

**Hybrid Organic-Inorganic Materials:
Synthesis, solid state characterisation and
solution studies of organoarsenate
and -phosphonate functionalised coordination
clusters and networks**

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*A thesis submitted to the University of Dublin for the degree of
Doctor of Philosophy*

School of Chemistry
University of Dublin
2013

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Camelia Ioana Onet

Acknowledgments

First and foremost, I would like to thank my supervisor Prof. Dr. Wolfgang Schmitt for offering me the possibility of joining his research group, for his guidance, and encouragement. I am really grateful for his understanding and support throughout my time here in Trinity College Dublin.

I am especially grateful to Dr. Tom McCabe, Dr. Lei Zhang and Dr. Nianying Zhu for their invaluable assistance with the X-ray diffraction measurements and crystal structure determinations. I also would like to express my gratitude to Prof. Rodolphe Cl  rac and Mathieu Rouz  res for the tireless effort they have put into the magnetic studies. I would sincerely like to thank Dr. J. Bernard Jean-Denis and Dr. Martin Feeney for their help with the ESI-MS measurements and to Dr. John O'Brien and Dr. Manuel R  ther for NMR measurements. Many thanks to all the academic, technical and administrative staff within the School of Chemistry for their help over the years.

Special thanks must go to my laboratory colleagues Lei, Ian, John, David, Giuseppe, Bartosz, Gerard, Adam, Anne Marie, Lukas, Theresa, Nianying, Mariyatra, Anil and Jian Di for all their support on both a professional and personal level. Thanks as well to all the project students who have joined us over the years, especially to Raphaele Clement and Pierre Heijboer. Also, I would like to thank all the members in Professor Draper's group.

I am very grateful to Mrs. Corinne Harrison for all her support during my years of study in Dublin and for treating me like her daughter while living at her house.

I would also like to thank SFI for their financial support and Trinity College Dublin for making my training here possible.

Finally, I would like to thank my family and friends for their support and encouragement.

Summary

The research presented in this thesis focuses on the development of novel hybrid organic-inorganic materials with potential applications in the areas of catalysis, gas sorption and separation, magnetism. The project involves the synthesis and structural characterisation of coordination complexes and networks stabilised by organophosphonate and -arsonate ligands. Solution studies were performed using electrospray ionisation mass spectrometry (ESI-MS). ESI-MS proved to be a very powerful analytical tool that allowed us to monitor the synthetic approach to hybrid organic-inorganic oxo-clusters and investigate their stability in solution. The physicochemical properties of the synthesised compounds have also been studied.

The first chapter of this work introduces the reader to the field of research, highlights main achievements of the field and puts the work into context.

The second chapter, “Hybrid Organic-Inorganic Polyoxomolybdates”, details the synthesis and characterisation of a series of hybrid polyoxomolybdates stabilised by organoarsonate and –phosphonate ligands: $(\text{NH}_4)_2\text{H}_2[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_5)_4]\cdot 5\text{H}_2\text{O}$ (1), $(\text{NH}_4)_2\text{H}_2[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4]\cdot \text{DMF}\cdot 4\text{H}_2\text{O}$ (2), $(\text{NH}_4)_5[\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_3\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]\cdot 9\text{H}_2\text{O}$ (3), $(\text{NH}_4)_4[\text{Mo}^{\text{VI}}_4\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_3\text{NO}_2\text{OH})_4]\cdot 2\text{H}_2\text{O}$ (4), $(\text{NH}_4)_4\text{H}_4\{\text{Mn}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (5), $(\text{NH}_4)_4\text{H}_4\{\text{Fe}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (6), $(\text{NH}_4)_4\text{H}_4\{\text{Co}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (7), $(\text{NH}_4)_4\text{H}_4\{\text{Ni}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (8) and $(\text{NH}_4)_4\text{H}_4\{\text{Mg}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (9). It has been demonstrated that slight perturbations of the ligand functionalities can be exploited to stabilise unprecedented core structures. Additionally, the electrospray ionisation mass spectrometry (ESI-MS) technique has been exploited to investigate the self-assembly process of hybrid organic-inorganic polyoxomolybdates that form upon partial reduction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in the presence of aromatic organoarsonates. Functionalised POMs were also obtained by incorporating d-block hetero-atoms (Mn, Fe, Co, Ni) and a main group element (Mg) into defined POM structures. We intended to explore how different heteroatoms would influence the structure and magnetic properties of the compounds.

The third chapter, “Polynuclear Manganese Coordination Complexes”, presents the synthesis and characterisation of a series of manganese cluster compounds stabilised by

organophosphonate ligands: $[\text{Mn}^{\text{III}}_{15}(\mu_2\text{-H}_2\text{O})_2(\text{CH}_3\text{OH})_{16}(\text{C}_6\text{H}_5\text{PO}_3)_{20}]\text{Cl}_5 \cdot 22\text{CH}_3\text{OH} \cdot 8\text{H}_2\text{O}$ (**10**), $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_5\text{Cl}]\cdot 3\text{H}_2\text{O}$ (**11**), $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_6]\text{Cl} \cdot 5\text{H}_2\text{O}$ (**12**), $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_6\text{H}_5\text{-C}_3\text{H}_6\text{-C}_5\text{H}_4\text{N})_6]\text{Cl} \cdot 5\text{H}_2\text{O}$ (**13**), $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Cl}_2 \cdot 3\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ (**14**), $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Br}_2 \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**15**) and $(\text{H}_3\text{O})_4[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_4\text{-O})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2\{(\text{C}_6\text{H}_5)_3\text{CPO}_3\}_6]\text{Cl}_2 \cdot 2\text{CH}_3\text{CN} \cdot 4\text{H}_2\text{O}$ (**16**). It has been shown that small changes to the reaction conditions result in drastic changes of the cluster nuclearity and topology. The ESI-MS technique was again used to screen the reaction mixtures of **10-16** in order to identify new polynuclear manganese species that form in solution. Magnetic studies performed for these compounds revealed that compounds **11-13** exhibit single molecule magnet (SMM) behaviour.

Chapter 4, describes the synthesis and characterisation of two coordination networks employing mononuclear SBUs and triphosphonate linkers: $(\text{H}_3\text{O})\{\text{Mn}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_2[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ (**17**) and $(\text{H}_3\text{O})\{\text{Cu}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ (**18**). The compounds exhibit a 2D layered architecture stabilised in the crystal structure by weak hydrogen bonds and $\pi\text{-}\pi$ interactions. The materials did not show any permanent porosity.

Chapter 5 provides a description of the applied materials and methods, and provides the experimental details for the synthesis of the compounds.

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List of compounds

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- 2 $(\text{NH}_4)_2\text{H}_2[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4]\cdot \text{DMF}\cdot 4\text{H}_2\text{O}$
- 3 $(\text{NH}_4)_5\cdot [\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_3\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]\cdot 9\text{H}_2\text{O}$
- 4 $(\text{NH}_4)_4\cdot [\text{Mo}^{\text{VI}}_4\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_3\text{NO}_2\text{OH})_4]\cdot 2\text{H}_2\text{O}$
- 5 $(\text{NH}_4)_4\cdot \text{H}_4\{\text{Mn}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$
- 6 $(\text{NH}_4)_4\cdot \text{H}_4\{\text{Fe}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$
- 7 $(\text{NH}_4)_4\cdot \text{H}_4\{\text{Co}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$
- 8 $(\text{NH}_4)_4\cdot \text{H}_4\{\text{Ni}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$
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- 10 $[\text{Mn}^{\text{III}}_{15}(\mu_2\text{-H}_2\text{O})_2(\text{CH}_3\text{OH})_{16}(\text{C}_6\text{H}_5\text{PO}_3)_{20}]\text{Cl}_5\cdot 22\text{CH}_3\text{OH}\cdot 8\text{H}_2\text{O}$
- 11 $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_5\text{Cl}]\cdot 3\text{H}_2\text{O}$
- 12 $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$
- 13 $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_6\text{H}_5\text{-C}_3\text{H}_6\text{-C}_5\text{H}_4\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$
- 14 $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Cl}_2\cdot 3\text{CH}_3\text{OH}\cdot 4\text{H}_2\text{O}$
- 15 $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Br}_2\cdot 2\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O}$
- 16 $(\text{H}_3\text{O})_4[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_4\text{-O})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2\{(\text{C}_6\text{H}_5)_3\text{CPO}_3\}_6]\text{Cl}_2\cdot 2\text{CH}_3\text{CN}\cdot 4\text{H}_2\text{O}$
- 17 $(\text{H}_3\text{O})\{\text{Mn}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_2[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\}\cdot x\text{CH}_3\text{OH}\cdot y\text{H}_2\text{O}$
- 18 $(\text{H}_3\text{O})\{\text{Cu}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\}\cdot x\text{CH}_3\text{OH}\cdot y\text{H}_2\text{O}$

Abbreviations

3D	three dimensional
ac	alternating current
a.m.u.	atomic mass units
ATR	attenuated total reflectance
BVS	bond valence sum analysis
C	Currie constant
CHN	carbon hydrogen nitrogen elemental analysis
D	zero-field splitting
dc	direct current
DMF	N,N'-dimethylformamide
DMSO	dimethyl sulfoxide
EDX	energy dispersive X-ray analysis
ESI-MS	electrospray ionization mass spectrometry
FTIR	Fourier-transform infrared
<i>g</i>	Landé <i>g</i> -factor
IR	infrared
<i>J</i>	exchange coupling constant
<i>M</i>	magnetisation
MALDI	matrix-assisted laser desorption ionisation
min	minutes
MOF	metal-organic framework
<i>m/z</i>	mass to charge ratio
NMR	nuclear magnetic resonance
Oe	Oersted
POM	polyoxometalate
P-MOF	polyoxometalate metal organic framework
<i>S</i>	ground spin state
SBU	secondary building unit
SMM	single molecule magnet
SQUID	superconducting quantum interference device
<i>T</i>	temperature
TGA	thermogravimetric analysis

TOF-MS	Time-of-flight mass spectrometer
U	spin reversal barrier
UV-vis	ultraviolet visible
XRD	X-ray diffraction
δ	chemical shift
χ	magnetic susceptibility
λ	wavelength
QTM	quantum tunnelling of the magnetisation

1. INTRODUCTION

1.1 POLYOXOMETALATES

Polyoxometalates (POMs) are anionic metal–oxide clusters of the early transition metals (V, Nb, Ta, Mo, W) in their highest oxidation state, and represent a class of compounds whose preparation is a very active area in chemical and materials research.¹⁻⁵

The interest in these compounds arises not only from their extraordinary structural characteristics but also from their unique intrinsic electronic, optical and chemical attributes (including redox and photochemical activity, charge distribution and band structures) which promote applications in many diverse disciplines such as catalysis, the development of sensors, photocatalysts, electrochromics, magnetic materials, energy storage and conversion devices.^{1, 4-16}

The field of polyoxometalate chemistry has evolved very rapidly in the last two decades and research developments are governed by newly developed synthetic methodologies that led to the synthesis and characterisation of ultra-large, molecular clusters that contain up to 368 metal atoms.¹⁷ Much of the interest in these molecules has arisen because such clusters represent molecular entities whose structures can be rationalised by consecutive condensation reactions of well defined sub-units. Variations of the reaction conditions can initiate aggregation reactions of specific molecular species producing oligomeric complexes and large nanoscale clusters.^{1, 17} The versatile nature of this class of compound in terms of structure, size, redox chemistry, photochemistry, and charge distribution, means that the chemistry of polyoxometalates is arguably one of the many areas in inorganic chemistry that is developing very rapidly.¹

While many of these systems can be easily prepared, the ability to functionalise polyoxometalates is an ongoing challenge.^{3, 18-20} The early transition metal ions are able to polarise terminal M-O bonds stabilising large molecular cage structures and other aggregates. These bonds that usually point radial to the outside of the 0-D cluster species are characterised by d- π contributions and double-bond character impeding functionalisation. Consequently many advanced developments of polyoxometalate-containing materials are hindered by the limited availability of functionalised POMs.²¹ Currently many research groups are developing synthetic approaches to functionalised POMs, whereby the preparation of hybrid POMs appears to be more challenging than ligand–stabilised compounds containing late transition metal ions.

1.1.1 Historical background of POMs

The history of polyoxometalate chemistry dates to the discovery of ammonium 12-molybdophosphate $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ by Berzelius in 1826. Many other heteropoly compounds were subsequently reported and analysed throughout the following decades, but the structure of most polyoxometalates remained not fully understood.²² The development of X-ray crystallographic techniques provided a breakthrough for the subject area allowing the detailed elucidation of POM structures and providing access to structure-property relationships.

In 1933 employing a powder X-ray diffraction study, J. F. Keggin solved the structure of $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$, a nowadays well-known 12:1 type heteropolyanion.²³ Named after its discoverer, the Keggin structure (Figure 1.1, a), contains 12 $\{\text{WO}_6\}$ octahedra linked by edge and corner sharing motifs, with the heteroatom occupying a tetrahedral coordination site in the centre of the oxo cluster. A further 6:1 type, the Anderson's heteropolyanion $[\text{Te}^{\text{VI}}\text{Mo}_6\text{O}_{24}]^{6-}$, was studied by single-crystal X-ray diffraction by Evans in 1948. This structure is now commonly called the Anderson-Evans structure²⁴ (Figure 1.1, b). It consists of six edge sharing $\{\text{MoO}_6\}$ octahedra adopting a hexagonal arrangement around a central octahedrally coordinated tellurium atom. Closely related to the Keggin structure, a 18:2 heteropolyanion $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ was reported in 1953 by Dawson²⁵, referred to as the Wells-Dawson's structure (Figure 1.1, c). This heteropolyanion consists of two identical subunits in which a central $\{\text{PO}_4\}$ tetrahedron is surrounded by 9 $\{\text{WO}_6\}$ octahedra linked by edge and corner sharing connectivity motifs.

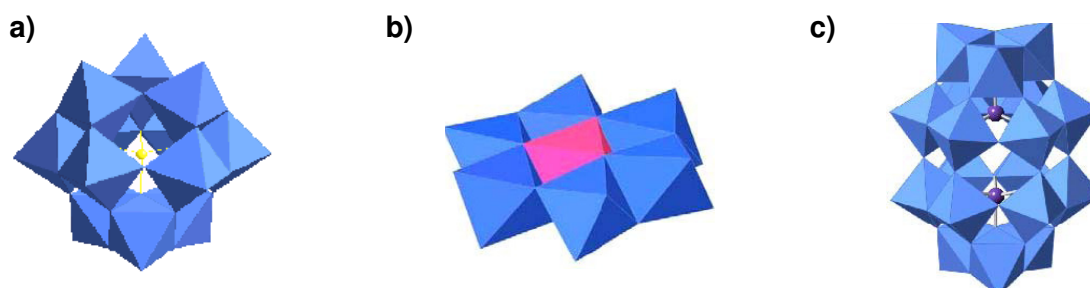


Figure 1.1 – Polyhedral representation of: (a) Keggin structure,²³ (WO_6 unit – blue polyhedra; P – yellow sphere); (b) Anderson-Evans structure,²⁴ (MoO_6 unit – blue polyhedra; Te – red polyhedron); (c) Wells-Dawson structure,²⁵ (WO_6 unit – blue polyhedra; P – purple spheres).

Another important POM cluster is the isopolyanion $[M_6O_{19}]^{n-}$, ($M = Mo, W, Nb, Ta, \text{ and } V$) discovered in 1952 by Lindqvist and known as the Lindqvist structure²⁶ (Figure 1.2).

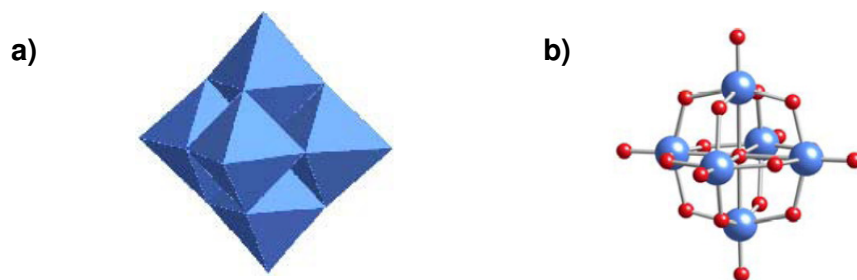


Figure 1.2 – The Lindqvist Structure: (a) polyhedral representation; (b) ball-and-stick representation.²⁶ Colour code: M blue, O red.

Lindqvist POMs have an overall octahedral geometry and consist of one central oxygen atom that is octahedrally surrounded by six metal ions. Each of these six metal atoms is μ_2 -bridged to other metal atoms by four different oxygen ligands and has one terminal oxygen atom.²⁶ One particular Lindqvist POM containing Mo metal ions, hexamolybdate $[Mo_6O_{19}]^{2-}$, is of importance, because it can be directly functionalised to incorporate organoimido ligands. This unique feature has made $[Mo_6O_{19}]^{2-}$ a very popular POM cluster that has been studied extensively in recent years.^{27, 28}

Recent exciting new developments in the field of polyoxometalates include:

- the discovery of large, highly symmetric polyoxomolybdates such as the wheel-shaped $[(MoO_3)_{176}(H_2O)_{80}H_{32}]$ cluster²⁹ (Figure 1.4, c), giant spherical clusters $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(CH_3COOH)\}_{30}]^{42-}$ (Figure 1.4, a)³⁰ and Keplerates $Na_{48}[H_{16}Mo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}] \cdot ca. 1000H_2O$ (Figure 1.4, d)¹⁷;
- hybrid organic-inorganic materials that contain POM cores;^{31, 32} new potential applications based on unusual magnetic⁷ and optical³³ properties of some POMs, and potential medical applications such as anti-tumor and anti-viral uses.³⁴

1.1.2 Condensation reactions as synthetic procedure

The main synthetic approaches used to produce oligomeric complexes or large nanoscale clusters of the early transition metal ions are simple and involve usually the acidification of aqueous solutions containing the relevant metal–oxide anions (molybdates, tungstates and vanadates).

However, the specific reaction variables and parameters that manipulate the synthesis of POMs are manifold and depend on the type of metal–oxide anion, the concentration, the pH and type of acid, the heteroatom concentration, the ligand types, the reducing agent, temperature and the solvent type. The synthesis of POM clusters is based on self assembly processes involving covalent linking of transferable building blocks, under "one-pot" conditions (Figure 1.3). These structural building blocks can assemble into pre-defined architectures, and consist of aggregates of metal–oxygen units that adopt a defined polyhedral arrangement with the metal ions in the centre and the oxygen ligands as vertices.^{1, 35-37}

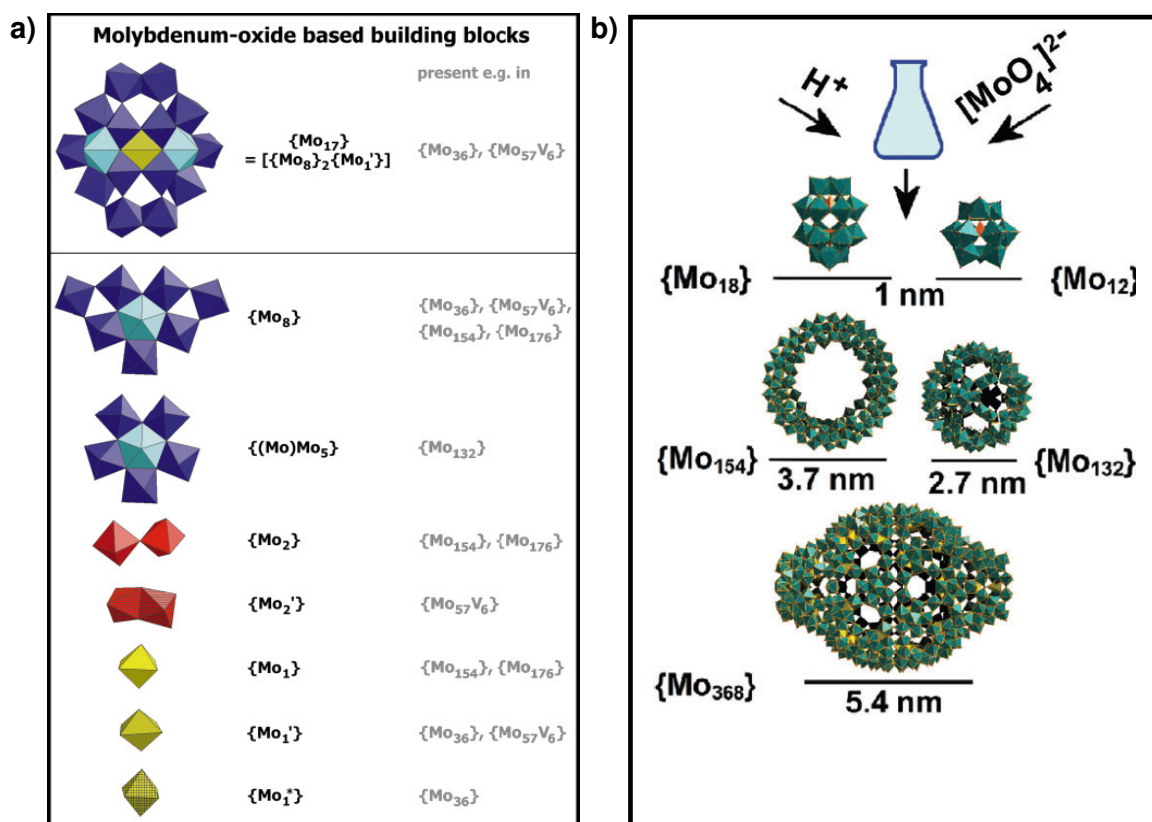


Figure 1.3 – (a) Fundamental units and building blocks;³⁸ (b) Self-assembly of polyoxometalate clusters from $\{Mo_{12}\}$ to the protein-sized $\{Mo_{368}\}$. The Mo centres are shown as green polyhedra.³⁵

The overall structure of the POM cluster can be visualised as a combination of a set of polyhedra that adopt corner and/or edge sharing modes. The formation reactions that often occur through a set of consecutive condensation reactions are mechanistically not yet fully understood. Therefore, the concept that regards metal-centered polyhedra as structural building blocks became extremely useful to rationalise the observed POM structures and their formation processes.^{35, 36, 38}

1.1.3 Polyoxomolybdates

Polyoxomolybdates represent a very important subclass of POM clusters. Research developments and synthetic approaches in this fascinating area of POM chemistry take advantage of a unique library of molybdenum-oxide based building blocks to generate a large variety of molecular architectures.³⁶ The fundamental units and building blocks of molybdenum-based POMs include $\{\text{Mo}_1\}$, $\{\text{Mo}_2\}$, $\{(\text{Mo})\text{Mo}_5\}$, $\{\text{Mo}_8\}$ and $\{\text{Mo}_{17}\} = [\{\text{Mo}_8\}_2\{\text{Mo}_1\}]$ units, as seen in Figure 1.3, a.³⁸ A huge diversity of structures, from small to large nanoscale clusters, can be produced upon combination of these building units. The broad range of polyoxomolybdate structures presently known include $\{\text{Mo}_6\}$,²⁴ $\{\text{Mo}_7\}$,³⁹ $\{\text{Mo}_8\}$,⁴⁰ $\{\text{Mo}_{10}\}$,⁴¹ $\{\text{Mo}_{12}\}$,⁴² $\{\text{Mo}_{18}\}$,⁴³ $\{\text{Mo}_{36}\}$,⁴⁴ $\{\text{Mo}_{37}\}$,⁴⁵ $\{\text{Mo}_{132}\}$,³⁰ $\{\text{Mo}_{154}\}$,⁴⁶ $\{\text{Mo}_{176}\}$,²⁹ $\{\text{Mo}_{248}\}$ ⁴⁷ and $\{\text{Mo}_{368}\}$ ¹⁷ oxo-clusters.

One of the most exciting developments in POM chemistry is represented by the discovery of a high-nuclearity cluster commonly known as the “big-wheel”, the $[\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-} \equiv \{\text{Mo}_{154}\}$ cluster, reported by Müller *et al.* in 1995.^{46, 48} The $\{\text{Mo}_{154}\}$ cluster anion has a ring topology and consists of 14 $\{\text{Mo}_8\}$ building units linked by 14 $\{\text{Mo}_2\}$ and 14 $\{\text{Mo}_1\}$ units, respectively (Figure 1.4, b). A structurally related wheel-shaped metal oxide cluster, the $[(\text{MoO}_3)_{176}(\text{H}_2\text{O})_{80}\text{H}_{32}] \equiv \{\text{Mo}_{176}\}$ cluster,²⁹ can be obtained by linking 16 instead of 14 sets of the above mentioned $\{\text{Mo}_8\}$, $\{\text{Mo}_2\}$ and $\{\text{Mo}_1\}$ building units, respectively (Figure 1.4, c). The $\{\text{Mo}_{154}\}$ cluster has an external diameter of 3.4 nm, while that of the $\{\text{Mo}_{176}\}$ cluster is 4.1 nm. The $\{\text{Mo}_8\}$ building block is itself built-up by a densely packed pentagonal unit $\{(\text{Mo})\text{Mo}_5\}$ and two more weakly bonded $\{\text{MoO}_6\}$ octahedra. The pentagonal unit $\{(\text{Mo})\text{Mo}_5\}$ consists of a central bipyramidal $\{\text{MoO}_7\}$ unit sharing edges with five $\{\text{MoO}_6\}$ octahedra. These pentagonal units are also key for the formation of giant spherical clusters or Keplerates, like the

$[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(CH_3COOH)\}_{30}]^{42-} \equiv \{Mo_{132}\}^{30}$ and the $[H_{16}Mo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-} \equiv \{Mo_{368}\}^{17}$ clusters. The $\{Mo_{368}\}$ cluster anion is the largest cluster known to date. It has an approximate D_4 symmetry and consists of 368 molybdenum atoms. It can be regarded as composed of 40 pentagonal $\{(Mo)Mo_5\}$ units, 32 dinuclear $\{Mo_2\}$ units and 64 mononuclear $\{Mo_1\}$ units (Figure 1.4, d).^{1, 48}

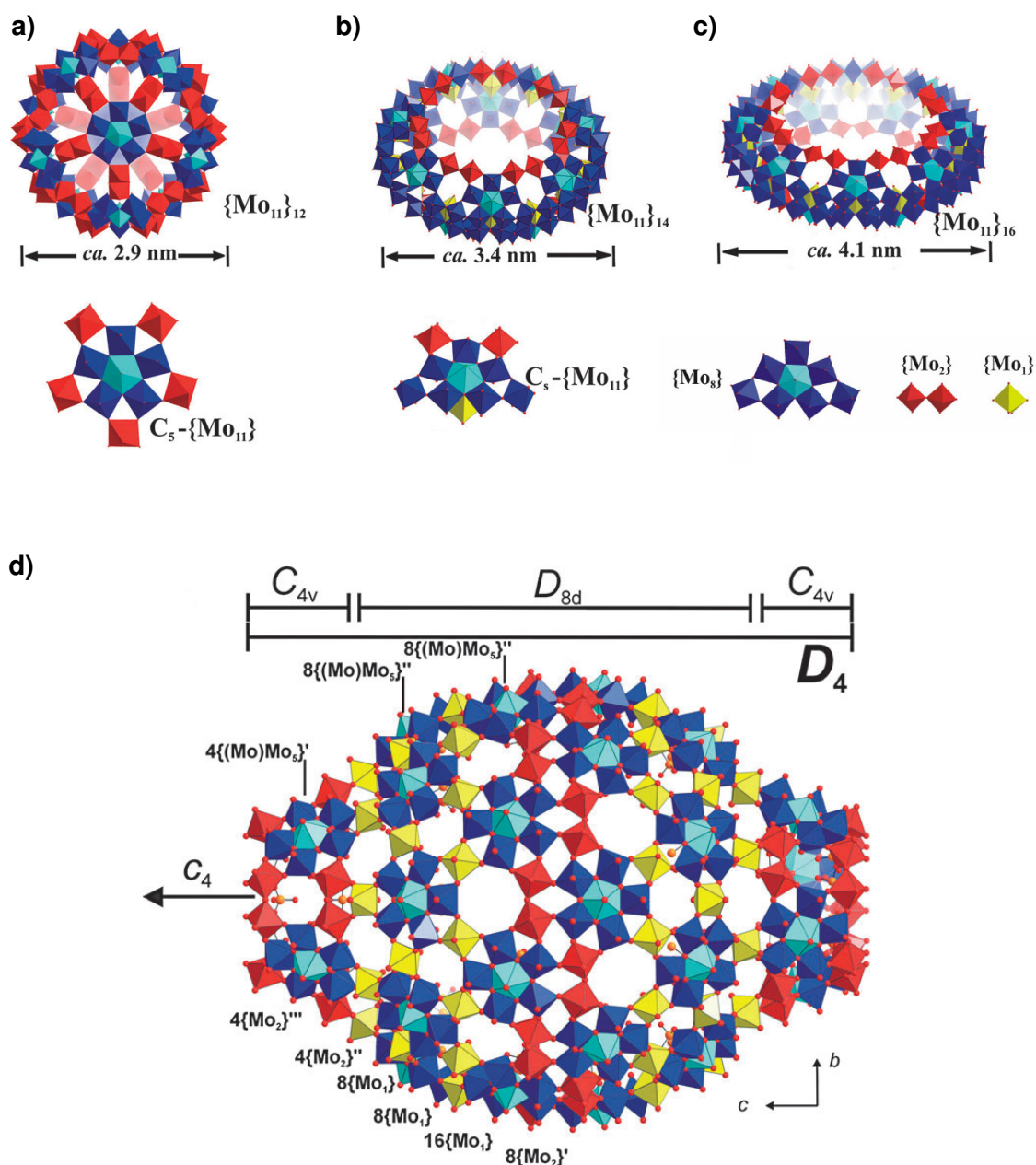


Figure 1.4 – Giant sphere- and wheel-shaped polyoxomolybdates: (a) The spherical $\{Mo_{132}\}$ cluster; (b,c) The wheel-shaped $\{Mo_{154}\}$ and $\{Mo_{176}\}$ clusters; (d) The $\{Mo_{368}\}$ cluster, highlighting the related pentagonal $\{(Mo)Mo_5\}$ (cyan and blue), dinuclear $\{Mo_2\}$ (red) and mononuclear $\{Mo_1\}$ (yellow) building units.⁴⁸

Despite the fact that the high nuclearity molybdenum clusters, $\{\text{Mo}_{132}\}$, $\{\text{Mo}_{154}\}$, $\{\text{Mo}_{176}\}$, $\{\text{Mo}_{248}\}$ and $\{\text{Mo}_{368}\}$, have complex nanoscale structures, they are quite easy to prepare and handle.^{1, 48} The versatile nature of polyoxomolybdate chemistry is due to the flexibility of the Mo-O-Mo bridges that allow “split and link” type processes,⁴⁸ the number of variable redox states of the molybdenum centers, different coordination numbers, strong hydration stabilisation and the presence of terminal Mo=O groups that ‘protect’ the entities to the outside stabilising discrete molecular clusters.⁴⁸

1.1.4 Functionalisation of POMs

The functionalisation of POMs may provide a tool to fine tune the electronic properties of the parent anions. This can be achieved by replacing the metal-oxo functionality of a POM by an alternate one, formal replacement of some oxo ligands, or grafting of a functional group at the surface of the polyanion.⁴⁹ The ability to functionalise polyoxometalate clusters is of great importance, as it aims to extend their utility.

1.1.4.1 Transition metal substituted POMs (TMSPs)

A simple approach to achieve POM functionalisation is to incorporate transition metal ions into the cluster. This allows us to influence their properties, such as magnetic behaviour^{50, 51} or catalytic activity⁴; examples are illustrated in Figure 1.5.

All first row and most of the second row transition metals have been incorporated into various POM clusters. Lacunary POM fragments are ideal for the incorporation of transition metals. The most stable lacunary POMs derive from Keggin and Wells-Dawson polyoxotungstates, which were intensively used for the preparation of TMSPs. On the other hand, TMSPs incorporating paramagnetic 3d metals Mn, Fe, Co, Ni and Cu are of particular interest due to their electronic and magnetic properties.⁵¹ For instance, the two Fe substituted polyoxotungstate clusters, $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{Fe}^{\text{III}}\text{W}_9\text{O}_{34})_2]^{10-}$ and $[(\text{Fe}^{\text{III}}_4\text{W}_9\text{O}_{34}(\text{H}_2\text{O}))_2(\text{Fe}^{\text{III}}\text{W}_6\text{O}_{26})]^{19-}$ (Figure 1.5, a, b) exhibit fascinating single molecule magnet (SMM) behaviour.⁵²

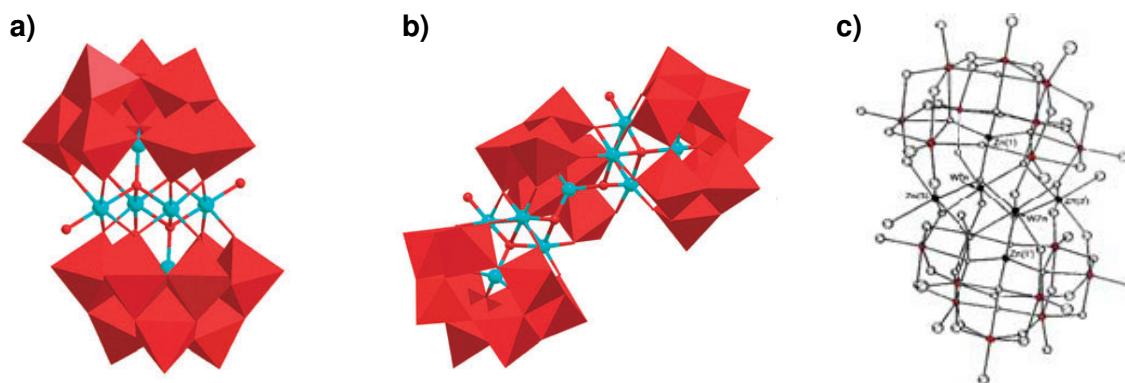


Figure 1.5 – Structural representations of: (a) $[\text{Fe}_4(\text{H}_2\text{O})_2(\text{FeW}_9\text{O}_{34})_2]^{10-}$ and (b) $[(\text{Fe}_4\text{W}_9\text{O}_{34}(\text{H}_2\text{O})_2)(\text{FeW}_6\text{O}_{26})_2]^{19-}$ POMs⁵² (displaying SMM behaviour) and (c) $[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ oxidation catalyst.⁴ Colour code: W red polyhedra, Fe blue spheres, O red spheres, Zn black.

1.1.4.2 Incorporation of main group elements into POMs

Polyoxometalates can also incorporate main group elements within their cluster structure. Examples of such main group derivatives are the halogenated POMs, which are useful precursors for further functionalisation.²⁰ This type of functionalised POMs have the halide ions occupying a terminal position, e.g. $[\text{Mo}_4\text{O}_{10}(\text{OMe})_4\text{Cl}_2]^{2-}$,⁵³ $[\text{W}_6\text{O}_{14}\text{Cl}_{10}]^{2-}$,⁵⁴ and $[\text{PW}_9\text{O}_{28}\text{Br}_6]^{3-}$.⁵⁵ However, there are also numerous examples of functionalised POMs in which the halide ions are incorporated within the cluster anion, e.g. $[\text{H}_2\text{NaW}_{18}\text{O}_{56}\text{F}_6]^{7-}$, or where the halide ion acts as a template for the self assembly of a larger cluster shell, e.g. $[\text{V}_{18}\text{O}_{42}\text{Cl}]^{13-}$.²⁰ Some examples are illustrated in Figure 1.6. Other examples of main group derivatives include Si, Sn or P containing POMs: $[\text{SiW}_{11}\text{O}_{39}\{\text{O}(\text{SiR})_2\}]^{4-}$, ($\text{R} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{C}_3\text{H}_5$), $[(\alpha\text{-A-XW}_9\text{O}_{34})(\text{SiR}_2)_3]^{(n-6)-}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$; $\text{X} = \text{Si}, n = 10$; $\text{X} = \text{P}$ or $\text{As}, n = 9$), $[\text{SiW}_9\text{O}_{34}(\text{SiEt})_3(\text{O}_3\text{SiEt})]^{4-}$, $[\text{SiM}_{11}\text{O}_{39}(\text{SnR})]^{5-}$ ($\text{M} = \text{W}, \text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{C}_3\text{H}_5, \text{C}_4\text{H}_9$; $\text{M} = \text{Mo}, \text{R} = \text{C}_2\text{H}_5$), $[\text{PW}_{10}\text{O}_{38}(\text{SnR})_2]^{5-}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$), $[\text{PW}_{11}\text{O}_{39}(\text{SnCl})]^{3-}$, $[\text{P}_2\text{W}_{16}\text{O}_{60}(\text{SnPh})_2]^{8-}$, $[\text{XW}_{11}\text{O}_{39}\text{Sn}]^{n-}$ ($\text{X} = \text{P}, \text{Si}, \text{Ge}, \text{B}, \text{Ga}$), $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\text{Sn}]^{8-}$.^{20, 56, 57}

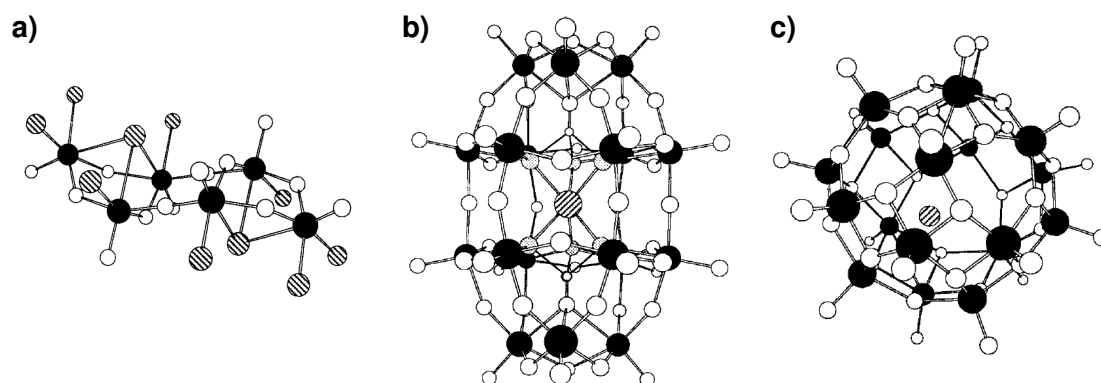


Figure 1.6 – Structural representations of: (a) $[\text{W}_6\text{O}_{14}\text{Cl}_{10}]^{2-}$; (b) $[\text{H}_2\text{NaW}_{18}\text{O}_{56}\text{F}_6]^{7-}$ and (c) $[\text{V}_{18}\text{O}_{42}\text{Cl}]^{13-}$ cluster anions.²⁰

1.1.4.3 Organic and organometallic derivatives of POMs

Numerous experimental studies have been devoted to the development of strategies to functionalise POM species using organic or organometallic precursors as functional groups. Main-group element, organic, and organometallic derivatives of polyoxometalates have been reviewed by A. Proust *et al.*,^{3, 20} highlighting several synthetic approaches to obtain such systems. One synthetic approach intensively exploited was the replacement of some terminal oxo ligands with various nitrogen-containing molecules such as nitrido, organoimido, diazenido ligands. The first nitrido POM derivative was reported by Zubietta and was a Lindqvist type POM $[\text{Mo}_6\text{O}_{18}\text{N}]^{3-}$. Later on, Maatta and Proust showed that Re- and Os-nitrido species can be incorporated in both Keggin and Dawson type POMs, $[\text{PW}_{11}\text{O}_{39}(\text{MN})]^{x-}$ and $[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{MN})]^{x-}$ ($\text{M} = \text{Re}, \text{Os}$) (Figure 1.7, a).^{3, 58, 59} Another exciting feature of the Lindqvist POM is the tendency to undergo multiple functionalisation steps upon reaction with organoimido ligands. Maatta *et al.* demonstrated that it is possible to replace successively all six terminal oxo groups of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion by 2,6-(diisopropyl)phenylimido moieties (Figure 1.7, b, c).^{3, 60, 61}

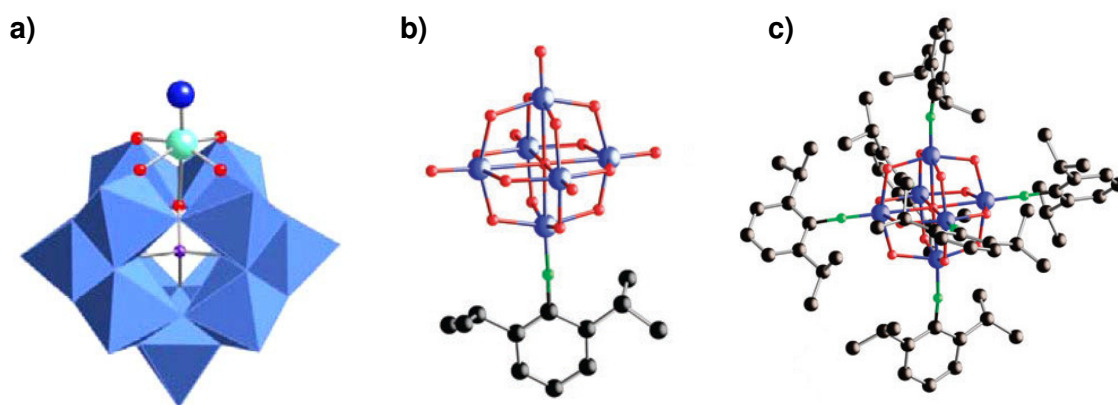


Figure 1.7 – Structural representations of: (a) the nitrido-Keggin ion $[\text{PW}_{11}\text{O}_{39}(\text{MN})]^{x-}$ (W blue polyhedra, M = Re, Os cyan, P purple, N blue spheres, O red); (b) $[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_3\text{-}2,6\text{-Me}_2)]^{2-}$ and (c) $[\text{HMo}_6\text{O}_{13}(\text{NC}_6\text{H}_3\text{-}2,6\text{-Me}_2)_6]^{2-}$ Lindqvist cluster anions (Mo blue, O red, N green, C black).²⁰

Most recent studies exploit the direct grafting of organic substrates and organic ligands at the nucleophilic oxygen atoms of the POM core. Examples of aromatic phosphonate and arsonate stabilised POMs are illustrated in Figure 1.8.^{18, 21, 62-66} In these compounds the aromatic ligands stabilise rather symmetrical cluster cores. The ligands

point into defined directions of space suggesting that these or related structures could be suitable building units for metal-organic frameworks.⁶¹

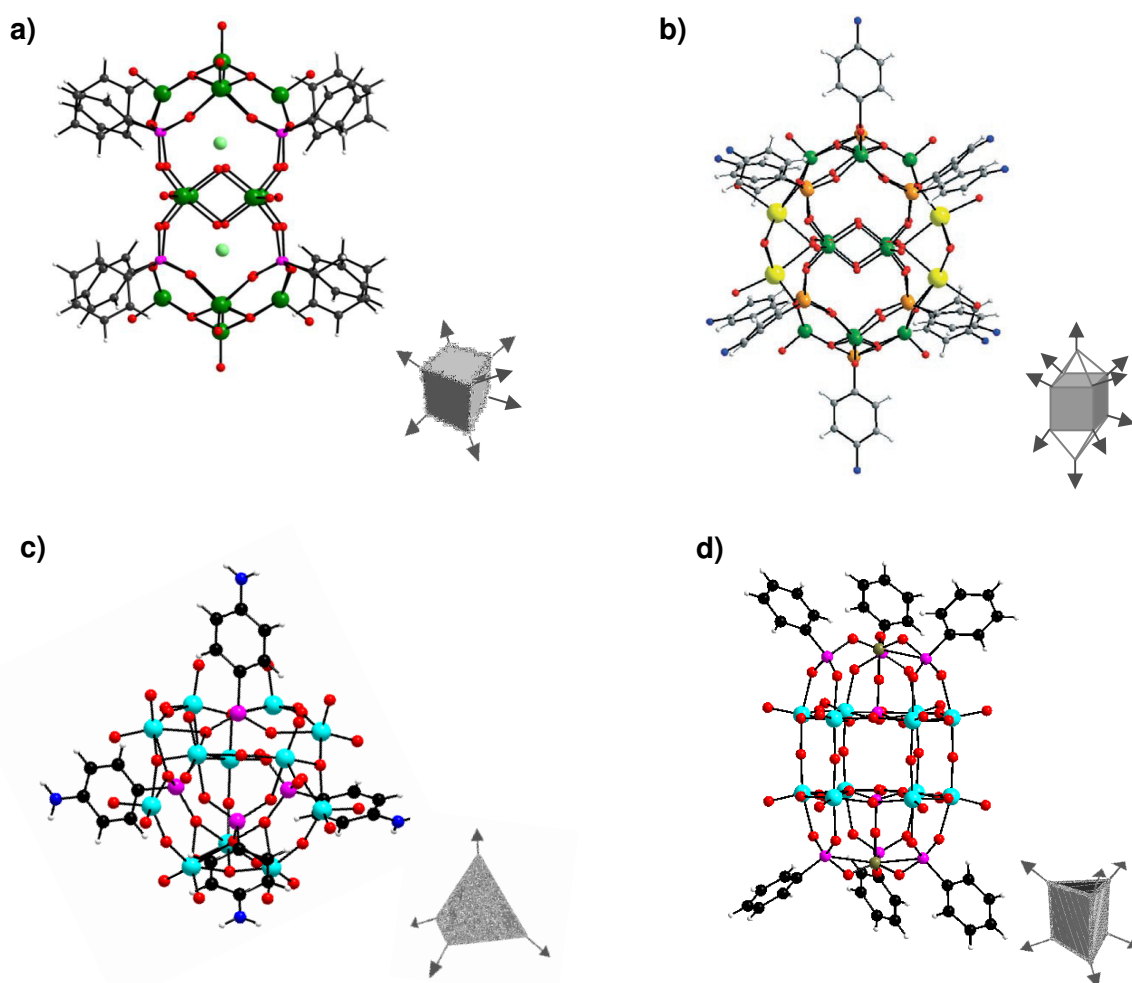


Figure 1.8 – Aromatic phosphonate/arsonate stabilised POMs with regular topology as potential SBUs for MOFs. (a) $[\text{Cl}_2\text{V}_{14}\text{O}_{22}(\text{OH})_4(\text{H}_2\text{O})_2(\text{C}_6\text{H}_5\text{PO}_3)_8]^{6-}$; ⁶² (b) $\{\text{Na}_4(\text{H}_2\text{O})_{10}\}[\text{V}_{12}\text{O}_{12}(\text{OH})_4(\text{H}_2\text{O})_2(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_{10}]$; ²¹ (c) $[\text{Mo}_{12}\text{O}_{34}(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4]^{4-}$; ⁶³ (d) $[\text{Mo}_{12}\text{O}_{30}(\text{BPO}_4)_2(\text{O}_3\text{PC}_6\text{H}_5)_6]^{5-}$. ⁶⁴ Colour code: V green, Mo cyan, O red, P purple, N blue, Cl light green, Na yellow, C black, H white.

1.1.4.4 Organophosphonate and -arsonate functionalised polyoxomolybdates

Metal organophosphonates and -arsonates have attracted considerable research interest due to their interesting coordination chemistry and potential applications as catalysts and ion exchange materials.⁶⁷ The structural diversity of these hybrid organic-inorganic materials spans over a range of structures from molecular clusters to three-dimensional (3D) frameworks.⁶⁸ A very important subclass of these materials is represented by organophosphonate and -arsonate functionalised polyoxometalates. The

tetrahedral functional group of the organophosphonate and -arsonate ligands displays geometrical and electronic similarities to metal-oxygen units in polyoxometalates suggesting that these ligands could be good candidates for POM functionalisation.

The $V/O/RPO_3^{2-}$ system proved to be quite fruitful in yielding a range of structurally unique clusters and extended compounds, while the corresponding $Mo/O/RPO_3^{2-}$ system remain relatively undeveloped, being mostly limited to some molecular species. The most common structural type of the $Mo/O/RPO_3^{2-}$ system is represented by the cyclic pentanuclear core structure, with the general formula $[Mo_5O_{15}(RPO_3)_2]^{4-}$.^{3, 61} These pentamolybdo-bisphosphonates were isolated using different phosphonate ligands ($R = CH_3, C_2H_5, C_6H_5, CH_2C_6H_5, C_2H_4NH_3^+, p-CH_2C_6H_4NH_3^+$). The $\{Mo_5\}$ clusters have a ring topology with two phosphonate ligands capping both sides of the ring (Figure 1.9, a).^{3, 20, 69}

Tetra-, hexa- and dodecanuclear architectures can also be isolated. Examples include $[Mo_4O_{10}(PhPO_3)_4]^{4-}$, $[Mo_6O_{18}(Bu^tPO_3)_2]^{4-}$, $[{(C_6H_5P)Mo_6O_{21}(H_2O)_3}_2]^{4-}$, $[RPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ ($R = OH, CH_3, C_2H_5$), $[(RPO_3)_4Mo_{12}O_{34}]^{4-}$ ($R = CH_3, C_2H_5$), $[Na\{Mo_6O_{12}(OH)_3(PhPO_3)_4\}_2]^{9-}$, $[Mo_{12}O_{30}(BPO_4)_2(O_3PC_6H_5)_6]^{5-}$.^{20, 61, 64, 69-71}

The tetranuclear complex $[Mo_4O_{10}(PhPO_3)_4]^{4-}$ consists of two $\{Mo_2O_{10}\}$ dinuclear units connected by two phosphonate ligands to form a six membered $\{Mo_4P_2\}$ ring. The remaining two phosphonate ligands cap both sides of the central cavity of the ring (Figure 1.9, b).²⁰ The core structure of the hexanuclear complexes, $[{(C_6H_5P)Mo_6O_{21}(H_2O)_3}_2]^{4-}$, $[RPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$, adopts a similar ring motif capped by only one organophosphonate ligand, while the $[Mo_6O_{18}(Bu^tPO_3)_2]^{4-}$ species adopts a non-planar conformation as seen in Figure 1.9, c.^{69, 70} The dodecanuclear complex $[(RPO_3)_4Mo_{12}O_{34}]^{4-}$ is stabilised by methyl- or ethyl- phosphonates and adopts a so-called inverted-Keggin structure (Figure 1.9, d).⁷¹ The sandwich type dodecanuclear compounds $[Na\{Mo_6O_{12}(OH)_3(PhPO_3)_4\}_2]^{9-}$ consist of two hexanuclear Mo^V moieties linked by a Na ion (Figure 1.9, e), while the dodecanuclear polyanion, $[Mo_{12}O_{30}(BPO_4)_2(O_3PC_6H_5)_6]^{5-}$ (Figure 1.8, d), is part of a class of POMs that resemble Dawson anions.^{20, 64, 72, 73}

The incorporation of diphosphonate ligands into POM structures was also investigated. Methylendiphosphonate $(O_3PCH_2PO_3)^{4-}$ was the first to be explored for this purpose. Dolbecq and Mialane reported a series of cyclic compounds with the general formula $\{(Mo^V_2O_4)(O_3PCH_2PO_3)_n\}$ ($n = 3, 4, 10$) (Figure 1.9, f).^{74, 75} The compounds

consist of alternating $\{\text{Mo}^{\text{V}}_2\text{O}_4\}$ units and diphosphonate ligands, and their geometry depends on the nature of the co-ligand used and the nature of the counterions (NH_4^+ , Na^+ , Li^+).⁶¹ The $[(\text{Mo}_2\text{O}_4)_{10}(\text{O}_3\text{PCH}_2\text{PO}_3)_{10}(\text{CH}_3\text{COO})_8(\text{H}_2\text{O})_4]^{28-}$ anion differentiates itself from conventional cyclic, adopting a double wheel architecture built from interconnected octa- and dodecanuclear wheels that are linked *via* two sodium ions (Figure 1.9, g).⁷⁵

Other diphosphonate functionalised POMs include $\{\text{Mo}_5\text{O}_{15}(\text{O}_3\text{P}(\text{CH}_2)_4\text{PO}_3)\}$, $[\text{Mo}^{\text{V}}_6\text{Mo}^{\text{VI}}\text{O}_{16}(\text{O}_3\text{PCH}_2\text{PO}_3)]^{8-}$ and $[\text{Mo}^{\text{V}}_7\text{Mo}^{\text{VI}}\text{O}_{16}(\text{O}_3\text{PPhPO}_3\text{H})]^{3-}$ (Figure 1.9, h).^{65, 76, 77}

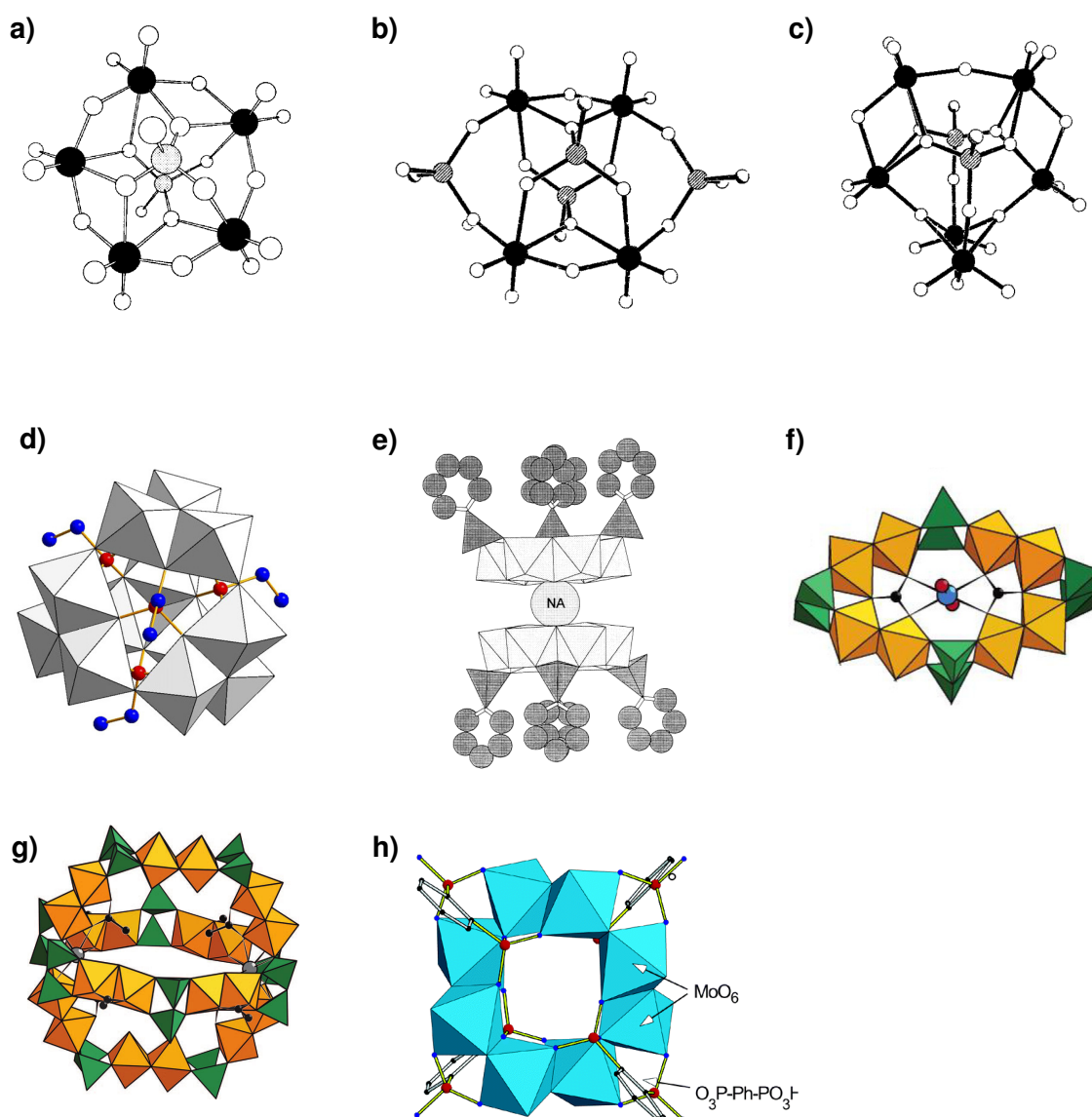


Figure 1.9 – (a) $[\text{Mo}_5\text{O}_{15}(\text{CH}_3\text{PO}_3)_2]^{4-}$;²⁰ (b) $[\text{Mo}_4\text{O}_{10}(\text{REO}_3)_4]^{4-}$ R = Ph, E = P, As;⁶⁹ (c) $[\text{Mo}_6\text{O}_{18}(\text{Bu}^1\text{PO}_3)_2]^{4-}$;⁶⁹ (d) $[(\text{EtPO}_3)_4\text{Mo}_{12}\text{O}_{34}]^{4-}$;⁷¹ (e) $[\text{Na}\{\text{Mo}_6\text{O}_{12}(\text{OH})_3(\text{PhPO}_3)_4\}_2]^{9-}$;^{72, 73} (f) $[(\text{Mo}_2\text{O}_4)_4(\text{O}_3\text{PCH}_2\text{PO}_3)_4(\text{CO}_3)_2]^{12-}$;⁷⁴ (g) $[(\text{Mo}_2\text{O}_4)_{10}(\text{O}_3\text{PCH}_2\text{PO}_3)_{10}(\text{CH}_3\text{COO})_8(\text{H}_2\text{O})_4]^{28-}$;⁷⁵ ($\{\text{MoO}_6\}$ orange octahedra, $\{\text{PO}_3\text{C}\}$ green tetrahedra, Na blue/gray spheres, C black spheres); (h) $[\text{Mo}^{\text{V}}_7\text{Mo}^{\text{VI}}\text{O}_{16}(\text{O}_3\text{PPhPO}_3\text{H})]^{3-}$.⁶⁵

Even though organoarsonates display reactivities and structural characteristics close to that of organophosphonates, organoarsonate-stabilised POM derivatives have far less been isolated.⁶¹ Examples of organoarsonate-functionalised polyoxomolybdates include $[\text{Mo}_4\text{O}_{10}(\text{RAsO}_3)_4]^{4-}$, $[\text{Mo}_5\text{O}_{15}(\text{RAsO}_3)_2]^{4-}$, $[\text{Mo}_6\text{O}_{18}(\text{RAsO}_3)_2]^{4-}$, $[\text{Mo}_{12}\text{O}_{34}(\text{RAsO}_3)_4]^{4-}$ ($\text{R} = \text{CH}_3, \text{C}_3\text{H}_7, \text{C}_6\text{H}_5, p\text{-C}_6\text{H}_4\text{NH}_3^+, \text{C}_2\text{H}_4\text{OH}, \text{C}_6\text{H}_4\text{COOH}$).^{3, 20, 78, 79} The $[\text{Mo}_{12}\text{O}_{34}(\text{RAsO}_3)_4]^{4-}$ (Figure 1.8, c) species are analogous to the organophosphonate derivatives that display an inverted-Keggin core with a tetrahedral arrangement of the organic ligands. These type of clusters may be suitable to be used as building units for metal-organic frameworks.⁶¹

1.2 METAL-ORGANIC FRAMEWORKS

Metal-organic frameworks (MOFs) represent a class of porous materials consisting of clusters or metal ions linked through rigid organic ligands. MOFs can be prepared using a fundamental construction principle, based on building block approaches where molecules, metal ions or clusters are considered as nodes, and coordination bonds represent node connectors. Choosing the desired combination of nodes and connectors, and using suitable building blocks, microporous networks with unprecedented surface areas can be obtained. The extraordinary low densities (1.00 to 0.20 gcm⁻³) and high surface areas (500 to 7000 m² g⁻¹) make MOFs ideal candidates for the storage and separation of gases (N₂, Ar, CO₂, CH₄, and H₂).⁸⁰⁻⁸²

The conceptual approach used to synthesise materials designed to have predetermined structures, compositions and properties is known as ‘the reticular synthetic approach’. This concept was described by O. M. Yaghi as “the process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures (networks), which are held together by strong bonding.”⁸³⁻⁸⁵ This approach requires the use of secondary building units (SBU). The term ‘secondary building unit’ refers to the geometry of the units (molecules, metal ions or clusters) defined by the points of extension (ligand coordination modes and metal coordination environments). These SBUs have intrinsic geometric properties that are used to direct the assembly of ordered frameworks. New materials with pre-desired structure, composition and properties can be obtainable by

linking these SBUs through coordination bonds. A few examples of inorganic and organic SBUs with varying geometries are presented in Figure 1.10.^{81, 83-87}

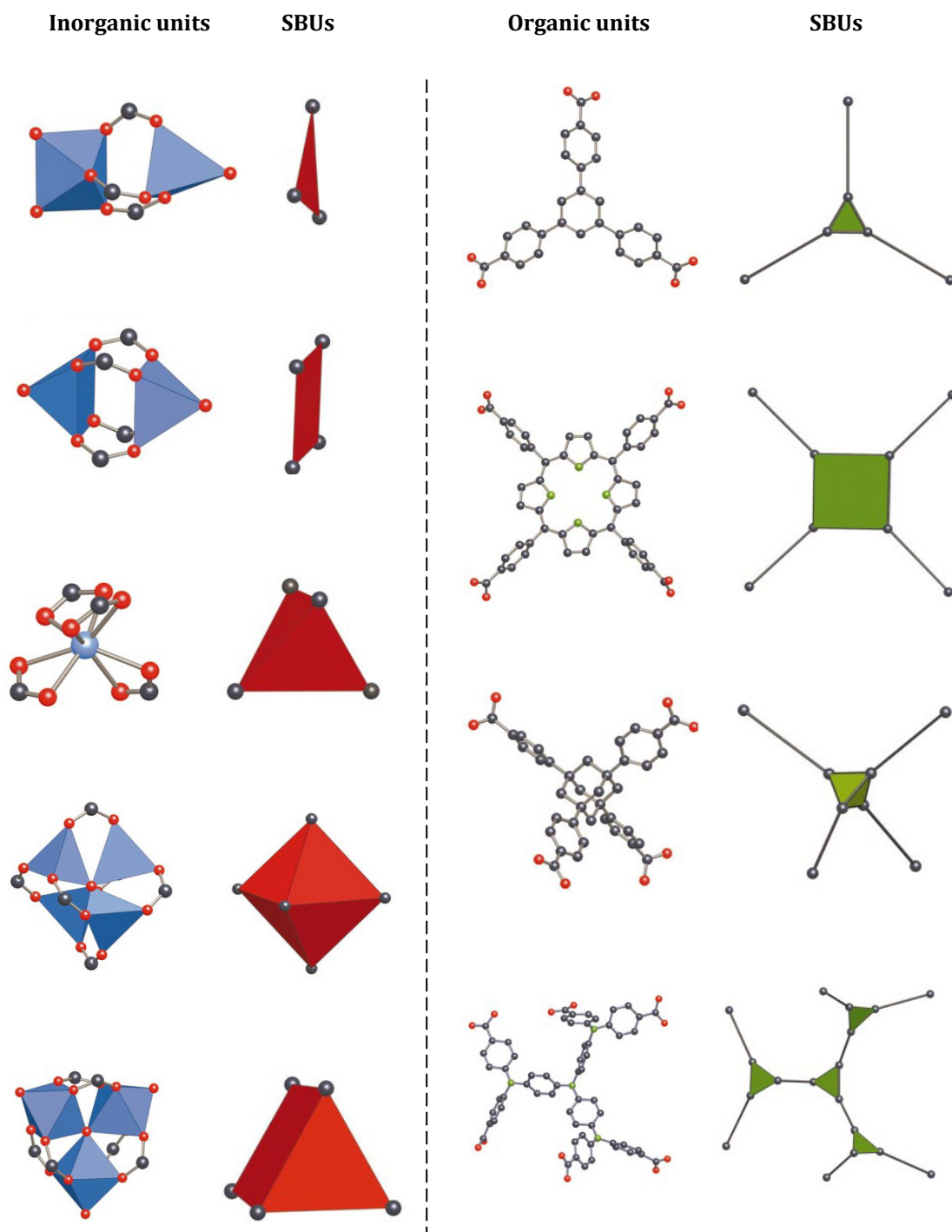


Figure 1.10 – Examples of SBUs from carboxylate MOFs. Colour code: O red, N green, C black. In inorganic units metal-oxygen polyhedra are blue.⁸³

The design of rigid frameworks based on such SBUs has been highly successful as demonstrated by Yaghi and co-workers. Their strategy was to use $\{Zn_4O(CO_2)_6\}$ octahedral units and polyaromatic carboxylate ligands (Figure 1.10) to assemble extended

network structures with high surface areas and permanent porosity (Figure 1.11).⁸³ For instance, by combining octahedral $\{Zn_4O(CO_2)_6\}$ units and large triangular tricarboxylate ligands, MOFs exhibiting exceptional porosity were generated. Examples include $[Zn_4O(BTB)_2]$ (MOF-177, $BTB^{3-} = 4,4',4''\text{-benzene-1,3,5-triyl-tribenzoate}$) (Figure 1.11), $[Zn_4O(BBC)_2]$ (MOF-200, $BBC^{3-} = 4,4',4''\text{-[benzene-1,3,5-triyl-tris(benzene-4,1-diyl)]tribenzoate}$) and $[Zn_4O(BTE)(BPDC)]$ (MOF-210, $BTE^{3-} = 4,4',4''\text{-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoate}$ and $BPDC^{2-} = \text{biphenyl-4,4'-dicarboxylate}$).⁸⁵ MOF-177 shows a surface area of $4500 \text{ m}^2 \text{ g}^{-1}$ and has a hydrogen gas uptake capacity of 7.5 wt % at 77 K.⁸⁵

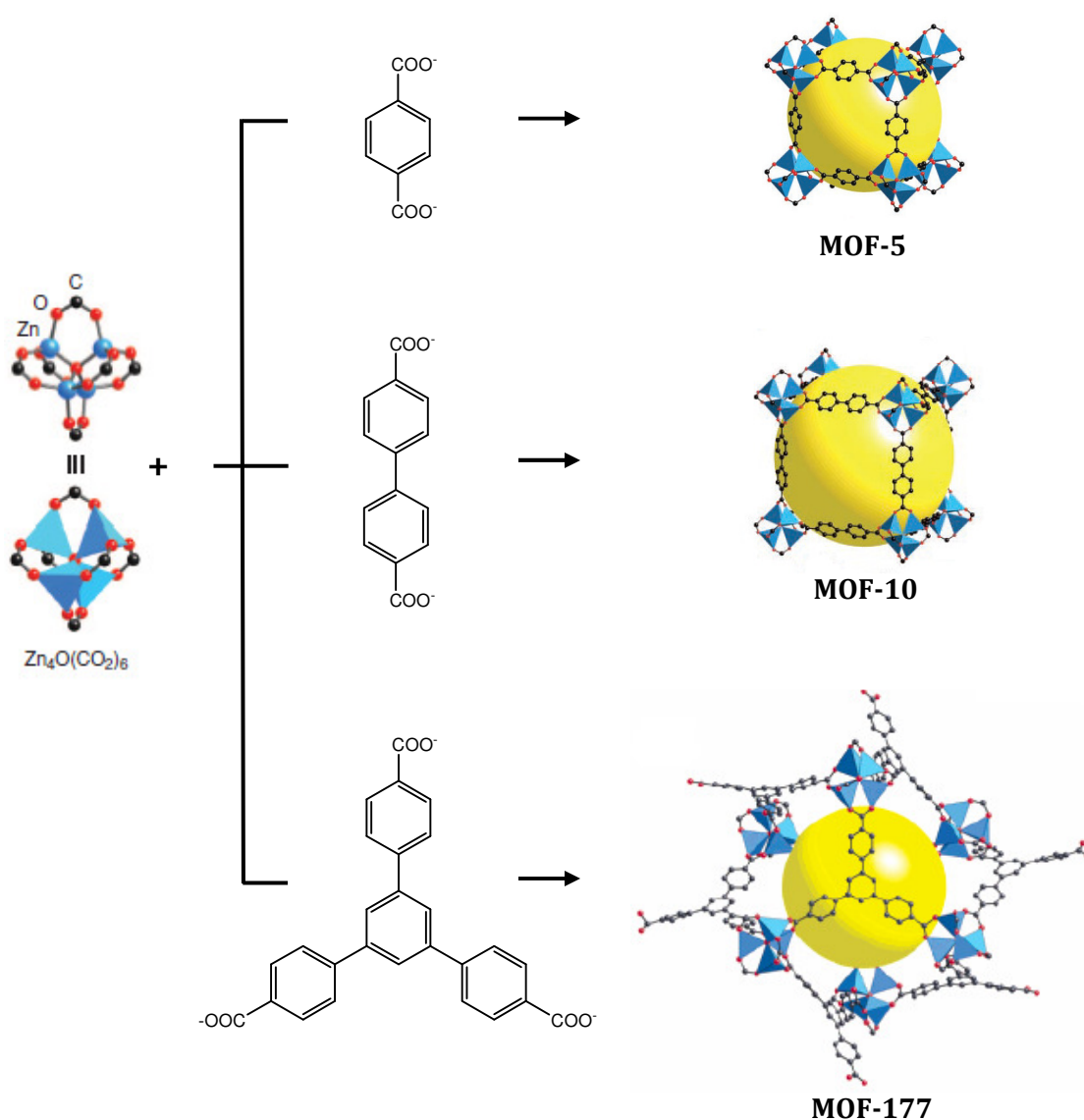


Figure 1.11 – Representation of the reticular synthesis concept which can be applied to prepare metal-organic frameworks.⁸³⁻⁸⁵

Current developments have led to the formation of metal-organic frameworks with ultrahigh surface areas. For instance, $[\text{Cu}_3(\text{L}^{6-}_{(109)})(\text{H}_2\text{O})_3]_n$ (NU-109, $\text{LH}_{6(109)} = 1,3,5\text{-tris}[(1,3\text{-carboxylic acid-5-(4-(ethynyl)phenyl))butadiynyl}]$ -benzene, Figure 1.12) and $[\text{Cu}_3(\text{L}^{6-}_{(110)})(\text{H}_2\text{O})_3]_n$ (NU-110, $\text{LH}_{6(110)} = 1,3,5\text{-tris}[(1,3\text{-carboxylic acid-5-(4-(ethynyl)phenyl))ethynyl}]$ -benzene) display the highest surface areas reported to date ($\sim 7000 \text{ m}^2 \text{ g}^{-1}$).⁸²

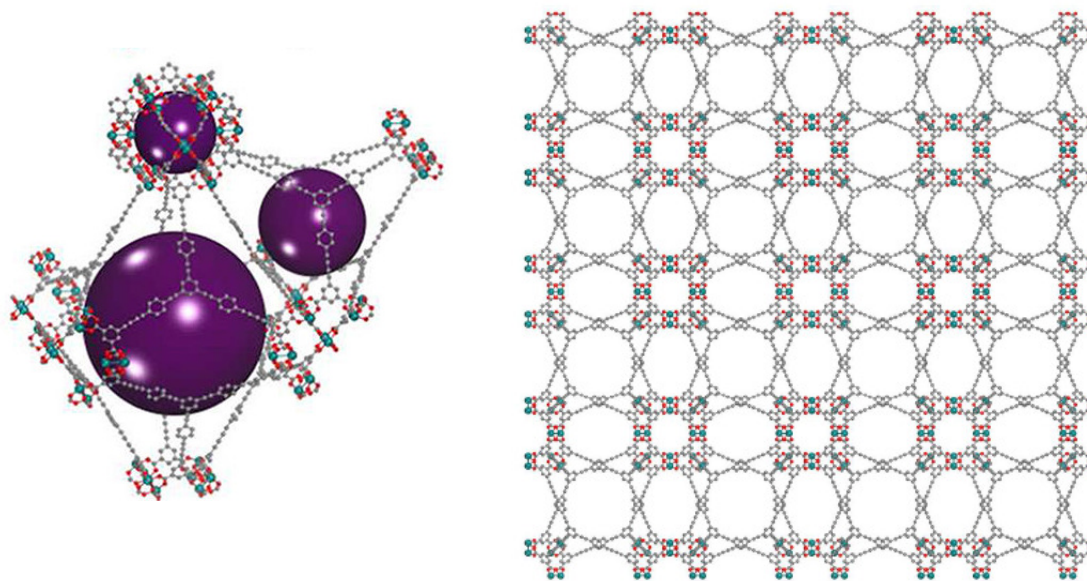


Figure 1.12 – NU-109 showing the presence of different types of cages within the structure and the packing arrangement viewed in the direction of the crystallographic *a*-axis.⁸²

The striking increase of the surface areas reported for MOFs is primarily due to the development of new SBUs with extended structures and multiple binding sites. However, it is to a certain extent surprising that the vast number of existing POM clusters have not yet been systematically exploited as building blocks for MOFs. Only a very limited number of polyoxometalate metal–organic frameworks (P-MOFs) have been reported.^{80, 88, 89} P-MOFs are hybrid organic-inorganic compounds that might be obtainable by functionalisation of POMs with rigid organic ligands. They may be regarded as a new generation of solid-state materials with promising attributes for advanced applications in the areas of gas storage materials and catalysis.⁸⁰ In contrast to traditional POMs, P-MOFs might provide additional functionalities arising from their organic components. Highly ordered and amendable cavities could give rise to shape-selectivity and may impact directly on important catalytic acid-base and redox processes.

1.3 MASS SPECTROMETRY IN COORDINATION CHEMISTRY

Mass spectrometry (MS) is a very powerful analytical technique used for both quantitative and qualitative investigations of a wide range of compounds ranging from small inorganic and organic molecules to biological macromolecules. MS technologies have faced huge progress in the past 20 years, leading to the development of highly sensitive mass spectrometers.⁹⁰⁻⁹²

The ability of MS to be used to analyse complex systems and labile solution species is due to the advances in the development of soft ionisation techniques such as electrospray ionisation (ESI) and matrix-assisted laser desorption ionisation (MALDI) processes. Furthermore, the sensitivity of a mass spectrometer is correlated to the mass analyser used, which separates the ions according to their mass-to-charge ratio (m/z). The most commonly used analysers are quadrupole and time of flight mass analysers. Different ionisation techniques and mass analysers have different advantages and disadvantages that one has to be aware of when performing MS analyses. For a specific class of compounds or for particular applications it is a requirement to choose the optimal ionisation technique and mass analyser.^{90, 91}

For instance, electrospray ionisation mass spectrometry (ESI-MS) has been successfully applied in the study of coordination compounds. The growing interest in the use of ESI-MS to characterise metal complexes arises from the simplicity of the technique which is capable of transferring non-volatile solution phase ions to the gas phase.⁹¹⁻⁹⁴ Furthermore, the soft character of ESI permits the transfer of the ions in the gas phase with minimum fragmentation, reflecting the actual species present in the solution. ESI-MS is a sensitive and direct method of detection that enables the analysis of highly diluted solutions and the examination of several species in solution simultaneously.^{91, 94, 95} Another attractive feature of ESI-MS is the flexibility with regard to the sample medium, as a wide range of solvents can be used and a wide pH range can be tolerated.⁹³

Mass spectrometry investigations of complex coordination clusters is furthermore facilitated by the large number of natural isotopes that some of the elements possess. As a result, the mass spectrum of metal complexes displays characteristic wide distributions of isotopic envelopes that can be used for the interpretation of the spectra. Thus, the isotopic distribution gives the possibility to identify the presence and the number of polyisotopic

metals by comparison of experimental spectra with theoretically calculated isotopic patterns.^{93, 95, 96} The shape of the isotopic envelope is determined by the type and number of polyisotopic elements present. A high number of polyisotopic elements, e.g. molybdenum (^{92}Mo , 14.8%; ^{94}Mo , 9.3%; ^{95}Mo , 15.9%; ^{96}Mo , 16.7%; ^{97}Mo , 9.6%; ^{98}Mo , 24.1%; ^{100}Mo , 9.6%) and tungsten isotopes (^{180}W , 0.1%; ^{182}W , 26.5%; ^{183}W , 14.3%; ^{184}W , 30.6%; ^{186}W , 28.4%) even can give rise to a Gaussian type distribution of the resulting isotopic envelope (see Figure 1.13). Some other non-metallic elements have distinct isotopic distributions that can be used as “fingerprints” for their identification, i.e. chlorine (^{35}Cl , 75.8%; ^{37}Cl , 24.2%) and bromine atoms (^{79}Br , 50.7%; ^{81}Br , 49.3%).^{95, 97}

An early example that demonstrated that a polynuclear cluster can be examined by ESI-MS was conducted by Colton and co-workers in 1992 using the heteropolyoxomolybdate $(\text{NEt}_4)_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ dissolved in acetonitrile solution. The study demonstrated that the intact $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ cluster ion can be observed in the mass spectrum and its isotopic pattern was compared with the calculated spectrum (Figure 1.13).⁹⁷

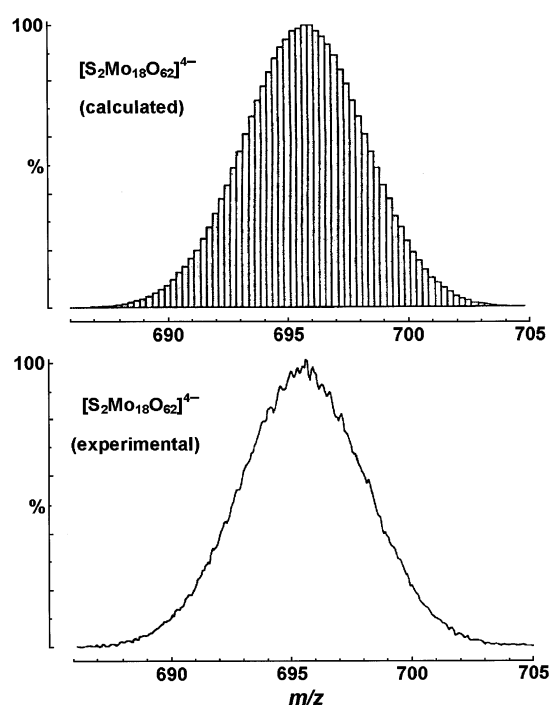


Figure 1.13 – Comparison of calculated and experimental negative-ion ESI mass spectral isotope pattern for $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$.⁹⁷

In addition to the here discussed main advantages of ESI-MS, a number of potential limitations must also be considered for data interpretation. Limitations when investigating

solution processes may include artefacts or signals in the mass spectrum due to ionisation processes or gas-phase reactions such as adduction, fragmentation or polymerisation, as well as redox processes.^{92, 93}

Until very recently, mass spectrometry in coordination chemistry was mainly used as a complementary tool for the characterisation of novel compounds. Such studies involved structural characterisations of metal complexes dissolved in various solvent systems.^{92, 93, 95} In these studies, MS was assisted by other techniques such as NMR, X-ray crystallography, electrochemistry, etc.^{92, 96} On the other hand, recent directions of MS demonstrate that this technique is also capable of monitoring reaction mixtures in order to investigate the formation processes and reactivity of complex coordination clusters in solution.⁹⁸⁻¹⁰⁰ Only a few studies of this kind were carried out to date. An early example of real-time monitoring of reacting polyoxometalate species in solution by ESI-MS is represented by the work performed by Howarth *et al.* in 1997.¹⁰¹ Aqueous solutions of two separate tungsten and molybdenum complexes were mixed and the ESI-MS spectra of the reaction mixture were recorded over a time period of 45 min (Figure 1.14). The experimental results showed that the two anions $[\text{HPW}_{12}\text{O}_{40}]^{2-}$ and $[\text{HPMo}_{12}\text{O}_{40}]^{2-}$ interchange metal ions with one another. The most intense signal in the mass spectrum recorded after 2 min after the solutions were mixed is due to the $[\text{HPW}_9\text{Mo}_3\text{O}_{40}]^{2-}$ ion. During a time period of 45 min the relative distribution of the metal species for the anions reaches an equilibrium and the most intense signal in the mass spectrum corresponds to the $[\text{HPW}_6\text{Mo}_6\text{O}_{40}]^{2-}$ ion.¹⁰¹

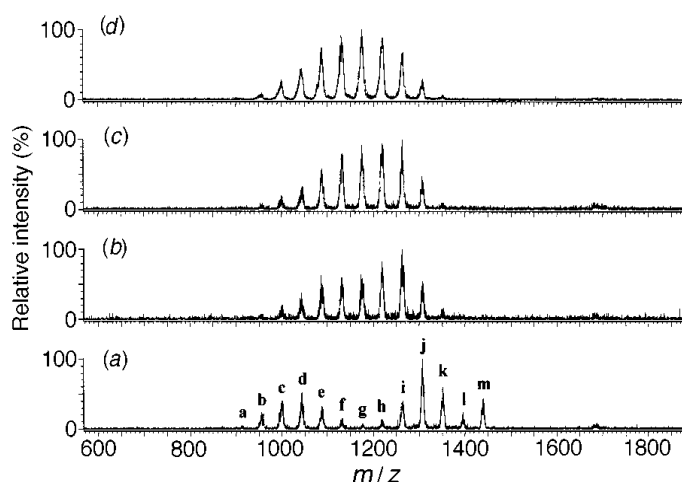


Figure 1.14 – The ESI mass spectra of mixtures of phosphododecatungstate and phosphododecamolybdate acquired (a) 2, (b) 17, (c) 32 and (d) 47 min after the two solutions were initially mixed. Labels **a-m** correspond, in order, to the formulae $[\text{HPW}_n\text{Mo}_{12-n}\text{O}_{40}]^{2-}$ with $n = 0$ to 12.¹⁰¹

These experiments indeed demonstrated that it is possible to monitor formation and possible rearrangement processes of polyoxometalate species that occur in solution.

The power of MS technique in the polyoxometalate field has recently been highlighted by Cronin *et al.*, who used it to study the self-assembly processes of polyoxometalate systems that emerge in solution. For example, cryospray ionisation mass spectrometry (CSI-MS) was used to analyse the reaction solution of the compound $((n\text{-C}_4\text{H}_9)_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}]_n$.⁹⁸

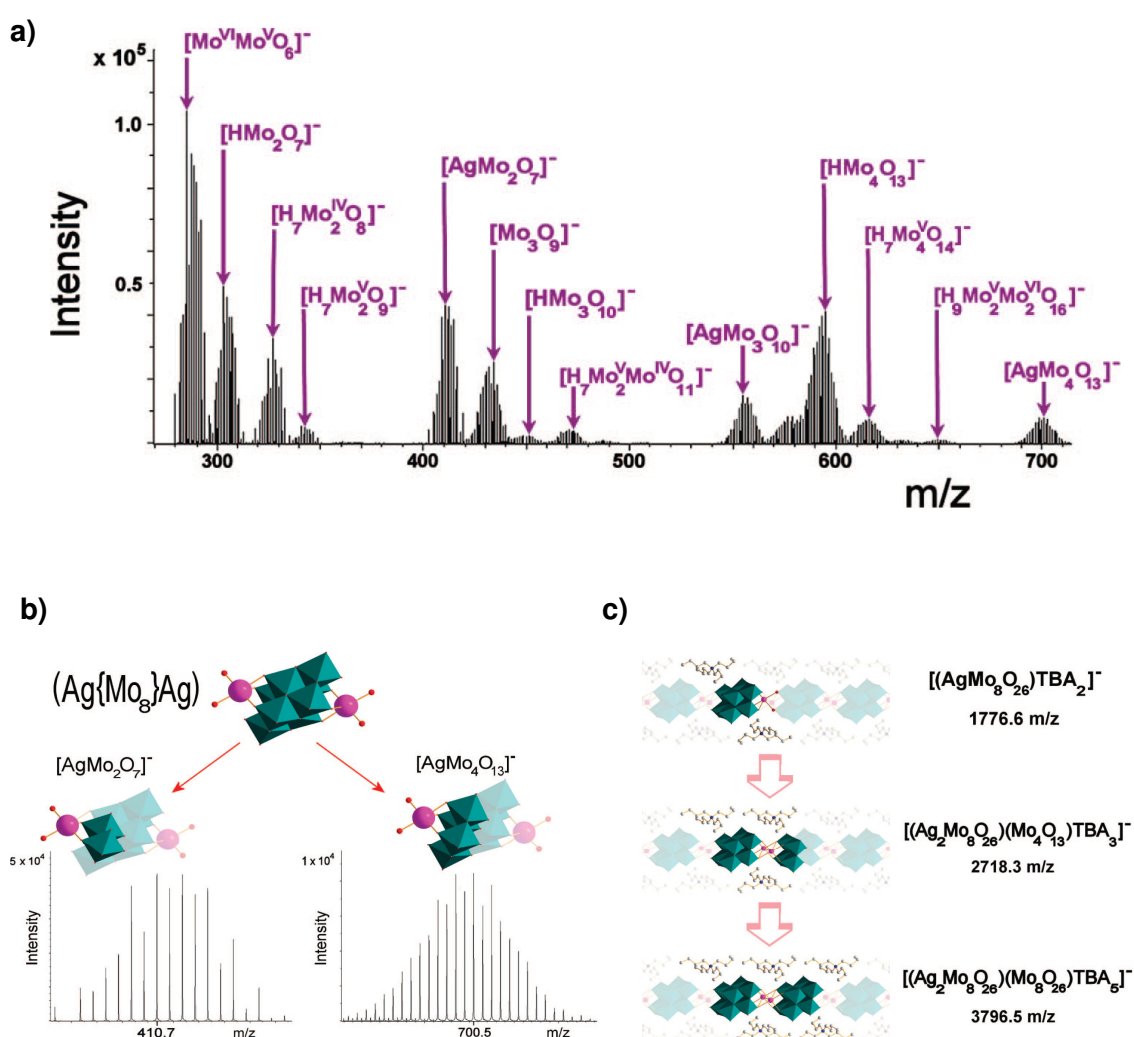


Figure 1.15 – (a) CSI-MS data collected of the reaction solution of $((n\text{-C}_4\text{H}_9)_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}]_n$; (b) Representation of the $[\text{AgMo}_2\text{O}_7]^-$ and $[\text{AgMo}_4\text{O}_{13}]^-$ species as building blocks of the $(\text{Ag}\{\text{Mo}_8\}\text{Ag})$ synthon showing the isotopic envelopes for their corresponding mass peaks at 410.7 m/z and 700.5 m/z, respectively; (c) Structural representation of the higher mass fragments identified within the CSI-MS analysis of the reaction solution of $((n\text{-C}_4\text{H}_9)_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}]_n$.⁹⁸

ESI-MS allowed access to direct observation of the rearrangement of Lindqvist anions into the (Ag{Mo₈}Ag) synthon units and subsequent addition of the organic cations. The mass spectrum of the reaction mixture is presented in Figure 1.15 and reveals the presence of six monoanionic series: [Mo_mO_{3m}][−] (*m* = 2, 3 or 5); [HMo_mO_{3m+1}][−] (*m* = 2 to 6); [H₇Mo_mO_{3m+2}][−] (*m* = 2 to 6); [H₇Mo_mO_{3m+3}][−] (*m* = 2 to 5); [H₉Mo_mO_{3m+4}][−] (*m* = 2 to 6); [AgMo_mO_{3m+1}][−] (*m* = 2 to 4). The detection of the [AgMo₂O₇][−] (signal at *m/z* = 410.7 a.m.u.) and [AgMo₄O₁₃][−] (signal at *m/z* = 700.5 a.m.u.) fragments of the (Ag{Mo₈}Ag) synthon units are particularly important in order to understand the formation of the compound. Also the detection of the species [(AgMo₈O₂₆)TBA₂][−] (signal at *m/z* = 1776.6 a.m.u.), [(Ag₂Mo₈O₂₆)(Mo₄O₁₃)TBA₃][−] (signal at *m/z* = 2718.3 a.m.u.), and [(Ag₂Mo₈O₂₆)(Mo₈O₂₆)TBA₅][−] (signal at *m/z* = 3796.5 a.m.u.) (Figure 1.15), containing an increasing number of organic cations is of great importance. The analysis demonstrates that the nuclearity of the chain-type compound increases with the number of organic cations present highlighting that the formation process involves “monomeric” units that assemble into larger fragments which eventually lead to crystals of ((*n*-C₄H₉)₄N)_{2n}[Ag₂Mo₈O₂₆]_{*n*}. The experimental results also demonstrate how organic cations can impose structure-directing effects on POM structures that assemble in solution.⁹⁸

A related study, reported in 2011, employs electrospray ionisation mass spectrometry (ESI-MS) to monitor in real-time the self-assembly of an organic-inorganic POM cluster. The reaction system involves the rearrangement of [α -Mo₈O₂₆]^{4−} into ((*n*-C₄H₉)₄N)₃[MnMo₆O₁₈((OCH₂)₃CNH₂)₂], a Mn-Anderson type cluster (Figure 1.16).⁹⁹ ESI-MS spectra of the reaction mixture containing ((*n*-C₄H₉)₄N)₃[MnMo₆O₁₈((OCH₂)₃CNH₂)₂] were recorded at different time intervals over the course of the reaction (~ 30 h), in order to identify different fragment ions present in the reaction mixture. A very important observation of the study is that the intensity of the signal attributed to the reactant ions decreases exponentially, whilst the intensity of the product signal increases at a lower rate over the course of the reaction. This suggests that the mechanism of formation of [Mn^{III}Mo₆O₁₈((OCH₂)₃CNH₂)₂TBA₂][−] proceeds through further intermediates. ESI-MS studies allowed the identification of intermediate fragment ions involved in the rearrangement of [α -Mo₈O₂₆]^{4−} into ((*n*-C₄H₉)₄N)₃[MnMo₆O₁₈((OCH₂)₃CNH₂)₂]. It was proposed that the rearrangement initially results in the formation of the [Mo₄O₁₃]^{2−} cluster species (i.e. [Mo₄O₁₃Na][−], *m/z* = 614.6 a.m.u. and [Mo₄O₁₃TBA][−], *m/z* = 833.8 a.m.u.) representing half-fragments of the {Mo₈} clusters. It is believed that further decomposition to smaller fragment ions (i.e. [Mo₂O₇H][−], *m/z* = 304.8 a.m.u. and [Mo₃O₁₀TBA][−], *m/z* =

690.0 a.m.u.) which subsequently bind to tris(hydroxymethyl)aminomethane ligands (TRIS) ($[\text{Mo}_2\text{O}_5((\text{OCH}_2)_3\text{CNH}_2)]^-$ $m/z = 389.8$ a.m.u.), manganese ions ($[\text{Mn}^{\text{III}}\text{Mo}_3\text{O}_8((\text{OCH}_2)_3\text{CNH}_2)_2]^-$ $m/z = 706.7$ a.m.u.), and anionic molybdate units, leads to the formation of the final Mn-Anderson-TRIS cluster, $[\text{Mn}^{\text{III}}\text{Mo}_6\text{O}_{18}((\text{OCH}_2)_3\text{CNH}_2)_2\text{TBA}_2]^-$ ($m/z = 1640.0$ a.m.u.) (Figure 1.16).⁹⁹

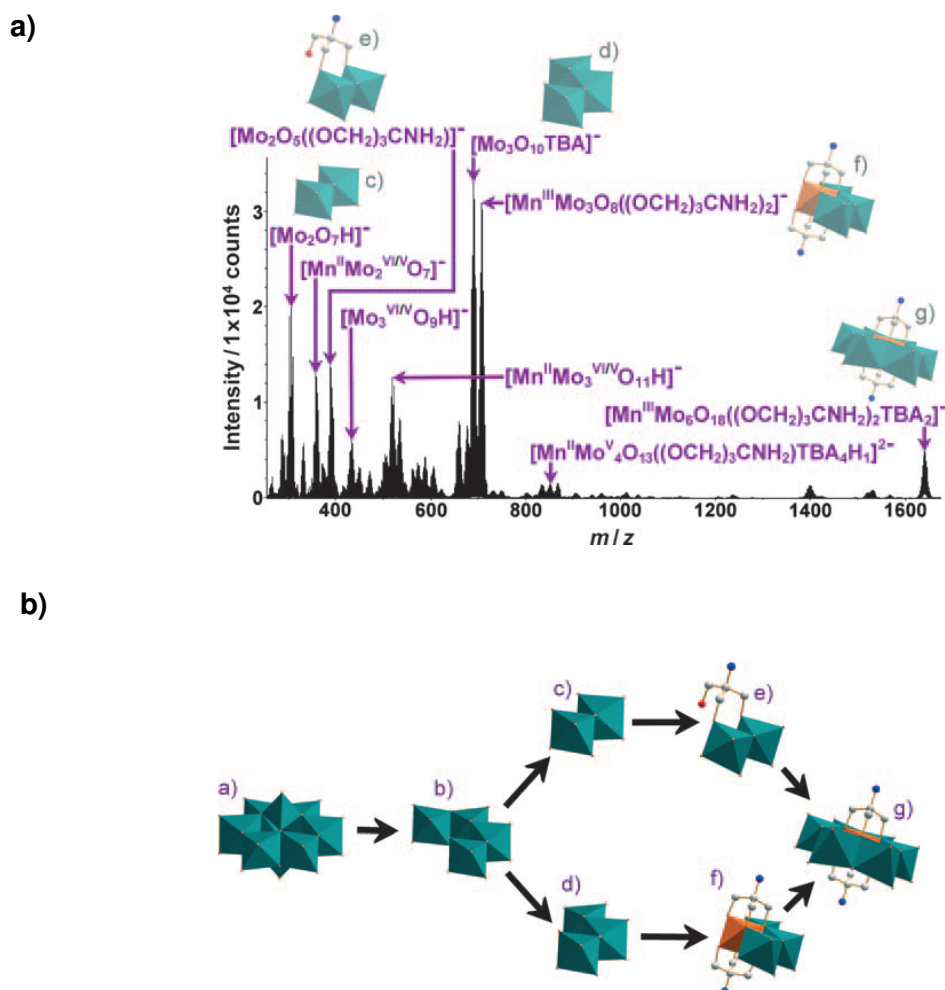


Figure 1.16 – (a) ESI mass spectrum recorded of the reaction mixture of $((n\text{-C}_4\text{H}_9)_4\text{N})_3[\text{MnMo}_6\text{O}_{18}((\text{OCH}_2)_3\text{CNH}_2)_2]$; spectrum was recorded after it has been heated at reflux (80°C) for approximately 30 h; (b) Illustration to visualize the prominent, intermediate fragment ions identified in this study (labelled b-f), which are involved in the rearrangement of the $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$ anion (labelled a), into the symmetrical Mn-Anderson anion $[\text{MnMo}_6\text{O}_{18}((\text{OCH}_2)_3\text{CNH}_2)_2]^{3-}$ (labelled g). Structures (b-f) represent the following fragment ions identified in the ESI-MS investigations: b) $[\text{Mo}_4\text{O}_{13}\text{TBA}]^-$, c) $[\text{Mo}_2\text{O}_7\text{H}]^-$, d) $[\text{Mo}_3\text{O}_{10}\text{TBA}]^-$, e) $[\text{Mo}_2\text{O}_5((\text{OCH}_2)_3\text{CNH}_2)]^-$, f) $[\text{Mn}^{\text{III}}\text{Mo}_3\text{O}_8((\text{OCH}_2)_3\text{CNH}_2)_2]^-$. Colour scheme: Mo green polyhedra, Mn orange polyhedra, O red, N blue, C gray spheres.⁹⁹

Mass spectrometry proves to be an indispensable tool in coordination chemistry which when used in combination with other techniques (i.e. X-ray crystallography, NMR

spectroscopy, electrochemistry, etc.) provides important information about the analyte (e.g. structure, purity and composition). Most remarkably the analytical technique provides the possibility of exploring real-time growth reactions of complex coordination clusters.^{91, 92, 100}

1.4 MOLECULAR MAGNETISM

Magnetic materials are considered to be indispensable in our daily lives finding applications in electronics, acoustic and telecommunication devices, data storage and readout devices, diagnostic equipment and medical therapy, etc.¹⁰²

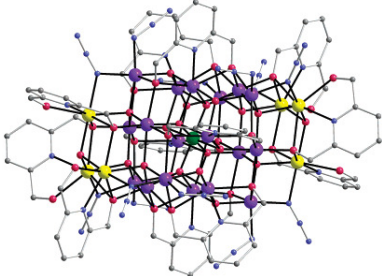
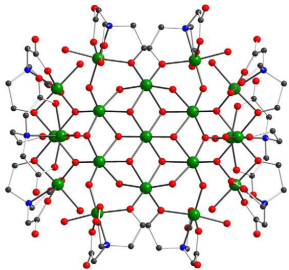
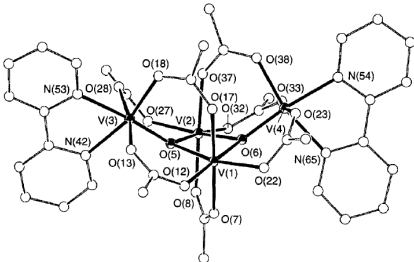
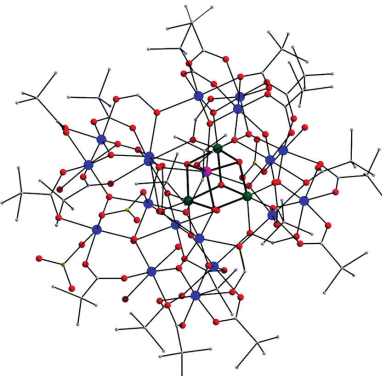
Molecular magnetism is an interdisciplinary area that deals with the design, synthesis, and characterisation of molecular-based magnetic materials.¹⁰³

Single molecule magnets (SMMs) are isolated molecules with a finite number of interacting spin centres. SMMs represent a class of compounds that combine a defined spin ground state (S) and a large and negative magnetic anisotropy (D). This type of compound shows slow relaxation of the magnetisation at low temperatures, due to the large spin reversal barrier (U).¹⁰²⁻¹⁰⁴

SMMs are fascinating materials as they show magnetic hysteresis effects as classical magnets do, but at the same time their nanoscopic nature gives rise to quantum effects. The combination of classical and quantum mechanical phenomena makes SMMs highly attractive for theoretical studies.^{102, 105} Furthermore, the well defined spin or quantum states of SMMs may lead to future prospective applications in the IT sector whereby information could be stored at high density using a single molecule. This conceptional approach could satisfy the need for the miniaturisation of electronic devices and increase the data storage capacity.^{102, 105, 106}

The most representative class of SMMs is based on manganese clusters.^{105, 107-109} Other large molecular clusters such as iron-oxo clusters¹¹⁰⁻¹¹², polyoxovanadates¹¹³⁻¹¹⁶ or lanthanide based compounds¹¹⁷⁻¹¹⁹ have also shown to give rise to SMM behaviour (Table 1.1).

Table 1.1 Examples of single molecule magnets.¹²⁰

Molecule	<i>S</i>	<i>D</i> (cm ⁻¹)	Ref.
$[\text{Mn}_{25}\text{O}_{18}(\text{OH})_2(\text{N}_3)_{12}(\text{pdm})_6(\text{pdmH})_6](\text{Cl})_2$ (pdmH ₂ = pyridine-2,6-dimethanol)  {Mn₂₅}	51/2	- 0.02	[109]
$[\text{Fe}_{19}\text{O}_6(\text{OH})_{14}(\text{metheidi})_{10}(\text{H}_2\text{O})_{12}]^+$ (metheidi = N-(1-hydroxymethylethyl)iminodiacetic acid)  {Fe₁₉}	33/2	- 0.04	[111]
$[\text{V}_4\text{O}_2(\text{EtCO}_2)_7(\text{bpy})_2]^+$ (bpy = 2,2'-bipyridine)  {V₄}	3	- 1.5	[113]
$[\text{Mn}_{21}\text{DyO}_{20}(\text{OH})_2(\text{Bu}^t\text{CO}_2)_{20}(\text{HCO}_2)_4(\text{NO}_3)_3(\text{H}_2\text{O})_7]$  {Mn₂₁Dy}	11	- 0.4	[119]

The first reported example of a single-molecule magnet is a dodecanuclear manganese cluster, $[\text{Mn}^{\text{IV}}_4\text{Mn}^{\text{III}}_8\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ (Figure 1.17), synthesised by Lis in 1980¹²¹ and intensively studied in the 1990s.^{106, 122, 123} In 1993 Novak *et al.* reported that the magnetisation of the $\{\text{Mn}_{12}\}$ cluster is highly anisotropic and that the relaxation time of the magnetisation becomes very long below 4K, giving rise to pronounced hysteresis effects (Figure 1.17).¹²³ The compound possesses a large spin ground state which arises from antiferromagnetic interactions between the spins of the four Mn^{IV} ions ($S = 3/2$) and the spins of the eight Mn^{III} ions ($S = 2$) to give a total spin of $S = [(4 \times 3/2) - (8 \times 2)] = 10$. The magnetisation relaxation half-life of the $\{\text{Mn}_{12}\}$ cluster is more than 2 months at 2 K. Unfortunately the relaxation time of the magnetisation decreases dramatically with increasing temperature and the hysteresis effects are no longer observed above 4 K.^{103, 104} The hysteresis loop observed for a single crystal at low temperature (Figure 1.17) shows step-like features that occur at values of the applied field where the energies of different spin states coincide. At these particular values of the field the relaxation from one spin state to another is enhanced, due to quantum tunnelling of the magnetisation (QTM) through the energy barrier U .^{104, 106}

Since the discovery of the first SMM, significant research work has been devoted to the development of molecule-based magnets that display spin reversal barriers (U) large enough to be able to show magnetic hysteresis effects at higher temperature.^{102, 104}

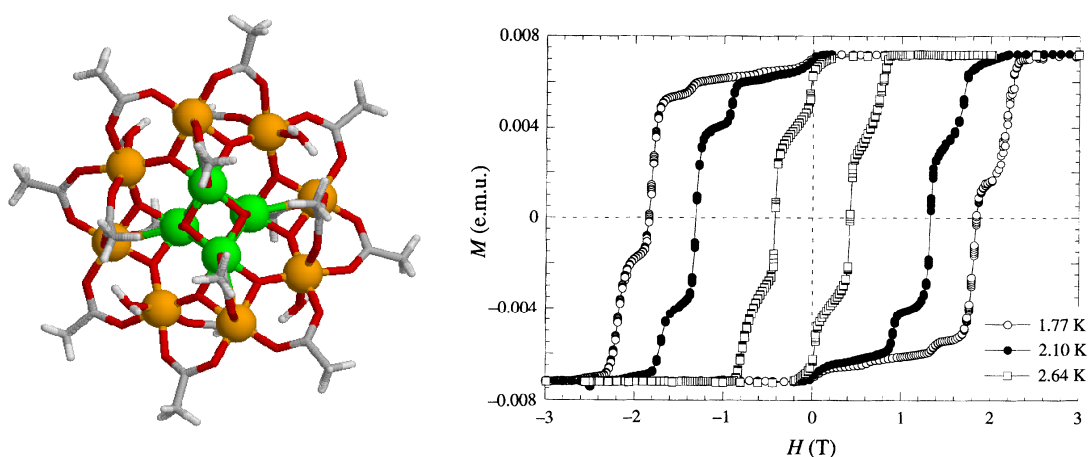


Figure 1.17 – The crystal structure of $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ and its magnetisation hysteresis loops measured at low temperature between magnetic fields of 5

Even though an increasing number of metal complexes have been demonstrated to behave as SMMs, $\{\text{Mn}_{12}\}$ still remains the SMM with the most striking features.

The largest SMM yet reported is a $\{\text{Mn}_{84}\}$ cluster, $[\text{Mn}_{84}\text{O}_{72}(\text{O}_2\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{42}(\text{OH})_6]$, synthesised by Christou *et al.* in 2004 (Figure 1.18).¹⁰⁵ The cluster adopts a circular torus motif with a diameter of ~ 4.2 nm, a height of ~ 1.2 nm and an inner free space with a diameter of ~ 1.9 nm. It has a ground state spin of $S = 6$ and exhibits both magnetic hysteresis and QTM.^{103, 105}

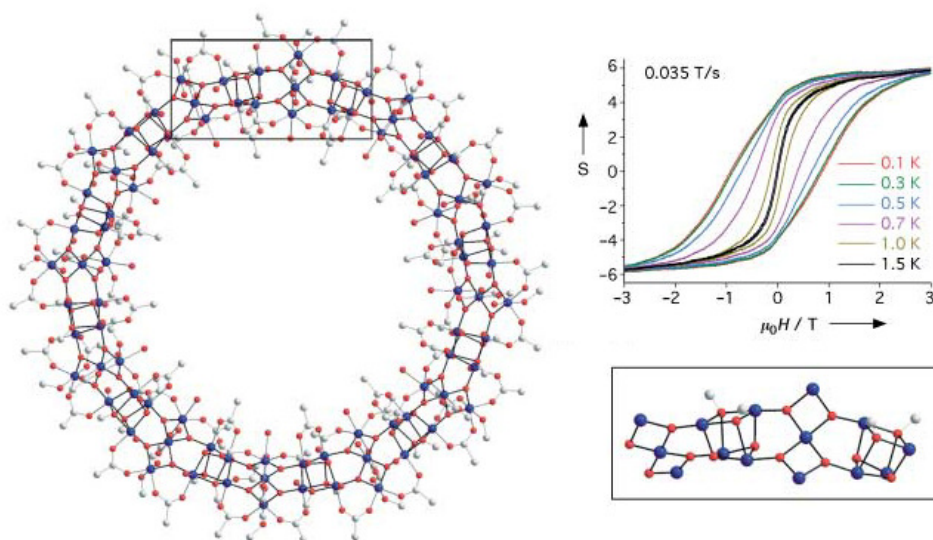


Figure 1.18 – The crystal structure of the $\{\text{Mn}_{84}\}$ torus. The rectangle shows the repeating $\{\text{Mn}_{14}\}$ unit that represents the contents of the asymmetric unit. Magnetisation hysteresis loops measured on single crystals of $\{\text{Mn}_{84}\}$ at low temperature showing SMM behaviour.¹⁰⁵

Another interesting SMM is a $\{\text{Mn}_6\}$ complex, $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh}(\text{Me})_2)_2(\text{EtOH})_6]$ ($\text{Et-saoH}_2 = 2\text{-hydroxyphenylpropane oxime}$), that exhibits the highest energy barrier for the reversal of the magnetisation $U_{\text{eff}} = 86.4$ K and a blocking temperature of ~ 4.5 K. This complex breaks the record held by the $\{\text{Mn}_{12}\}$ family which was known to show the highest blocking temperatures (~ 3.5 K). $\{\text{Mn}_6\}$ has a ground state spin of $S = 12$ and exhibits both magnetic hysteresis and QTM (Figure 1.19).¹²⁴

The greatest spin ground state of $S = 83/2$ was achieved in a $\{\text{Mn}_{19}\}$ complex, $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu_4\text{-O})_8(\mu_3, \eta^1\text{-N}_3)_8(\text{HL})_{12}(\text{MeCN})_6]\text{Cl}_2 \cdot 10\text{MeOH} \cdot \text{MeCN}$ ($\text{H}_3\text{L} = 2,6\text{-bis(hydroxymethyl)-4-methylphenol}$), which comprises twelve Mn^{III} ($S = 2$) and seven Mn^{II} ($S = 5/2$) ions. Despite this large spin, $\{\text{Mn}_{19}\}$ does not exhibit SMM behaviour due to a very small positive D .¹²⁵ Anisotropy can be introduced in the $\{\text{Mn}_{19}\}$ complex by

replacing the central Mn^{II} with a Dy^{III} ion to generate a $\{\text{Mn}_{18}\text{Dy}\}$ complex, $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_6\text{Dy}^{\text{III}}(\mu_4\text{-O})_8(\mu_3\text{-Cl})_{6.5}(\mu_3\text{-N}_3)_{1.5}(\text{HL})_{12}(\text{MeOH})_6]\text{Cl}_3 \cdot 25\text{MeOH}$, with the same core topology but showing SMM behaviour (Figure 1.20).¹¹⁷

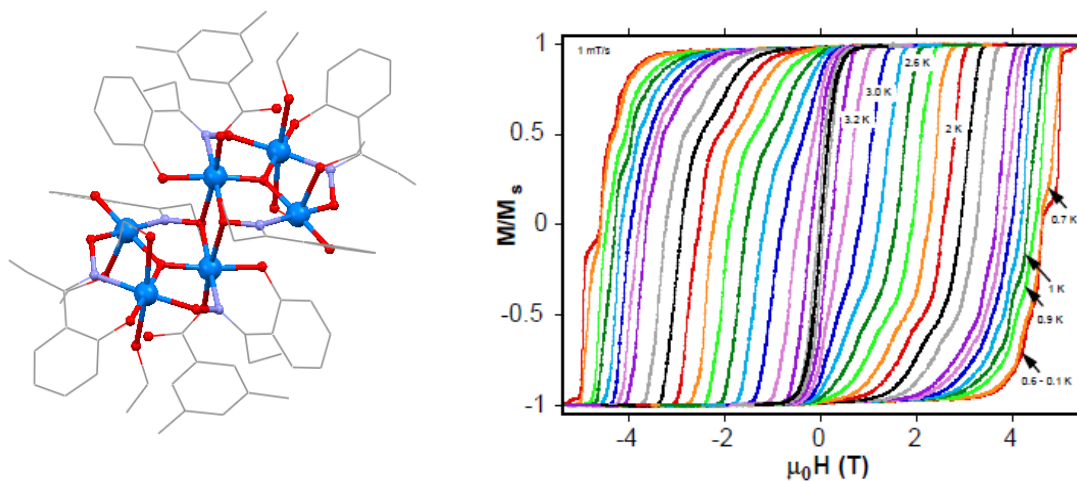


Figure 1.19 – The crystal structure of the $\{\text{Mn}_6\}$ complex and its hysteresis loops measured at a constant field sweep rate of 1 mT s^{-1} at low temperature.¹²⁴

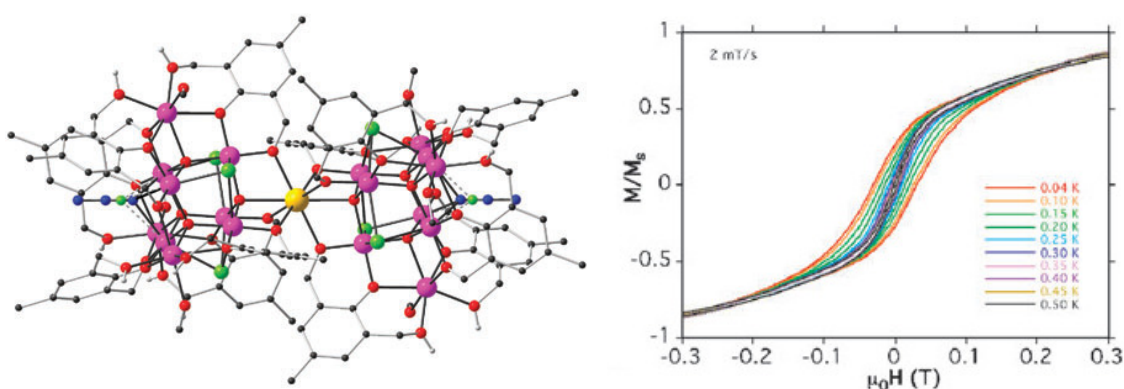


Figure 1.20 – The crystal structure of the $\{\text{Mn}_{18}\text{Dy}\}$ complex and its hysteresis loops measured at a field scan rate of 2 mT s^{-1} in the temperature range 0.5–0.04 K.¹¹⁷

1.5 AIMS AND OBJECTIVES

The main aim of this research project is to synthesise hybrid organic-inorganic materials using a series of mono- and trifunctional organophosphonate and -arsonate ligands. These products could possess advantageous properties which could lend themselves to applications in the areas of catalysis, gas sorption and separation, magnetism. The research developed in the course of this project is focused on the solution behaviour, synthesis and structure elucidation of novel hybrid organic-inorganic materials.

In the first part of the work we set out to explore the formation of mixed-valent molybdates in the presence of organoarsonates and -phosphonates. As already discussed in the previous sections of the introduction, early transition metal ions in their higher oxidation states have the ability to polarise terminal O^{2-} ligands efficiently, often resulting in stable purely ‘inorganic’ oxo-clusters.²¹ The terminal metal-oxygen bonds limit the functionalisation of these clusters and advanced applications, for instance in catalysis are hampered by the limited availability of hybrid polyoxometalates that contain organic molecules. Organophosphonates and -arsonates appear to be good candidates for POM functionalisation as they have tetrahedral binding sites which display geometrical and electronic similarities to metal-oxygen units in polyoxometalates. Functionalisation of spherical clusters with rigid polyphosphonate and -arsonate ligands that point in defined directions of space might link the clusters into polyoxometalate metal-organic frameworks (P-MOFs) that are highly desired for catalysis, gas sorption and separation studies.

The second part of this project is focused on the preparation of novel polynuclear manganese clusters stabilised by organophosphonates. The resulting coordination clusters may display interesting magnetic properties. The chemistry of manganese coordination clusters has drawn much attention due to their potential to exhibit properties of single molecule magnets. Carboxylate ligands have previously been intensively exploited to stabilise high-nuclearity molecular compounds of manganese, whereas organophosphonates have rarely been employed.¹²⁶ However, organophosphonates appear to be good candidates to stabilise such species as they are versatile ligands that show high binding affinities towards metal ions.^{67, 127-129}

A third aspect of the project explores the use of rigid extended triphosphonate ligands for the formation of supramolecular coordination networks. Porous hybrid organic-

inorganic materials are of particular interest for potential applications in catalysis, gas storage and separation. Several classes of MOFs have been explored, of which the carboxylate-based compounds are the most studied. This class of MOFs may possess high surface areas and uniform pore size distribution, but unfortunately the structural stability of many MOFs can be quite limited. This prompted us to explore the preparation of network structures using organic triphosphonate ligands. Organophosphonates are known to form stronger bonds with metal ions than carboxylates and therefore have a greater potential to form robust porous solids.⁶⁷ Furthermore, the multidentate binding mode of the triphosphonate ligands makes them ideal for the preparation of hybrid materials with unprecedented topologies or enhanced porosity.

Another aspect of the work aims to investigate the stability, formation processes and the reactivity of complex polynuclear clusters in solution. For this study we decided to take advantage of electrospray ionisation mass spectrometry (ESI-MS) which is a very powerful analytical tool. ESI-MS proved to be very efficient in monitoring complex reaction mixtures in order to gain a better understanding of how polynuclear clusters form and how we can influence the formation processes towards desired materials. Solution studies of polyoxometalates that involve ESI-MS screening of reaction mixtures is still at its infancy, while ESI-MS studies that investigate complex Mn coordination cluster systems have not been reported in the literature. This analytical technique was also applied to investigate the stability of the synthesised compounds in solution, an essential requirement for potential applications, e.g. as homogeneous catalysts.

The organophosphonate and -arsonate ligands used for the preparation of these materials are presented in Figure 1.21.

In order to accomplish the main aims of the research project, we initially set out to attain the following specific objectives:

- To synthesise and characterise rigid polyphosphonate and -arsonate ligands;
- To stabilise supramolecular coordination complexes and networks using organophosphonates and -arsonates;
- To monitor the formation of these compounds *via* mass spectrometry and to investigate the stability of these compounds in solution;
- To structurally characterise the compounds using single crystal and powder X-ray diffraction;

- To investigate the magnetic properties of all relevant compounds;
- To determine other supplemental physicochemical properties (optical properties, thermal stability, surface areas etc.) of the compounds.

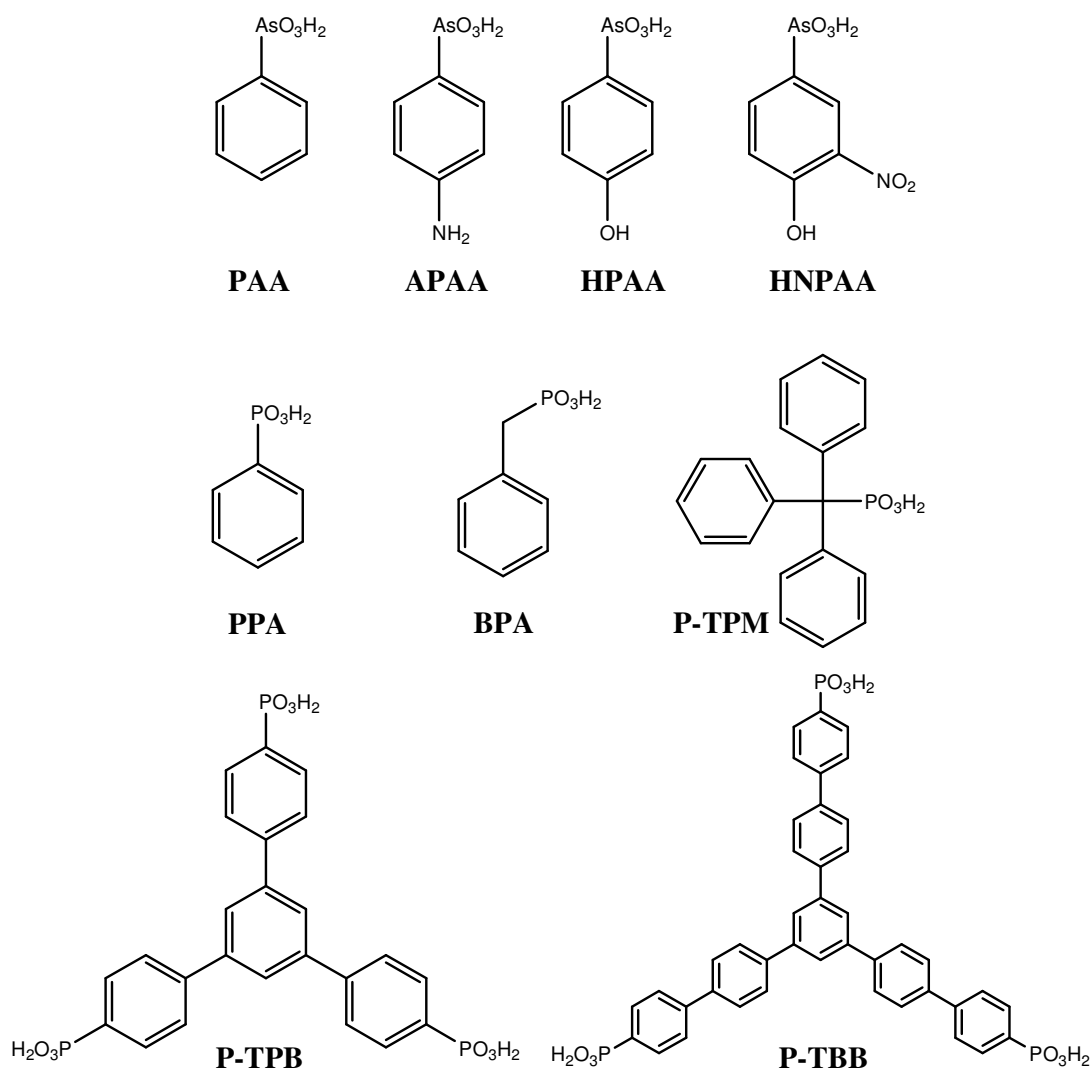


Figure 1.21 – Phosphonate and arsonate ligands used to stabilise supramolecular coordination complexes and networks: PAA – phenylarsonic acid; APAA – (4-aminophenyl)arsonic acid (*p*-arsanilic acid); HPAA – (4-hydroxyphenyl)arsonic acid; HNPA – (4-hydroxy-3-nitrophenyl)arsonic acid; PPA – phenylphosphonic acid; BPA – benzylphosphonic acid; P-TPM – triphenylmethylphosphonic acid; P-TPB – 1,3,5-tris(4-phosphonophenyl)benzene; P-TBB – 1,3,5-tris(4'-phosphonobiphenyl-4-yl)benzene.

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2. HYBRID ORGANIC-INORGANIC POLYOXOMOLYBDATES

2.1 INTRODUCTION AND MOTIVATION

The chemistry of the polyoxometalates (POMs) is one of the most active and rapidly advancing areas of inorganic chemistry.¹⁻⁴ Functionalisation approaches to generate hybrid polyoxometalate structures or advanced inorganic materials remain an ongoing challenge and new synthetic and analytical approaches are pivotal to the progress of the field.²⁻⁵

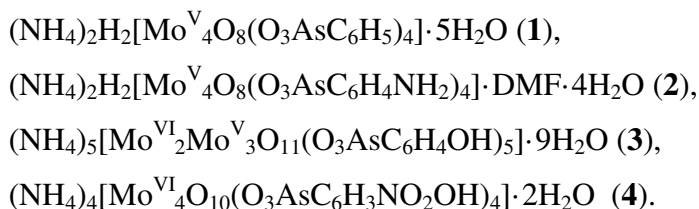
We are interested in the chemistry of hybrid organic-inorganic materials, and we decided to explore the formation of mixed-valent molybdates in the presence of organoarsonates and phosphonates. Hybrid organic-inorganic polyoxomolybdates would combine the characteristics of both the inorganic oxo clusters and the organic moieties resulting in new products with potentially new or even enhanced properties. Organophosphonate and -arsonate stabilised oxo clusters that contain redox-active metal centres are of interest for applications in catalysis.^{2, 6, 7} A limited number of organoarsonate and -phosphonate stabilised molybdates have previously been reported in the literature.⁸⁻¹⁹

Despite an ever increasing interest in POM complexes, it is surprising that their solution behaviour, i.e. formation reactions that often prevail through a set of consecutive condensation reactions, are often fairly poorly understood. However, speciation within POM solutions is not only important to devise rational synthetic approaches to desired products but it is moreover a pre-requisite to improve catalytic processes that draw on the active sites or electronic characteristics of POMs. Recent accounts demonstrate that electrospray ionisation mass spectrometry (ESI-MS) provides a very powerful analytical tool to characterise the formation and the reactivity of complex polyoxometalate clusters in solution.²⁰⁻³³

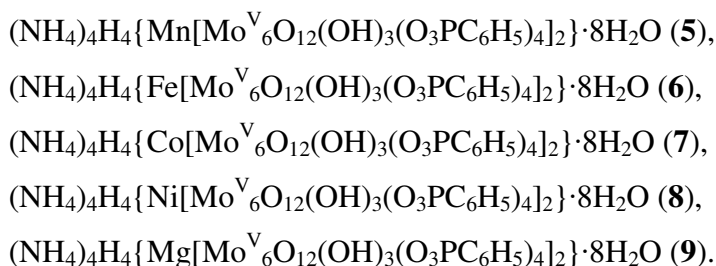
We decided to use electrospray ionisation mass spectrometry (ESI-MS) to investigate the self-assembly process of hybrid polyoxomolybdates that form upon partial reduction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in the presence of aromatic organoarsonates. We were interested in exploring how perturbations of the ligand functionality influence the formation of unprecedented species, and we used ESI-MS to screen the reaction mixtures prior to crystallisation attempts. Although, several arsonate stabilised molybdates have previously been reported,^{9, 11, 34-39} this mass spectrometry-guided approach allowed us to

selectively identify species with unprecedented core structures. The structure and composition of these species were later confirmed by single crystal XRD studies.

The first part of this chapter presents the synthesis and characterisation of four unprecedented hybrid cluster compounds stabilised by organoarsenate ligands:



Stimulated by the interest in transition metal functionalised POMs and in so-called “sandwiched atoms” involving POMs,⁴⁰ we additionally decided to explore how d-block hetero-atoms can be incorporated into defined POM structures. A known molybdenum phosphonate is $(\text{NH}_4)_5\text{Na}_4\{\text{Na}[\text{Mo}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 6\text{H}_2\text{O}$, in which two $\{\text{Mo}_6\}$ fragments are linked through a Na ion.¹³ Considering this, we sought to investigate if transition metal ions could be used to link the hexanuclear subunits to produce sandwich-type compounds. We intended to explore how different heteroatoms would influence the structure and magnetic properties of the compounds. This part of the chapter presents the synthetic approach, the structure characterisation and properties of five isostructural compounds (4 transition metal derivatives and 1 main group compound) that self-assemble under closely related reaction conditions:



2.2 FUNCTIONALISATION OF POLYOXOMOLYBDATES USING ORGANO-ARSONATES AND -PHOSPHONATES

2.2.1 Synthesis and characterisation of organoarsonate functionalised polyoxomolybdate clusters

2.2.1.1 The Phenylarsonic Acid – Mo^{VI}/Mo^V Reaction System

(NH₄)₂H₂[Mo^V₄O₈(O₃AsC₆H₅)₄]·5H₂O (**1**)

Partial reduction of (NH₄)₆Mo₇O₂₄·4H₂O in the presence of phenylarsonic acid and acetic acid using N₂H₄·H₂SO₄ results in a deep blue solution from which dark red crystals of (NH₄)₂H₂[Mo^V₄O₈(O₃AsC₆H₅)₄]·5H₂O (**1**) separate within a time period of three weeks.

Single crystal X-ray analysis reveals that **1** crystallises in the triclinic crystal system in the space group $P\bar{1}$ and contains a tetranuclear Mo^V complex in which the Mo atoms and bridging O donors adopt a typical [Mo₄(μ₃-O)₄]¹²⁺ cubane structure. The structure is shown in Figure 2.1. In this structure, the four Mo atoms are situated diagonally across from each other, occupying four corners of a cube. Four O²⁻ oxo ligands occupy the remaining four corners of the cube, and each one binds to three Mo atoms. The structure is further stabilised by four fully deprotonated phenylarsonic acid ligands that each bind in a η¹:η¹:μ₂ bridging mode to two Mo ions, resulting in an overall octanuclear compound (the As atoms are also considered to be core atoms). The slightly distorted octahedral coordination environment of each of the four Mo ions in **1** comprises of three μ₃-O oxo ligands, two O donors originating from two different arsonate ligands and is completed by a terminal Mo=O bond. The distorted nature of the octahedra arises from the geometrical restrictions of the binding ligands and can be observed from the bond angles and bond lengths of the Mo^V metal centres. The bond lengths of the Mo=O bonds range between 1.660(4) Å – 1.679(4) Å and are, as expected, significantly shorter than the Mo–(μ₃-O) distances of 1.969(4) Å – 2.424(4) Å and the Mo–O_{arsonate} bond distances of 2.043(4) Å – 2.090(4) Å, (Table 2.1). The following bond angles: O(12)-Mo(1)-O(6), O(7)-Mo(1)-O(10) and O(8)-Mo(1)-O(11) of 170.50(17)°, 152.42(14)° and 151.57(14)°, respectively, deviate from the ideal octahedral angle of 180°, while the bond angles O(12)-Mo(1)-O(7), O(12)-Mo(1)-O(11), O(8)-Mo(1)-O(7), O(7)-Mo(1)-O(11), O(8)-Mo(1)-O(10), O(7)-Mo(1)-O(6) and

O(8)-Mo(1)-O(6) of $110.67(16)^\circ$, $97.79(19)^\circ$, $88.68(17)^\circ$, $86.42(17)^\circ$, $85.21(16)^\circ$, $76.37(14)^\circ$ and $75.74(15)^\circ$, respectively, deviate from the ideal angle of 90° . Similar values can be found for the bond angles of the Mo(2), Mo(3) and Mo(4) ions, which are summarized in Table 2.2.

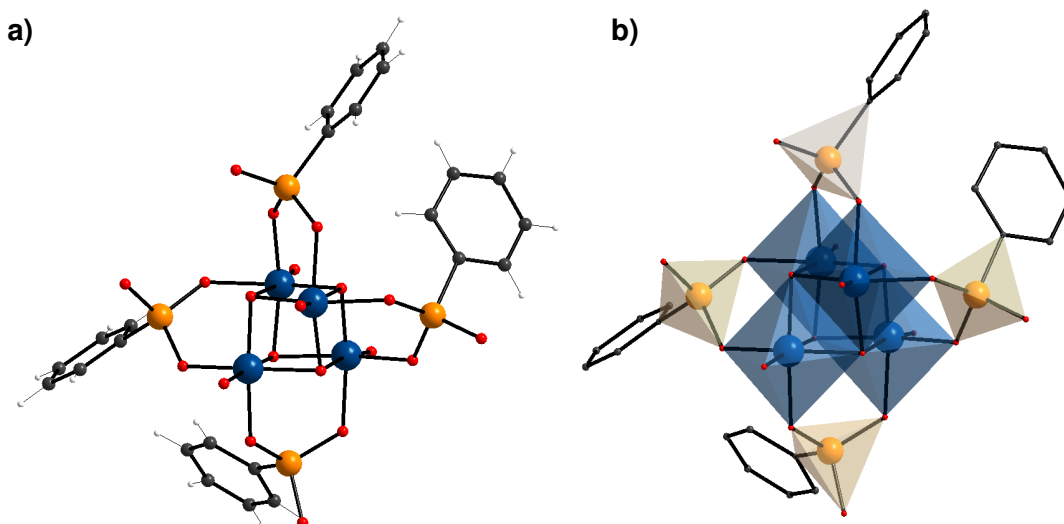


Figure 2.1 – Crystal structure of the tetranuclear Mo complex in **1**: (a) ball-and-stick representation, (b) polyhedral presentation. Colour code: Mo^V blue, As orange, O red, C grey, H white (hydrogen atoms have been omitted for clarity in b).

The $[\text{Mo}_4(\mu_3\text{-O})_4]^{12+}$ core structure deviates slightly from the geometry of an ideal cube. The Mo–O–Mo and O–Mo–O angles range between $83.82(3)^\circ$ – $104.04(1)^\circ$ and $76.18(1)^\circ$ – $89.72(3)^\circ$, respectively, differing from the ideal angle of 90° . Bond valence sum analysis⁴¹ confirms that all four Mo atoms in **1** adopt the oxidation state +V. Short Mo(1)-Mo(2) and Mo(3)-Mo(4) contacts of $2.647(1) \text{ \AA}$ and $2.642(1) \text{ \AA}$, respectively, are in agreement with the assigned +V oxidation states. The cluster is further stabilised by weak intramolecular π - π interactions⁴² with an interplanar separation distance that range between $3.604(21) \text{ \AA}$ – $4.091(19) \text{ \AA}$.

The packing arrangement of the $[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_5)_4]^{4-}$ clusters in the crystal structure is stabilised by weak hydrogen bonds between the cluster anions and constitution water molecules (O–O distances: $2.769(48) \text{ \AA}$ – $2.915(57) \text{ \AA}$) and also between the cluster anions and NH_4^+ counterions (N–O distances: $2.698(36) \text{ \AA}$ – $3.045(30) \text{ \AA}$). The solvent molecules are situated in small channels that run in the direction of the crystallographic *a*-axis (Figure 2.3). Very weak intermolecular π - π interactions (shortest contact $3.975(28) \text{ \AA}$) of the aromatic rings of the arsonate ligands also contribute to the stability of **1** in the solid state.

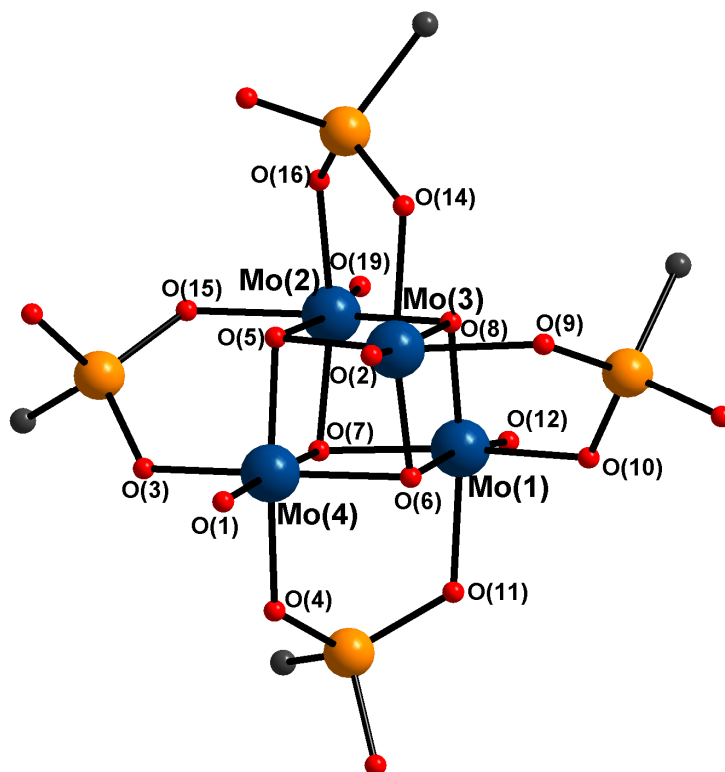


Figure 2.2 – The core structure of the tetranuclear Mo complex in **1**. Colour code: Mo^V blue, As orange, O red, C grey.

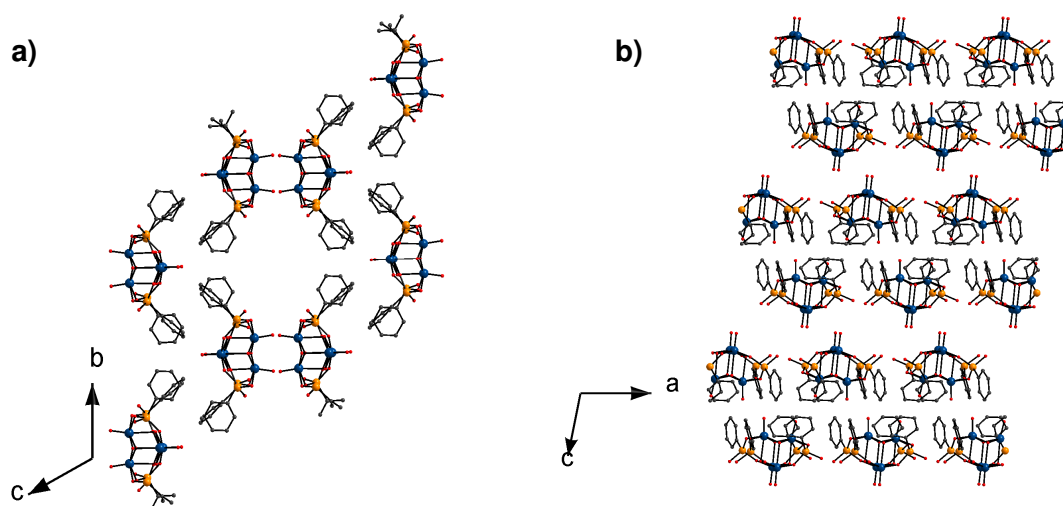


Figure 2.3 – Packing arrangement of **1** in the crystal structure viewed in the direction of the crystallographic: (a) *a*-axis and (b) *b*-axis. Colour code: Mo^V blue, As orange, O red, C grey (crystallization water molecules, NH₄⁺ counterions and hydrogen atoms have been omitted for clarity).

Table 2.1 – Selected bond lengths [Å] and bond valence sum (BVS) for compound 1.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mo(1)	Mo(1)-O(12)	1.660(4)	5.159	+5
	Mo(1)-O(7)	1.989(4)		
	Mo(1)-O(8)	1.983(4)		
	Mo(1)-O(11)	2.055(4)		
	Mo(1)-O(10)	2.065(4)		
	Mo(1)-O(6)	2.405(4)		
Mo(2)	Mo(2)-O(19)	1.673(4)	5.161	+5
	Mo(2)-O(7)	1.974(4)		
	Mo(2)-O(8)	1.986(4)		
	Mo(2)-O(15)	2.043(4)		
	Mo(2)-O(16)	2.046(4)		
	Mo(2)-O(5)	2.424(4)		
Mo(3)	Mo(3)-O(2)	1.667(4)	5.165	+5
	Mo(3)-O(5)	1.970(4)		
	Mo(3)-O(6)	1.983(4)		
	Mo(3)-O(14)	2.047(4)		
	Mo(3)-O(9)	2.090(4)		
	Mo(3)-O(8)	2.364(4)		
Mo(4)	Mo(4)-O(1)	1.679(4)	5.085	+5
	Mo(4)-O(5)	1.969(4)		
	Mo(4)-O(6)	1.972(4)		
	Mo(4)-O(3)	2.066(4)		
	Mo(4)-O(4)	2.087(4)		
	Mo(4)-O(7)	2.386(4)		
Mo(1) ... Mo(2)		2.647(1)		
Mo(3) ... Mo(4)		2.642(1)		

Structurally related cubane structures were previously isolated using squaric acid ((ColMe)₄[Mo₄O₈(C₄O₄)₄]·2MeOH·2Col, (ColH)₄(PyEt)[Mo₄O₈(C₄O₄)₄]Br; Col = 2,4,6-collidine), diphenylphosphinic acid (Mo₄(μ₃-O)₄(μ-O₂PPh₂)₄O₄) and dimethylphosphinic acid (Mo₄(μ₃-O)₄(μ-O₂PMe₂)₄O₄) as ligands.⁴³⁻⁴⁵ However, it is noteworthy that the cubane arrangement of Mo^V atoms is far less frequently observed than the structurally related rhombic planar arrangement.⁴³

Table 2.2 – Selected bond angles [°] for compound 1.

Bond Angle (°)		Bond Angle (°)	
O(12)-Mo(1)-O(6)	170.50(17)	O(19)-Mo(2)-O(5)	171.66(17)
O(7)-Mo(1)-O(10)	152.42(14)	O(7)-Mo(2)-O(16)	154.38(15)
O(8)-Mo(1)-O(11)	151.57(14)	O(8)-Mo(2)-O(15)	152.70(14)
O(12)-Mo(1)-O(7)	110.67(16)	O(19)-Mo(2)-O(7)	109.20(17)
O(12)-Mo(1)-O(11)	97.79(19)	O(19)-Mo(2)-O(15)	98.17(17)
O(8)-Mo(1)-O(7)	88.68(17)	O(19)-Mo(2)-O(16)	96.04(18)
O(7)-Mo(1)-O(11)	86.42(17)	O(7)-Mo(2)-O(8)	89.02(16)
O(8)-Mo(1)-O(10)	85.21(16)	O(8)-Mo(2)-O(16)	86.95(16)
O(7)-Mo(1)-O(6)	76.37(14)	O(16)-Mo(2)-O(5)	77.54(15)
O(8)-Mo(1)-O(6)	75.74(15)	O(8)-Mo(2)-O(5)	76.61(14)
O(2)-Mo(3)-O(8)	170.03(19)	O(1)-Mo(4)-O(7)	170.26(17)
O(5)-Mo(3)-O(9)	154.78(15)	O(5)-Mo(4)-O(4)	154.73(14)
O(6)-Mo(3)-O(14)	154.28(16)	O(6)-Mo(4)-O(3)	152.73(14)
O(2)-Mo(3)-O(6)	109.62(19)	O(1)-Mo(4)-O(6)	109.66(17)
O(2)-Mo(3)-O(9)	95.60(18)	O(1)-Mo(4)-O(3)	96.97(18)
O(5)-Mo(3)-O(6)	89.45(16)	O(5)-Mo(4)-O(6)	89.81(18)
O(6)-Mo(3)-O(9)	88.05(17)	O(5)-Mo(4)-O(3)	87.12(16)
O(14)-Mo(3)-O(9)	84.41(17)	O(3)-Mo(4)-O(4)	82.92(16)
O(5)-Mo(3)-O(8)	78.38(15)	O(5)-Mo(4)-O(7)	77.92(15)
O(14)-Mo(3)-O(8)	77.62(14)	O(3)-Mo(4)-O(7)	75.73(15)

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

Infrared spectroscopy was used as a basic tool for preliminary characterisation of compound **1**. The IR spectrum of **1** (Figure 2.4) reveals some characteristic stretches of the organoarsenate ligands. These include signals at 1093 cm^{-1} attributed to As–C vibrations and 1439 cm^{-1} associated with C–C skeletal vibrations of the phenyl rings. Additionally observed bands arising from the molybdenum-oxygen and arsenic-oxygen stretching vibrations appear in the $1000 - 650\text{ cm}^{-1}$ region.^{8, 15, 37, 46-48}

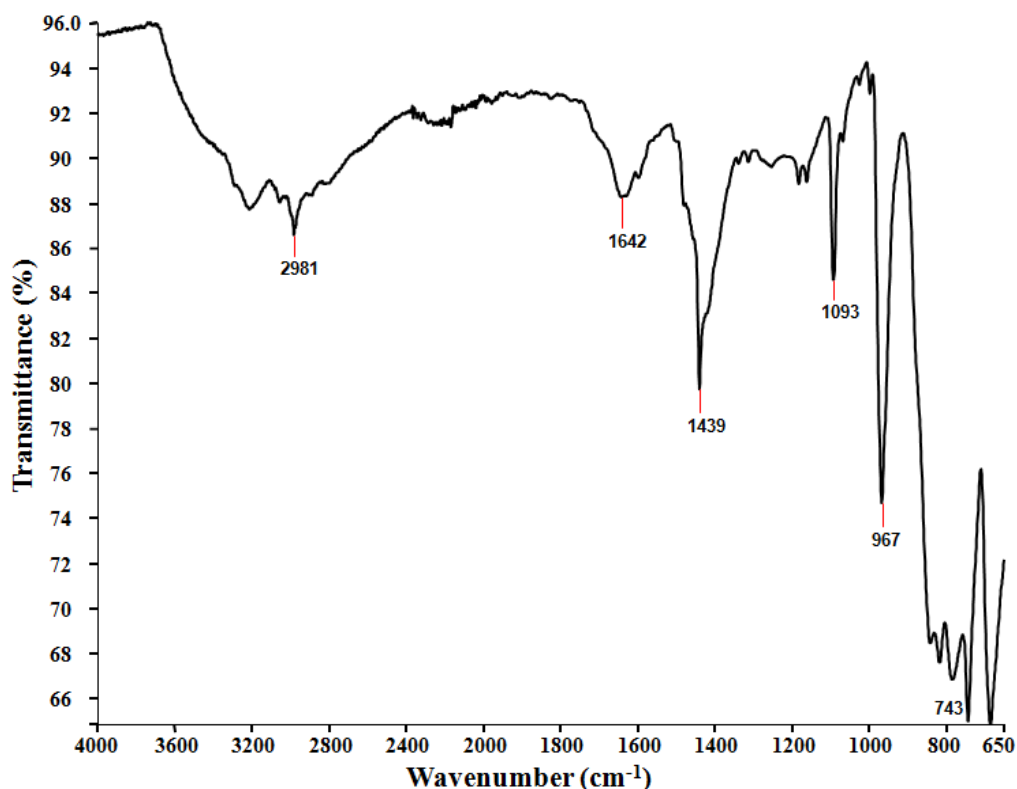


Figure 2.4 – Infrared spectrum of **1**.

- *Thermogravimetric analysis*

The thermal stability of compound **1** was investigated by thermogravimetric analysis (TGA) using a freshly prepared crystalline sample. The analysis was carried out in the temperature range between 30 and 900 °C, in an N₂ atmosphere. The TGA of **1** reveals a weight loss of 6.4 % in the temperature range between 30 – 90 °C. This

thermogravimetric step can be attributed to the loss of five water molecules (calcd: 6.2 %). A further increase in the temperature up to 500 °C produces a weight loss that occurs in a two step process. This weight loss can be associated with the decomposition of the organic ligands of the cluster. The weight loss centered at *ca.* 770 °C is most likely being associated with the formation of oxides.

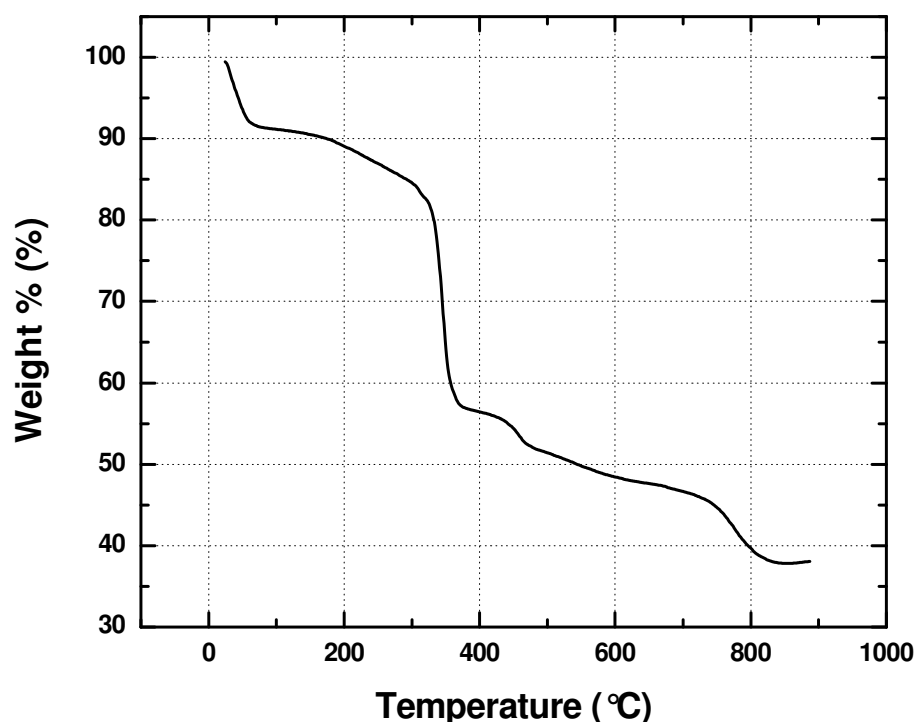


Figure 2.5 – Thermogravimetric analysis of **1**.

- *Mass spectrometry*

The stability of compound **1** in solution was investigated by electrospray ionization mass spectrometry (ESI-MS). The negative mode ESI-MS spectrum of compound **1** dissolved in DMSO is presented in Figure 2.6. The mass spectrum displays only one major isotopic envelope in the high molecular mass region, centered at $m/z = 1315.3$ a.m.u. The signal was assigned to the $\{H_3[Mo^V_4O_8(O_3AsC_6H_5)_4]\}^-$ species. The expected signal was modelled (Figure 2.6, Inset) and good fits between the experimental and simulated isotopic envelopes confirm the assignment.

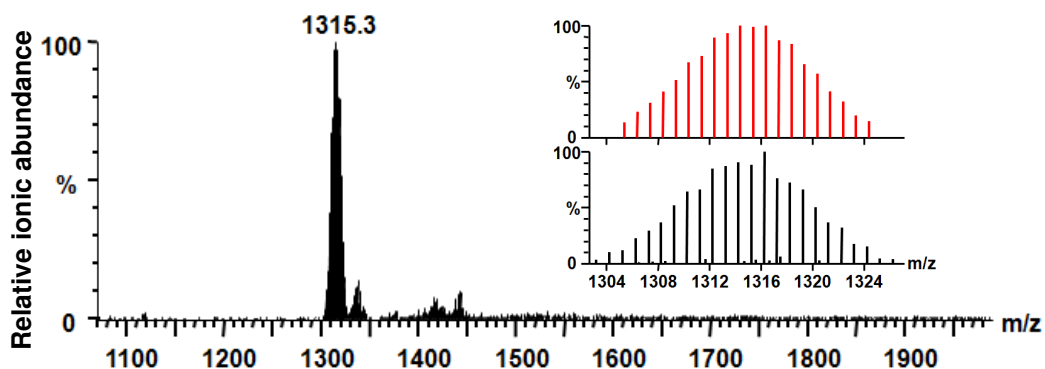


Figure 2.6 – Negative-mode ESI-MS spectra for crystals of **1** dissolved in DMSO. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{H_3[Mo_4^V O_8(O_3AsC_6H_5)_4]\}^-$ centered at $m/z = 1315.3$ a.m.u. (cone voltage: 30 V).

- *NMR spectroscopy*

The 1H NMR spectrum of **1** recorded in deuterated DMSO further confirms the stability of the compound in DMSO environment. The spectrum of **1** exhibits resonance shifts at 7.97 ppm (d, 8H) and 7.67 ppm (m, 12H) corresponding to aromatic H-atoms of the arsonate ligands. A section of the 1H NMR spectrum of **1** is presented in Figure 2.7.

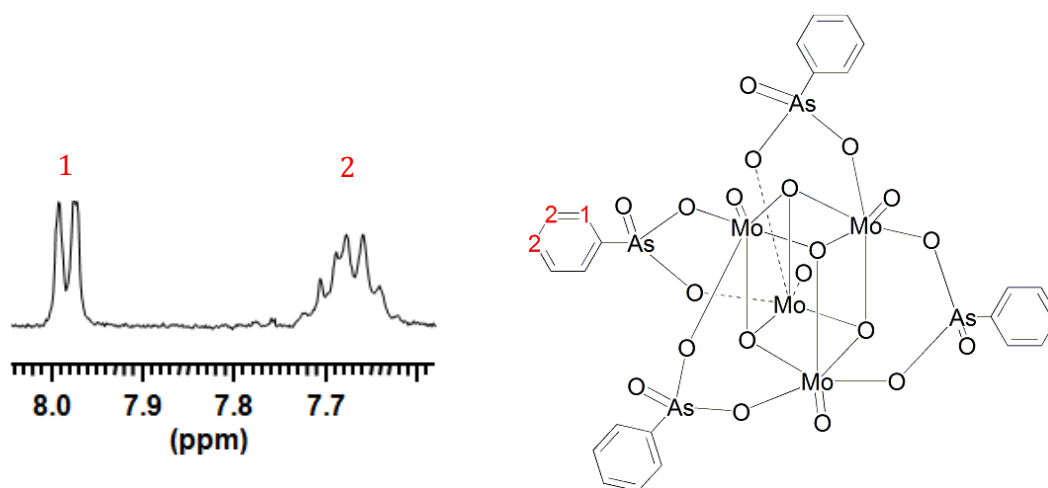


Figure 2.7 – A section of the 1H NMR (400MHz, DMSO) spectrum showing the assignment for **1**.

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **1** was recorded in DMF (Figure 2.8). The spectrum displays an absorption band at *ca.* 457 nm ($\epsilon = 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$) due to d – d transitions involving the Mo^{V} metal centers. These d – d transitions can be assigned to a ${}^2\text{E}_g \leftarrow {}^2\text{T}_{2g}$ transition for the octahedral Mo^{V} ions within **1**.³⁸

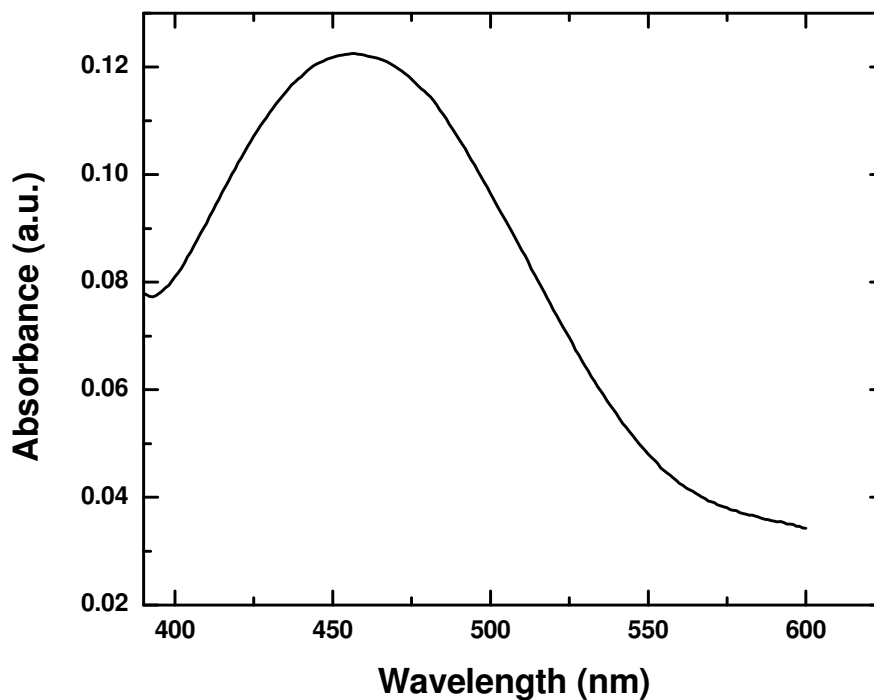


Figure 2.8 –A section of the UV-Vis spectrum of a 10^{-4} M solution of **1** in DMF.

Table 2.3 – Crystal data and structural refinement parameters for 1.

Compound 1	
Empirical formula	C ₂₄ H ₄₀ As ₄ Mo ₄ N ₂ O ₂₅
Molecular mass/g mol ⁻¹	1440.02
Crystal colour/shape	Red / triangular plate
Crystal size/mm ³	0.20×0.20×0.05
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	10.009(4)
b/ Å	15.767(5)
c/ Å	17.287(5)
α /°	117.09(2)
β /°	96.03(2)
γ /°	98.454(18)
V/ Å ³	2356.1(14)
Z	2
Temperature (K)	118(2)
Density/Mg m ⁻³	2.001
Absorp. coef./mm ⁻¹	3.906
F(000)	1356
2 θ_{max} /°	50
Reflections collected	36989
Independent reflections	8303 [R(int) = 0.1174]
Data / restraints / parameters	8303 / 2128 / 577
S on F^2	1.036
R ₁ , wR ₂ [I>2 σ (I)]	0.0985, 0.2684
R ₁ , wR ₂ (all data)	0.1171, 0.2869
Largest diff. peak and hole/e.Å ⁻³	2.217 and -2.503

2.2.1.2 The *p*-Aminophenylarsonic Acid – Mo^{VI}/Mo^V Reaction System (NH₄)₂H₂[Mo^V₄O₈(O₃AsC₆H₄NH₂)₄]·DMF·4H₂O (**2**)

Encouraged by these results we decided to alter the ligand functionality and introduced an amino group in the *para* position to the arsonate functionality. When this ligand is used to control the self-assembly process upon reduction of (NH₄)₆Mo₇O₂₄·4H₂O, a blue solution is obtained, as in the previous case. During a time period of one week, rod-shaped red crystals of (NH₄)₂H₂[Mo^V₄O₈(O₃AsC₆H₄NH₂)₄]·DMF·4H₂O (**2**) were obtained. **2** was characterised by single crystal X-ray diffraction measurements.

2 crystallises in the triclinic crystal system in the space group $P\bar{1}$. The core structure within **2** (Figure 2.10) is almost isostructural to the cluster core found in **1**, having only slightly different structural and geometrical parameters. The bond valence sums and underlying M–O and Mo–Mo distances agree very well with those observed for **1**. Selected interatomic distances and angles for compound **2** are given in Table 2.4 and Table 2.5, respectively. Similar to **1** the core structure within **2**, [Mo₄(μ₃-O)₄]¹²⁺, deviates slightly from the geometry of an ideal cube. The Mo–O–Mo and O–Mo–O angles range between 83.19(29)° – 104.78(30)° and 75.16(27)° – 90.33(30)°, respectively, differing from the ideal angle of 90°.

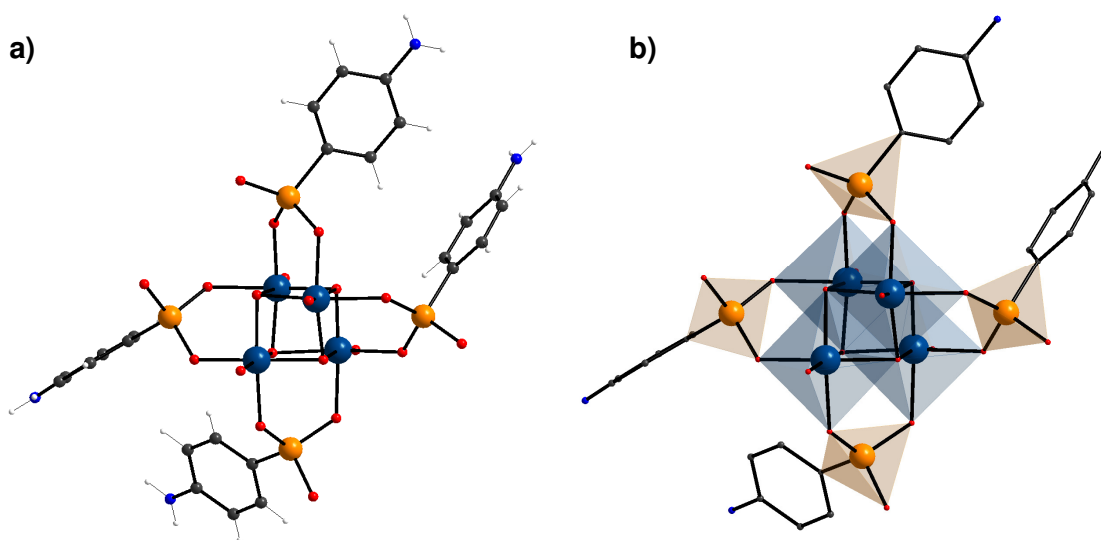


Figure 2.9 – Crystal structure of the tetranuclear Mo complex in **2**: (a) ball-and-stick representation, (b) polyhedral presentation. Colour code: Mo^V blue, As orange, O red, N light blue, C grey, H white (hydrogen atoms have been omitted for clarity in b).

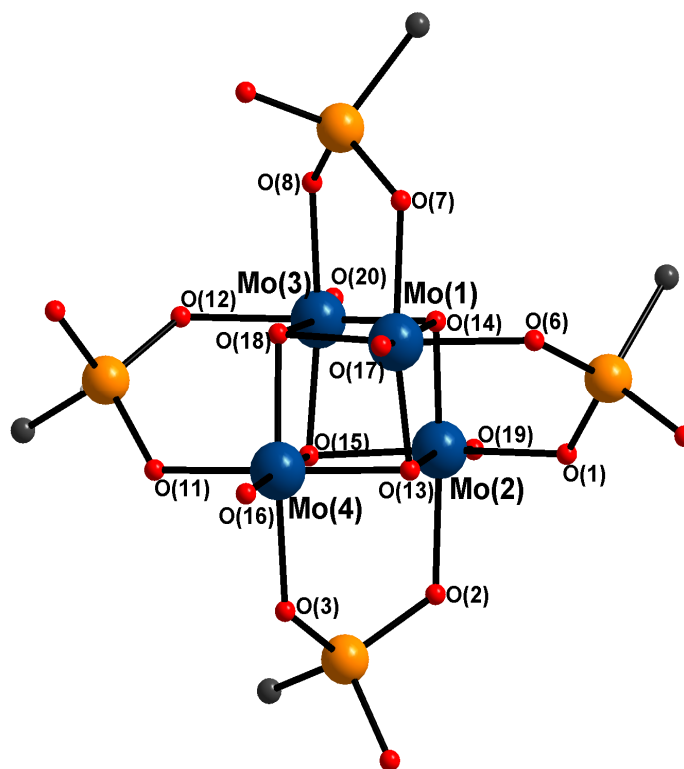


Figure 2.10 – The core structure of the tetranuclear Mo complex in **2**. Colour code: Mo^V blue, As orange, O red, C grey.

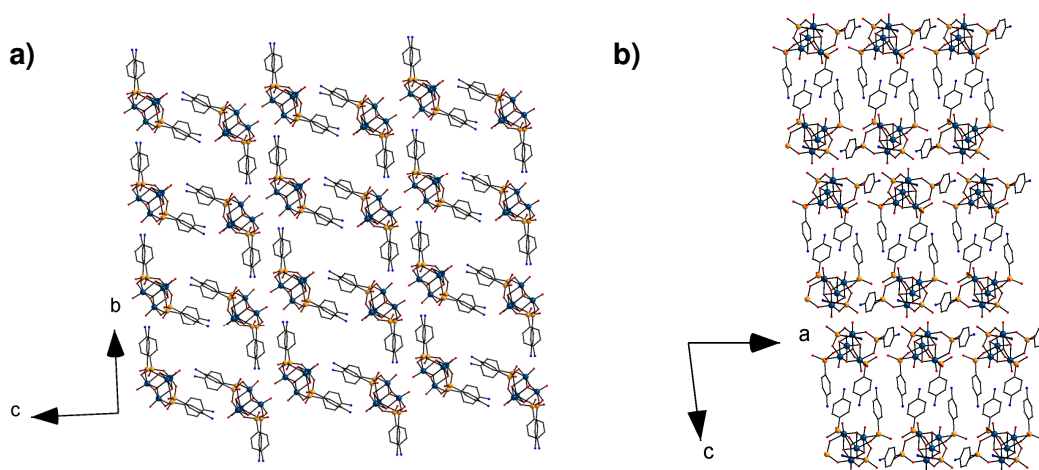


Figure 2.11 – Packing arrangement of **2** in the crystal structure viewed in the direction of the crystallographic: (a) *a*-axis and (b) *b*-axis. Colour code: Mo^V blue, As orange, O red, N light blue, C grey (crystallisation solvent molecules, NH₄⁺ counterions and hydrogen atoms have been omitted for clarity).

The amine functionalities of the organic ligands only impose an influence on the packing arrangement of the clusters in the crystal structure, resulting in a grid-like packing arrangement, with small intercluster cavities (filled with solvent molecules and NH₄⁺ counterions) running in the direction of the crystallographic *a*-axis (Figure 2.11). The

packing arrangement of the clusters in the crystal structure is stabilised by weak hydrogen bonds between the cluster anions and constitution solvent molecules (O-O distances: 2.847(21) Å – 3.060(24) Å) and also between the cluster anions and NH_4^+ counterions (N-O distances: 2.861(19) Å – 3.083(23) Å). Very weak offset π - π interactions⁴² between two adjacent clusters with interplanar separation distances that range between 3.475(29) Å – 4.145(32) Å also contribute to the stability of **2** in the solid state.

The protonation of the tetranuclear Mo clusters in **1** and **2**, respectively, are in agreement with the elemental analysis and the constitutional representation in the form of $H_x[\text{clustercore}]$ is commonly applied in this field of research.⁹

Table 2.4 – Selected bond lengths [Å] and bond valence sum (BVS) for compound 2.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mo(1)	Mo(1)-O(17)	1.679(9)	5.122	+5
	Mo(1)-O(18)	1.978(8)		
	Mo(1)-O(13)	1.976(7)		
	Mo(1)-O(7)	2.024(8)		
	Mo(1)-O(6)	2.079(8)		
	Mo(1)-O(14)	2.420(8)		
Mo(2)	Mo(2)-O(19)	1.663(9)	5.227	+5
	Mo(2)-O(15)	1.966(7)		
	Mo(2)-O(14)	1.967(8)		
	Mo(2)-O(2)	2.060(8)		
	Mo(2)-O(1)	2.084(8)		
	Mo(2)-O(13)	2.353(8)		
Mo(3)	Mo(3)-O(20)	1.678(8)	5.112	+5
	Mo(3)-O(14)	1.978(8)		
	Mo(3)-O(15)	1.985(8)		
	Mo(3)-O(8)	2.036(8)		
	Mo(3)-O(12)	2.067(8)		
	Mo(3)-O(18)	2.411(8)		
Mo(4)	Mo(4)-O(16)	1.674(9)	5.110	+5
	Mo(4)-O(13)	1.984(7)		
	Mo(4)-O(18)	1.983(8)		
	Mo(4)-O(11)	2.044(7)		
	Mo(4)-O(3)	2.074(8)		
	Mo(4)-O(15)	2.393(8)		
Mo(1) ... Mo(4)		2.630(1)		
Mo(2) ... Mo(3)		2.615(1)		

Table 2.5 – Selected bond angles [°] for compound 2.

Bond Angle (°)		Bond Angle (°)	
O(17)-Mo(1)-O(14)	171.1(3)	O(19)-Mo(2)-O(13)	170.0(3)
O(18)-Mo(1)-O(6)	155.5(3)	O(14)-Mo(2)-O(2)	155.9(3)
O(13)-Mo(1)-O(7)	152.0(3)	O(15)-Mo(2)-O(1)	154.7(3)
O(17)-Mo(1)-O(13)	109.6(4)	O(19)-Mo(2)-O(14)	109.4(4)
O(17)-Mo(1)-O(7)	97.9(3)	O(19)-Mo(2)-O(1)	95.7(4)
O(17)-Mo(1)-O(6)	95.0(3)	O(15)-Mo(2)-O(14)	90.6(3)
O(13)-Mo(1)-O(18)	89.5(3)	O(2)-Mo(2)-O(1)	88.1(3)
O(7)-Mo(1)-O(6)	87.4(3)	O(15)-Mo(2)-O(2)	85.7(3)
O(13)-Mo(1)-O(6)	85.4(3)	O(2)-Mo(2)-O(13)	78.7(3)
O(6)-Mo(1)-O(14)	78.0(3)	O(15)-Mo(2)-O(13)	77.5(3)
O(20)-Mo(3)-O(18)	171.4(3)	O(16)-Mo(4)-O(15)	171.5(3)
O(15)-Mo(3)-O(8)	155.2(3)	O(18)-Mo(4)-O(3)	155.9(3)
O(14)-Mo(3)-O(12)	153.9(3)	O(13)-Mo(4)-O(11)	152.0(3)
O(20)-Mo(3)-O(15)	108.9(4)	O(16)-Mo(4)-O(13)	109.3(4)
O(20)-Mo(3)-O(12)	97.0(4)	O(16)-Mo(4)-O(11)	98.2(3)
O(20)-Mo(3)-O(8)	95.6(4)	O(16)-Mo(4)-O(3)	94.7(4)
O(14)-Mo(3)-O(15)	89.7(3)	O(18)-Mo(4)-O(13)	89.1(3)
O(15)-Mo(3)-O(12)	86.8(3)	O(3)-Mo(4)-O(15)	79.0(3)
O(14)-Mo(3)-O(8)	85.8(3)	O(18)-Mo(4)-O(15)	76.9(3)
O(8)-Mo(3)-O(18)	78.8(3)	O(11)-Mo(4)-O(15)	75.8(3)

- PHYSICOCHEMICAL CHARACTERISATION

- FT-IR spectroscopy

The IR spectrum of **2** is presented in Figure 2.12 and reveals some characteristic stretches of the organic ligands. The set of bands observed between $1600 - 1400\text{ cm}^{-1}$ can be attributed to C–C skeletal vibrations of the phenyl rings while the signal at 1095 cm^{-1} can be associated with As–C vibrations. Other characteristic stretches observed in the IR spectrum of **2** appear as strong bands in the $1000 - 650\text{ cm}^{-1}$ region. Some of these bands can be attributed to the molybdenum-oxygen and arsenic-oxygen stretching vibrations. The O–H stretching vibrations and H–O–H bending vibrations of the crystallisation water molecules engaged in H-bonds appear as broad bands centered at *ca.* 3200 cm^{-1} and *ca.* 1630 cm^{-1} , respectively. Stretches relating to NH_2 group of the organic ligands are expected to appear in the same region as the O–H stretches of the crystallisation water molecules.^{8, 15, 37, 46-48}

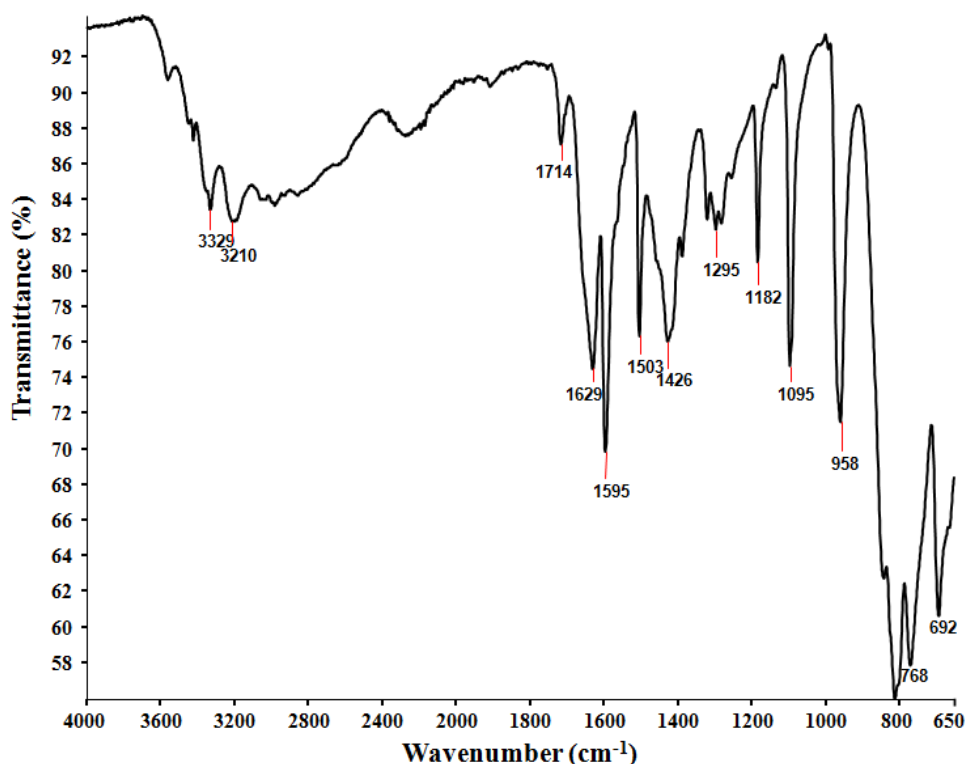


Figure 2.12 – Infrared spectrum of **2**.

- *Thermogravimetric analysis*

The thermal stability of **2** was investigated by thermogravimetric analysis using a freshly prepared crystalline sample (Figure 2.13). Compound **2** reveals a weight loss of about 9.7 % below 150 °C corresponding to the loss of four water and one DMF molecules (calcd: 9.3 %). From 150 to 600 °C a gradual weight loss is associated with the decomposition of organic moieties finally producing oxide materials.

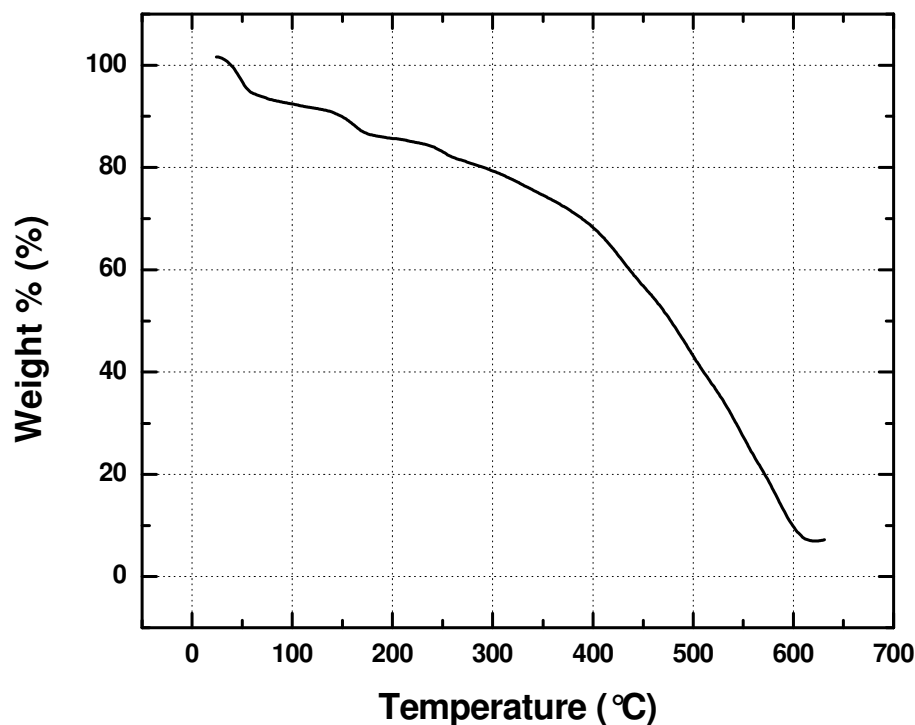


Figure 2.13 – Thermogravimetric analysis of **2**.

- *Mass spectrometry*

ESI-MS studies on pristine crystals of **2** dissolved in DMSO were performed in order to investigate the stability of the molybdenum cluster in solution. Similar to compound **1**, the mass spectrum of **2** (Figure 2.14) reveals only one major isotopic envelope in the high molecular mass region of the spectrum. The signal is centered at $m/z = 1374.4$ a.m.u. and corresponds to the $\{H_3[Mo^V_4O_8(O_3AsC_6H_4NH_2)_4]\}^-$ species. Again, the signal of the species was modelled and a comparison of the experimental isotopic envelopes with the simulated envelope is presented in Figure 2.14, Inset. It is noteworthy that both compounds **1** and **2** are insoluble in H_2O .

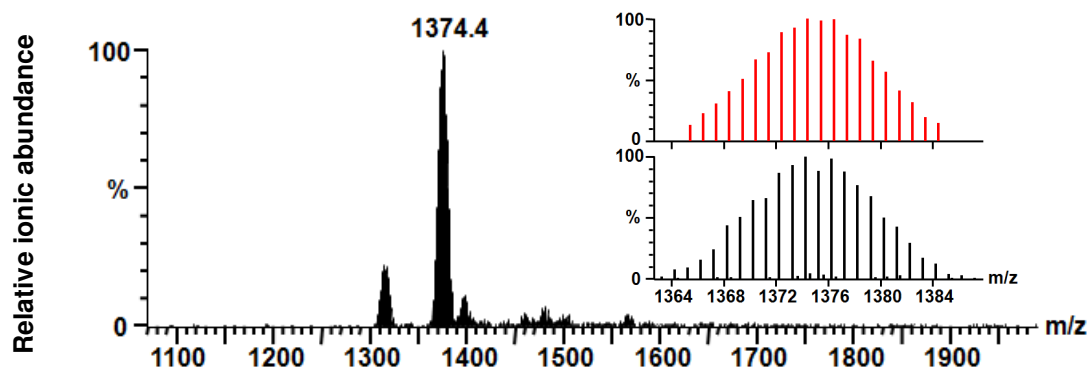


Figure 2.14 – Negative-mode ESI-MS spectra for crystals of **2** dissolved in DMSO. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{H_3[Mo^V_4O_8(O_3AsC_6H_4NH_2)_4]\}^-$ centered at $m/z = 1374.4$ a.m.u. (cone voltage: 30 V).

- *NMR spectroscopy*

Similar to **1**, the cluster of **2** appears to be stable in a DMSO environment. The 1H NMR spectrum of **2** (Figure 2.15) exhibits signals at 7.56 ppm (d, 8H), 6.73 ppm (d, 8H) and 5.80 ppm (s, 8H). The two most downfield signals were assigned to the aromatic H-atoms of the (4-aminophenyl)arsonate ligands, while the signal at 5.80 ppm was assigned to the amine H-atoms of the organic ligands.

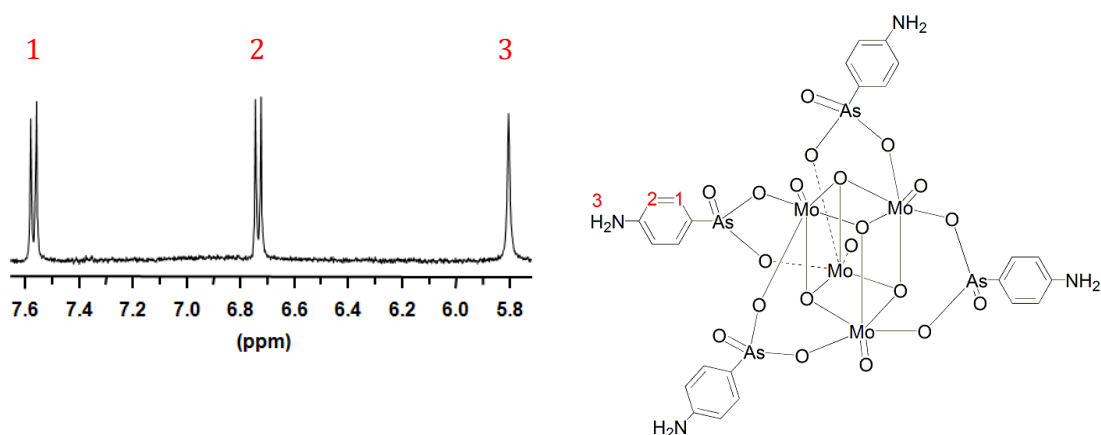


Figure 2.15 – A section of the 1H NMR (400MHz, DMSO) spectrum showing the assignment for **2**.

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **2** recorded in DMF is similar to that of **1** displaying an absorption band at *ca.* 460 nm ($\epsilon = 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$). This signal most likely originates from d – d transitions that can be assigned to ${}^2\text{E}_g \leftarrow {}^2\text{T}_{2g}$ transitions involving the octahedrally coordinated Mo^{V} ions within **2**.³⁸

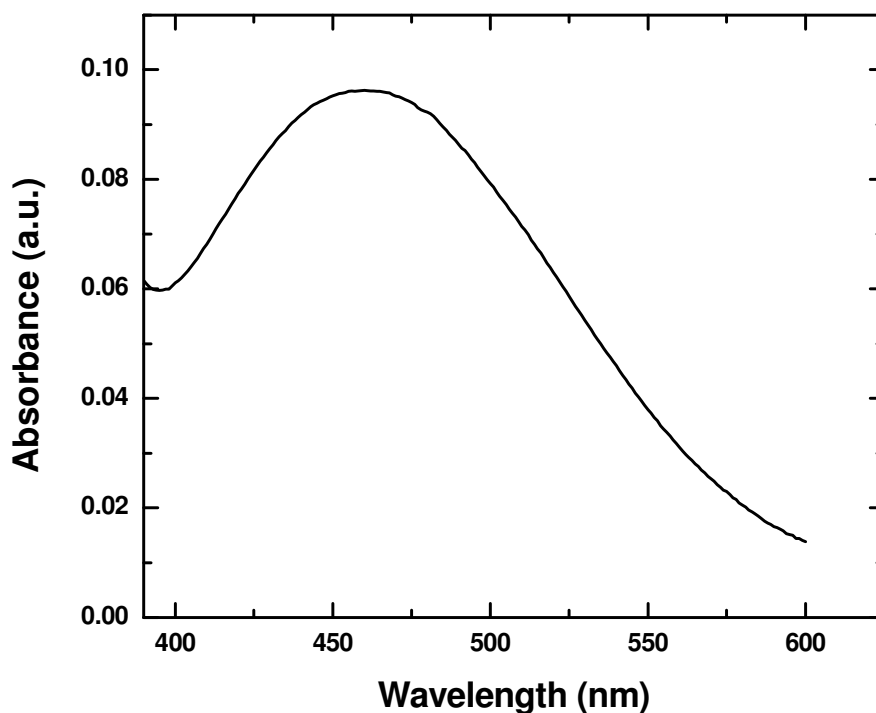


Figure 2.16 –A section of the UV-Vis spectrum of a 10^{-4} M solution of **2** in DMF.

Table 2.6 – Crystal data and structural refinement parameters for 2.

Compound 2	
Empirical formula	C ₂₇ H ₄₉ As ₄ Mo ₄ N ₇ O ₂₅
Molecular mass/g mol ⁻¹	1555.16
Crystal colour/shape	Red / rod-shaped
Crystal size/mm ³	0.20×0.15×0.10
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	10.207(4)
b/ Å	13.740(5)
c/ Å	19.700(8)
α /°	87.426(13)
β /°	82.265(10)
γ /°	71.005(11)
V/ Å ³	2588.6(17)
Z	2
Temperature (K)	118(2)
Density/Mg m ⁻³	1.978
Absorp. coef./mm ⁻¹	3.567
F(000)	1494
2 θ_{max} /°	50
Reflections collected	39817
Independent reflections	9114 [R(int) = 0.1044]
Data / restraints / parameters	9114 / 13 / 604
S on F^2	1.006
R ₁ , wR ₂ [I>2 σ (I)]	0.0836, 0.1961
R ₁ , wR ₂ (all data)	0.0892, 0.2006
Largest diff. peak and hole/e.Å ⁻³	2.238 and -1.076

2.2.1.3 The *p*-Hydroxyphenylarsonic Acid – Mo^{VI}/Mo^V Reaction System (NH₄)₅[Mo^{VI}₂Mo^V₃O₁₁(O₃AsC₆H₄OH)₅]·9H₂O (**3**)

Surprisingly when *p*-hydroxyphenylarsonic acid is used as a stabilising ligand under the same reaction conditions as described above, we obtain a reaction mixture from which blue crystals of (NH₄)₅[Mo^{VI}₂Mo^V₃O₁₁(O₃AsC₆H₄OH)₅]·9H₂O (**3**), separate within a time period of one week. The structure of **3** is significantly different to that of **1** and **2**.

Single crystal X-ray diffraction measurements reveal that compound **3** crystallises in the triclinic crystal system in the space group $P\bar{1}$, and contains a pentanuclear, mixed-valent cluster stabilised by five *p*-hydroxyphenyl arsonate ligands. The structure of the cluster anion is shown in Figure 2.17. All Mo ions in the structure are distorted octahedrally surrounded by O donors. The coordination spheres of Mo(1) and Mo(2), each consist of three bridging μ_2 -O²⁻ oxo ligands, two O donors that derive from two deprotonated organoarsonate ligands and are completed by a terminal Mo=O bonds. The bond distances between these Mo ions and the bridging μ_2 -O²⁻ oxo ligands range between 1.930(5) Å – 2.060(5) Å. The bond distances between the Mo ions and the O donors originating from the organic arsonate ligands range between 2.083(5) Å – 2.299(5) Å, while the Mo=O bond distances between Mo(1)-O(9) and Mo(2)-O(10) are 1.701(5) Å and 1.685(5) Å, respectively (Table 2.7). The remaining Mo ions in **3**, Mo(3), Mo(4) and Mo(5), also show distorted octahedral geometries each consisting of two bridging μ_2 -O²⁻ oxo ligands, three O_{arsonate} donors and a terminal Mo=O bond. The Mo – (μ_2 -O) bond distances range between 1.817(5) Å – 1.998(5) Å; the Mo – O_{arsonate} bond distances range between 2.013(5) Å – 2.312(5) Å, while the Mo=O bond distances between Mo(3)-O(11), Mo(4)-O(12) and Mo(5)-O(13) are 1.701(5) Å, 1.671(5) Å and 1.682(5) Å, respectively. The distorted nature of the octahedral geometries of the coordinated metal centres can also be observed from their bond angles that deviate from the ideal octahedral geometry. The bond angle O(2)-Mo(1)-O(7) of 155.3(2)° shows the greatest deviation from the ideal octahedral angle of 180°, while the bond angle O(9)-Mo(1)-O(2) of 106.5(2)° shows the greatest deviation from the ideal octahedral angle of 90°. Selected bond lengths and bond angles for the Mo ions in **3** are listed in Table 2.7 and Table 2.8.

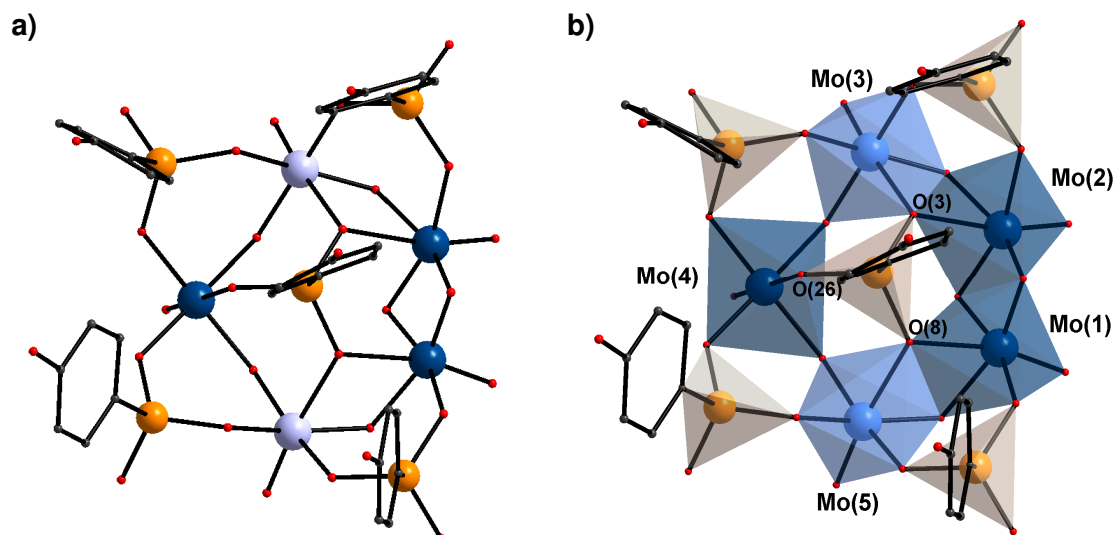


Figure 2.17 – Crystal structure of the pentanuclear Mo complex in **3**: (a) ball-and-stick representation, (b) polyhedral presentation. Colour code: Mo^{VI} lavender blue, Mo^V blue, As orange, O red, C grey (hydrogen atoms have been omitted for clarity).

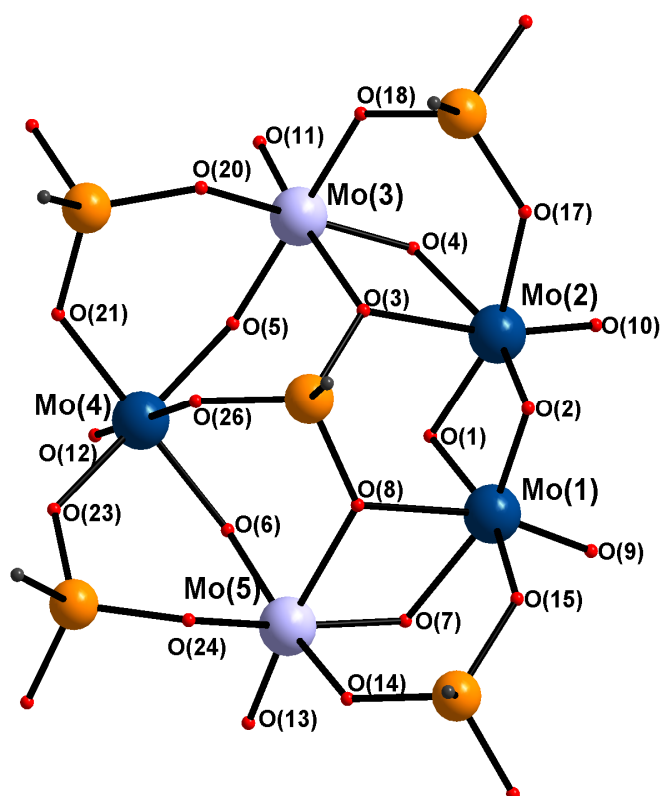


Figure 2.18 – The core structure of the pentanuclear Mo complex in **3**. Colour code: Mo^{VI} lavender blue, Mo^V blue, As orange, O red, C grey.

The coordination polyhedra of Mo(1), Mo(2), Mo(3) and Mo(5) share common edges. The polyhedron of Mo(4), shares common vertices with the polyhedra of Mo(3) and Mo(5) and closes the resulting circular entity in **3**. Four organic ligands are situated on the outer side of the ring, and each binds *via* its deprotonated arsonate functionalities in a $\eta^1:\eta^1:\mu_2$ bridging mode to two Mo ions. The organic ligands bridge between Mo(2) and Mo(3), Mo(3) and Mo(4), Mo(4) and Mo(5) and Mo(5) and Mo(1), respectively. The fifth ligand is situated above the centre of the {Mo₅} ring and binds with its three O atoms to all Mo ions (O(26) binds to Mo(4), and O(3) and O(8) bridge between Mo(2) and Mo(3), and Mo(5) and Mo(1), respectively). The aromatic ring systems of the ligands all point in one direction and project perpendicularly to the virtual plane of the {Mo₅} ring. The phenolic OH functionalities of the organic ligands remain protonated and are engaged in hydrogen bonding within the crystal structure.

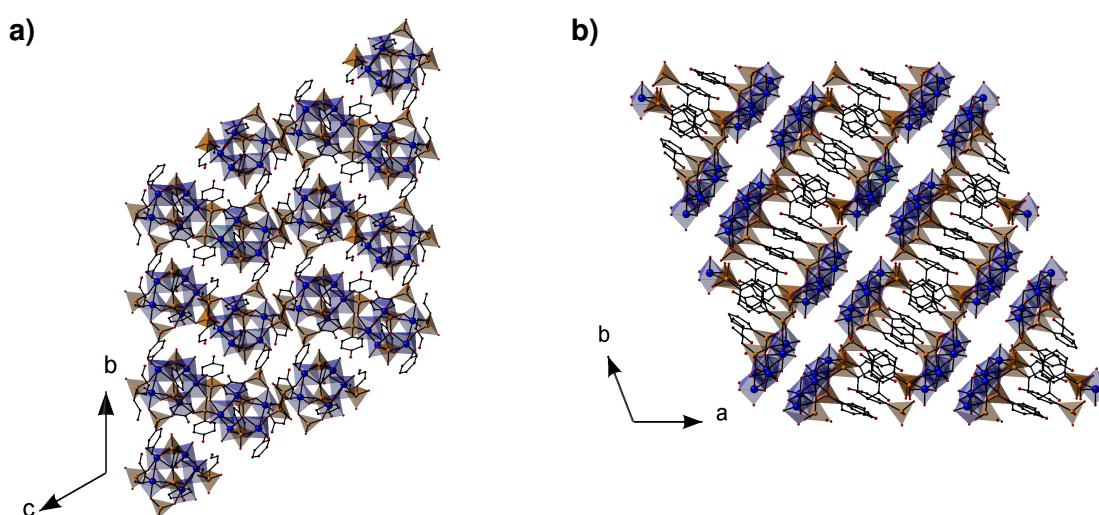


Figure 2.19 – Packing arrangement of **3** in the crystal structure viewed in the direction of the crystallographic: (a) *a*-axis and (b) *c*-axis. Colour code: Mo blue, As orange, O red, C grey (crystallisation water molecules, NH₄⁺ counterions and hydrogen atoms have been omitted for clarity).

The Mo–O bond distances of Mo(3) and Mo(5) are significantly shorter than the corresponding distances of the other Mo ions in the structure. Further bond valence sum analyses confirm that these two Mo ions adopt the oxidation state +VI, while Mo(1), Mo(2) and Mo(4) are in the oxidation state +V. The assignment of the oxidation states is further substantiated by the observed Mo–Mo distances within **3**. The short interatomic distance of 2.574(1) Å between Mo(1) and Mo(2) is indicative for Mo–Mo contacts and in agreement with the +V oxidation states. Comparable Mo^V–Mo^{VI} distances are expectedly

significantly longer (Mo(1)-Mo(5) 3.359(1) Å, Mo(2)-Mo(3) 3.353(3) Å, Mo(3)-Mo(4) 3.680(2) Å and Mo(4)-Mo(5) 3.671(5) Å). Its mixed valence nature distinguishes **3** from many other organoarsenate-stabilised polyoxomolybdates, which tend to exist, with few exceptions,^{38, 39} predominantly in their fully oxidised forms.

Table 2.7 – Selected bond lengths [Å] and bond valence sum (BVS) for compound 3.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mo(1)	Mo(1)-O(9)	1.701(5)	5.251	+5
	Mo(1)-O(1)	1.930(5)		
	Mo(1)-O(2)	1.954(5)		
	Mo(1)-O(7)	2.060(5)		
	Mo(1)-O(15)	2.083(5)		
	Mo(1)-O(8)	2.252(5)		
Mo(2)	Mo(2)-O(10)	1.685(5)	5.277	+5
	Mo(2)-O(2)	1.938(5)		
	Mo(2)-O(1)	1.940(5)		
	Mo(2)-O(4)	2.053(5)		
	Mo(2)-O(17)	2.101(6)		
	Mo(2)-O(3)	2.299(5)		
Mo(3)	Mo(3)-O(11)	1.701(5)	5.919	+6
	Mo(3)-O(5)	1.826(5)		
	Mo(3)-O(4)	1.828(5)		
	Mo(3)-O(18)	2.033(6)		
	Mo(3)-O(20)	2.069(5)		
	Mo(3)-O(3)	2.312(5)		
Mo(4)	Mo(4)-O(12)	1.671(5)	5.462	+5
	Mo(4)-O(5)	1.980(5)		
	Mo(4)-O(6)	1.998(5)		
	Mo(4)-O(21)	2.013(5)		
	Mo(4)-O(23)	2.022(5)		
	Mo(4)-O(26)	2.183(5)		
Mo(5)	Mo(5)-O(13)	1.682(5)	5.981	+6
	Mo(5)-O(6)	1.817(5)		
	Mo(5)-O(7)	1.843(5)		
	Mo(5)-O(24)	2.045(5)		
	Mo(5)-O(14)	2.085(5)		
	Mo(5)-O(8)	2.272(5)		
Mo(1) ... Mo(2)		2.574(1)		

Table 2.8 – Selected bond angles [°] for compound 3.

Bond Angle (°)		Bond Angle (°)	
O(9)-Mo(1)-O(8)	165.6(2)	O(10)-Mo(2)-O(3)	166.9(2)
O(1)-Mo(1)-O(15)	161.5(2)	O(1)-Mo(2)-O(17)	161.0(2)
O(2)-Mo(1)-O(7)	155.3(2)	O(2)-Mo(2)-O(4)	153.6(2)
O(9)-Mo(1)-O(2)	106.5(2)	O(10)-Mo(2)-O(2)	106.4(2)
O(9)-Mo(1)-O(7)	97.6(2)	O(10)-Mo(2)-O(4)	99.4(2)
O(1)-Mo(1)-O(2)	94.7(2)	O(2)-Mo(2)-O(1)	94.9(2)
O(7)-Mo(1)-O(15)	87.3(2)	O(2)-Mo(2)-O(17)	86.7(2)
O(1)-Mo(1)-O(7)	84.5(2)	O(1)-Mo(2)-O(3)	85.1(2)
O(2)-Mo(1)-O(15)	85.9(2)	O(2)-Mo(2)-O(3)	81.8(2)
O(15)-Mo(1)-O(8)	77.56(19)	O(17)-Mo(2)-O(3)	76.3(2)
O(11)-Mo(3)-O(3)	175.1(2)	O(12)-Mo(4)-O(26)	178.8(2)
O(5)-Mo(3)-O(18)	158.2(2)	O(5)-Mo(4)-O(23)	166.1(2)
O(4)-Mo(3)-O(20)	156.3(2)	O(6)-Mo(4)-O(21)	165.6(2)
O(11)-Mo(3)-O(5)	101.1(2)	O(12)-Mo(4)-O(21)	97.1(2)
O(11)-Mo(3)-O(20)	99.0(2)	O(12)-Mo(4)-O(5)	96.8(2)
O(11)-Mo(3)-O(18)	96.4(2)	O(5)-Mo(4)-O(6)	95.4(2)
O(4)-Mo(3)-O(18)	88.3(2)	O(5)-Mo(4)-O(21)	88.8(2)
O(20)-Mo(3)-O(3)	83.64(18)	O(6)-Mo(4)-O(23)	86.6(2)
O(18)-Mo(3)-O(3)	80.1(2)	O(5)-Mo(4)-O(26)	83.72(19)
O(4)-Mo(3)-O(3)	75.4(2)	O(21)-Mo(4)-O(26)	81.7(2)
O(13)-Mo(5)-O(8)	172.6(2)		
O(6)-Mo(5)-O(14)	157.4(2)		
O(7)-Mo(5)-O(24)	155.9(2)		
O(6)-Mo(5)-O(7)	103.7(2)		
O(13)-Mo(5)-O(7)	99.3(2)		
O(13)-Mo(5)-O(14)	97.2(2)		
O(6)-Mo(5)-O(24)	87.8(2)		
O(6)-Mo(5)-O(8)	84.2(2)		
O(14)-Mo(5)-O(8)	78.76(19)		
O(7)-Mo(5)-O(8)	74.3(2)		

The pentanuclear polyoxomolybdate cluster in **3** carries an overall charge of -5, which is compensated for by NH_4^+ counterions. In the crystal structure, the cluster packs to form a layered lamellar structure with alternating inorganic and organic areas. This structure, viewed in the direction of the crystallographic *c*-axis, is shown in Figure 2.19, b. The counterions and the crystallisation water molecules are engaged in hydrogen bonds (O-O distances: 2.497(67) Å – 3.142(95) Å, N-O distances: 2.589(74) Å – 3.122(66) Å) and prevail in the hydrophilic part of the structure.

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

The IR spectrum of **3** (Figure 2.20) is similar to that of **1** and **2**. Characteristic C–C skeletal vibrations of the phenyl rings can be observed in the range $1600 - 1400\text{ cm}^{-1}$. The signal at 1093 cm^{-1} can be associated with As–C vibrations, while some bands in the $1000 - 650\text{ cm}^{-1}$ region can be attributed to the molybdenum-oxygen and arsenic-oxygen stretching vibrations.^{8, 15, 37, 46-48}

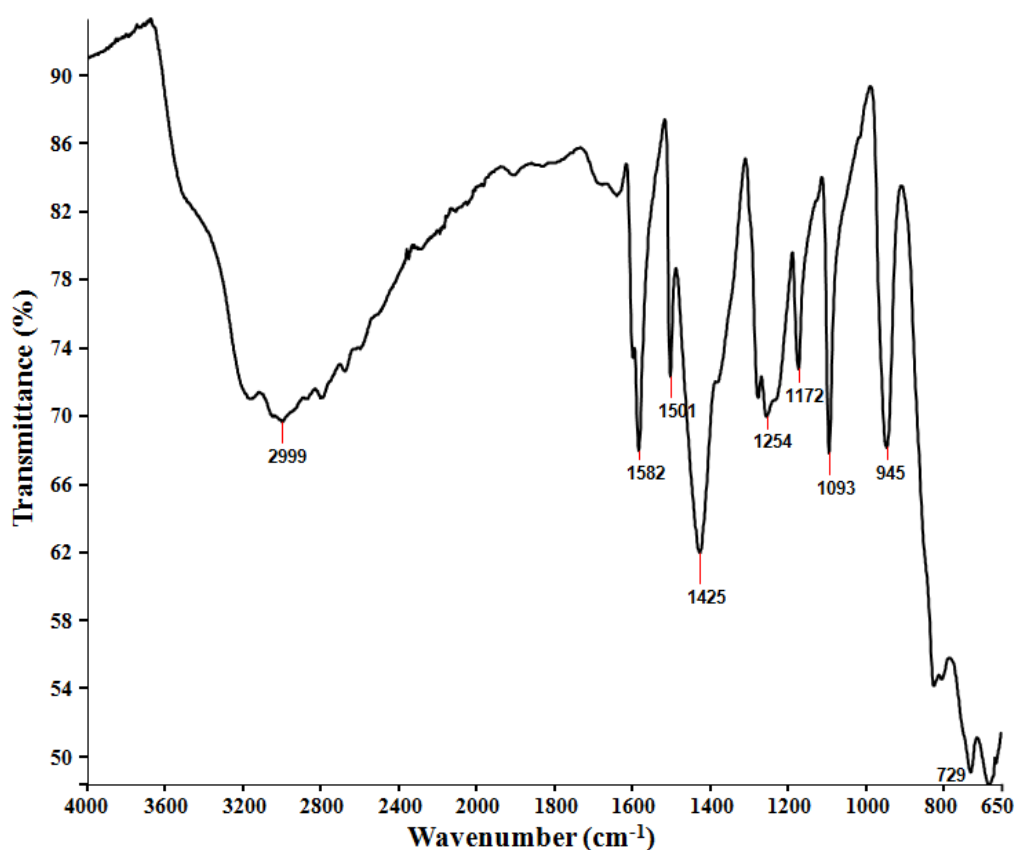


Figure 2.20 – Infrared spectrum of **3**.

- *Thermogravimetric analysis*

The thermal stability of compound **3** was investigated by thermogravimetric analysis in the temperature range between 30 and 900 °C, in a N₂ atmosphere (Figure 2.21). Upon thermolysis, **3** decomposes in a similar sequence as **2**. A weight loss of about 8.3 % occurs below 150 °C. This weight loss can be attributed to the loss of nine water molecules (calcd: 8.1 %). Decomposition of the organic ligands occurs between 200 – 400 °C and a step at 700 °C indicates the transformation into oxides.

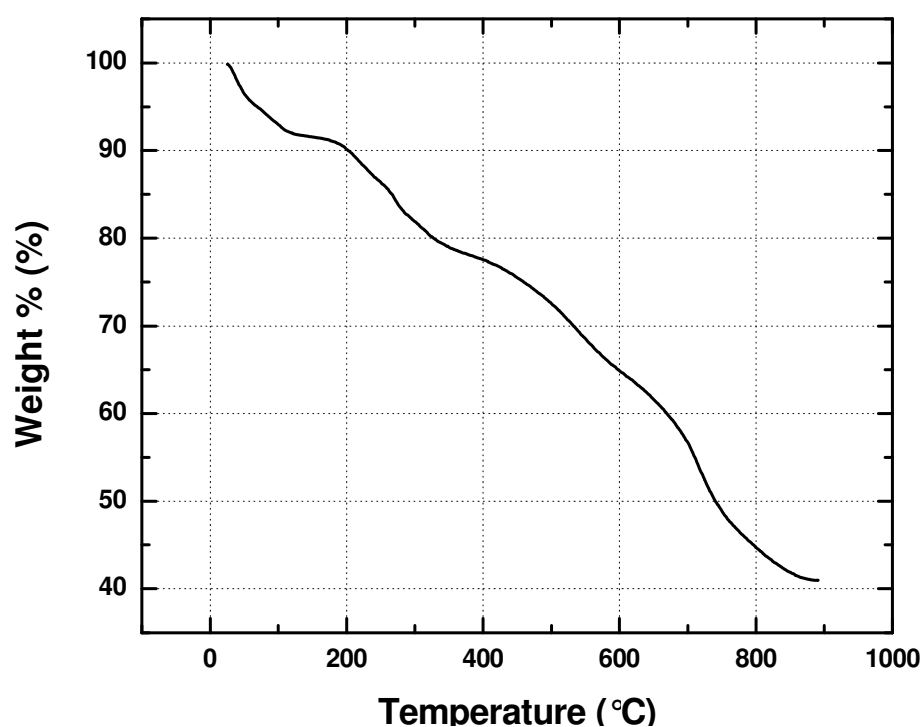


Figure 2.21 – Thermogravimetric analysis of **3**.

- Magnetism

The assignments of the oxidation states of the Mo atoms in **3** are in agreement with the observed magnetic properties. In the {Mo₅} units, three $S = \frac{1}{2}$ Mo^V (light pink) and two diamagnetic Mo^{VI} (purple) metal ions are present (Figure 2.22 a). Considering the topology of the complex, two different magnetic exchange pathways could possibly be envisaged for the {Mo₅} core. These magnetic pathways are highlighted in Figure 2.22. Moreover, it is worth noting that the interaction denoted with J' will likely be very strong as two oxo bridges mediate the magnetic interactions between Mo^V centres.

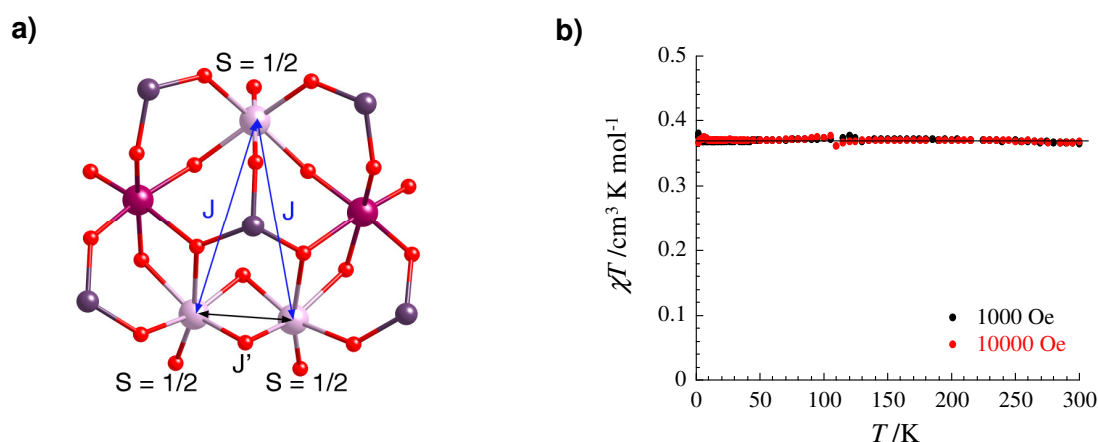


Figure 2.22 – (a) {Mo₅} units of compound **3** showing: the $S = \frac{1}{2}$ Mo(V) (light pink), the diamagnetic Mo(VI) (purple) metal ions, and the J and J' magnetic interactions; (b) Temperature dependence of the χT product (with χ defined as the magnetic susceptibility and equal to M/H after diamagnetic and experimental corrections) at 0.1 and 1 T.

The temperature dependence of the χT product of **3** is shown in Figure 2.22, b. At room temperature, the χT product is $0.37 \text{ cm}^3 \text{ K mol}^{-1}$ which is in good agreement with the presence of one $S = \frac{1}{2}$ Mo^V metal ion (expected value: $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2$). The two other Mo^V ions appear to be magnetically silent as expected for two spin centres that are strongly antiferromagnetically coupled ($|J'| \gg 500 \text{ K}$) to give a diamagnetic dinuclear unit. Such strong antiferromagnetic exchange is common in polyoxomolybdates that feature edge- and face-sharing dinuclear molybdenum octahedra.^{49, 50} When the temperature is lowered, the χT product at 1000 Oe remains constant at $0.37 \text{ cm}^3 \text{ K mol}^{-1}$ down to 1.8 K indicating a Curie type paramagnetism. From the Curie constant ($0.37 \text{ cm}^3 \text{ K mol}^{-1}$), the g value is estimated to be very close to 2.

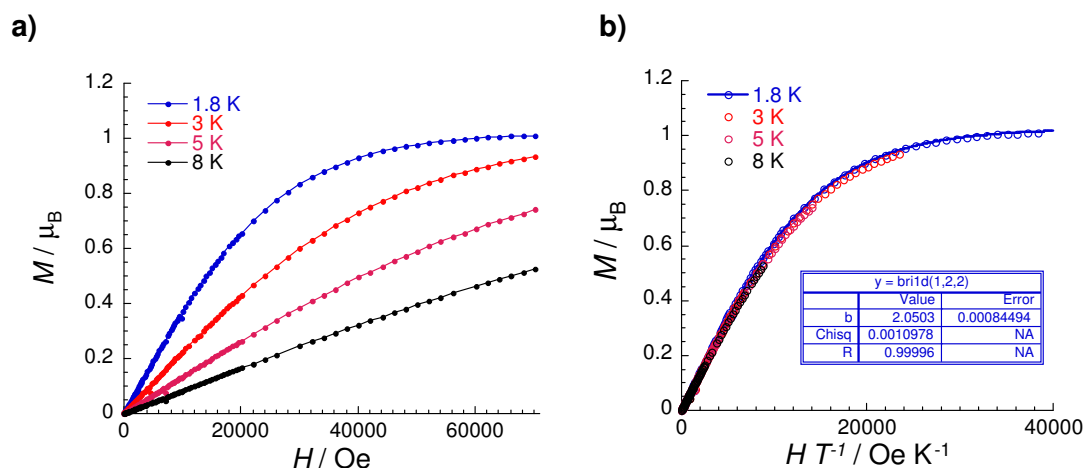


Figure 2.23 – (a) M vs H and (b) M vs H/T data below 8 K. The solid lines are guides for eyes on the left figure while the blue line on the right figure is the best fit obtained with an $S = 1/2$ Brillouin function and $g = 2.05$.

The magnetisation as a function of field at low temperatures has been measured up to 7 T between 1.8 and 8 K (Figure 2.23). It is worth noting that no hysteresis effect were detected even at 1.8 K and that the magnetisation plotted as a function of H/T is perfectly superimposed on a single master curve, as expected for isotropic systems. At 7 T and 1.8 K, the magnetic moment saturates at $1.01 \mu_B$ in perfect agreement with the presence of an $S = 1/2$ spin. The $S = 1/2$ spin ground state of the $\{\text{Mo}_5\}$ unit is confirmed by the fit of the magnetisation to an $S = 1/2$ Brillouin function that reproduces very well the experimental data with $g = 2.05$.

- *Mass spectrometry*

Negative mode ESI-MS spectra of compound **3** dissolved in a suitable solvent (H₂O and DMSO, respectively), were recorded. ESI-MS studies using the crystalline material reveal that compound **3** undergoes structural transformations when dissolved in distilled water but is stable in a DMSO environment. The mass spectrum of **3** dissolved in DMSO (Figure 2.24) reveals the presence of a signal centered at $m/z = 1739.1$ a.m.u. which corresponds to the $\{\text{H}_3[\text{Mo}^{\text{VI}}_3\text{Mo}^{\text{V}}_2\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]\}^-$ species. A comparison of the experimental isotopic envelopes with simulated patterns is presented in Figure 2.24 and confirms our assignment.

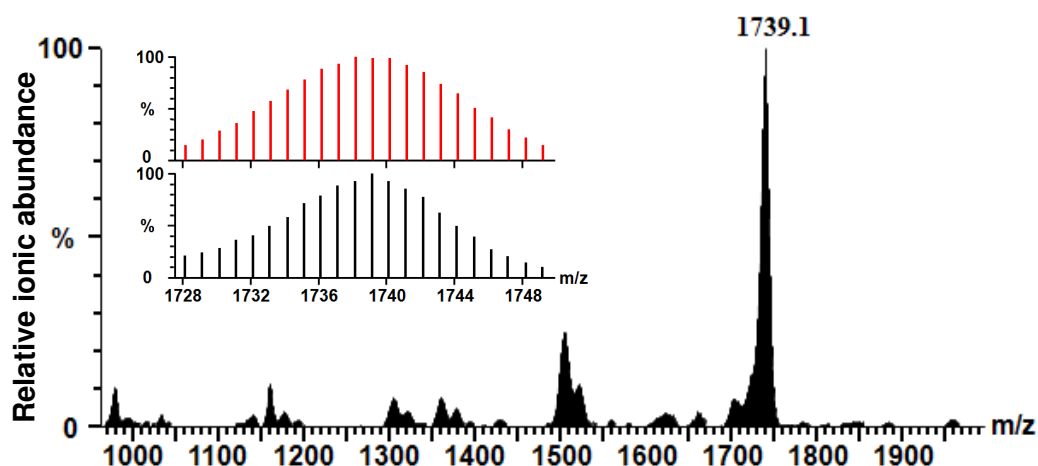


Figure 2.24 – Negative-mode ESI-MS spectra for crystals of **3** dissolved in DMSO. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated envelope (red spectrum) for $\{\text{H}_3[\text{Mo}^{\text{VI}}_3\text{Mo}^{\text{V}}_2\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]\}^-$ centered at $m/z = 1739.1$ a.m.u. (cone voltage: 30 V).

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **3** recorded in DMF displays an absorption band at *ca.* 531 nm ($\epsilon = 2700 \text{ L mol}^{-1} \text{ cm}^{-1}$). Compared to **1** and **2**, the absorption band observed for **3** is much broader and shifted to higher wavelengths. Thus, this band is a result of two different types of absorptions: d – d transitions involving the Mo^{V} metal centers and intervalence charge transfer between Mo^{V} and Mo^{VI} *via* an oxo bridge. The d – d transitions can be assigned to a ${}^2\text{E}_g \leftarrow {}^2\text{T}_{2g}$ transition of the octahedrally coordinated Mo^{V} ions.^{38, 51, 52}

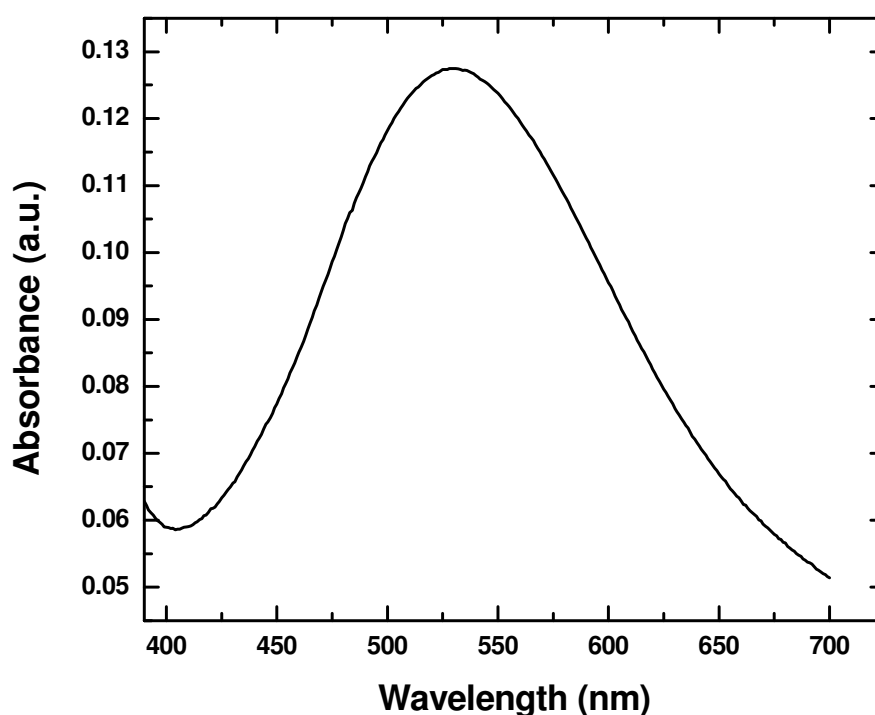


Figure 2.25 – A section of the UV-Vis spectrum of a 10^{-4} M solution of **3** in DMF.

Table 2.9 – Crystal data and structural refinement parameters for 3.

Compound 3	
Empirical formula	C ₃₀ H ₆₃ As ₅ Mo ₅ N ₅ O ₄₀
Molecular mass/g mol ⁻¹	1988.13
Crystal colour/shape	Blue / rectangular plate
Crystal size/mm ³	0.50×0.40×0.40
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	19.417(4)
b/ Å	21.040(4)
c/ Å	21.562(4)
α /°	113.09(3)
β /°	112.90(3)
γ /°	99.16(3)
V/ Å ³	6941(2)
Z	2
Temperature (K)	108(2)
Density/Mg m ⁻³	1.864
Absorp. coef./mm ⁻¹	3.334
F(000)	3732
2 $\theta_{\max}$ /°	50
Reflections collected	103006
Independent reflections	24429 [R(int) = 0.0648]
Data / restraints / parameters	24429 / 15280 / 1587
S on F^2	1.059
R ₁ , wR ₂ [I>2 σ (I)]	0.0704, 0.1844
R ₁ , wR ₂ (all data)	0.0789, 0.1930
Largest diff. peak and hole/e.Å ⁻³	2.729 and -2.598

2.2.1.4 The (4-Hydroxy-3-Nitrophenyl)arsonic Acid – Mo^{VI}/Mo^{VI} Reaction System (NH₄)₄[Mo^{VI}₄O₁₀(O₃AsC₆H₃NO₂OH)₄]·2H₂O (**4**)

It was decided to investigate the influence of a disubstituted arsonate ligand on the self-assembly process of hybrid polyoxomolybdates under the same outlined reaction conditions that led to the formation of **1–3**. Using a substituted arsonate ligand with a hydroxyl group in the *para* position and a nitro group in the *meta* position, a dark-green solution is obtained, which undergoes a colour change to red-orange within approximately ten days. Orange crystals of (NH₄)₄[Mo^{VI}₄O₁₀(O₃AsC₆H₃NO₂OH)₄]·2H₂O (**4**) were obtained from the reaction mixture within a time period of three weeks, and single crystal X-ray studies were performed.

4 crystallises in the triclinic crystal system in the space group $P\bar{1}$. The anionic cluster [Mo^{VI}₄O₁₀(O₃AsC₆H₃NO₂OH)₄]⁴⁻ in **4** (Figure 2.26) contains two {Mo₂O₁₀}⁸⁻ subunits in which octahedrally coordinated Mo atoms share a common edge (Mo(1) with Mo(2) and Mo(1') with Mo(2')). The dimeric units are connected by four deprotonated arsonate ligands. Two of the ligands have their As atoms (As(3) and As(3')) arranged nearly coplanar to the four Mo atoms. Each of the ligands is bridging between two Mo ions in a μ_2 -*syn, syn* bridging mode to form a six membered {As₂Mo₄} ring. The remaining two arsonate ligands cap both sides of the central cavity of the ring and each provides one μ_2 -bridging O-donor (O(4) and O(4')) of the common edges of the {Mo₂O₁₀}⁸⁻ dimer moieties. The other two O atoms of the tetrahedral arsonate functionality of each of the ligands (O(7), O(13) and O(7'), O(13')) respectively) link to the adjacent {Mo₂O₁₀}⁸⁻ moiety and interconnect the dimeric subunits. The involved O donors bridge in a μ_2 -*syn, syn* bridging mode and occupy two apical positions of the octahedrally coordinated Mo atoms within the dimer units. All four Mo atoms show distorted octahedral coordination environments. Each Mo ion in **4** is involved in two short Mo=O bonds (range between 1.692(3) - 1.720(3) Å), three elongated Mo–O_{arsonate} bonds that range between 2.009(3) - 2.427(3) Å and one Mo–(μ_2 -O) bond with a bond length of 1.915(3) Å for Mo(1)-O(1) and 1.894(3) Å for Mo(2)-O(1) (Table 2.10). The distorted nature of the octahedral coordination environments of the Mo ions can be exemplified by examining the bond lengths and bond angles of the metal centres. The bond angles O(1)-Mo(1)-O(5) and O(1)-Mo(1)-O(4) of 156.65(11)° and 75.20(10)°, respectively, show the greatest deviation from the ideal octahedral geometry (Table 2.11).

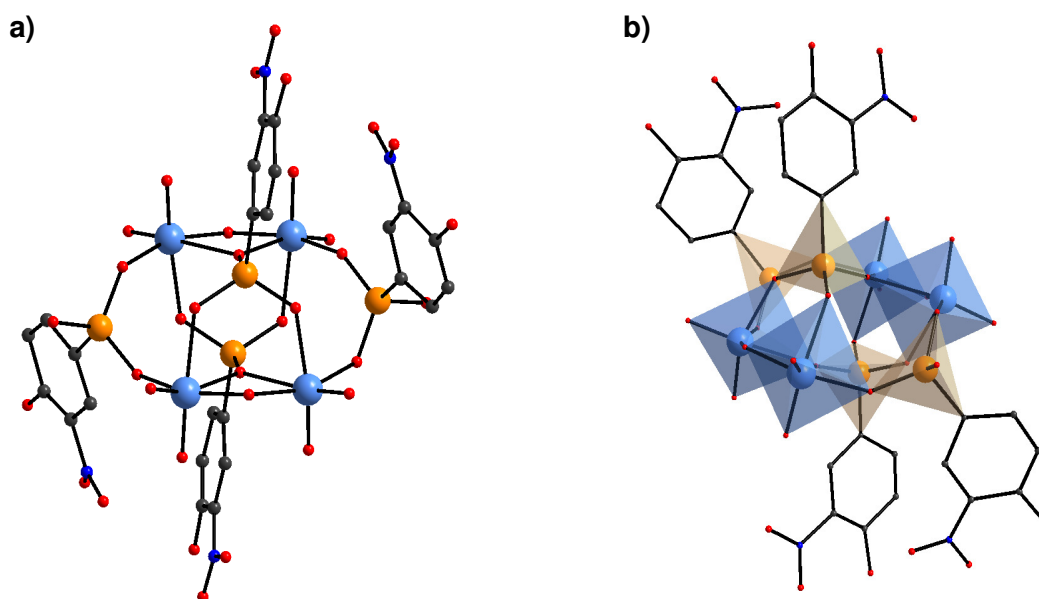


Figure 2.26 – Crystal structure of the tetranuclear Mo complex in **4**: (a) ball-and-stick representation, (b) polyhedral presentation. Colour code: Mo^{VI} sky blue, As orange, O red, N light blue, C grey (hydrogen atoms have been omitted for clarity).

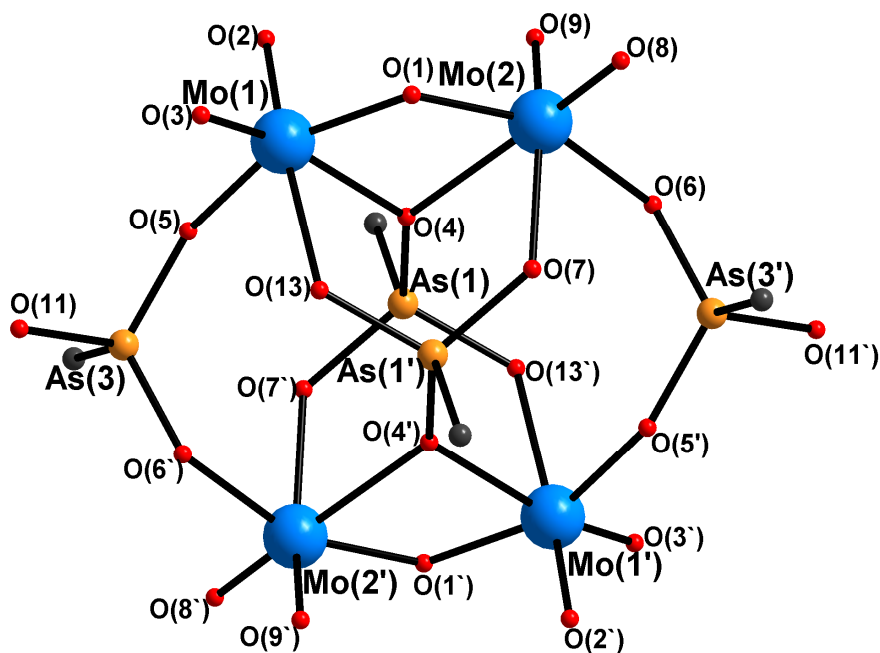


Figure 2.27 – The core structure of the tetranuclear Mo complex in **4**. Colour code: Mo^{VI} sky blue, As orange, O red, C grey.

The core structure of **4** is related to those observed in $(\text{Et}_3\text{NH})_4[\text{Mo}_4\text{O}_{10}(\text{C}_6\text{H}_5\text{PO}_3)_4]\cdot 2\text{CH}_3\text{CN}$ and $(\text{Et}_3\text{NH})_4[\text{Mo}_4\text{O}_{10}(\text{C}_6\text{H}_5\text{AsO}_3)_4]\cdot 4\text{H}_2\text{O}$,

respectively.¹¹ In these compounds the anionic clusters share a common structural motif but are stabilised by different organic ligands.

Bond valence sum analyses confirm that all four Mo atoms in **4** adopt the oxidation state +VI (Table 2.10).

Table 2.10 – Selected bond lengths [Å] and bond valence sum (BVS) for compound 4.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mo(1)	Mo(1)-O(3)	1.692(3)	5.979	+6
	Mo(1)-O(2)	1.720(3)		
	Mo(1)-O(1)	1.915(3)		
	Mo(1)-O(5)	2.009(3)		
	Mo(1)-O(13)	2.223(3)		
	Mo(1)-O(4)	2.276(3)		
Mo(2)	Mo(2)-O(8)	1.707(3)	5.937	+6
	Mo(2)-O(9)	1.714(3)		
	Mo(2)-O(1)	1.894(3)		
	Mo(2)-O(6)	2.049(3)		
	Mo(2)-O(7)	2.113(3)		
	Mo(2)-O(4)	2.427(3)		

Table 2.11 – Selected bond angles [°] for compound 4.

Bond Angle (°)		Bond Angle (°)	
O(2)-Mo(1)-O(13)	167.73(12)	O(8)-Mo(2)-O(4)	169.07(12)
O(3)-Mo(1)-O(4)	162.67(12)	O(9)-Mo(2)-O(7)	154.73(13)
O(1)-Mo(1)-O(5)	156.65(11)	O(1)-Mo(2)-O(6)	158.36(12)
O(3)-Mo(1)-O(2)	104.73(14)	O(8)-Mo(2)-O(9)	104.19(14)
O(3)-Mo(1)-O(5)	98.60(13)	O(8)-Mo(2)-O(1)	99.20(13)
O(2)-Mo(1)-O(1)	97.13(13)	O(8)-Mo(2)-O(6)	96.61(13)
O(2)-Mo(1)-O(4)	92.55(12)	O(6)-Mo(2)-O(4)	90.51(10)
O(3)-Mo(1)-O(13)	86.93(12)	O(9)-Mo(2)-O(6)	88.55(13)
O(5)-Mo(1)-O(4)	82.40(11)	O(6)-Mo(2)-O(7)	77.79(11)
O(1)-Mo(1)-O(4)	75.20(10)	O(7)-Mo(2)-O(4)	74.87(10)

As expected, the di-substituted arsonate ligand imposes an influence on the self-assembly process under the investigated conditions that produce **1** and **2**. In fact, the composition of the cluster anion **4** is closely related to that of **1** and **2**. However, it seems

that the -OH and -NO₂ functionalities of the organic ligands enforce a rearrangement of the cubane core structure. The rearrangement can formally be explained by an intramolecular condensation reaction under acidic conditions (Figure 2.28).

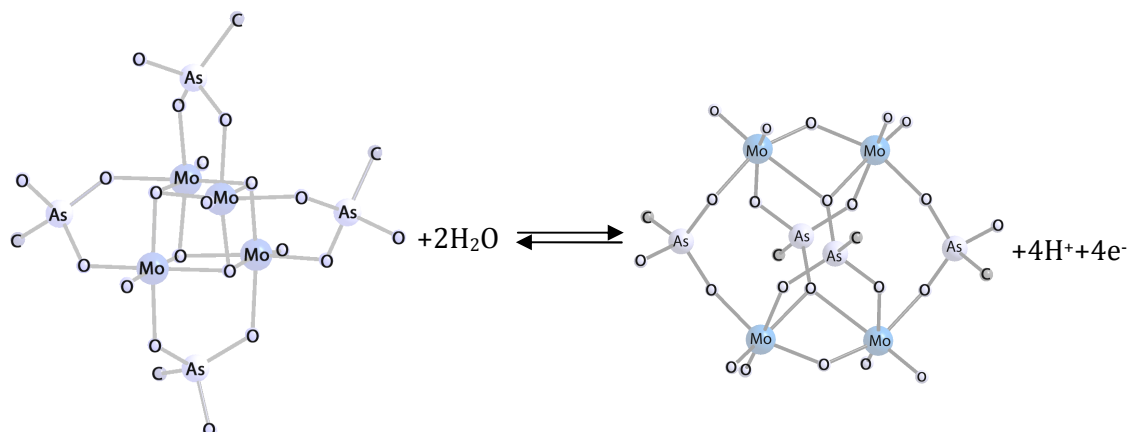


Figure 2.28 – Formal rearrangement of the {Mo₄} core structure in **1** or **2** to give **4**.

The packing arrangement of the [Mo^{VI}₄O₁₀(O₃AsC₆H₃NO₂OH)₄]⁴⁻ clusters in the crystal structure is characterised by small intercluster channels (filled with constitution water molecules and NH₄⁺ counterions) that run in the direction of the crystallographic *a*-axis (Figure 2.29). The counterions and the crystallisation water molecules are engaged in H bonds whose N-O and O-O contacts range between 2.697(10) Å – 3.112(34) Å.

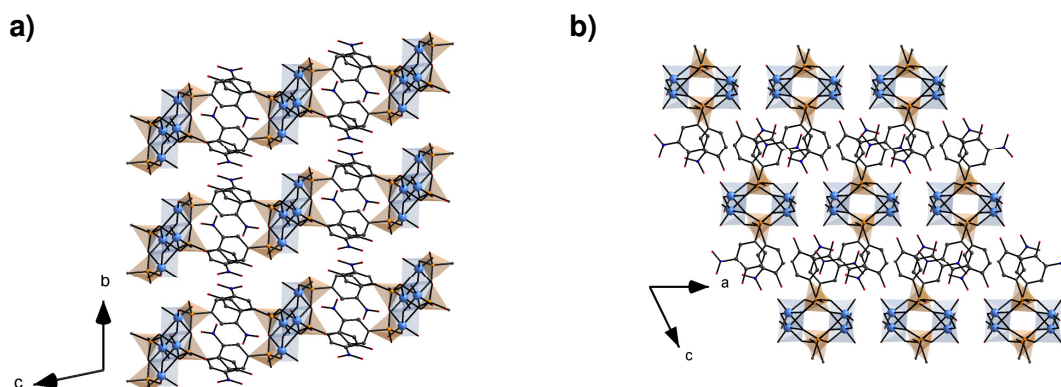


Figure 2.29 – Packing arrangement of **4** in the crystal structure viewed in the direction of the crystallographic: (a) *a*-axis and (b) *b*-axis. Colour code: Mo^{VI} sky blue, As orange, O red, N light blue, C grey (crystallisation water molecules, NH₄⁺ counterions and hydrogen atoms have been omitted for clarity).

- PHYSICOCHEMICAL CHARACTERISATION

- FT-IR spectroscopy

The IR spectrum of **4** shown in Figure 2.30 is comparable to that of **1** – **3**. Notably, the 1620 – 1050 cm^{-1} region of the spectrum is quite crowded displaying a set of sharp bands of medium intensity. These bands arise from C–C skeletal vibrations of the phenyl rings, As–C vibrations and N–O stretches of the organoarsonate ligands.^{8, 15, 37, 46-48}

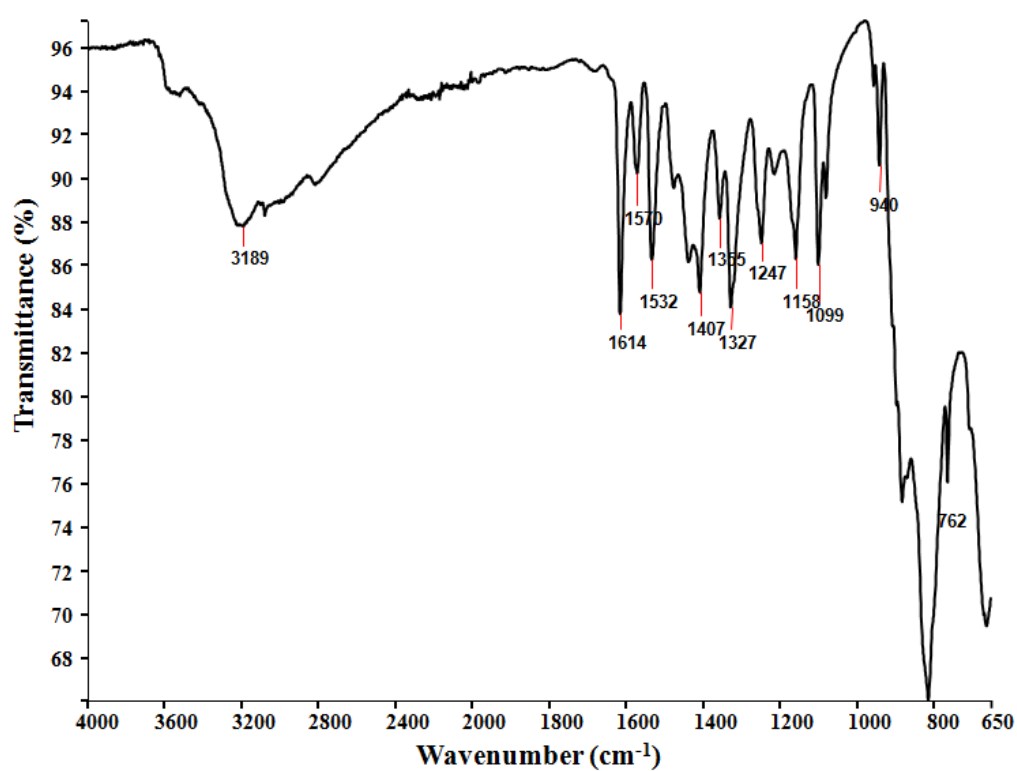


Figure 2.30 – Infrared spectrum of **4**.

- *Thermogravimetric analysis*

Compound **4** was also analysed by TGA (Figure 2.31). A gradual weight loss of 2.3 % observed below 200 °C which corresponds to the loss of two water molecules (calcd: 2.1 %). A further weight loss between 200 – 450 °C indicates the decomposition of the organic moieties, while the thermogravimetric step between 450 – 550 °C can be associated with the decomposition into oxides.

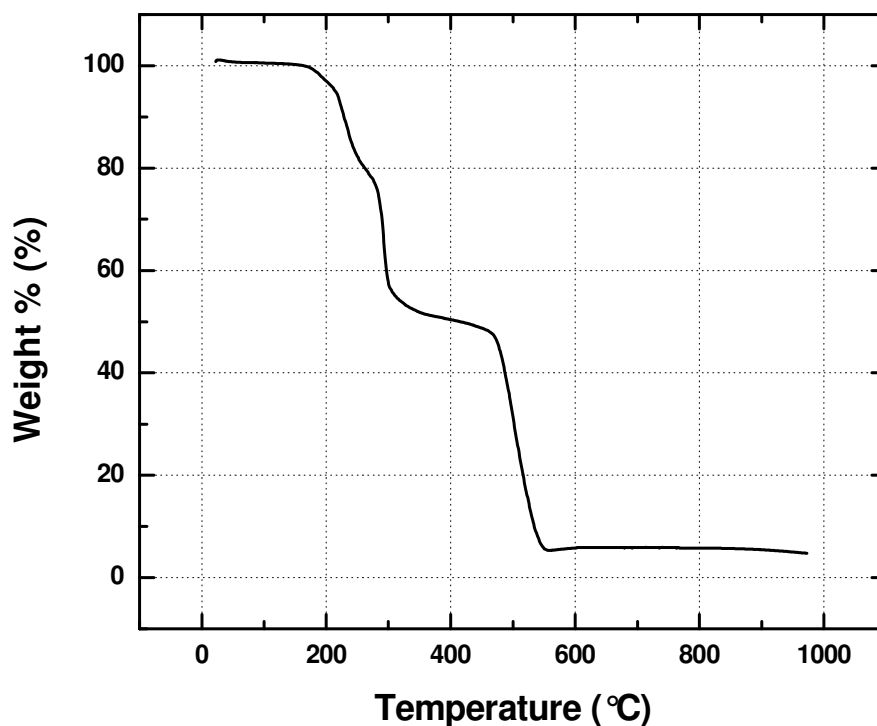


Figure 2.31 – Thermogravimetric analysis of **4**.

ESI-MS studies reveal that **4** is unstable in solution. The compound most likely decomposes into insoluble inorganic or polymeric materials when dissolved in H₂O or DMSO.

Table 2.12 – Crystal data and structural refinement parameters for 4.

Compound 4	
Empirical formula	C ₂₄ H ₃₆ As ₄ Mo ₄ N ₈ O ₃₆
Molecular mass/g mol ⁻¹	1696.02
Crystal colour/shape	Orange / rectangular plate
Crystal size/mm ³	0.20×0.20×0.20
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	10.7255(19)
b/ Å	10.937(3)
c/ Å	12.000(3)
α /°	89.474(13)
β /°	66.129(10)
γ /°	63.926(7)
V/ Å ³	1131.6(5)
Z	1
Temperature (K)	108(2)
Density/Mg m ⁻³	2.465
Absorp. coef./mm ⁻¹	4.109
F(000)	808
$2\theta_{\max}$ /°	50.04
Reflections collected	14710
Independent reflections	3987 [R(int) = 0.0313]
Data / restraints / parameters	3987 / 3 / 343
S on F^2	1.036
R ₁ , wR ₂ [I>2 σ (I)]	0.0282, 0.0817
R ₁ , wR ₂ (all data)	0.0303, 0.0831
Largest diff. peak and hole/e.Å ⁻³	1.502 and -0.739

2.2.2 Synthesis and characterisation of organophosphonate functionalised heteropolyoxomolybdate clusters

2.2.2.1 The Phenylphosphonic Acid – Mo^{VI}/Mo^V Reaction System (NH₄)₄H₄{Mn[Mo^VO₁₂(OH)₃(O₃PC₆H₅)₄]₂}·8H₂O (**5**)

Partial reduction of molybdic acid using N₂H₄·H₂O in the presence of phenylphosphonic acid and MnCl₂·4H₂O results in a red-brown solution from which orange octahedral crystals of (NH₄)₄H₄{Mn[Mo^VO₁₂(OH)₃(O₃PC₆H₅)₄]₂}·8H₂O (**5**) separate within a time period of three days.

Single crystal X-ray analysis reveals that **5** crystallises in the orthorhombic crystal system in the space group *Pbca*. The structure consists of two [Mo^VO₁₂(OH)₃(O₃PC₆H₅)₄]⁵⁻ fragments linked through a Mn^{II} ion (Figure 2.32). Within each fragment, six Mo ions form distorted octahedral coordination polyhedra, each sharing two common edges with adjacent polyhedra to form a six membered ring. Three organophosphonate ligands are situated on the periphery of the resulting ring, each bridging two Mo ions in a $\eta^1:\eta^1:\mu_2$ bridging mode. The O donors of a fourth organic ligand cap the central cavity of the ring and provide μ_2 bridging O donors (O(2), O(4) and O(12)) to three, dimeric edges-sharing subunits (Mo(2) and Mo(3), Mo(4) and Mo(5), and Mo(6) and Mo(1), respectively). The aromatic moieties of the four organic ligands are arranged approximately perpendicular to the mean plane of the six membered ring. The six molybdenum atoms within the ring display distorted octahedral coordination environments. This distortion mainly results from the presence of short Mo=O bonds (range between 1.678(7) - 1.699(6) Å) situated in *trans* positions to significantly longer Mo-(μ_2 -O) bonds (range between 2.302(6) - 2.333(6) Å). The μ_2 bridging O-donors (O(2), O(4) and O(12)) engaged in these elongated bonds originate from the phosphonate functionality of the central ligand. The remaining coordination sites of the Mo ions are occupied by one O donor originating from a peripheral organic ligand, two μ_2 -O²⁻ ions that bridge between two Mo ions and a μ_3 -O²⁻ ligand bridging between two Mo ions and the central Mn ion. The bond distances between the Mo ions and the O donors of these peripheral phosphonate ligands range between 2.066(6) Å – 2.093(7) Å, the Mo-(μ_2 -O²⁻) bond distances range between 1.941(7) Å – 2.135(6) Å, while the Mo-(μ_3 -O²⁻) bond distances range between 1.972(6) Å – 1.989(6) Å. The distorted octahedral coordination environment of the Mo

ions in **5** can also be exemplified by examining the bond angles that deviate from the ideal octahedral geometry. Selected bond lengths and bond angles for the Mo ions in **5** are listed in Table 2.13, Table 2.14.

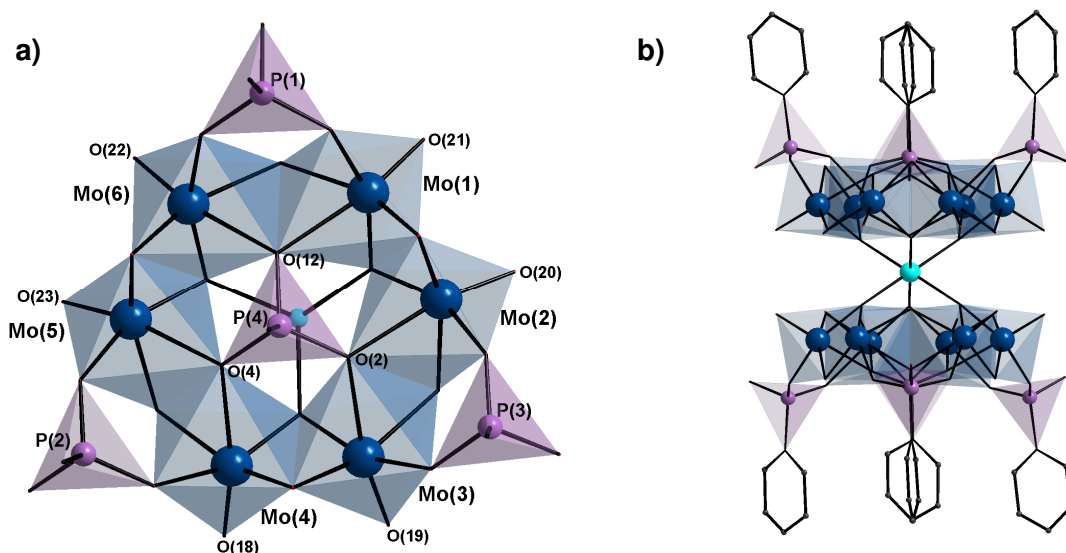


Figure 2.32 – Crystal structure of the dodecanuclear Mo complex in **5**. Colour code: Mo^V blue, P purple, O red, Mn cyan, C grey (hydrogen atoms have been omitted for clarity).

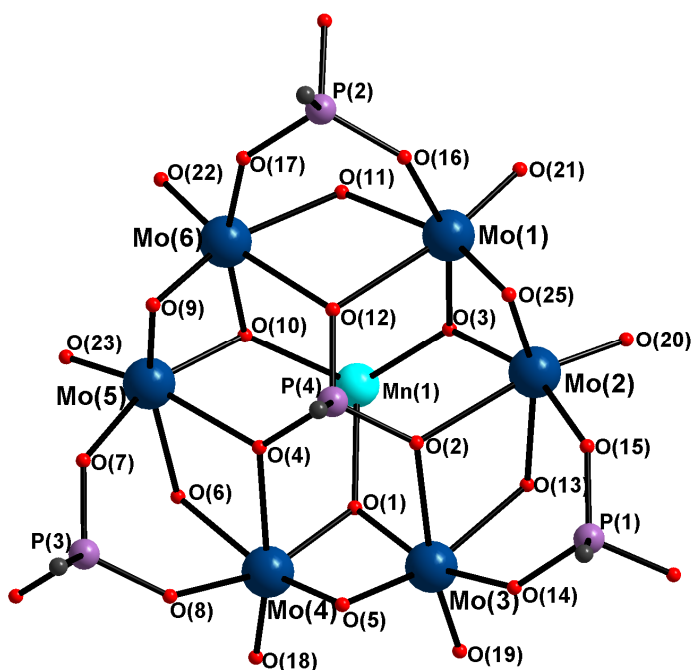


Figure 2.33 – The {Mn[Mo^V₆O₁₂(OH)₃(O₃PC₆H₅)₄]}³⁻ fragment in **5**. Colour code: Mo^V blue, P purple, O red, Mn cyan, C grey.

Table 2.13 – Selected bond lengths [$\text{\AA}$] and bond valence sum (BVS) for compound **5.**

Atom	Bond	Bond distances ($\text{\AA}$)	BVS	Assigned oxidation state
Mo(1)	Mo(1)-O(21)	1.699(6)	5.174	+5
	Mo(1)-O(25)	1.951(7)		
	Mo(1)-O(3)	1.987(6)		
	Mo(1)-O(16)	2.084(7)		
	Mo(1)-O(11)	2.127(6)		
	Mo(1)-O(12)	2.326(6)		
Mo(2)	Mo(2)-O(20)	1.689(7)	5.047	+5
	Mo(2)-O(25)	1.945(7)		
	Mo(2)-O(3)	1.987(6)		
	Mo(2)-O(15)	2.093(7)		
	Mo(2)-O(13)	2.109(6)		
	Mo(2)-O(2)	2.302(6)		
Mo(3)	Mo(3)-O(19)	1.678(7)	5.134	+5
	Mo(3)-O(5)	1.943(7)		
	Mo(3)-O(1)	1.972(6)		
	Mo(3)-O(14)	2.079(7)		
	Mo(3)-O(13)	2.118(6)		
	Mo(3)-O(2)	2.318(6)		
Mo(4)	Mo(4)-O(18)	1.689(7)	5.001	+5
	Mo(4)-O(5)	1.941(7)		
	Mo(4)-O(1)	1.989(6)		
	Mo(4)-O(8)	2.092(7)		
	Mo(4)-O(6)	2.127(6)		
	Mo(4)-O(4)	2.333(6)		
Mo(5)	Mo(5)-O(23)	1.692(7)	5.044	+5
	Mo(5)-O(9)	1.943(6)		
	Mo(5)-O(10)	1.978(6)		
	Mo(5)-O(7)	2.068(6)		
	Mo(5)-O(6)	2.135(6)		
	Mo(5)-O(4)	2.320(6)		
Mo(6)	Mo(6)-O(22)	1.687(7)	5.091	+5
	Mo(6)-O(9)	1.945(6)		
	Mo(6)-O(10)	1.978(6)		
	Mo(6)-O(17)	2.066(6)		
	Mo(6)-O(11)	2.117(6)		
	Mo(6)-O(12)	2.325(6)		
Mo(1) ... Mo(2)		2.6058(14)		
Mo(3) ... Mo(4)		2.6027(14)		
Mo(5) ... Mo(6)		2.5934(15)		

Bond valence sum analysis confirms that all six Mo atoms in **5** adopt the oxidation state +V. In the crystal structure of **5**, the molecular entities pack to form a layered lamellar structure with alternating hydrophobic organic and hydrophilic inorganic regions (Figure 2.34). The NH_4^+ counterions and the crystallisation water molecules are situated in the hydrophilic part of the structure being engaged in hydrogen bonds (O-O and O-N distances: 2.901(26) $\text{\AA}$ – 3.084(21) $\text{\AA}$). Weak offset π - π interactions between two adjacent

clusters with an interplanar separation distance of about 3.9 Å also contribute to the stability of **5** in the solid state.

Table 2.14 – Selected bond angles [°] for compound **5**.

Bond Angle (°)		Bond Angle (°)	
O(21)-Mo(1)-O(12)	169.8(3)	O(20)-Mo(2)-O(2)	168.7(3)
O(3)-Mo(1)-O(16)	160.2(3)	O(3)-Mo(2)-O(15)	159.3(3)
O(25)-Mo(1)-O(11)	155.6(3)	O(25)-Mo(2)-O(13)	155.9(3)
O(21)-Mo(1)-O(25)	106.2(3)	O(20)-Mo(2)-O(25)	105.9(3)
O(21)-Mo(1)-O(11)	97.3(3)	O(20)-Mo(2)-O(15)	97.5(3)
O(25)-Mo(1)-O(3)	95.4(3)	O(25)-Mo(2)-O(3)	95.6(3)
O(25)-Mo(1)-O(16)	86.5(3)	O(3)-Mo(2)-O(13)	86.5(3)
O(16)-Mo(1)-O(11)	84.1(3)	O(15)-Mo(2)-O(13)	84.6(3)
O(3)-Mo(1)-O(12)	81.3(2)	O(3)-Mo(2)-O(2)	80.9(2)
O(11)-Mo(1)-O(12)	73.0(2)	O(13)-Mo(2)-O(2)	72.1(2)
O(19)-Mo(3)-O(2)	168.1(3)	O(1)-Mo(4)-O(8)	160.6(3)
O(1)-Mo(3)-O(14)	159.5(3)	O(18)-Mo(4)-O(4)	169.8(3)
O(5)-Mo(3)-O(13)	155.1(3)	O(5)-Mo(4)-O(6)	155.8(3)
O(19)-Mo(3)-O(5)	106.7(3)	O(18)-Mo(4)-O(5)	106.1(3)
O(19)-Mo(3)-O(13)	96.9(3)	O(18)-Mo(4)-O(6)	97.3(3)
O(5)-Mo(3)-O(1)	95.4(3)	O(5)-Mo(4)-O(1)	94.9(3)
O(1)-Mo(3)-O(13)	86.6(3)	O(5)-Mo(4)-O(8)	87.2(3)
O(5)-Mo(3)-O(2)	84.2(2)	O(8)-Mo(4)-O(6)	84.0(3)
O(1)-Mo(3)-O(2)	80.7(2)	O(1)-Mo(4)-O(4)	81.5(2)
O(13)-Mo(3)-O(2)	71.7(2)	O(6)-Mo(4)-O(4)	73.0(2)
O(23)-Mo(5)-O(4)	169.5(3)	O(22)-Mo(6)-O(12)	169.0(3)
O(10)-Mo(5)-O(7)	158.6(3)	O(10)-Mo(6)-O(17)	158.9(3)
O(9)-Mo(5)-O(6)	156.9(3)	O(9)-Mo(6)-O(11)	156.8(3)
O(23)-Mo(5)-O(9)	105.5(3)	O(22)-Mo(6)-O(9)	105.9(3)
O(23)-Mo(5)-O(7)	97.6(3)	O(22)-Mo(6)-O(17)	97.1(3)
O(9)-Mo(5)-O(10)	95.5(2)	O(9)-Mo(6)-O(10)	95.4(3)
O(9)-Mo(5)-O(7)	86.6(3)	O(9)-Mo(6)-O(17)	86.4(3)
O(7)-Mo(5)-O(6)	84.6(3)	O(17)-Mo(6)-O(11)	84.3(3)
O(10)-Mo(5)-O(4)	80.5(2)	O(10)-Mo(6)-O(12)	80.4(2)
O(6)-Mo(5)-O(4)	73.2(2)	O(11)-Mo(6)-O(12)	73.2(2)

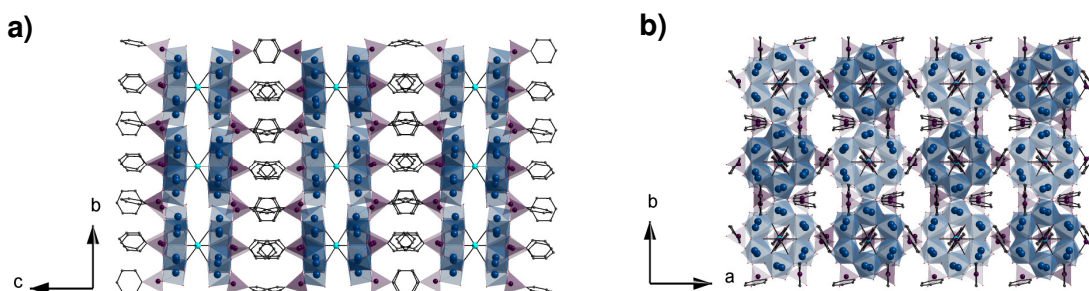
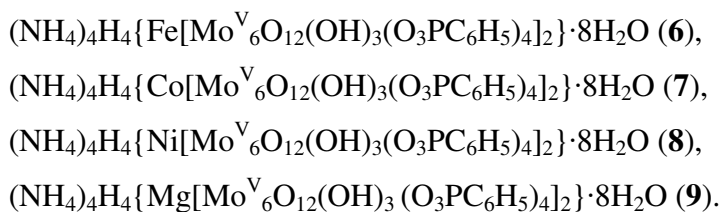


Figure 2.34 – Packing arrangement of **5** in the crystal structure viewed in the direction of the crystallographic: (a) *a*-axis and (b) *c*-axis. Colour code: Mo^V blue, P purple, O red, Mn cyan, C grey (crystallisation water molecules, NH₄⁺ counterions and hydrogen atoms have been omitted for clarity).

Several of these sandwich-type compounds were successfully synthesised using similar synthetic procedure as for **5**, but replacing the Mn^{II} ion with Fe^{III} , Co^{II} , Ni^{II} , and Mg^{II} metal ions, respectively, in order to link the two $\{\text{Mo}_6\}$ fragments:



The resulting compounds are isostructural to **5** and have very similar structural and geometrical parameters. A single crystal X-ray diffraction study was carried out on the Fe^{III} complex, confirming the expected sandwich structure (Table 2.16). XRD powder diffraction analyses were performed on the Co^{II} , Ni^{II} , and Mg^{II} complexes to certify that the compounds are isostructural. The measured powder pattern of each compound fits to the simulated pattern which is based on the single crystal X-ray diffraction data of **5** (Figure 2.35).

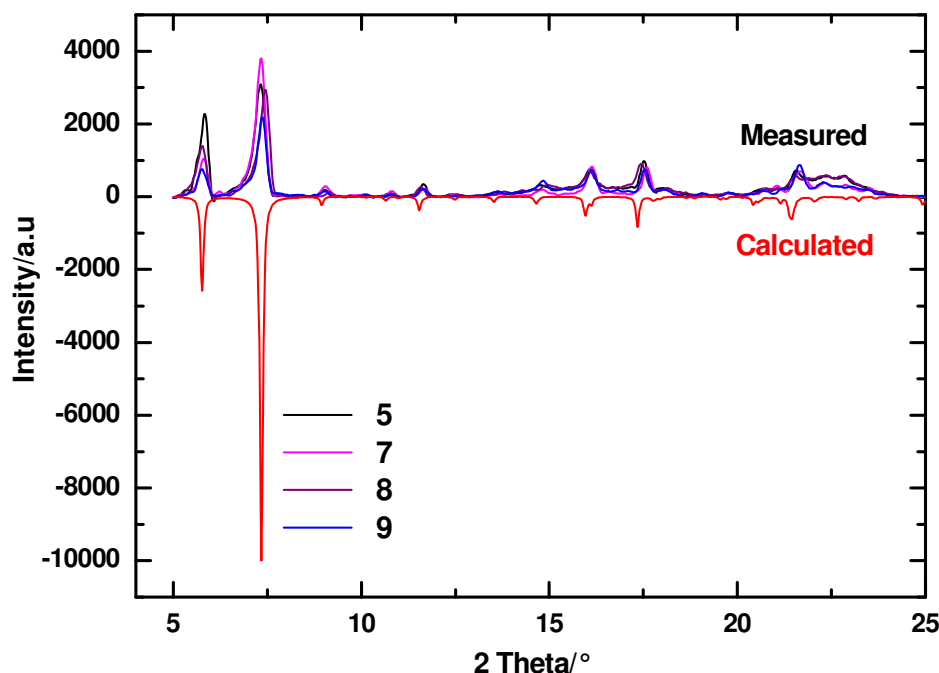


Figure 2.35 – X-ray powder diffraction analysis, comparing the experimental patterns of **5** (black), **7** (pink), **8** (purple) and **9** (blue) complexes with simulated pattern (red) based on the single crystal X-ray diffraction data of **5**.

EDX analyses further confirm the presence of the transition metal ions within the corresponding compounds.

- PHYSICOCHEMICAL CHARACTERISATION

- FT-IR spectroscopy

The IR spectrum of **5** is presented in Figure 2.36 and reveals some characteristic stretches of the organophosphonate ligands. The C–C skeletal vibrations of the phenyl rings can be identified in the range $1600 - 1400\text{ cm}^{-1}$, while some of the bands in the $800 - 650\text{ cm}^{-1}$ region arise from C–H out-of-plane bending vibrations of the aromatic rings. Different P–O stretching vibrations of the phosphonate groups can be observed in the range $1200 - 1000\text{ cm}^{-1}$. The very strong band at *ca.* 950 cm^{-1} is characteristic of Mo=O stretching vibrations. Finally, the broad bands at *ca.* 3200 cm^{-1} and *ca.* 1600 cm^{-1} arise from O–H stretching vibrations and H–O–H bending vibrations of the crystallisation water molecules engaged in H-bonds.^{13, 48, 53, 54}

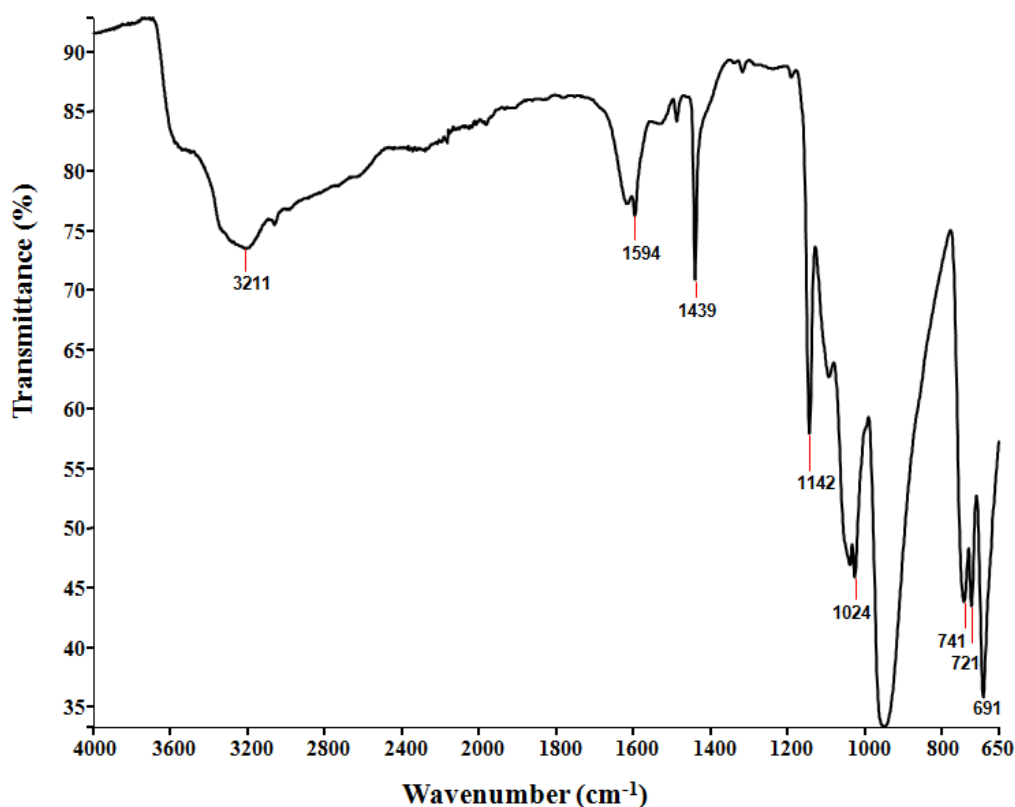


Figure 2.36 – Infrared spectrum of **5**.

- *Thermogravimetric analysis*

The TGA curve of compound **5** is presented in Figure 2.37. It reveals a weight loss of 4.6 % below 100 °C, which was attributed to the loss of eight water molecules (calcd: 4.5 %). The decomposition of the organic ligands occurs between 300 – 600 °C and further cluster degradation processes result in the formation of metal oxides. The thermal stability of compounds **6**, **7**, **8** and **9** was also investigated. As expected, all five isostructural compounds reveal similar decomposition behaviour.

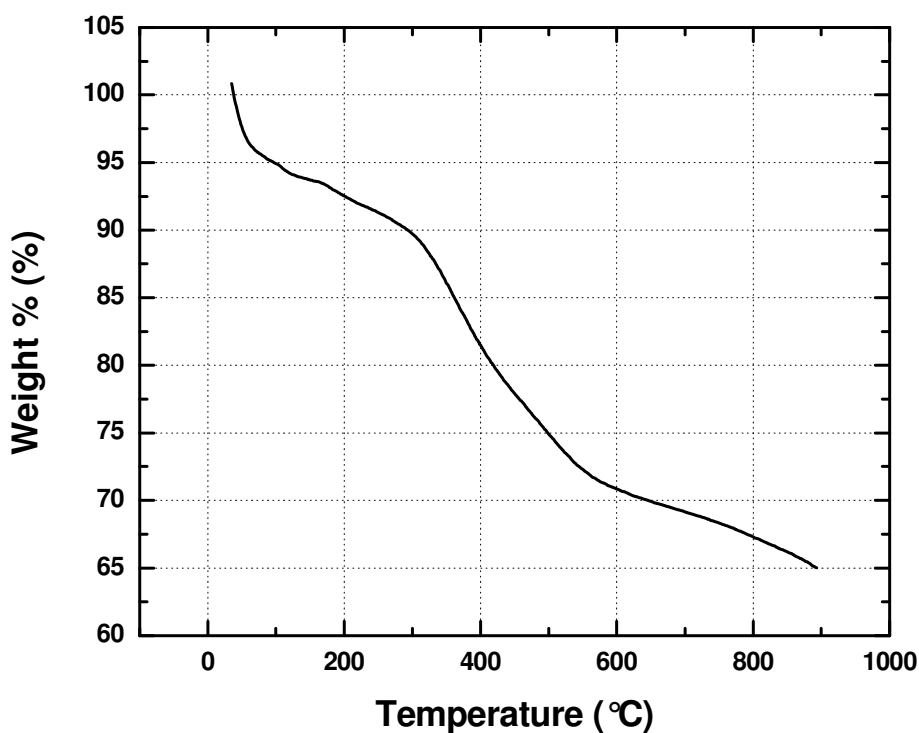


Figure 2.37 – Thermogravimetric analysis of **5**.

The CHN analysis of the compounds is also in good agreement with the composition of the compounds.

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **5** recorded in CH₃CN is presented in Figure 2.38. The strong absorption band observed at *ca.* 305 nm ($\epsilon = 11000 \text{ L mol}^{-1} \text{ cm}^{-1}$) is due to charge transfer transitions involving either the phosphonate ligands or the {Mo-O} moieties. A very weak absorption band can also be observed at *ca.* 443 nm ($\epsilon = 1050 \text{ L mol}^{-1} \text{ cm}^{-1}$) involving a d – d transition that can be assigned to $^2\text{E}_g \leftarrow ^2\text{T}_{2g}$ transitions of the octahedrally coordinated Mo^V ions within **5**. Compounds **6**, **7**, **8** and **9** display similar absorption spectra as **5** showing characteristic charge transfer absorptions around 300 nm and very weak absorption bands due to d – d transitions at *ca.* 450 nm.^{38, 55}

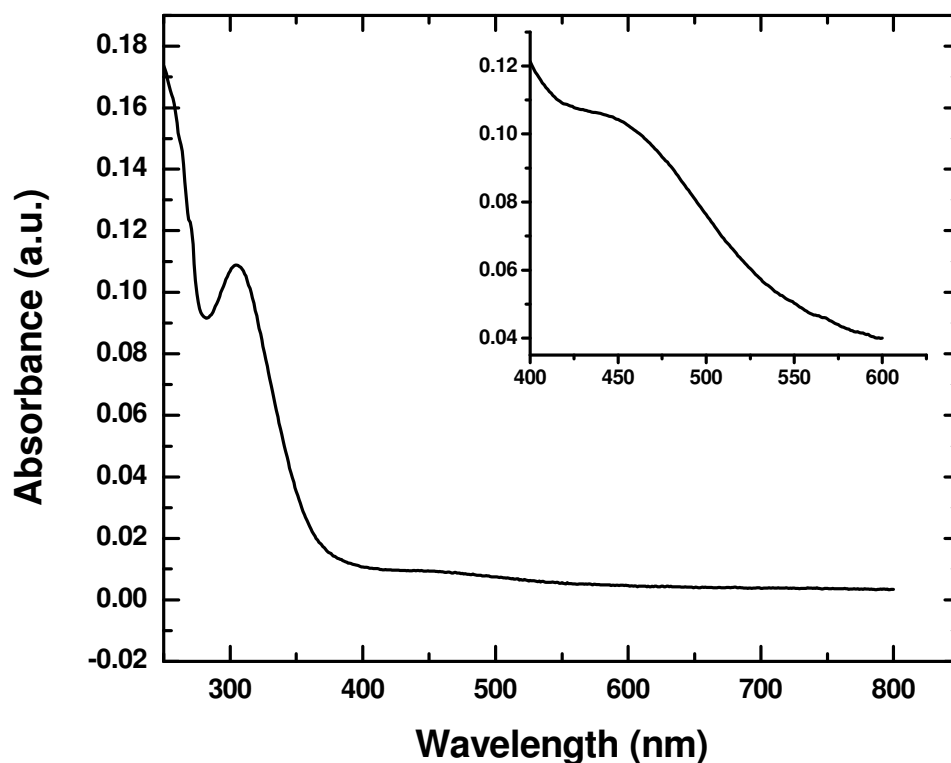


Figure 2.38 – UV-Vis spectrum of a 10^{-5} M solution of **5** in CH₃CN. Inset: A section of the UV-Vis spectrum of a 10^{-4} M solution of **5** in CH₃CN.

Table 2.15 – Crystal data and structural refinement parameters for 5.

Compound 5	
Empirical formula	C ₄₈ H ₈₂ MnMo ₁₂ N ₄ O ₆₂ P ₈
Molecular mass/g mol ⁻¹	3161.16
Crystal colour/shape	Orange / octahedral
Crystal size/mm ³	0.25×0.25×0.10
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> / Å	19.757(7)
<i>b</i> / Å	17.463(6)
<i>c</i> / Å	30.649(10)
α /°	90
β /°	90
γ /°	90
<i>V</i> / Å ³	10574(6)
<i>Z</i>	1
Temperature (K)	108(2)
Density/Mg m ⁻³	2.085
Absorp. coef./mm ⁻¹	1.718
<i>F</i> (000)	6404
$2\theta_{\text{max}}$ /°	50
Reflections collected	41398
Independent reflections	9259 [R(int) = 0.0438]
Data / restraints / parameters	9259 / 0 / 664
<i>S</i> on <i>F</i> ²	1.073
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0763, 0.2084
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0863, 0.2185
Largest diff. peak and hole/e.Å ⁻³	1.859 and -1.627

Table 2.16 – Crystal data and structural refinement parameters for 6.

Compound 6	
Empirical formula	C ₄₈ H ₈₂ FeMo ₁₂ N ₄ O ₆₂ P ₈
Molecular mass/g mol ⁻¹	3162.07
Crystal colour/shape	Red brown / polygonal
Crystal size/mm ³	0.15×0.15×0.25
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> / Å	19.601(8)
<i>b</i> / Å	17.357(6)
<i>c</i> / Å	30.430(12)
α /°	90
β /°	90
γ /°	90
<i>V</i> / Å ³	10353(7)
<i>Z</i>	1
Temperature (K)	108(2)
Density/Mg m ⁻³	2.071
Absorp. coef./mm ⁻¹	1.767
<i>F</i> (000)	6170
$2\theta_{\text{max}}$ /°	50
Reflections collected	58886
Independent reflections	9089 [R(int) = 0.0648]
Data / restraints / parameters	9089 / 0 / 646
<i>S</i> on <i>F</i> ²	1.049
<i>R</i> ₁ , <i>wR</i> ₂ [I>2σ(I)]	0.0964, 0.2517
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1057, 0.2613
Largest diff. peak and hole/e.Å ⁻³	1.807 and -1.966

2.3 ESI-MS STUDIES OF COMPLEX REACTION MIXTURES TO INVESTIGATE THE FORMATION OF HYBRID ORGANIC-INORGANIC POLYOXOMOLYBDATES

2.3.1 Investigation of the reaction system that led to the formation of the cubane structures in **1** and **2**

Partial reduction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in the presence of phenylarsonic acid and acetic acid using $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ resulted in a deep blue solution. When the initial reaction mixture is examined by ESI-MS, the spectrum reveals isotopic envelopes in the high molecular mass region centered at $m/z = 1315.3$ a.m.u. and $m/z = 1659.2$ a.m.u. (Figure 2.41). Within a time period of three weeks, dark red crystals of **1**, $(\text{NH}_4)_2\text{H}_2[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_5)_4]\cdot 5\text{H}_2\text{O}$ separate from this reaction mixture (Figure 2.39).

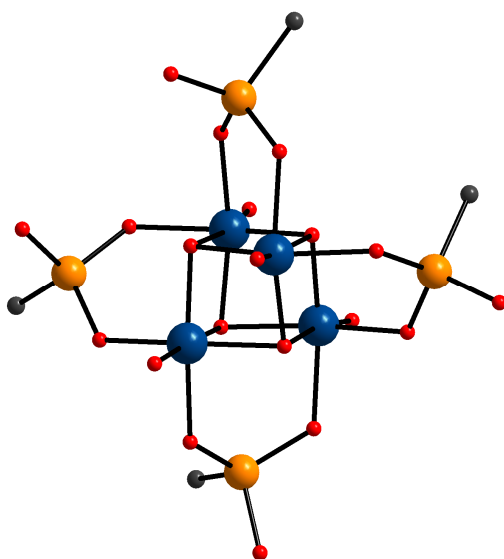


Figure 2.39 – The core structure of the tetranuclear Mo complexes in **1** and **2**. Colour code: Mo^{V} blue, As orange, O red, C grey.

The signal at $m/z = 1315.3$ a.m.u. in the mass spectrum of the reaction mixture that produced **1** is in agreement with the crystallographically determined formula of the cluster anion in **1** (Table 2.17). The signal can be reproduced by recording a spectrum of pristine crystals of **1** dissolved in dimethyl sulfoxide (DMSO), further confirming that the cluster core of **1** is stable in this polar solution as seen in section 2.2.1 of this chapter. Lower

molecular mass signals in the ESI-MS spectrum centered at $m/z = 816.6$ a.m.u. and $m/z = 646.6$ a.m.u. originate from the cubane cluster and can be assigned to the species $\{H_9[Mo^V_4O_{14}(O_3AsC_6H_5)]\}^-$ and $[Mo^{VI}_4O_{16}H_7]^-$, respectively. The ESI-MS spectrum of the reaction mixture further contains a high molecular mass signal centered at $m/z = 1659.2$ a.m.u. We were able to assign this signal to a $\{Mo_6\}$ species with the formula $\{(NH_4)_2H_4[Mo^V_4Mo^{IV}_2O_{12}(OH)_3(O_3AsC_6H_5)_4]\}^-$. A closely related core structure that is stabilised by phosphonates has previously been isolated in a compound $\{Na[Mo^V_6O_{12}(OH)_3(O_3PC_6H_5)_4]_2\}^{9-}$.¹³ It can be crystallised from comparable reaction mixtures that contain alkali metal ions, producing a solid state structure in which two $[Mo^V_6O_{12}(OH)_3(O_3PC_6H_5)_4]^{5-}$ fragments are linked through monovalent ions. We have successfully isolated the hexanuclear molybdenum fragments in compounds **5-9** and a description of the $\{Mo_6\}$ core structure was presented in section 2.2.2.

Table 2.17 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **1**.

	m/z	Species attributed	
Reaction mixture of 1	646.6	$[Mo^{VI}_4O_{16}H_7]^-$	$\rightarrow \{Mo_4\}$
	816.6	$\{H_9[Mo^V_4O_{14}(O_3AsC_6H_5)]\}^-$	$\rightarrow \{Mo_4\}$
	1315.3	$\{H_3[Mo^V_4O_8(O_3AsC_6H_5)_4]\}^-$	$\rightarrow \{Mo_4\}$
	1659.2	$\{(NH_4)_2H_4[Mo^V_4Mo^{IV}_2O_{12}(OH)_3(O_3AsC_6H_5)_4]\}^-$	$\rightarrow \{Mo_6\}$

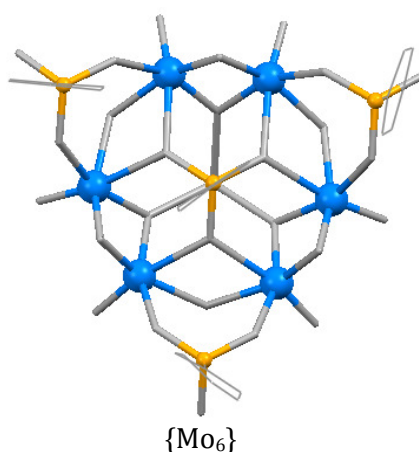


Figure 2.40 – Representation of a structural motif that agrees with the constitutional assignment for the $\{Mo_6\}$ species identified in the mass spectrum of the reaction mixture that led to the crystallisation of **1**. Colour code: Mo blue, As orange, C grey, O light grey.

We successfully simulated the isotopic envelopes for all of the identified species and decomposition products of **1** that originate from the reaction mixture (Figure 2.41),

and good fits between experimental and theoretical data further confirm our structural and constitutional assignments. The ESI-MS analysis further supports the assignment of the oxidation states and, in addition, suggests the presence of other relatively labile species in the solution.

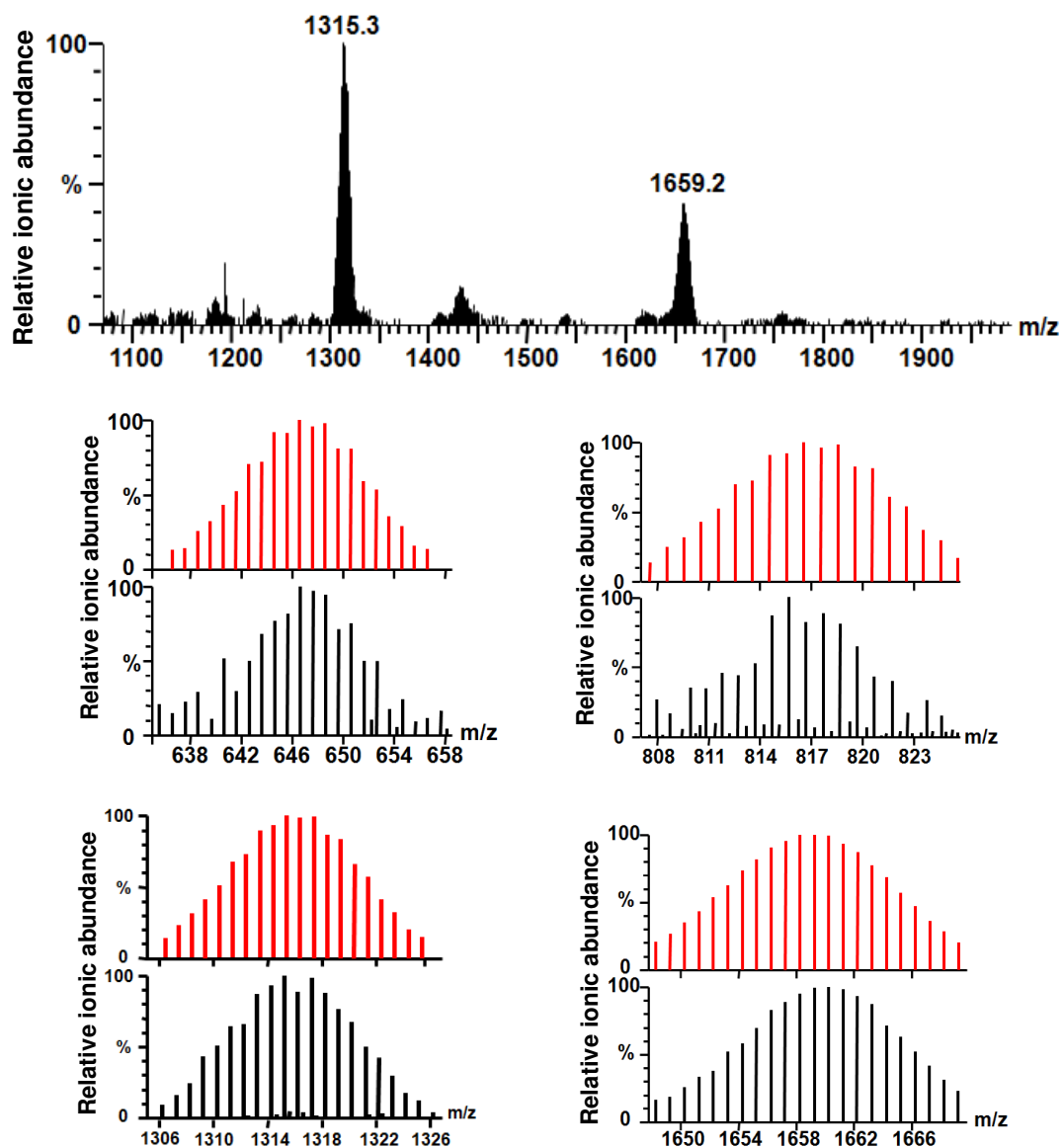


Figure 2.41 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **1** (24 h after preparation). Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $[\text{Mo}^{\text{VI}}_4\text{O}_{16}\text{H}_7]^-$ centered at $m/z = 646.6$ a.m.u., $\{\text{H}_9[\text{Mo}^{\text{V}}_4\text{O}_{14}(\text{O}_3\text{AsC}_6\text{H}_5)]\}^-$ centered at $m/z = 816.6$ a.m.u., $\{\text{H}_3[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_5)_4]\}^-$ centered at $m/z = 1315.3$ a.m.u. and $\{(\text{NH}_4)_2\text{H}_4[\text{Mo}^{\text{V}}_4\text{Mo}^{\text{IV}}_2\text{O}_{12}(\text{OH})_3(\text{O}_3\text{AsC}_6\text{H}_5)_4]\}^-$ centered at $m/z = 1659.2$ a.m.u. (cone voltage: 30 V).

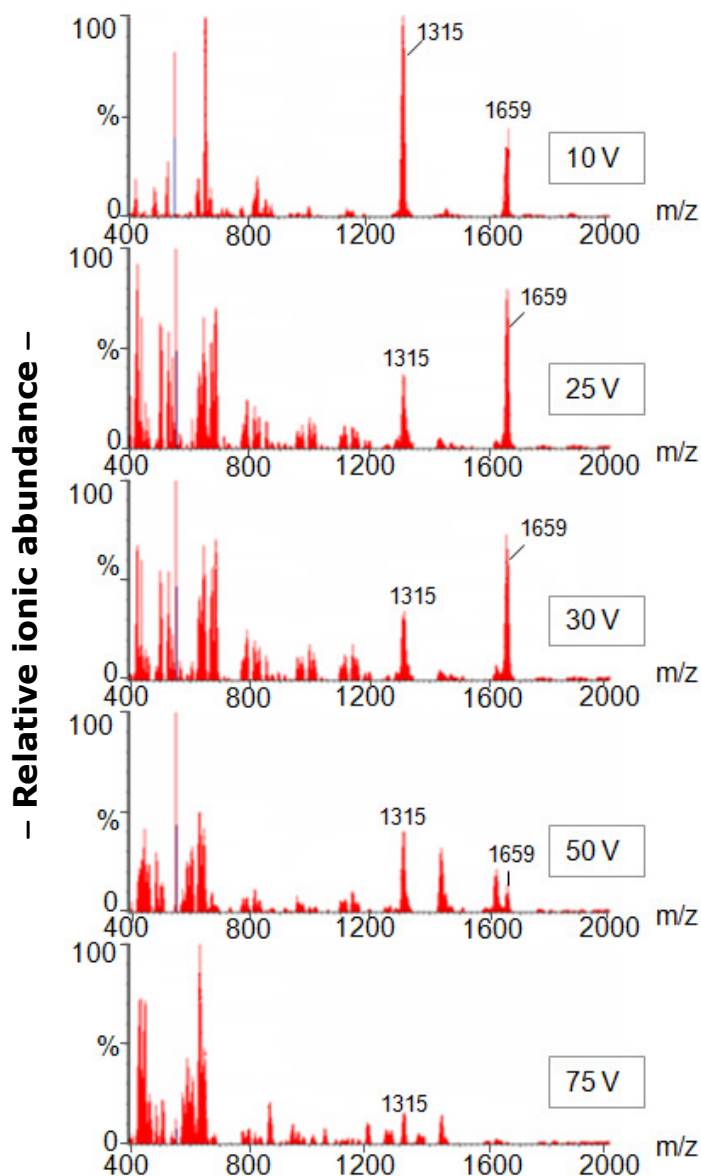


Figure 2.42 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **1** at different cone voltages: 10V, 25V, 30V, 50V and 75V, respectively.

Cone voltage (CV) variation experiments were performed in order to investigate its effect on the ESI-MS spectra (Figure 2.42). According to literature observations, through (CV) variations one can distinguish between the signals originating from the parent ions that form in solution and the fragment ions produced within the spraying chamber. Upon increasing the CV values during the ESI-MS experiments, the relative ionic abundance of the parent species that form in solution decreases, while the abundance of the fragment ions that form in the gas phase, increases. We and others observe that higher cone voltages result in the defragmentation of the coordination clusters within the spraying chamber.^{56, 57}

As seen in Figure 2.42, the relative ionic abundances of $\{\text{Mo}_4\}$ and $\{\text{Mo}_6\}$ species decrease with increasing CV values. These experimental observations suggest that $\{\text{Mo}_4\}$ and $\{\text{Mo}_6\}$ species form in the same reaction mixture. The $\{\text{Mo}_6\}$ species appears to be structurally related to the hexanuclear molybdenum units in **5-9**, while the $\{\text{Mo}_4\}$ species is structurally related to the cubane structure in **1** which crystallises out from this reaction mixture. The most probable structural arrangement for $\{\text{Mo}_6\}$ species is represented in Figure 2.40.

When *p*-aminophenylarsonic acid was used as a stabilising ligand under the same reaction conditions that produced **1**, we obtained a blue solution. The ESI-MS spectrum of this reaction mixture (Figure 2.43) only contains one isotopic envelope in the high mass region of the spectrum. The signal is centered at $m/z = 1374.4$ a.m.u. and corresponds to the cubane structure in **2**, $(\text{NH}_4)_2\text{H}_2[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4] \cdot \text{DMF} \cdot 4\text{H}_2\text{O}$, which crystallises from this solution as red rod-shaped crystals.

Table 2.18 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **2**.

	m/z	Species attributed	
Reaction mixture of 2	1374.4	$\{\text{H}_3[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4]\}^-$	$\rightarrow \{\text{Mo}_4\}$

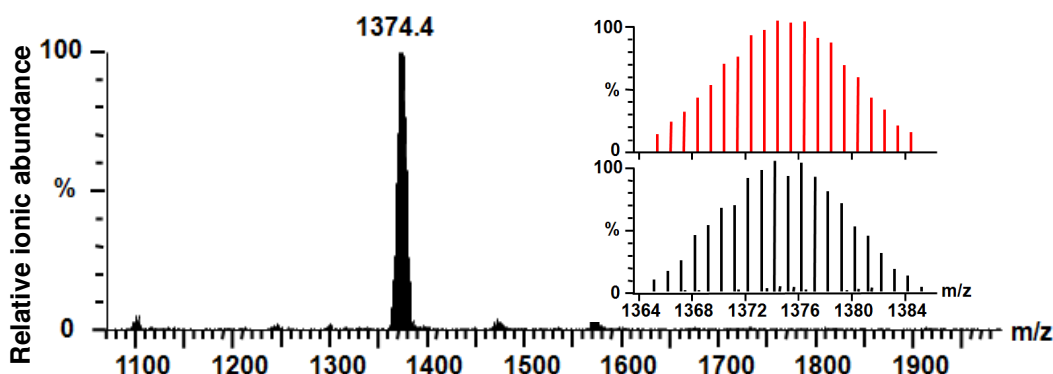


Figure 2.43 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **2** (24 h after preparation). Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_3[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4]\}^-$ centered at $m/z = 1374.4$ a.m.u. (cone voltage: 30 V).

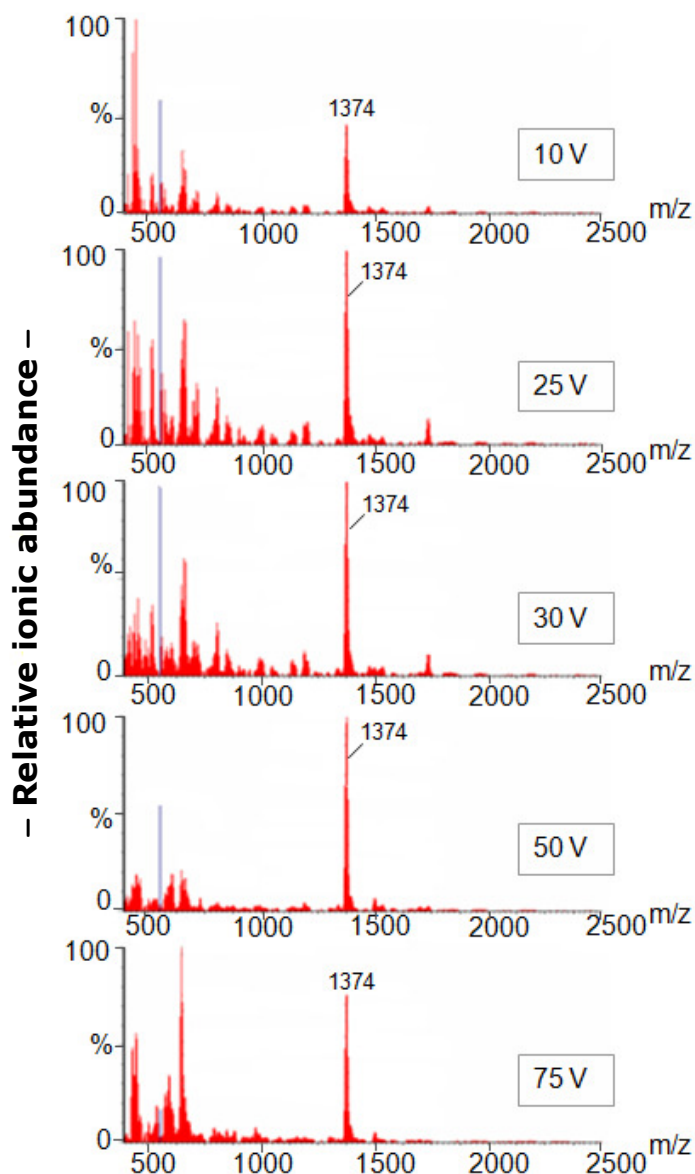


Figure 2.44 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **2** at different cone voltages: 10V, 25V, 30V, 50V and 75V, respectively.

ESI-MS and NMR analyses of the isolated compound in DMSO, presented in section 2.2.1, further confirm our assignments.

ESI-MS cone voltage variation experiments performed on the reaction mixture that led to the crystallisation of **2**, show that the signal attributed to the $\{\text{Mo}_4\}$ species is independent on CV variations up to 75 V (Figure 2.44), and the relative ionic abundance of this species start to decrease in intensity at CV greater than 100 V. These observations further confirm that the $\{\text{Mo}_4\}$ species form in solution and is structurally related to the cubane structure in **2**.

2.3.2 Investigation of the reaction system that led to the formation of the {Mo₅} complex in **3**

Compound **3**, (NH₄)₅[Mo^{VI}₂Mo^V₃O₁₁(O₃AsC₆H₄OH)₅].9H₂O crystallises under the same reaction conditions that led to the formation of **1** and **2**, but using *p*-hydroxyphenylarsonic acid as a stabilising ligand. The ESI-MS spectrum of this reaction mixture is complex and is characterised by four major isotopic envelopes centred at m/z = 1377.3 a.m.u., m/z = 1522.2 a.m.u., m/z = 1704.1 a.m.u. and m/z = 1740.2 a.m.u. in the higher mass region of the spectrum (Figure 2.46).

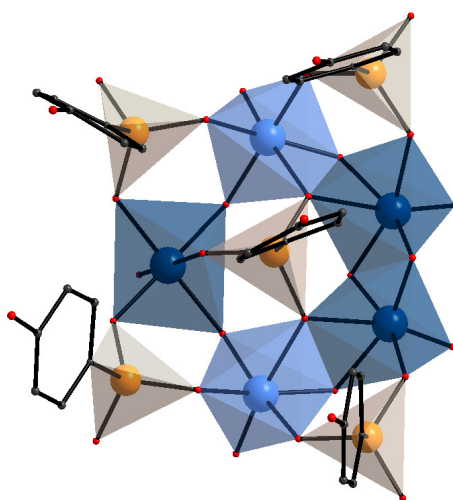


Figure 2.45 – Crystal structure of the pentanuclear Mo complex in **3**. Colour code: Mo^{VI} lavender blue, Mo^V blue, As orange, O red, C grey (hydrogen atoms have been omitted for clarity).

The spectrum proved to be very interesting, as we were able to identify three different species, a {Mo₄}, a {Mo₅} and a {Mo₆} species, in the high molecular mass region of the spectrum (Table 2.19). The signal at m/z = 1377.3 a.m.u. can be assigned to the cubane structure, also observed in the previously examined reaction mixtures, whilst the high molecular mass signal centered at m/z = 1740.2 a.m.u. originates from a new pentanuclear mixed valent Mo cluster in **3**. The signal at m/z = 1522.2 a.m.u. can be attributed to a defragmentation product of **3**, in which one organic ligand is abstracted from the cluster anion. The ESI-MS spectrum of the reaction mixture of **3** displays a fourth signal at m/z = 1704.1 a.m.u. which can be assigned to a hexanuclear compound {(NH₄)H₃[Mo^V₆O₁₂(OH)₃(O₃AsC₆H₄OH)₄]}⁻. A similar compound was also observed during analysis of the previously described reaction systems.

Table 2.19 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **3**.

	<i>m/z</i>	Species attributed	
Reaction mixture of 3	1377.3	$\{\text{H}_3[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_4]\}^-$	$\rightarrow \{\text{Mo}_4\}$
	1522.2	$\{\text{H}_2[\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_3\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_4]\}^-$	$\rightarrow \{\text{Mo}_5\}$
	1704.1	$\{(\text{NH}_4)\text{H}_3[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_4]\}^-$	$\rightarrow \{\text{Mo}_6\}$
	1740.2	$\{\text{H}_4[\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_3\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]\}^-$	$\rightarrow \{\text{Mo}_5\}$

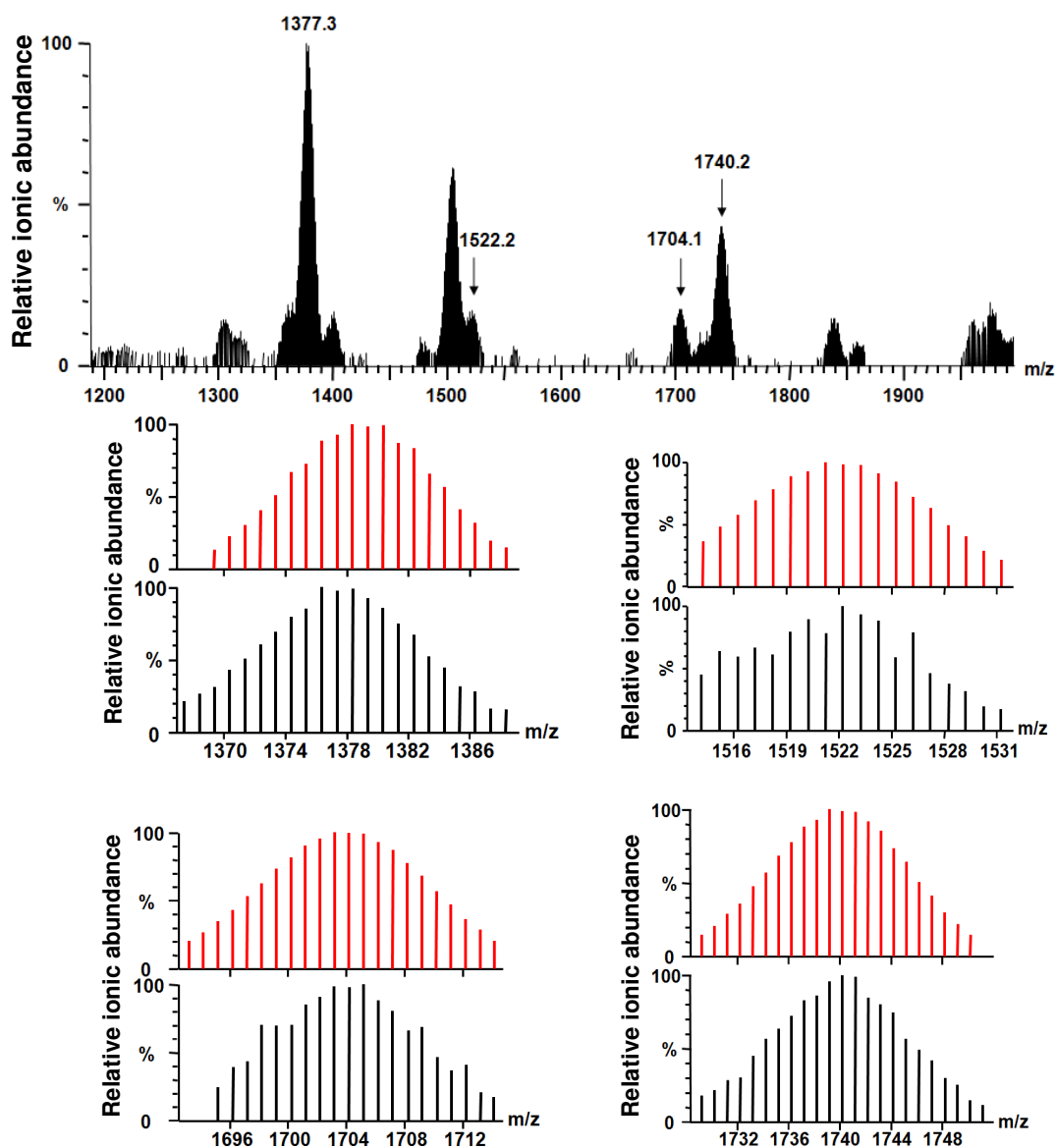


Figure 2.46 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **3** (24 h after preparation). Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_3[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_4]\}^-$ centered at $m/z = 1377.3$ a.m.u., $\{\text{H}_2[\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_3\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_4]\}^-$ centered at $m/z = 1522.2$ a.m.u., $\{(\text{NH}_4)\text{H}_3[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_4]\}^-$ centered at $m/z = 1704.1$ a.m.u. and $\{\text{H}_4[\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_3\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]\}^-$ centered at $m/z = 1740.2$ a.m.u. (cone voltage: 30 V).

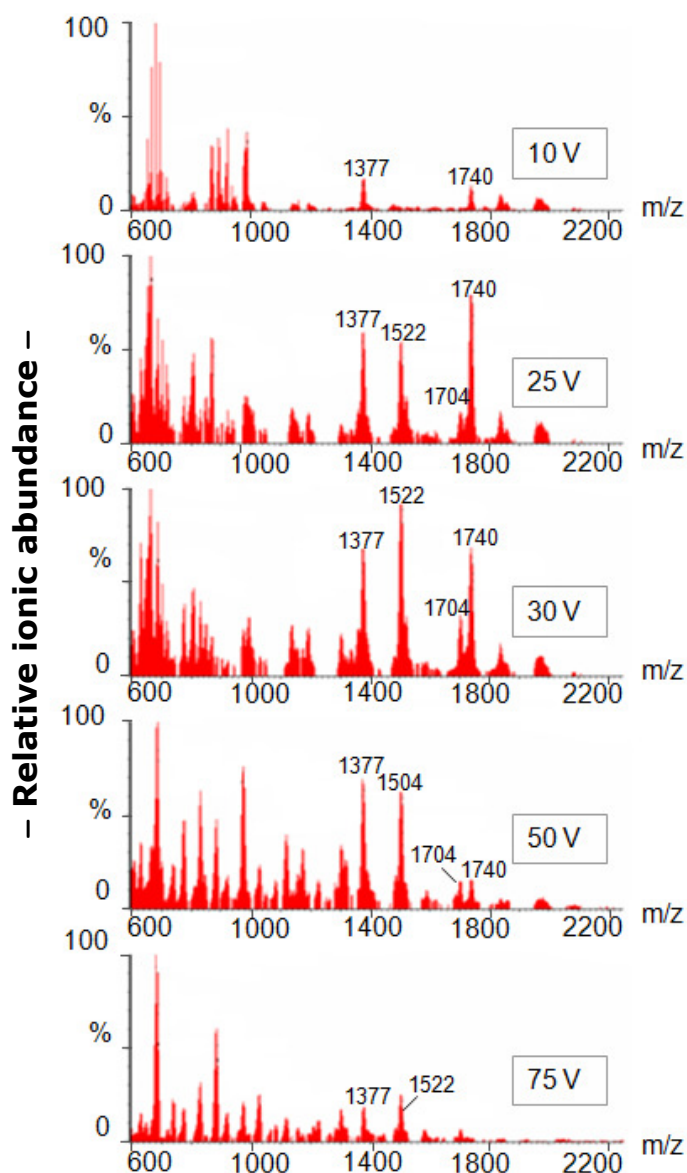


Figure 2.47 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **3** at different cone voltages: 10V, 25V, 30V, 50V and 75V, respectively.

ESI-MS analyses including cone voltage variations clearly confirm that the tetranuclear cubane structure and the pentanuclear complex **3** form in solution in the same reaction mixture.

We successfully simulated the isotopic envelopes for all of the identified species and decomposition products of the pentanuclear cluster, and good fits between experimental and theoretical data further substantiate our assignments (Figure 2.46).

2.3.3 Investigation of the reaction system that led to the formation of the {Mo₄} complex in **4**

The same reaction conditions that led to the formation of **1-3** but using a disubstituted arsonate ligand to control the self-assembly process, gave a dark green solution from which compound **4**, (NH₄)₄[Mo^{VI}₄O₁₀(O₃AsC₆H₃NO₂OH)₄]·2H₂O, was obtained. The ESI-MS spectrum of this reaction mixture is complex, showing the presence of multiple species in the higher mass region of the spectrum. We were able to identify unambiguously the composition of one of these species. Its isotopic envelope is centered at $m/z = 1615.4$ a.m.u. and corresponds to the formula of a tetranuclear molybdenum complex with the composition {H₉[Mo^V₂Mo^{IV}₂O₁₀(O₃AsC₆H₃NO₂OH)₄]·H₂O}[−] (Figure 2.49, Table 2.20). Orange crystals of a closely related compound **4** were obtained from the reaction mixture within a time period of three weeks, and single crystal X-ray studies were performed.

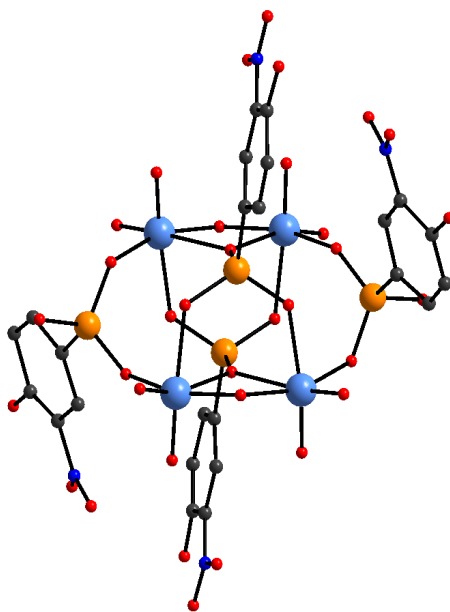


Figure 2.48 – Crystal structure of the tetranuclear Mo complex in **4**. Colour code: Mo^{VI} sky blue, As orange, O red, N light blue, C grey (hydrogen atoms have been omitted for clarity).

Table 2.20 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **4**.

	m/z	Species attributed
Reaction mixture of 4	1615.4	$\{H_9[Mo^V_2Mo^{IV}_2O_{10}(O_3AsC_6H_3NO_2OH)_4]\cdot H_2O\}^- \rightarrow \{Mo_4\}$

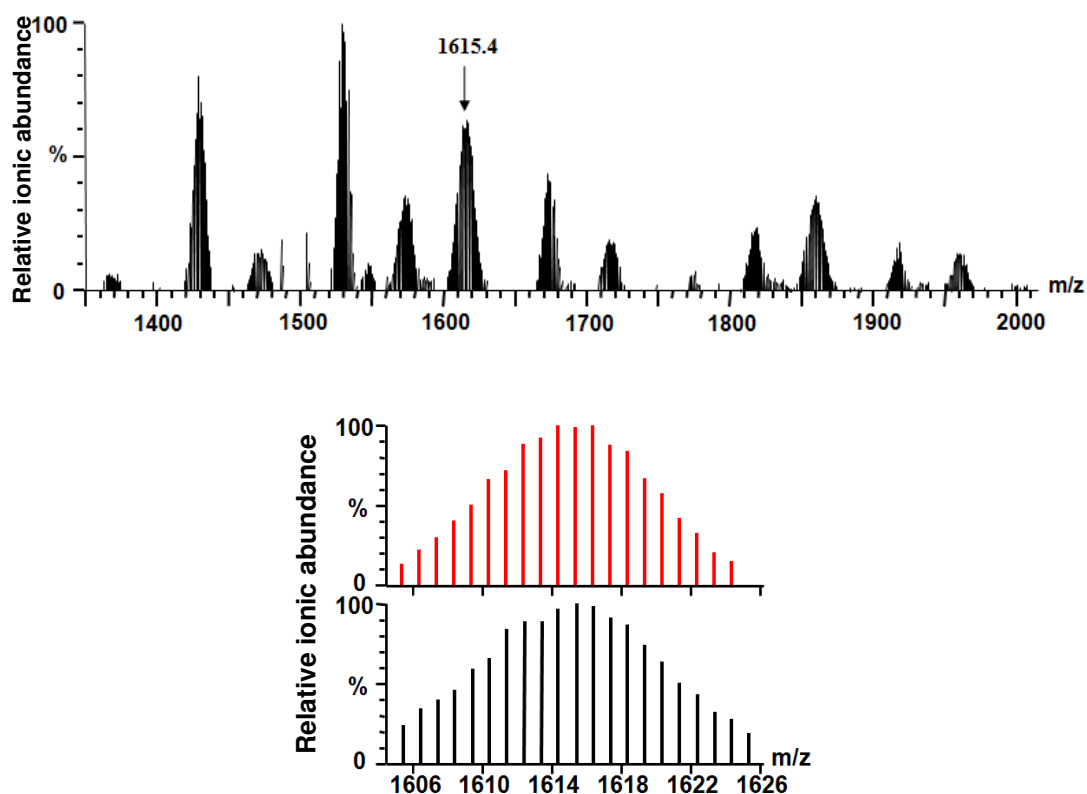


Figure 2.49 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **4** (24 h after preparation). Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{H_9[Mo^V_2Mo^{IV}_2O_{10}(O_3AsC_6H_3NO_2OH)_4]\cdot H_2O\}^-$ centered at $m/z = 1615.4$ a.m.u. (cone voltage: 30 V).

2.4 CONCLUSION AND FUTURE WORK

In this chapter we present a facile synthetic approach to functionalise polyoxomolybdate clusters. The approach involves the partial reduction of Mo^{VI} salts in the presence of organoarsenate and phosphonate ligands.

We demonstrate how slight perturbations of the ligand functionalities can be exploited to stabilise unprecedented core structures. Our investigations underline the stability of **1-3** in solution, an essential requirement for potential applications as catalysts. Redox-active transition metals that adopt cubane as observed in **1** and **2** or related structures are of particular interest to scientists because of their resemblance to active sites of enzymes, and it has recently been suggested that such oxo clusters might hold the key to catalysing the splitting of water,⁵⁸⁻⁶² a process that might have an impact on future energy requirements providing a conceptional solution to climate issues. We demonstrate that the cubane structures tolerate amine functional groups in the *para* position to the arsonate group, a characteristic that might allow the tethering of clusters to surfaces, for instance, electrodes. We isolated an unprecedented pentanuclear ring structure in **3** when *p*-hydroxyphenyl arsenic acid is employed as a ligand. The mixed-valent oxo-cluster is characterised by strong antiferromagnetic interactions between the Mo^{V} centres. The use of (4-hydroxy-3-nitrophenyl)arsonic acid as a ligand promotes the formation of a rhombic planar arrangement in a tetranuclear complex in **4** which can formally be related to the rearrangement of the cube-type structures in **1** and **2**.

Another aspect of the work focused on the synthesis of hybrid organic-inorganic heteropolyoxomolybdates that incorporate additional d-block elements (Mn, Fe, Co, Ni). The secondary transition metal ions serve as a bridging linker between two polyoxomolybdate moieties leading to sandwich structures. We synthesised and isolated a series of isostructural transition metal compounds and a main group derivative (Mg^{2+} compound). Our investigations include the structure determination and some physicochemical characterisations of the compounds. Preliminary studies of the magnetic properties of compounds **5-9** suggest that the $S = \frac{1}{2}$ Mo^{V} centres in these compounds are strongly antiferromagnetically coupled at room temperature leading to magnetically silent hexanuclear subunits. The temperature dependence of the susceptibility of the compounds is mainly determined by the presence of the transition metal ions. Based on the results of our synthetic efforts it appears feasible that f-block elements such as lanthanide ions (Tb,

Dy, Ho) could also be utilised to link the two {Mo₆} fragments. The resulting heteropolyoxomolybdates might exhibit interesting photophysical and magnetic properties.

Future work will involve the synthesis of hybrid organic-inorganic heteropolyoxomolybdates that incorporate f-block elements (Tb, Dy, Ho) in order to expand the family of clusters **5-9**. We also intend to use a series of rigid extended polyphosphonate and –arsonate ligands which could give rise to the formation of porous polyoxometalate metal–organic frameworks (P-MOFs). The electrochemical and catalytic properties of the compounds will also be investigated.

The ESI-MS study of complex reaction mixtures presented in the last section of this chapter aims to investigate the formation processes of hybrid organic-inorganic polyoxomolybdates. We have demonstrated that ESI-MS, in combination with X-ray crystallography, provides an extremely powerful tool to identify and characterise new species that form in solution. Our approach allowed us to use simple, common, well-investigated, and commercially available ligands and to screen their involvement in condensation reactions, providing us with a time-effective protocol to selectively isolate and structurally characterise a series of novel species (structures described in section 2.2.1). The effectiveness of mass spectrometry in this field of science has only recently been highlighted, and our efforts extend accomplishments to complex hybrid structures. Our results underline the possibility of exploring real-time growth reactions of polyoxometales that emerge in solution, transforming from small or oligonuclear species and aggregating into larger molecular clusters. A summary of the ESI-MS assignment for the reaction mixtures that led to the formation of the cubane structures in **1** and **2**, and also to the {Mo₅} complex in **3** highlighting related structural motifs is presented in Figure 2.50. We observe the {Mo₄} cubane species in the ESI-MS spectra of the reaction mixture that led to the crystallisation of **1**, **2** and **3**. A {Mo₆} species is observed in the ESI-MS spectra of the reaction mixture that led to the crystallisation of **1** and **3** and seems to be structurally related to the hexanuclear molybdenum units in **5-9**. The third species observed in the ESI-MS spectrum of the reaction mixture that led to the crystallisation of **3**, {Mo₅}, forms in solution and structurally relates to the pentanuclear molybdenum cluster that crystallises from this reaction mixture.

Our efforts focus on the application of analytical techniques that allow us to monitor and direct complex condensation reactions to produce novel functionalised hybrid materials.

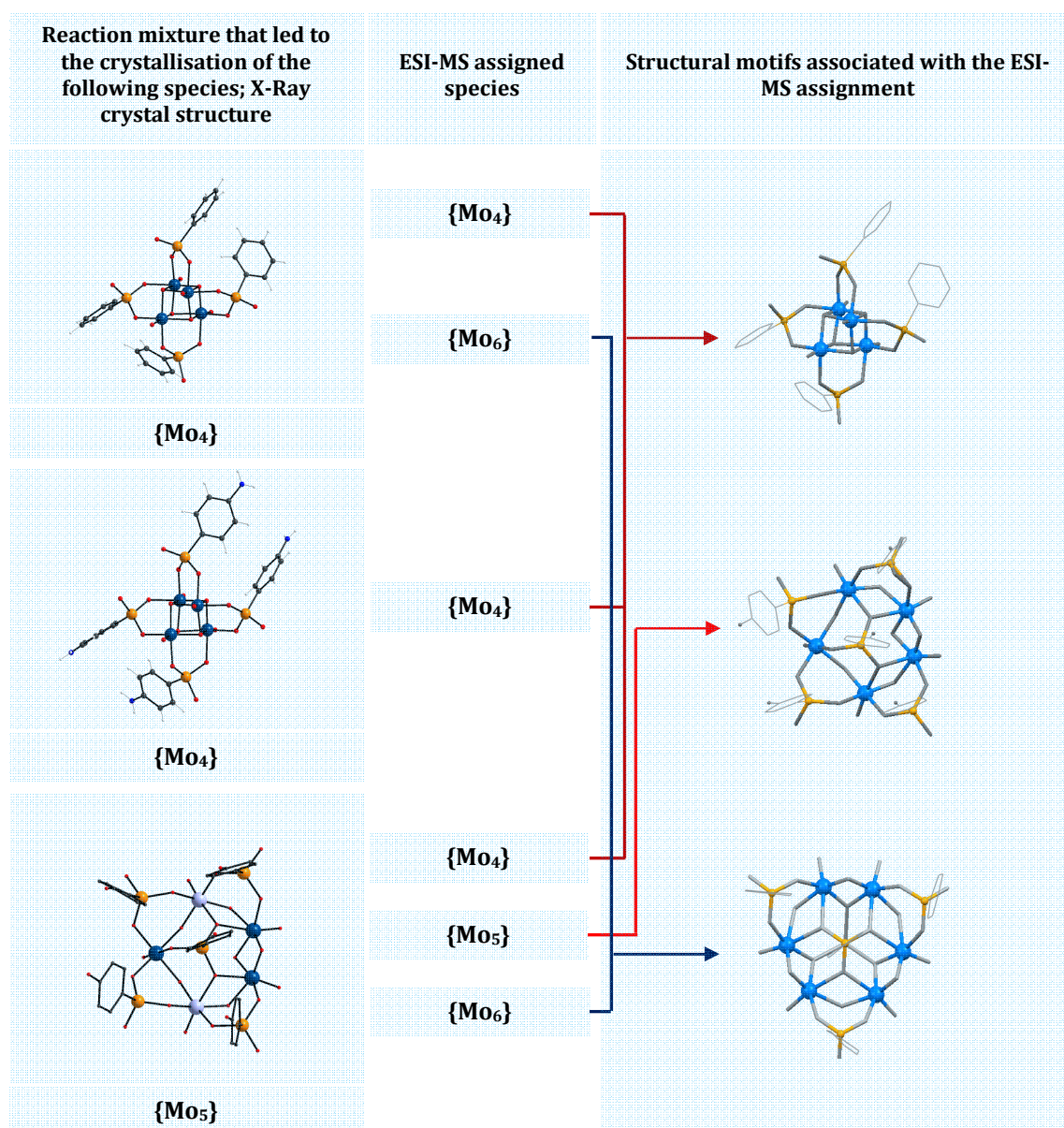


Figure 2.50 – Summary of the ESI-MS assignment for the reaction mixtures that led to the formation of the cubane structures in **1** and **2**, and also, to the {Mo₅} complex in **3** highlighting related structural motifs.

In conclusion, we demonstrated that the topological features of the described hybrid molybdenum phosphonates and –arsonates are strongly dependent on the nature of the employed organic ligand. The described approach provides an efficient protocol to prepare hybrid polyoxomolybdates. Our results provide a solid foundation for research objectives whereby rigid extended poly-phosphonate and –arsonate ligands could give rise to the formation of porous polyoxometalate metal–organic frameworks (P-MOFs). These systems would be interesting for catalysis, gas sorption and separation applications.⁸⁰

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3. POLYNUCLEAR MANGANESE COORDINATION COMPLEXES

3.1 INTRODUCTION AND MOTIVATION

The chemistry of Mn coordination clusters has gained considerable attention during the last decades due to their relevance to bioinorganic chemistry and potential applications as molecular magnetic materials. Manganese is an essential redox active element in biology, playing an important role in the active sites of many proteins and enzymes responsible for carrying out vital chemical transformations. For example, the photosynthetic water oxidation is catalyzed within photosystem II (PSII) by a $\{\text{Mn}_4\text{O}_4\text{Ca}\}$ cluster species.¹⁻⁵

Mn complexes with various nuclearities and topologies have been intensively studied for their fascinating physical properties and, also for the intrinsic architectural beauty they often possess.⁶ Depending on the oxidation states, the nuclearity, topology and bridging modes, these coordination clusters can reveal properties of single molecule magnets (SMMs) that exhibit superparamagnetic behaviour below a certain blocking temperature. This type of materials show potential future applications in high-density magnetic storage devices and molecular electronics.⁶⁻¹¹

A large number of Mn complexes have been prepared using carboxylate ligands, whereas phosphonates have only rarely been employed.⁶ However, the versatile nature of these potential ligands and their high binding affinity towards metal ions renders this class of organic molecules to be highly suitable to stabilise low-dimensional molecular species.¹²⁻¹⁵

Based on these considerations we set out to investigate the influence of different phosphonate ligands on the Mn coordination cluster formation and to explore the properties of the resulting materials. Our aim was to develop new Mn coordination clusters that may display interesting magnetic properties. Thus, we selected a set of three different ligands with different characteristics: phenylphosphonic acid, benzylphosphonic acid and triphenylmethylphosphonic acid. Benzylphosphonic acid contains, in comparison to phenylphosphonic acid, a flexible $-\text{CH}_2-$ group that can freely rotate to meet the steric requirements imposed by the coordination geometries of aggregating Mn ions. In contrast, triphenylmethylphosphonic acid represents a more bulky ligand, which might restrict oligomerisation and lead to the formation of discrete cages.

The preparation of new Mn coordination clusters and SMMs is predominantly based on serendipitous synthetic approaches. In order to produce novel materials with interesting magnetic properties, one needs to understand the formation processes of such complex molecular entities and to be able to control the reaction systems to generate targeted species. There is a need to develop rational synthetic approaches for the formation of single molecule magnets.^{11, 16} Additionally, suitable characterisation tools, that would allow the identification of new and interesting species in solution, or would give the possibility to identify building units and monitor their aggregations, are required.¹⁷

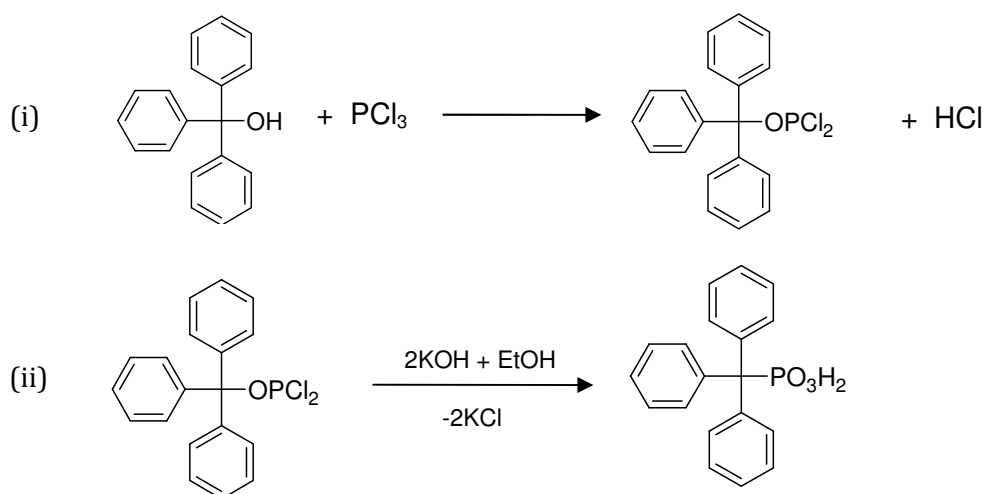
NMR spectroscopy is one of the main techniques which can provide detailed information about the structure, reaction state, chemical environment of molecules, etc., but, is of little use when a large number of paramagnetic metal centres are involved. Other techniques must be employed in such cases. Generally, a combination of techniques provides the most complete picture of the chemistry of the reaction system under study.^{18, 19} Mass spectrometry in combination with X-ray crystallography proved to be an extremely powerful approach to identify and characterize new species that form in solution. It was previously used to study the self-assembly processes of polyoxometalate systems that emerge in solution.²⁰⁻²⁵ Based on these considerations, we decided to exploit the ESI-MS technique and apply it to characterise manganese-phosphonate coordination clusters system. Surprisingly ESI-MS studies that investigate complex Mn coordination cluster systems have not been reported in the literature.

Our aim was to investigate the formation processes of polynuclear manganese clusters. The characterisation of complex reaction mixtures might provide insights into underlying condensation reactions and might lead the development of more rational approaches for the design of single molecule magnets.

In this chapter, we demonstrate how electrospray ionisation mass spectrometry can be used to screen complex Mn reaction mixtures in order to identify new polynuclear manganese species that form in solution. Some of these species were isolated and their structures and other physicochemical properties were characterised.

3.2 PHOSPHONATE LIGANDS

A set of different aromatic phosphonates were used to prepare a series of polynuclear manganese coordination complexes. Phenylphosphonic acid and benzylphosphonic acid, which were commercially available, and triphenylmethylphosphonic acid that was prepared according to literature procedures.²⁶⁻²⁸ For the synthesis of triphenylmethylphosphonic acid, triphenylcarbinol was treated with phosphorus trichloride to give the corresponding phosphorous acid dichloride according to the equation (i) in Scheme 3.1. Then, the desired phosphonic acid was produced by treating the triphenylmethoxyphosphorous dichloride with an alcoholic solution of potassium hydroxide (Scheme 3.1 (ii)).



Scheme 3.1 – Reaction scheme for the synthesis of triphenylmethylphosphonic acid.

These phosphonate ligands were then reacted with manganese salts in comproportionation reactions with the aim of generating manganese phosphonate coordination clusters. The geometrical characteristics of the functional group of the organophosphonates and the strong coordination capability of these ligands towards metal ions were expected to promote the formation of unprecedented core structures with novel properties.

3.3 POLYNUCLEAR MANGANESE COMPLEXES STABILISED BY ORGANOPHOSPHONATES

3.3.1 Synthesis and characterisation of a pentadecanuclear manganese complex

3.3.1.1 $[\text{Mn}^{\text{III}}_{15}(\mu_2\text{-H}_2\text{O})_2(\text{CH}_3\text{OH})_{16}(\text{C}_6\text{H}_5\text{PO}_3)_{20}]\text{Cl}_5 \cdot 22\text{CH}_3\text{OH} \cdot 8\text{H}_2\text{O}$ (**10**)

Compound **10**, $[\text{Mn}^{\text{III}}_{15}(\mu_2\text{-H}_2\text{O})_2(\text{CH}_3\text{OH})_{16}(\text{C}_6\text{H}_5\text{PO}_3)_{20}]\text{Cl}_5 \cdot 22\text{CH}_3\text{OH} \cdot 8\text{H}_2\text{O}$, was prepared by a comproportionation reaction between $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 , in MeOH , in the presence of phenylphosphonic acid. The reaction mixture was stirred for five hours, filtered and left undisturbed for four days at room temperature. Then, the reaction mixture was transferred into a refrigerator. Rectangular, red-brown crystals of **10** were obtained after keeping the reaction mixture at about 2 °C for another four days. The crystal structure of **10** was determined by single crystal X-ray diffraction measurements.

10 crystallises in the triclinic crystal system in the space group $P\bar{1}$ and contains a pentadecanuclear Mn^{III} complex (Figure 3.1). The manganese cluster core in **10** is centrosymmetric, consisting of two symmetry equivalent $\{\text{Mn}^{\text{III}}_5\text{O}_{25}\}$ units, (Figure 3.1, **A**), linked by a central $\{\text{Mn}^{\text{III}}_5\text{O}_{28}\}$ unit (Figure 3.1, **B**) to give the $\{\text{Mn}_{15}\}$ core structure. Within the $\{\text{Mn}^{\text{III}}_5\text{O}_{25}\}$ unit four Mn ions (Mn(1), Mn(3), Mn(4) and Mn(6)) are connected through eight phosphonate ligands to form a twelve membered ring (As ions included). The fifth Mn ion (Mn(2)) caps one side of the ring (Figure 3.2). The “basketlike” $\{\text{Mn}^{\text{III}}_5\text{O}_{25}\}$ unit is further stabilized by five CH_3OH ligands. Each Mn ion in **A** displays a square pyramidal coordination environment in which four O donors are provided by four different phosphonate ligands whilst the remaining O donor arises from a CH_3OH molecule. All Mn ions in **A** adopt the oxidation state +III as calculated using bond valence sum analysis²⁹ based on the bond distances between the Mn centers and the surrounding O donors. The bond distances between the Mn ions and the O donors originating from the organic phosphonate ligands vary between 1.875(7) Å – 1.934(7) Å, whilst the remaining Mn-O_{methanol} bond lengths are 2.171(7) Å, 2.211(7) Å, 2.139(7) Å, 2.116(8) Å and 2.156(8) Å.

Å, respectively for Mn(1)-O(33), Mn(2)-O(36), Mn(3)-O(38), Mn(4)-O(34) and Mn(6)-O(35) (Table 3.1).

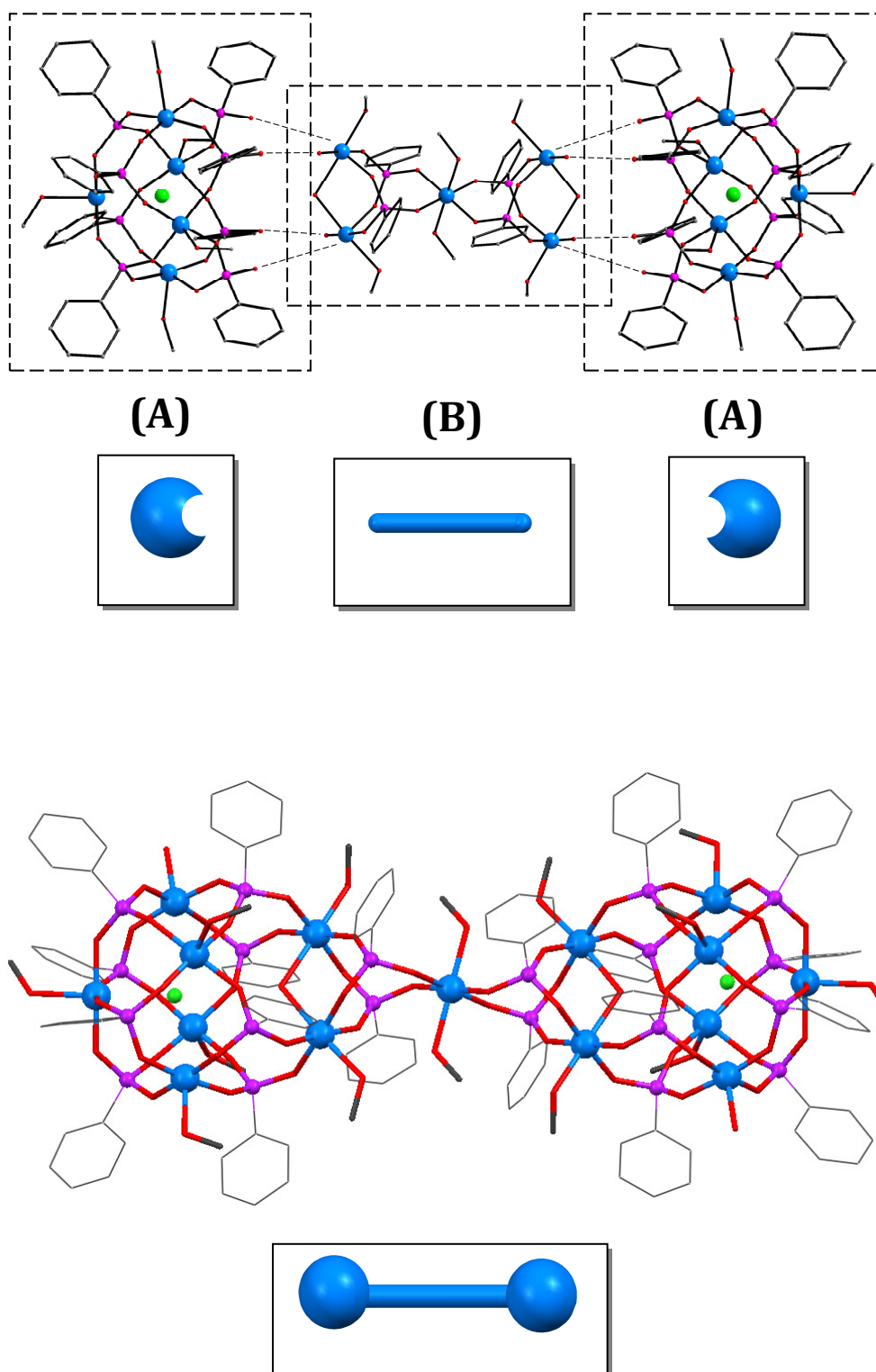


Figure 3.1 – Crystal structure of the pentadecanuclear Mn^{III} complex in **10** formally constructed of two $\{\text{Mn}^{\text{III}}_5\text{O}_{25}\}$ units **A** and a connecting $\{\text{Mn}^{\text{III}}_5\text{O}_{28}\}$ unit **B**; (schematic representation $\{\text{Mn}^{\text{III}}_5\text{O}_{25}\}$ – blue sphere, $\{\text{Mn}^{\text{III}}_5\text{O}_{28}\}$ – blue rod). Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green (hydrogen atoms have been omitted for clarity).

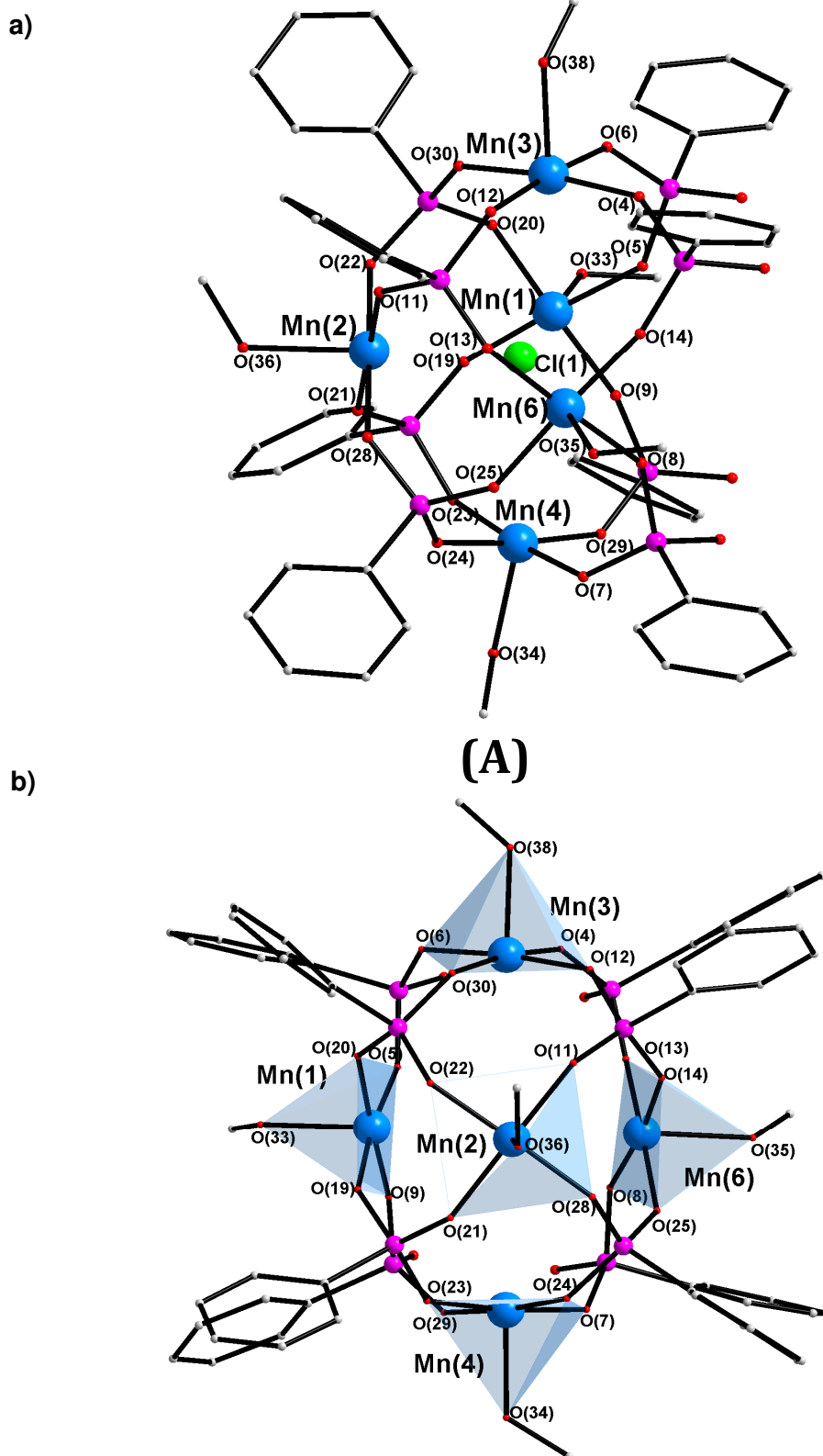


Figure 3.2 – Different views of the $\{\text{Mn}^{\text{III}}_5\text{O}_{25}\}$ unit A. (a) Ball-and-stick and (b) polyhedral representation. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green (hydrogen atoms have been omitted for clarity).

Table 3.1 – Selected bond lengths [Å] and bond valence sum (BVS) for compound 10.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mn(1)	Mn(1)-O(19)	1.888(7)	3.066	+3
	Mn(1)-O(9)	1.890(7)		
	Mn(1)-O(20)	1.894(7)		
	Mn(1)-O(5)	1.928(7)		
	Mn(1)-O(33)	2.171(7)		
Mn(2)	Mn(2)-O(28)	1.898(7)	2.956	+3
	Mn(2)-O(22)	1.904(7)		
	Mn(2)-O(11)	1.905(7)		
	Mn(2)-O(21)	1.934(7)		
	Mn(2)-O(36)	2.211(7)		
Mn(3)	Mn(3)-O(30)	1.876(7)	3.182	+3
	Mn(3)-O(4)	1.876(7)		
	Mn(3)-O(12)	1.892(7)		
	Mn(3)-O(6)	1.909(7)		
	Mn(3)-O(38)	2.139(7)		
Mn(4)	Mn(4)-O(24)	1.875(7)	3.222	+3
	Mn(4)-O(29)	1.882(7)		
	Mn(4)-O(23)	1.885(7)		
	Mn(4)-O(7)	1.902(8)		
	Mn(4)-O(34)	2.116(8)		
Mn(5)	Mn(5)-O(31)	1.884(7)	3.299	+3
	Mn(5)-O(10)	1.889(7)		
	Mn(5)-O(27)	1.893(8)		
	Mn(5)-O(26)	1.903(7)		
	Mn(5)-O(37)	2.191(9)		
Mn(6)	Mn(5)-O(39)	2.364(8)	3.077	+3
	Mn(6)-O(25)	1.890(7)		
	Mn(6)-O(14)	1.886(8)		
	Mn(6)-O(13)	1.896(7)		
	Mn(6)-O(8)	1.929(7)		
Mn(7)	Mn(6)-O(35)	2.156(8)	3.212	+3
	Mn(7)-O(2)	1.892(7)		
	Mn(7)-O(15)	1.900(8)		
	Mn(7)-O(3)	1.902(7)		
	Mn(7)-O(16)	1.919(8)		
Mn(8)	Mn(7)-O(32)	2.210(8)	3.320	+3
	Mn(7)-O(39)	2.345(7)		
	Mn(8)-O(1)	1.877(7)		
	Mn(8)-O(1')	1.877(7)		
	Mn(8)-O(17')	1.912(8)		
	Mn(8)-O(17)	1.912(7)		
	Mn(8)-O(18')	2.243(8)		
	Mn(8)-O(18)	2.243(8)		
	Mn(1) ... Cl(1)	2.644(3)		
	Mn(2) ... Cl(1)	2.651(3)		
	Mn(6) ... Cl(1)	2.640(3)		

The $\{\text{Mn}^{\text{III}}_5\text{O}_{28}\}$ unit **B** (Figure 3.3) consists of two $\{\text{Mn}^{\text{III}}_2\text{O}_{11}\}$ symmetry equivalent subunits connected to each other through a central $\{\text{MnO}_6\}$ unit involving four

bridging phosphonate ligands. The $\{\text{Mn}^{\text{III}}_5\text{O}_{28}\}$ unit is further stabilized by six CH_3OH ligands. The position of the central Mn(8) atom coincides with the position of an inversion symmetry centre.

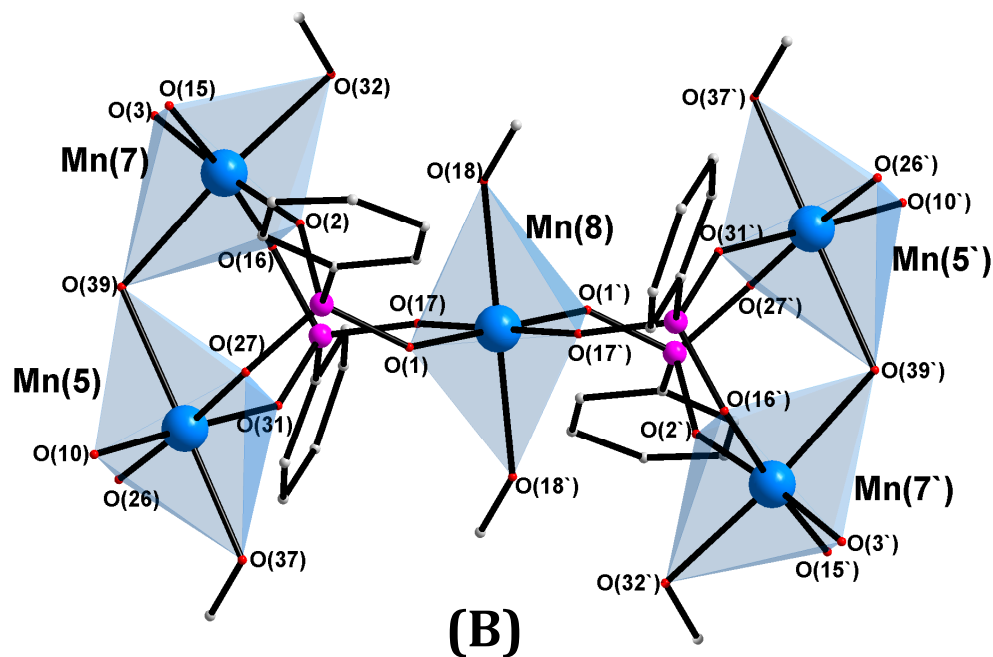


Figure 3.3 – Polyhedral representation of the $\{\text{Mn}^{\text{III}}_5\text{O}_{28}\}$ unit **B**. Colour code: Mn^{III} blue, P purple, O red, C grey (hydrogen atoms have been omitted for clarity).

Within the $\{\text{Mn}^{\text{III}}_2\text{O}_{11}\}$ subunit two Mn ions (Mn(5) and Mn(7)) share a common vertex (O(39)) of their distorted octahedral coordination environment. The O(39) donor arises from a bridging H_2O ligand, whilst the remaining coordination sites are occupied by one $\text{O}_{\text{methanol}}$ and four O donors originating from four distinct phosphonate ligands. The distorted nature of the octahedra can be observed from the bond angles and bond lengths of the Mn^{III} metal centres. The following bond angles: O(37)-Mn(5)-O(39), O(31)-Mn(5)-O(10) and O(27)-Mn(5)-O(26) of $178.8(3)^\circ$, $178.0(3)^\circ$ and $176.6(3)^\circ$ respectively, deviate from the ideal octahedral angle of 180° , whilst the bond angles O(31)-Mn(5)-O(39), O(26)-Mn(5)-O(39), O(10)-Mn(5)-O(26), O(10)-Mn(5)-O(39), O(10)-Mn(5)-O(27) and O(27)-Mn(5)-O(39) of $91.6(3)^\circ$, $91.1(3)^\circ$, $91.0(3)^\circ$, $90.3(3)^\circ$, $87.8(3)^\circ$ and $85.7(3)^\circ$ respectively, deviate from the ideal angle of 90° (Table 3.2). Similar values can be found for the bond angles of the Mn(7) ion, which are summarized in Table 3.2. The four Mn-O bond distances between Mn ions and O donors originating from the organic ligands, vary between $1.884(7) \text{ \AA}$ – $1.919(8) \text{ \AA}$, whilst the remaining two bond lengths involving *trans* located MeOH and H_2O ligands of the octahedral coordination environment are slightly elongated. Thus, the Mn(5) and Mn(7) ions display Jahn-Teller (JT) axial elongation

typical for Mn^{III} ions.³⁰ Mn-O_{methanol} bond distances, Mn(5)-O(37) and Mn(7)-O(32) are 2.191(9) Å and 2.210(8) Å, respectively, and the bond lengths between Mn(5), Mn(7) and the μ_2 -H₂O ligand, O(39), are 2.364(8) Å and 2.345(7) Å (Table 3.1). The central Mn(8) ion located on an inversion center displays a more regular octahedral coordination polyhedron compared to those of Mn(5) and Mn(7) ions. The bond angles of the Mn(8) ion are very close to the ideal octahedral angle of 180° and 90°, as seen in Table 3.2. However, substantial distortion can be observed due to the elongated Mn-O_{methanol} bonds of 2.243(8) Å occupying the apical positions of the Jahn-Teller distorted Mn^{III} ion.

Table 3.2 – Selected bond angles [°] for compound 10.

Bond Angle (°)		Bond Angle (°)	
O(37)-Mn(5)-O(39)	178.8(3)	O(2)-Mn(7)-O(3)	175.8(3)
O(31)-Mn(5)-O(10)	178.0(3)	O(15)-Mn(7)-O(16)	175.5(3)
O(27)-Mn(5)-O(26)	176.6(3)	O(32)-Mn(7)-O(39)	174.3(3)
O(31)-Mn(5)-O(39)	91.6(3)	O(3)-Mn(7)-O(39)	93.8(3)
O(26)-Mn(5)-O(39)	91.1(3)	O(15)-Mn(7)-O(3)	91.3(3)
O(10)-Mn(5)-O(26)	91.0(3)	O(2)-Mn(7)-O(39)	90.4(3)
O(10)-Mn(5)-O(39)	90.3(3)	O(15)-Mn(7)-O(39)	89.5(3)
O(10)-Mn(5)-O(27)	87.8(3)	O(3)-Mn(7)-O(16)	88.3(3)
O(27)-Mn(5)-O(39)	85.7(3)	O(16)-Mn(7)-O(39)	86.1(3)
O(17')-Mn(8)-O(17)	180.0(2)		
O(1)-Mn(8)-O(1')	179.999(4)		
O(18')-Mn(8)-O(18)	179.997(1)		
O(1)-Mn(8)-O(17)	93.9(3)		
O(17')-Mn(8)-O(18)	93.4(3)		
O(1)-Mn(8)-O(18)	92.2(3)		
O(1)-Mn(8)-O(18')	87.8(3)		
O(17)-Mn(8)-O(18)	86.6(3)		
O(1)-Mn(8)-O(17')	86.1(3)		

Each of the twenty PhPO₃²⁻ moieties in **10** bridge between three Mn atoms in a $\eta^1:\eta^1:\eta^1:\mu_3$ bridging mode. The oxidation states of the Mn ions and the protonation of the bridging donor species, i.e. H₂O ligands were established by Mn and O bond valence sum calculations (Table 3.1), close examination of the geometric parameters and detection of Mn^{III} Jahn-Teller (JT) elongation axes. The Mn – (μ_2 -H₂O) distances in **10** are comparable to those observed in other reported aqua-bridged dimanganese complexes (2.25 Å – 2.18 Å).³¹⁻³⁴ These distances are found to be significantly longer than the Mn – (μ_2 -OH⁻) distances of 2.05 Å – 2.09 Å and the Mn – (μ_2 -O²⁻) distances of 1.78 Å – 1.81 Å. The overall charge of the cluster is compensated by five chlorine ions. Two of the chlorine ions are encapsulated within the {Mn^{III}₅O₂₅} units and may serve as templates promoting the

cluster formation. The distances between the chlorine ion Cl(1) and Mn(1), Mn(2) and Mn(6) are 2.644(3) Å, 2.651(3) Å and 2.640(3) Å, respectively (Table 3.1).

In the solid state, the packing arrangement of the clusters is stabilized by weak hydrogen bonding interactions between the coordinated methanol molecules and constitutional solvent molecules. A detailed analysis of these interactions was not possible due to the large number of disordered solvent molecules and the complexity of the cluster entity. Weak offset π - π interactions³⁵ between two adjacent clusters can also be observed. These involve the phenyl rings of the phosphonate ligands from the coordination sphere of Mn(2) and its symmetry related partners, resulting in an interplanar separation distance of 4.144(2) Å. The clusters are further linked through halogen bonding interactions between Cl(3) and two hydrogen atoms of two phosphonate rings of two adjacent coordination clusters (2.763(5) Å and 2.805(5) Å, respectively). In addition some weak interaction between Cl(3), Cl(4), Cl(5) and hydrogen atoms of some constitutional solvent molecules prevail. The crystal structure displays small intercluster cavities which are filled with solvent molecules. These channels extend in the direction of the crystallographic *b*-axis as can be seen in Figure 3.4 (b).

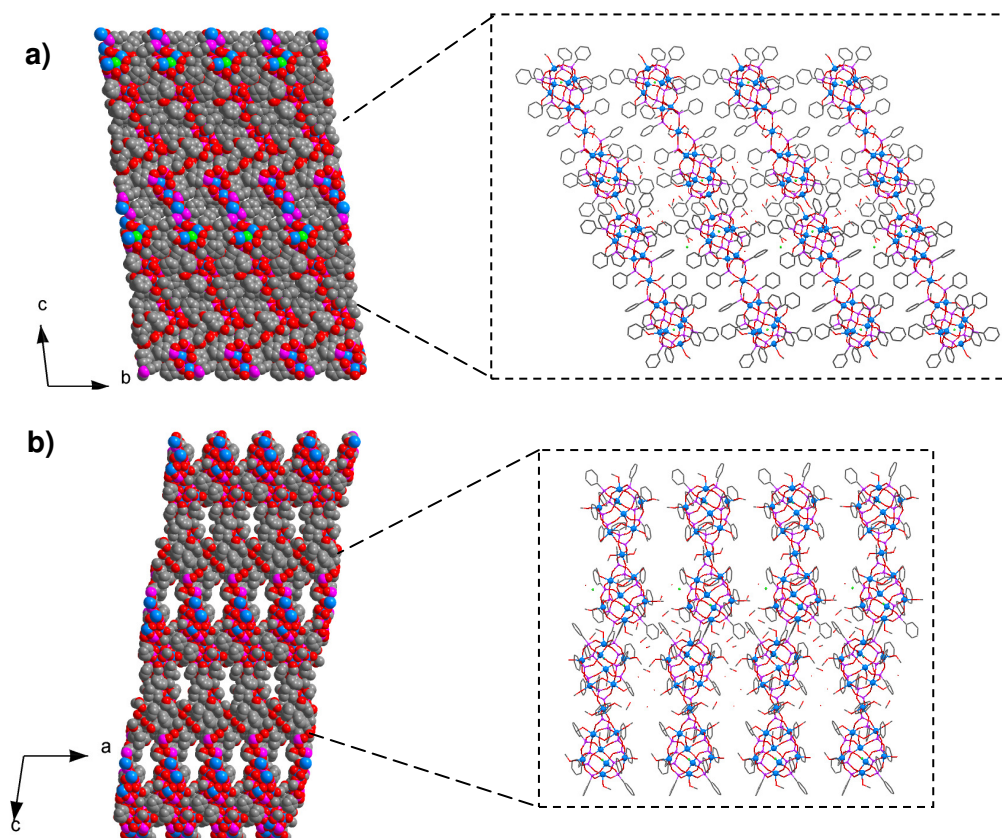


Figure 3.4 – Packing arrangement of the pentadecanuclear Mn^{III} clusters in **10**, viewed in the direction of the crystallographic: (a) *a*-axis and (b) *b*-axis. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green (crystallization solvent molecules and hydrogen atoms have been omitted for clarity).

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

Compound **10** was characterized by infrared spectroscopy. The IR spectrum of **10** is shown in Figure 3.5 and reveals some characteristic stretches of the organophosphonate ligands. The set of bands observed between $3000 - 2800\text{ cm}^{-1}$ can be attributed to C–H stretching vibrations, while the bands between $1500 - 1430\text{ cm}^{-1}$ are most likely due to C–C skeletal vibrations of the phenyl rings. Typical C–H out-of-plane bending vibrations of the aromatic rings can be found between $800 - 650\text{ cm}^{-1}$ as sharp bands. The set of bands between $1200 - 900\text{ cm}^{-1}$ are due to the different P–O stretching vibrations of the phosphonate groups. Finally, the corresponding O–H stretching vibrations and H–O–H bending vibrations of the crystallization water molecules engaged in H-bonds appear as broad bands centered at *ca.* 3266 cm^{-1} and *ca.* 1628 cm^{-1} , respectively.³⁶⁻⁴⁰

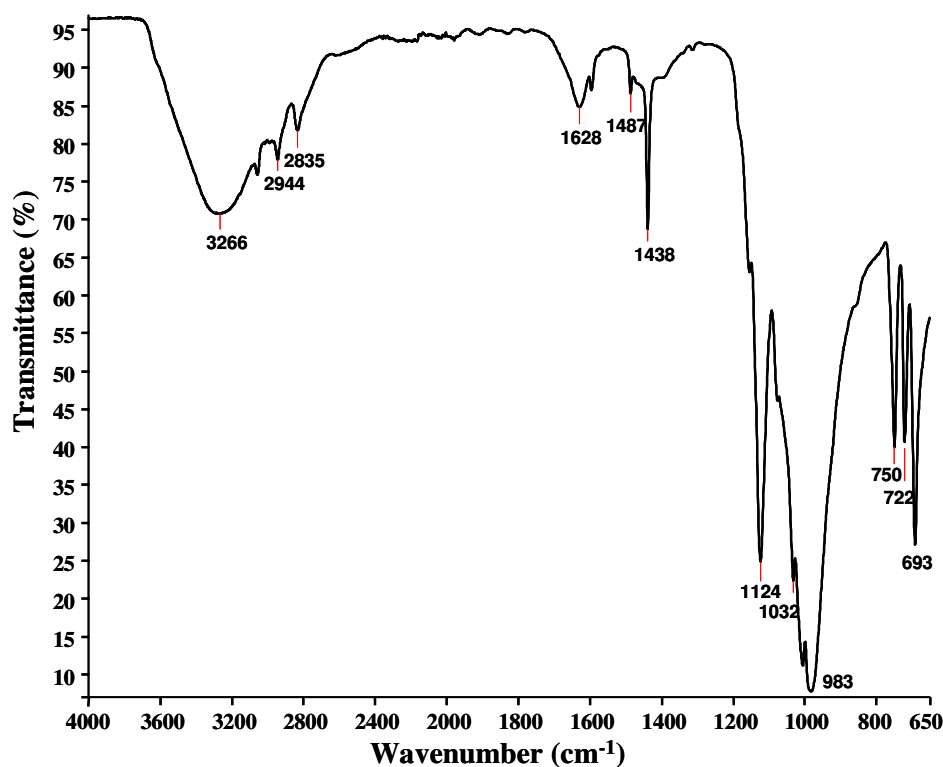


Figure 3.5 – Infrared spectrum of **10**.

- *Thermogravimetric analysis*

The thermal stability of compound **10** was investigated by thermogravimetric analysis (TGA) using a freshly prepared crystalline sample. The analysis was carried out in the temperature range between 30 and 900 °C, in an N₂ atmosphere. The TGA curve of **10** shown in Figure 3.6 exhibits an initial weight loss of 10.9 % between 30 – 200 °C that can be attributed to the removal of sixteen coordination CH₃OH molecules (calcd: 11.0 %). The other crystallization solvent molecules of **10** may have been lost prior to the TGA during the storage of the sample at room temperature. A further increase of the temperature affected a gradual weight loss between 200 – 500 °C corresponding to the decomposition of the organic ligands, followed by further cluster degradation above 500 °C.

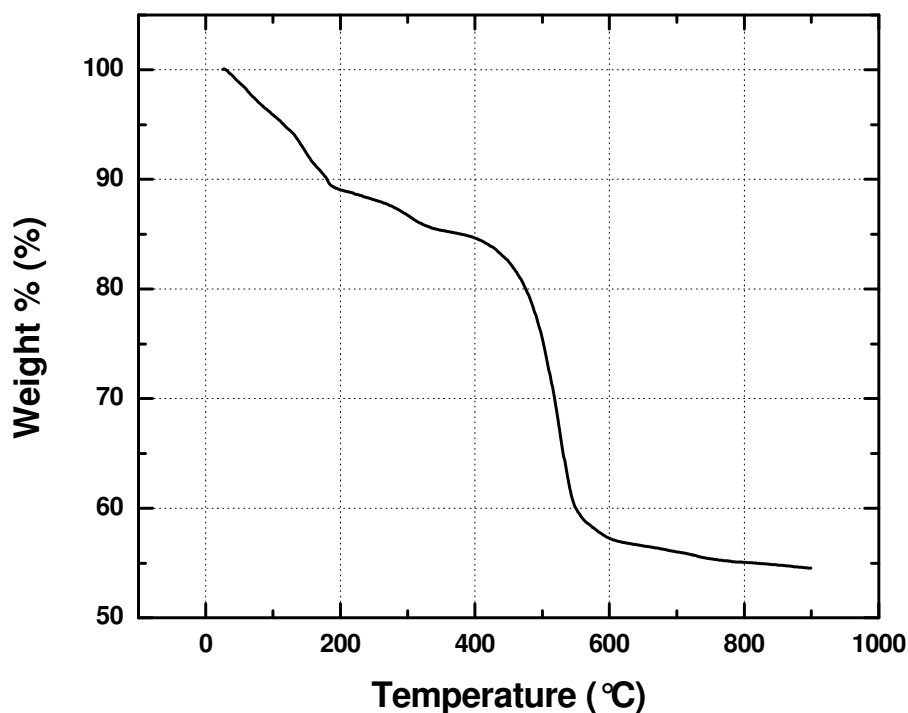


Figure 3.6 – Thermogravimetric analysis of **10**.

- Magnetism

The magnetic properties for compound **10** were studied on a powdered microcrystalline sample. The temperature dependence of the magnetic susceptibility of **10** was measured between 298 and 1.8 K (Figure 3.7). The χT value of $22.4 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature is significantly lower than the expected value of $45 \text{ cm}^3 \text{ K mol}^{-1}$ for the presence of fifteen $S = 2 \text{ Mn}^{\text{III}}$ carriers ($C = \frac{N_{\text{Mn}}^2 \mu_{\text{B}}^2}{3k_{\text{B}}} S(S+1)$ with $\frac{N_{\text{Mn}}}{3k_{\text{B}}} = 0.12505 \text{ cm}^3 \text{ K mol}^{-1}$ and $g = 2$).⁴¹ This result is characteristic for predominately strong antiferromagnetic (AF) exchange parameters between spins carriers. Upon lowering the temperature, the χT product decreases down to a minimum of *ca.* $0.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. This thermal behavior confirms the presence of dominant AF interactions between spin carriers and the low temperature χT value suggests an $S_{\text{T}} = 0$ ground state. This result does not exclude the presence of ferromagnetic interactions but only suggests that the AF interactions are dominant.

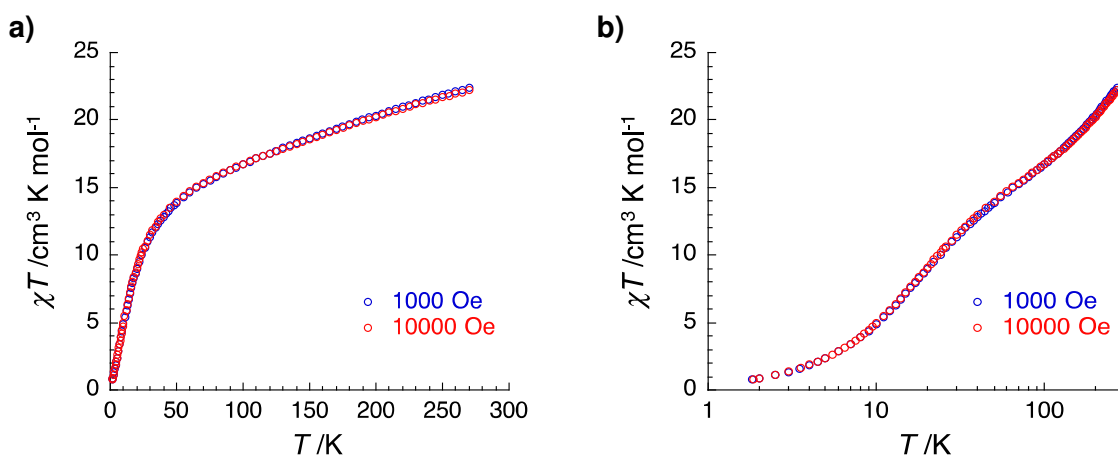


Figure 3.7 – (a) Temperature dependence of the χT product of **10** at 0.1 and 1 T. (b) A magnified view of the χT product in (a) between 1 and 100 K.

Unfortunately the experimental data can not be fitted to a Curie-Weiss law probably because the magnetic exchange parameters within the cluster core are so large and thus a mean-field model can not be used for this molecular system.

The field dependence of the magnetisation for this compound has been measured at low temperatures between 1.8 and 8 K (Figure 3.8). The M vs H plot is typical of a complex with diamagnetic ground state characterised by weak magnetisation values, almost linear field dependence and no saturation even at high field.

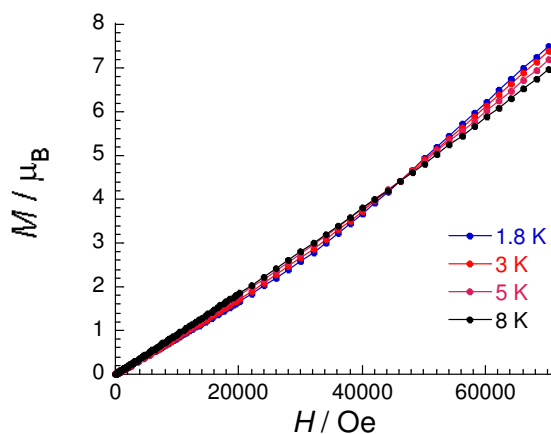


Figure 3.8 – Field dependence of the magnetisation at and below 8 K.

It is worth noting that no hysteresis effects upon measuring the field-dependence of the magnetisation (M vs H , 100 – 200 Oe/min) and no ac susceptibility in zero dc field (at 1000 Hz) have been observed above 1.8 K.

- *Mass spectrometry*

The stability of compound **10** in solution was investigated by electrospray ionization mass spectrometry which provides a very powerful analytical tool for the characterization of coordination compounds in solution.⁴²⁻⁴⁸ Negative mode ESI-MS spectra of compound **10** dissolved in a suitable solvent (CH₃CN, DMF and DMSO, respectively), were recorded (Table 3.3, Figure 3.9). The mass spectra of these solutions reveal only one major isotopic envelope in the high molecular mass region, centered at $m/z = 1684.3$ a.m.u. This signal can be assigned to the $\{H_{17}[Mn^{IV}_6Mn^{III}O_{15}(C_6H_5PO_3)_6]Cl_3\}^-$ species, which was modelled (Figure 3.9, inset) and good fits between the experimental and simulated patterns could be found. The entire $\{Mn_{15}\}$ complex could not be identified in the ESI-MS spectrum, presumably due to a facile dissociation involving the partially solvated, central Mn(8) ion (Figure 3.3) .

Table 3.3 – ESI-MS assignment for compound **10**.

	Solvent	m/z	Species attributed	
Crystals of 10 in:	CH ₃ CN	1684.3	$\{H_{17}[Mn^{IV}_6Mn^{III}O_{15}(C_6H_5PO_3)_6]Cl_3\}^-$	→ $\{Mn_7\}$
	DMF	1684.3	$\{H_{17}[Mn^{IV}_6Mn^{III}O_{15}(C_6H_5PO_3)_6]Cl_3\}^-$	→ $\{Mn_7\}$
	DMSO	1684.3	$\{H_{17}[Mn^{IV}_6Mn^{III}O_{15}(C_6H_5PO_3)_6]Cl_3\}^-$	→ $\{Mn_7\}$

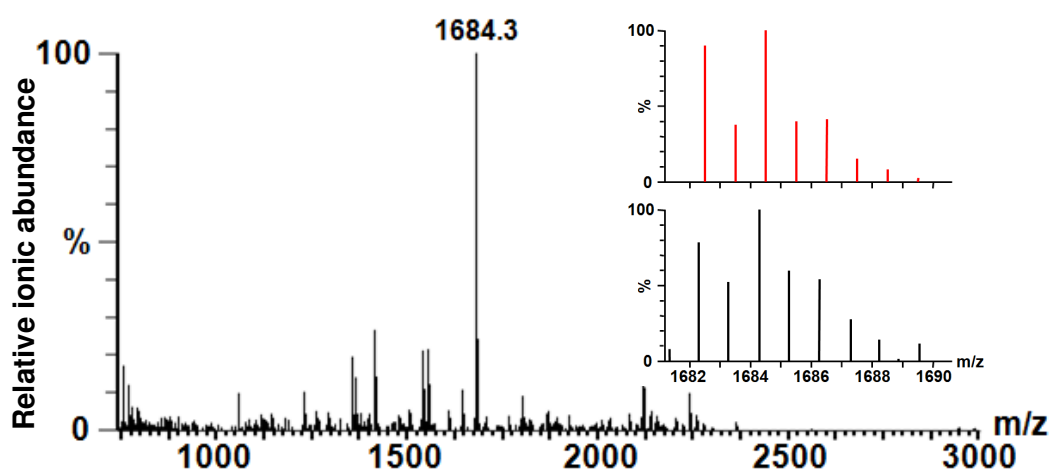


Figure 3.9 – Negative-mode ESI-MS spectra for crystals of **10** dissolved in DMF. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{H_{17}[Mn^{IV}_6Mn^{III}O_{15}(C_6H_5PO_3)_6]Cl_3\}^-$ centered at $m/z = 1684.3$ a.m.u. (cone voltage: 30 V).

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **10** recorded in CH₃CN can be seen in Figure 3.10. The shoulder observed at *ca.* 280 nm ($\epsilon = 34000 \text{ L mol}^{-1} \text{ cm}^{-1}$) can be attributed to $\pi - \pi^*$ transitions of the phosphonate ligands, while the weak band at *ca.* 465 nm ($\epsilon = 6400 \text{ L mol}^{-1} \text{ cm}^{-1}$) involve a d – d transition that can be assigned to a ${}^5\text{T}_{2g} \leftarrow {}^5\text{E}_g$ transition for the octahedral Mn^{III} ions within **10**.⁴⁹⁻⁵²

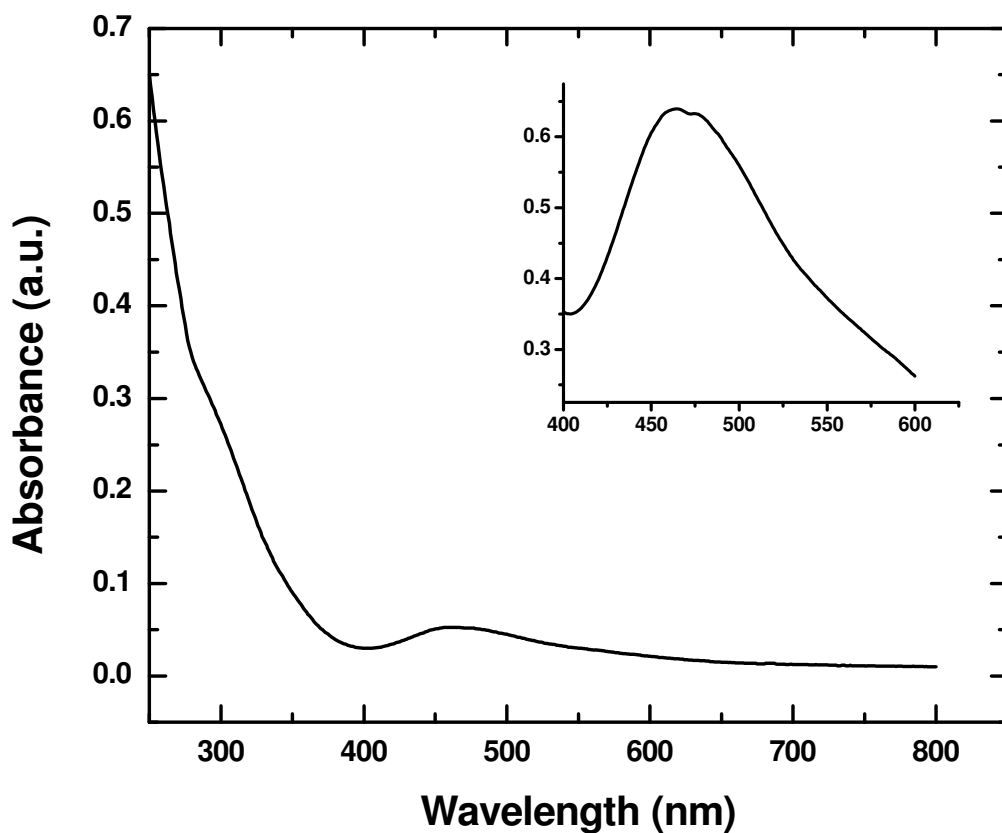


Figure 3.10 – UV-Vis spectrum of a 10^{-5} M solution of **10** in CH₃CN. Inset: A section of the UV-Vis spectrum of a 10^{-4} M solution of **10** in CH₃CN.

Table 3.4 – Crystal data and structural refinement parameters for 10.

Compound 10	
Empirical formula ^a	C ₁₃₆ H ₁₆₈ Cl ₅ Mn ₁₅ O ₇₈ P ₂₀
Molecular mass/g mol ⁻¹ ^a	4671.55
Crystal colour/shape	Red brown / rectangular block
Crystal size/mm ³	0.50×0.20×0.20
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	14.5661(5)
b/ Å	16.5025(5)
c/ Å	51.7573(16)
α /°	95.1300(10)
β /°	97.2120(10)
γ /°	102.500(2)
V/ Å ³	11962.6(7)
Z	1
Temperature (K)	150(2)
Density/Mg m ⁻³	1.379
Absorp. coef./mm ⁻¹	0.974
F(000)	5044
2 $\theta_{\max}$ /°	50
Reflections collected	93851
Independent reflections	41381 [R(int) = 0.0329]
Data / restraints / parameters	41381 / 0 / 2782
S on <i>F</i> ²	1.079
R ₁ , wR ₂ [I>2 σ (I)]	0.1236, 0.2785
R ₁ , wR ₂ (all data)	0.1286, 0.2813
Largest diff. peak and hole/e.Å ⁻³	2.823 and -2.275

^aExcluding solvate molecules

3.3.2 Synthesis and characterisation of tridecanuclear manganese complexes

3.3.2.1 $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_5\text{Cl}]\cdot 3\text{H}_2\text{O}$ (**11**)

Compound **11** was prepared using a similar synthetic procedure that led to the formation of **10**. $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ and KMnO_4 were reacted with phenylphosphonic acid in a $\text{MeOH}/\text{CH}_3\text{CN}$ solution and pyridine was added as an organic base. After stirring the reaction mixture for five hours, it was filtered and left at room temperature for slow evaporation of the solvent. During a time period of one week small rhombic red-brown crystals of $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_5\text{Cl}]\cdot 3\text{H}_2\text{O}$ (**11**) were obtained and characterized by single crystal X-ray diffraction measurements.

11 crystallises in the orthorhombic crystal system in the space group $P2_12_12_1$. It contains a tridecanuclear Mn^{III} complex that is shown in Figure 3.11. The core structure of **11** features a three layered metal-centered distorted cuboctahedron (Figure 3.11, Figure 3.12). The triangular units **A** and **A'** are staggered in a trigonal antiprismatic fashion. They consist of three Mn^{III} ions ($\text{Mn}(9)$, $\text{Mn}(10)$ and $\text{Mn}(11)$, and $\text{Mn}(4)$, $\text{Mn}(8)$ and $\text{Mn}(12)$, respectively) connected through a $\mu_2\text{-OH}^-$ moiety and three phosphonate ligands (Figure 3.13). Unit **A** is further stabilised by two pyridine molecules, one chloride ion and two methanol molecules, while unit **A'** is further stabilised by three pyridine and two methanol molecules. Two of the three Mn ions in **A** and **A'** ($\text{Mn}(9)$ and $\text{Mn}(10)$, $\text{Mn}(8)$ and $\text{Mn}(12)$, respectively) adopt distorted square pyramidal geometries that share a common vertex $\text{O}(33)$ and $\text{O}(10)$, respectively. The coordination spheres of $\text{Mn}(9)$, $\text{Mn}(10)$, $\text{Mn}(8)$ and $\text{Mn}(12)$, each consist of one $\mu_2\text{-OH}^-$ group, three O donors from three distinct phosphonate ligands and a N atom from a pyridine molecule.

The bond distances between Mn ions and the $\mu_2\text{-OH}^-$ are 1.899(13) Å, 1.960(13) Å, 1.897(13) Å, and 1.953(13) Å for $\text{Mn}(9)\text{-O}(33)$, $\text{Mn}(10)\text{-O}(33)$, $\text{Mn}(8)\text{-O}(10)$ and $\text{Mn}(12)\text{-O}(10)$, respectively. The bond distances between these latter Mn ions and the O donors originating from the organic phosphonate ligands range between 1.868(11) Å – 1.934(12) Å, while the bond distances between $\text{Mn}(9)\text{-N}(2)$, $\text{Mn}(10)\text{-N}(3)$, $\text{Mn}(8)\text{-N}(5)$ and $\text{Mn}(12)\text{-N}(6)$ are 2.195(14) Å, 2.243(17) Å, 2.255(17) Å and 2.231(15) Å, respectively (Table 3.5).

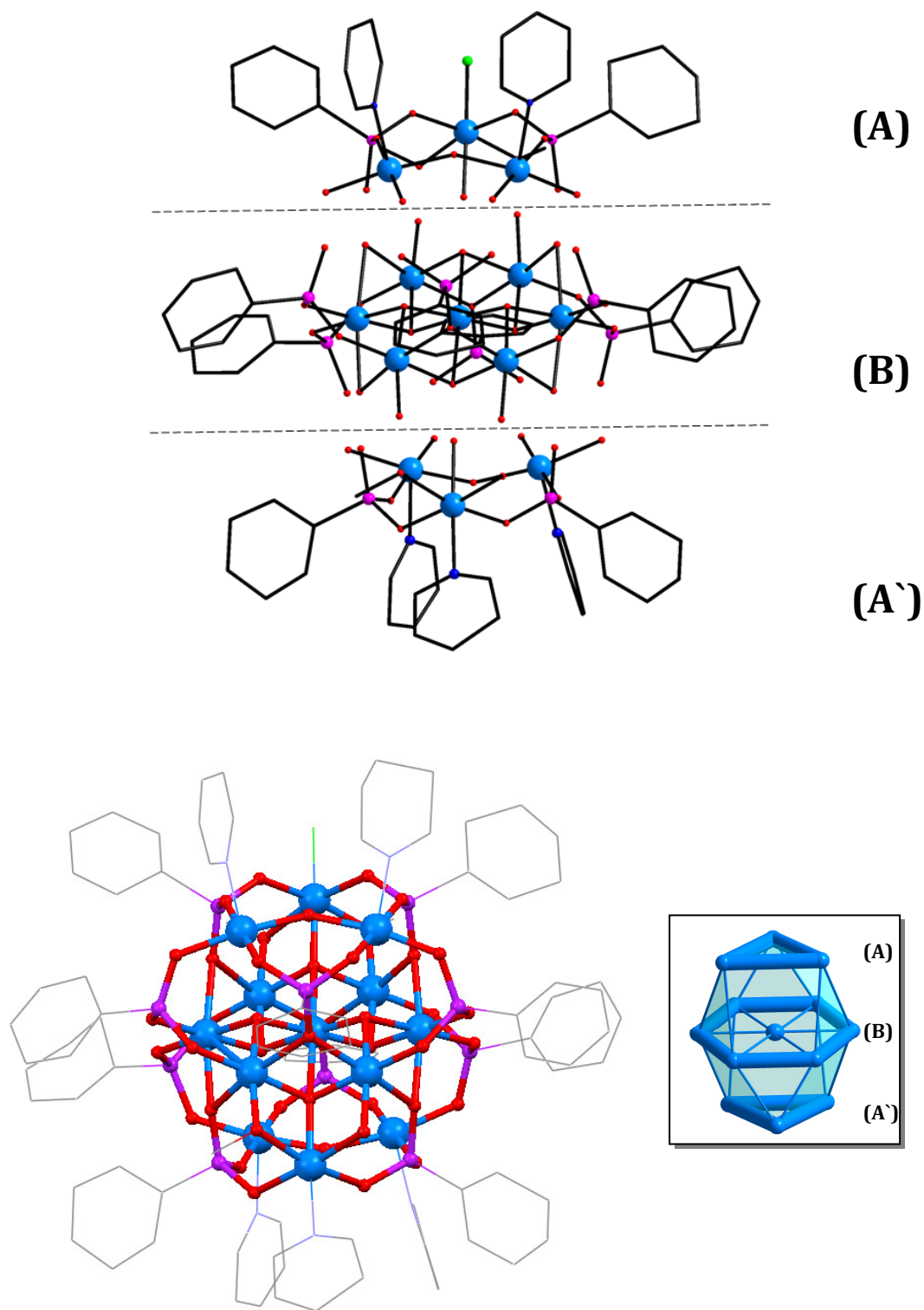


Figure 3.11 – Crystal structure of the tridecanuclear manganese complex in **11** showing the triangular units **A** and the hexagonal unit **B**. Colour code: Mn^{III} blue, P purple, O red, Cl green, C grey (hydrogen atoms have been omitted for clarity).

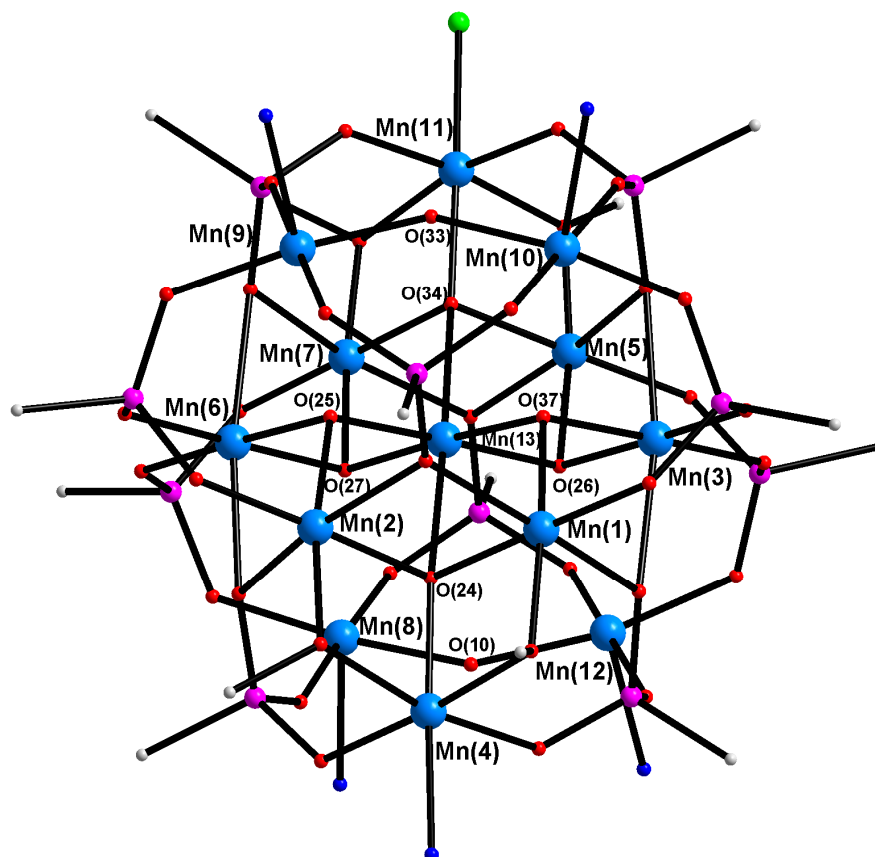


Figure 3.12 – The core structure of the tridecanuclear manganese complex in **11**. Colour code: Mn^{III} blue, P purple, O red, Cl green, C grey.

The third Mn^{III} ion in the **A** and **A'** moieties, Mn(11) and Mn(4) respectively, displays a distorted octahedral coordination environment. The distortion arises from the geometrical restrictions of the binding ligands and the nature of the Mn^{III} Jahn-Teller ion, and can be exemplified by examining the bond angles and bond lengths that deviate from the ideal octahedral geometry. Selected bond angles for Mn(11) and Mn(4) ions are listed in Table 3.7. The distorted octahedral geometry of Mn(11) and Mn(4) ions consists of two O_{phosphonate} donors forming Mn-O bond lengths that range between 1.905(11) Å – 2.092(13) Å, two O_{methanol} donors which engage in Mn-O bonds that range between 1.943(10) Å – 2.141(13) Å, and a μ_4 -O²⁻ ion forming Mn-O bond lengths of 1.959(10) Å and 1.928(10) Å, for Mn(11)-O(34) and Mn(4)-O(24), respectively. The coordination environment of Mn(11) is completed by a Cl ion that forms a Mn(11)-Cl(1) bond of 2.281(7) Å, while the coordination environment of Mn(4) is completed by a N atom from a pyridine molecule that forms a Mn(4)-N(1) bond of 2.208(11) Å (Table 3.5). The Mn(11)-Cl(1) and Mn(4)-N(1) bonds are about 0.1 – 0.3 Å longer than the other bonds of the coordination environments of Mn(11) and Mn(4), respectively. In addition it is worth noting that the bond angles O(6)-Mn(11)-O(17), O(16)-Mn(11)-O(6), O(22)-Mn(4)-O(8) and O(22)-

Mn(4)-N(1) of $168.6(5)^\circ$, $95.5(5)^\circ$, $167.2(5)^\circ$ and $97.9(4)^\circ$, respectively, show the greatest deviation from the ideal octahedral geometry.

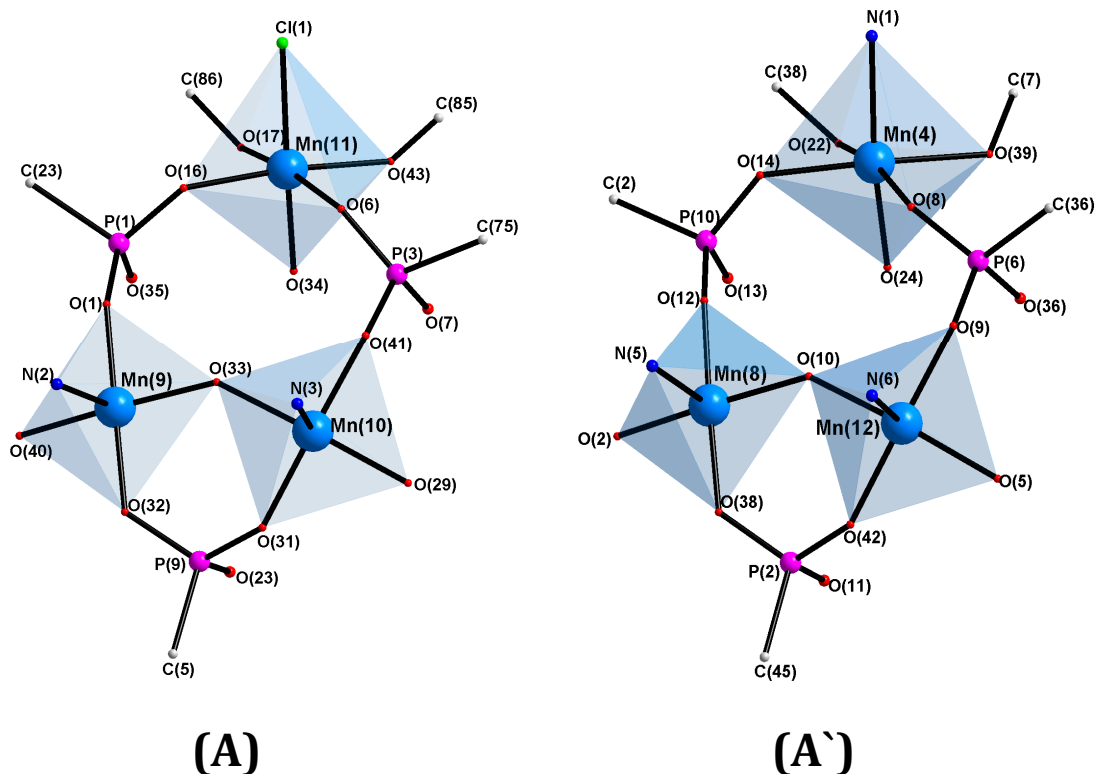


Figure 3.13 – Polyhedral representation of the triangular units **A** and **A'** in **11**. Colour code: Mn^{III} blue, P purple, O red, Cl green, C grey.

The hexagonal unit **B** (Figure 3.14) consists of six Mn atoms (Mn(1), Mn(2), Mn(3), Mn(5), Mn(6), Mn(7)) and one Mn atom located in the centre (Mn(13)). All Mn ions in **B** adopt a near-octahedral geometry, with an obvious Jahn–Teller (JT) distortion (axial elongation) further supporting the assignment of the +III oxidation state of the Mn ions.³⁰ The distorted octahedral geometry of Mn(1), Mn(2), Mn(5), and Mn(7) consists of three O_{phosphonate} donors, one O_{methanol} donor, one μ_4 -O²⁻ ion and a μ_3 -O²⁻ ion. The Mn-O_{phosphonate} bond distances range between 1.913(10) Å – 2.253(11) Å, the Mn-O_{methanol} bond distances range between 1.871(12) Å – 1.932(11) Å, the Mn-(μ_4 -O²⁻) bond distances range between 1.901(9) Å – 1.946(9) Å, while the Mn-(μ_3 -O²⁻) bond distances range between 1.908(10) Å – 1.971(12) Å. The distorted octahedral geometry of Mn(3) and Mn(6) consists of four O_{phosphonate} donors and two μ_3 -O²⁻ ions. The Mn-O_{phosphonate} bond distances range between 1.906(10) Å – 2.240(11) Å, while the Mn-(μ_3 -O²⁻) bond distances range between 1.904(11) Å – 1.937(9) Å. Finally, the octahedral coordination sphere of Mn(13)

compress two $\mu_4\text{-O}^{2-}$ ions and four $\mu_3\text{-O}^{2-}$ ions. The $\text{Mn}(\mu_4\text{-O}^{2-})$ bond distances are 2.369(10) Å and 2.423(10) Å for Mn(13)-O(34) and Mn(13)-O(24) , respectively, while the $\text{Mn}(\mu_3\text{-O}^{2-})$ bond distances range between 1.935(9) Å – 1.967(9) Å. The distorted nature of the octahedral geometry of the metal ions within the hexagonal sub-unit can be observed from the bond lengths and the bond angles of the Mn^{III} metal centres that deviate from the ideal octahedral geometry. Selected bond lengths and bond angles for the Mn ions in **11** are listed in Table 3.5 and Table 3.7.

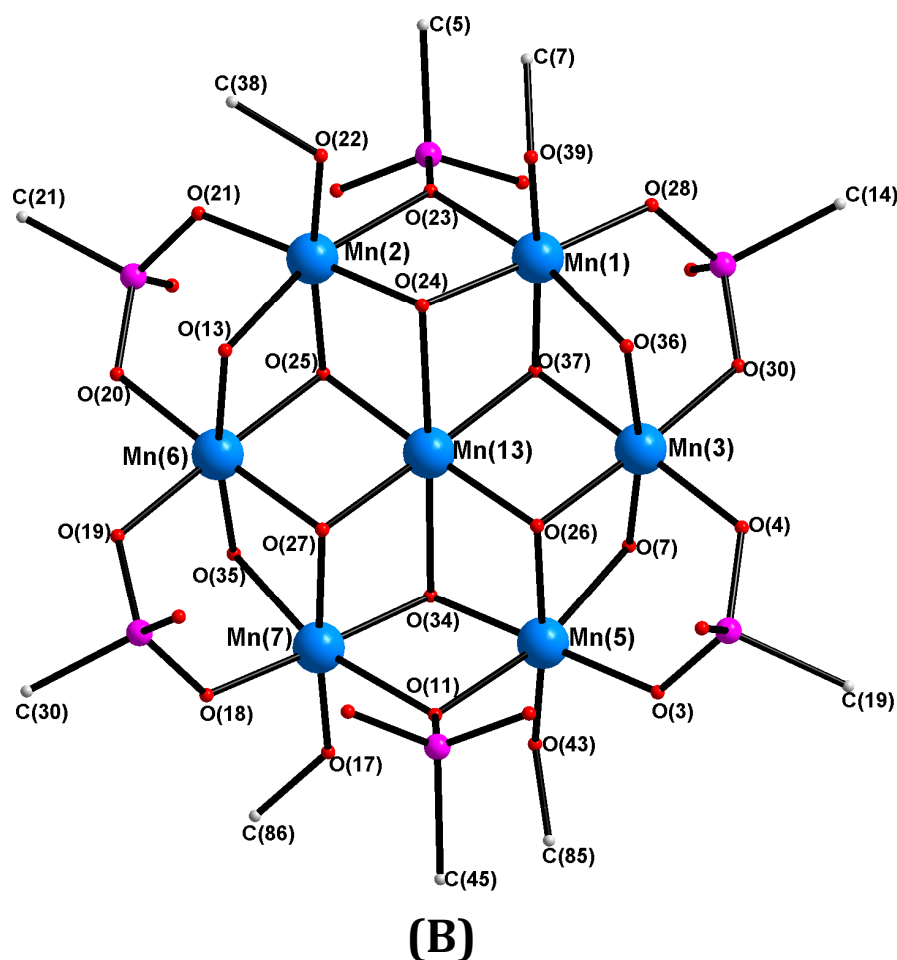


Figure 3.14 – Ball-and-stick representation of the hexagonal unit **B** in **11**. Colour code: Mn^{III} blue, P purple, O red, C grey.

The hexagonal unit **B** is stabilized to the outside by six phosphonate ligands and four methanol molecules. The units **A** and **B** are connected to each other by a combination of O^{2-} , CH_3O^- and phosphonate ligands to give the $\{\text{Mn}_{13}\}$ core structure. All four methanol molecules are deprotonated and bridge between two Mn ions (Mn(1) and Mn(4) , Mn(2) and Mn(4) , Mn(5) and Mn(11) , Mn(7) and Mn(11) , respectively).

Table 3.5 – Selected bond lengths [Å] and bond valence sum (BVS) for compound 11.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mn(1)	Mn(1)-O(37)	1.908(10)	3.271	+3
	Mn(1)-O(39)	1.909(12)		
	Mn(1)-O(28)	1.921(11)		
	Mn(1)-O(24)	1.946(9)		
	Mn(1)-O(36)	2.156(10)		
	Mn(1)-O(23)	2.162(11)		
Mn(2)	Mn(2)-O(22)	1.882(12)	3.281	+3
	Mn(2)-O(24)	1.901(9)		
	Mn(2)-O(21)	1.913(10)		
	Mn(2)-O(25)	1.926(11)		
	Mn(2)-O(13)	2.209(9)		
	Mn(2)-O(23)	2.229(10)		
Mn(3)	Mn(3)-O(26)	1.904(11)	3.238	+3
	Mn(3)-O(4)	1.906(10)		
	Mn(3)-O(30)	1.909(12)		
	Mn(3)-O(37)	1.928(10)		
	Mn(3)-O(7)	2.194(11)		
	Mn(3)-O(36)	2.240(11)		
Mn(4)	Mn(4)-O(24)	1.928(10)	2.799	+3
	Mn(4)-O(14)	2.020(12)		
	Mn(4)-O(22)	2.072(11)		
	Mn(4)-O(39)	2.073(11)		
	Mn(4)-O(8)	2.092(13)		
	Mn(4)-N(1)	2.208(11)		
Mn(5)	Mn(5)-O(34)	1.913(9)	3.127	+3
	Mn(5)-O(3)	1.926(9)		
	Mn(5)-O(43)	1.932(11)		
	Mn(5)-O(26)	1.971(12)		
	Mn(5)-O(11)	2.154(11)		
	Mn(5)-O(7)	2.220(10)		
Mn(6)	Mn(6)-O(27)	1.920(10)	3.117	+3
	Mn(6)-O(20)	1.924(9)		
	Mn(6)-O(19)	1.926(11)		
	Mn(6)-O(25)	1.937(9)		
	Mn(6)-O(13)	2.226(10)		
	Mn(6)-O(35)	2.226(12)		
Mn(7)	Mn(7)-O(17)	1.871(12)	3.153	+3
	Mn(7)-O(18)	1.930(12)		
	Mn(7)-O(34)	1.934(10)		
	Mn(7)-O(27)	1.967(11)		
	Mn(7)-O(11)	2.181(10)		
	Mn(7)-O(35)	2.253(11)		
Mn(8)	Mn(8)-O(12)	1.868(11)	3.122	+3
	Mn(8)-O(10)	1.897(13)		
	Mn(8)-O(2)	1.910(15)		
	Mn(8)-O(38)	1.911(12)		
	Mn(8)-N(5)	2.255(17)		
Mn(9)	Mn(9)-O(1)	1.880(13)	3.200	+3
	Mn(9)-O(32)	1.887(11)		
	Mn(9)-O(33)	1.899(13)		
	Mn(9)-O(40)	1.911(12)		
	Mn(9)-N(2)	2.195(14)		

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mn(10)	Mn(10)-O(29)	1.881(13)	3.082	+3
	Mn(10)-O(31)	1.884(10)		
	Mn(10)-O(41)	1.893(13)		
	Mn(10)-O(33)	1.960(13)		
	Mn(10)-N(3)	2.243(17)		
Mn(11)	Mn(11)-O(16)	1.905(11)	3.340	+3
	Mn(11)-O(43)	1.943(10)		
	Mn(11)-O(34)	1.959(10)		
	Mn(11)-O(6)	2.057(12)		
	Mn(11)-O(17)	2.141(13)		
	Mn(11)-Cl(1)	2.281(7)		
Mn(12)	Mn(12)-O(9)	1.871(12)	3.019	+3
	Mn(12)-O(42)	1.901(11)		
	Mn(12)-O(5)	1.934(12)		
	Mn(12)-O(10)	1.953(13)		
	Mn(12)-N(6)	2.231(15)		
Mn(13)	Mn(13)-O(26)	1.935(9)	2.766	+3
	Mn(13)-O(25)	1.945(9)		
	Mn(13)-O(27)	1.946(11)		
	Mn(13)-O(37)	1.967(9)		
	Mn(13)-O(34)	2.369(10)		
	Mn(13)-O(24)	2.423(10)		
Mn(1) ... Mn(4)	2.940(4)	Mn(3) ... Mn(5)	3.031(4)	
Mn(1) ... Mn(3)	3.023(4)	Mn(5) ... Mn(11)	2.929(4)	
Mn(1) ... Mn(2)	3.099(3)	Mn(5) ... Mn(7)	3.072(3)	
Mn(1) ... Mn(13)	3.119(4)	Mn(5) ... Mn(13)	3.087(4)	
Mn(2) ... Mn(4)	2.944(4)	Mn(6) ... Mn(13)	2.895(4)	
Mn(2) ... Mn(6)	3.023(4)	Mn(6) ... Mn(7)	3.033(4)	
Mn(2) ... Mn(13)	3.147(4)	Mn(7) ... Mn(11)	2.993(4)	
Mn(3) ... Mn(13)	2.905(3)	Mn(7) ... Mn(13)	3.106(4)	

Table 3.6 – Bond valence sum (BVS) calculations for some O atoms in 11.

Atom	BVS	Assignment ^a
O(24)	2.090	$\mu_4\text{-O}^{2-}$
O(34)	2.063	$\mu_4\text{-O}^{2-}$
O(26)	1.866	$\mu_3\text{-O}^{2-}$
O(37)	1.877	$\mu_3\text{-O}^{2-}$
O(27)	1.825	$\mu_3\text{-O}^{2-}$
O(25)	1.865	$\mu_3\text{-O}^{2-}$
O(10)	1.284	$\mu_2\text{-OH}^{\cdot}$
O(33)	1.269	$\mu_2\text{-OH}^{\cdot}$

^a An oxygen BVS in the ~1.8-2.0, ~1.0-1.2, and ~0.2-0.4 ranges is indicative of non-, single- and double protonation, respectively.^{7, 53}

Table 3.7 – Selected bond angles [°] for compound 11.

Bond Angle (°)		Bond Angle (°)	
O(28)-Mn(1)-O(24)	178.1(5)	O(4)-Mn(3)-O(37)	178.2(4)
O(39)-Mn(1)-O(37)	171.2(5)	O(30)-Mn(3)-O(26)	176.8(4)
O(23)-Mn(1)-O(36)	169.1(4)	O(7)-Mn(3)-O(36)	170.8(4)
O(28)-Mn(1)-O(23)	97.5(4)	O(4)-Mn(3)-O(36)	98.3(5)
O(39)-Mn(1)-O(28)	94.0(5)	O(30)-Mn(3)-O(7)	97.2(4)
O(39)-Mn(1)-O(23)	93.5(5)	O(30)-Mn(3)-O(37)	93.3(4)
O(39)-Mn(1)-O(36)	91.8(5)	O(26)-Mn(3)-O(36)	90.2(4)
O(37)-Mn(1)-O(23)	89.5(4)	O(30)-Mn(3)-O(4)	88.4(4)
O(39)-Mn(1)-O(24)	84.3(5)	O(30)-Mn(3)-O(36)	89.2(4)
O(24)-Mn(1)-O(23)	81.8(4)	O(37)-Mn(3)-O(36)	81.2(4)
O(14)-Mn(4)-O(39)	175.3(5)	O(16)-Mn(11)-O(43)	172.4(5)
O(24)-Mn(4)-N(1)	171.4(4)	O(34)-Mn(11)-Cl(1)	171.3(4)
O(22)-Mn(4)-O(8)	167.2(5)	O(6)-Mn(11)-O(17)	168.6(5)
O(22)-Mn(4)-N(1)	97.9(4)	O(16)-Mn(11)-O(6)	95.5(5)
O(24)-Mn(4)-O(14)	96.6(4)	O(17)-Mn(11)-Cl(1)	95.4(4)
O(8)-Mn(4)-N(1)	94.9(4)	O(43)-Mn(11)-Cl(1)	95.0(4)
O(39)-Mn(4)-N(1)	92.0(4)	O(6)-Mn(11)-Cl(1)	95.0(4)
O(14)-Mn(4)-O(8)	93.1(5)	O(16)-Mn(11)-O(34)	92.4(4)
O(14)-Mn(4)-N(1)	90.6(4)	O(16)-Mn(11)-Cl(1)	91.8(4)
O(14)-Mn(4)-O(22)	87.4(5)	O(16)-Mn(11)-O(17)	88.8(5)
O(34)-Mn(13)-O(24)	178.0 (4)		
O(26)-Mn(13)-O(25)	177.4(6)		
O(37)-Mn(13)-O(27)	176.6(6)		
O(26)-Mn(13)-O(24)	105.2(4)		
O(27)-Mn(13)-O(24)	102.4(4)		
O(26)-Mn(13)-O(27)	98.9(4)		
O(26)-Mn(13)-O(37)	81.6(4)		
O(26)-Mn(13)-O(34)	76.4(4)		
O(37)-Mn(13)-O(24)	74.2(4)		
O(25)-Mn(13)-O(24)	72.5(4)		

The phosphonate ligands bridge between the hexagonal unit **B** and the triangular units **A** in $\eta^1:\eta^1:\eta^1:\mu_3$ (P(4), P(5), P(7) and P(8)), and $\eta^1:\eta^1:\eta^2:\mu_4$ (P(1), P(2), P(3), P(6), P(9), and P(10)) bridging modes (Figure 3.15). The oxidation states of the Mn ions and the protonation states of O ions were assigned by bond valence sum analysis (Table 3.5, Table 3.6).

In the solid state the tridecanuclear clusters are intermolecularly linked by weak hydrogen bonds involving constitution solvent molecules resulting in a relatively densely packed structure that can be seen in Figure 3.16.

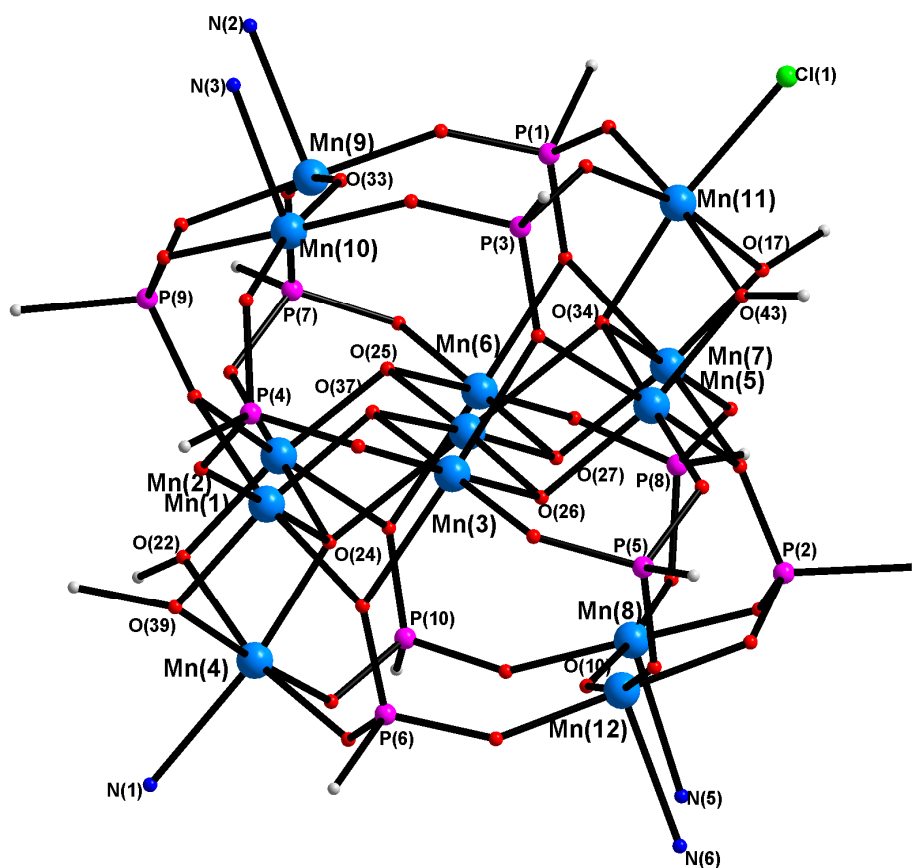


Figure 3.15 – Ball-and-stick representation of the $\{\text{Mn}_{13}\}$ core structure in **11**, showing the phosphonates' bridging modes. Colour code: Mn^{III} blue, P purple, O red, Cl green, C grey.

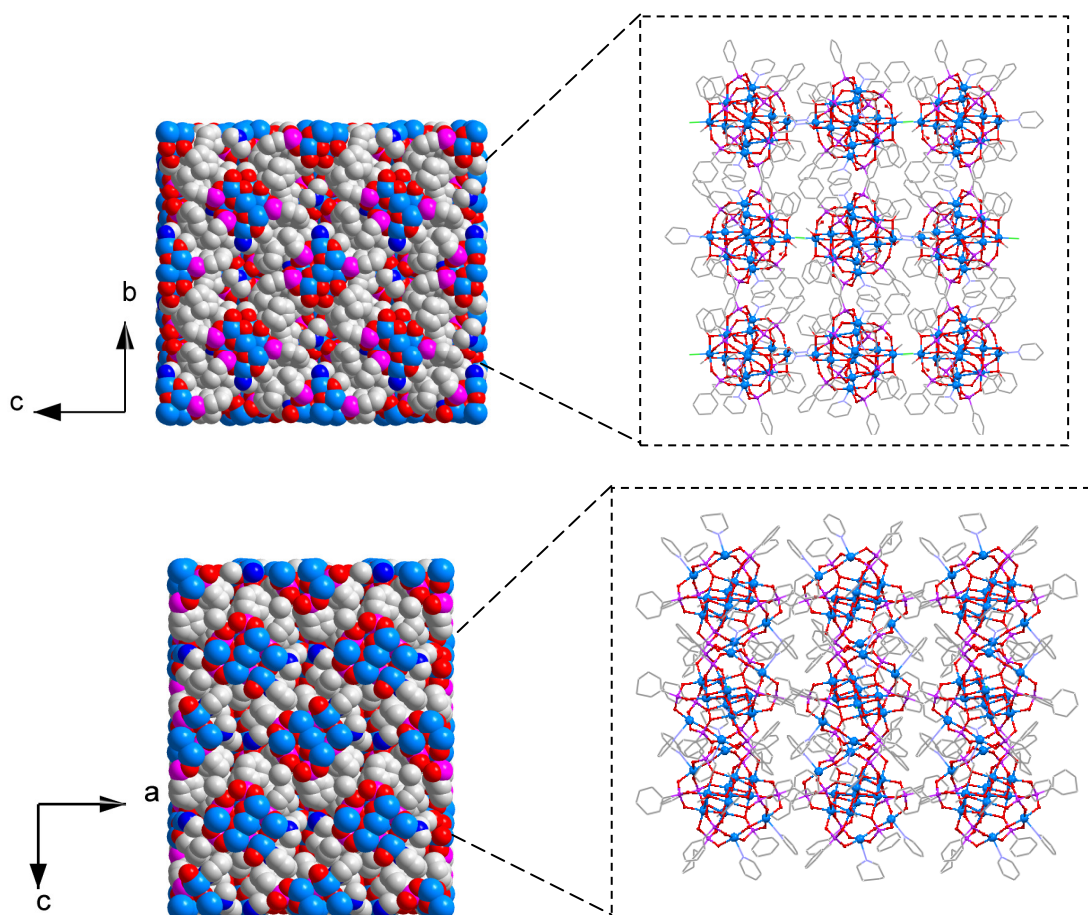


Figure 3.16 – Packing arrangement of the tridecanuclear manganese clusters in **11** viewed in the direction of the crystallographic *a*- and *b*-axis. Colour code: Mn blue, P purple, O red, C grey, (crystallization solvent molecules and hydrogen atoms have been omitted for clarity).

The metal-centered cuboctahedral core structure of **11** is unprecedented but can be regarded as a member of a family of $\{\text{Mn}_{13}\}$ complexes stabilised by carboxylate and phosphonate ligands, such as: $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_6\text{O}_8(\text{O}_2\text{CPh})_{12}(\text{OEt})_6]$, $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_6\text{O}_8(\text{OH})_6(\text{ndc})_6]$, $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_6\text{O}_8(\text{OEt})_5(\text{OH})(\text{ndc})_6]$, $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_6\text{O}_8(\text{OMe})_6(\text{ndc})_6]$, (ndcH_2 = 1,8-naphthalenedicarboxylic acid), $[\text{Mn}_{13}\text{O}_8(\text{OEt})_6(\text{O}_2\text{CC}_6\text{H}_4\text{OPh})_{12}]$, $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_{12}\text{O}_6(\text{OH})_6(\text{O}_3\text{PC}_6\text{H}_{11})_{10}(\text{py})_6]$, $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_{12}\text{O}_8\text{Cl}_6(\text{t-BuPO}_3)_8][\text{Mn}^{\text{II}}(\text{CH}_3\text{CN})_6]\text{Cl}_2$, $[\text{Mn}^{\text{III}}_{13}\text{O}_6(\text{t-BuPO}_3)_{10}(\text{OH})_2(\text{N}_3)_6(\text{MeCOOH})_2(\text{H}_2\text{O})_2]^-$.^{12, 48, 53-55} Amongst these $\{\text{Mn}_{13}\}$ complexes the neutral $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_{12}\text{O}_6(\text{OH})_6(\text{O}_3\text{PC}_6\text{H}_{11})_{10}(\text{py})_6]$ compound reported by Zheng *et al.* reveals the closest similarity to **11**.¹² Zheng used cyclohexyl phosphonic acid as a stabilising ligand and obtained a mixed-valent $\{\text{Mn}_{13}\}$ cluster in which the central Mn ion adopts the oxidation state +II. There are a number of other elements that differentiate Zheng's compound from compound **11**. The triangular units in Zheng's compound consist of one square pyramidally and two octahedrally coordinated

Mn^{III} ions. In contrast to **11** in the reported compound four μ_4 -O²⁻ and two μ_3 -O²⁻ ligands bridge between the triangular and hexagonal units. In addition the four μ_2 -CH₃O⁻ ligands in **11** are replaced with four μ_2 -OH⁻ ligands in Zheng's compound.

The [Mn^{III}₁₃O₆(t-BuPO₃)₁₀(OH)₂(N₃)₆(MeCOOH)₂(H₂O)₂]⁻ coordination cluster reported by Chen *et al.* also shows similarities to the here presented complex. It comprises of thirteen octahedrally coordinated Mn^{III} ions connected through six μ_4 -O²⁻ oxo bridges, ten t-BuPO₃²⁻, two OH⁻, six N₃⁻, two CH₃COOH and two H₂O ligands.^{48, 55} Another {Mn₁₃} complex with metal centred cuboctahedral cluster-cores stabilised by *tert*-butylphosphonates, [Mn^{II}Mn^{III}₁₂(μ_4 -O₈)(μ_4 -Cl₆)(t-BuPO₃)₈], was reported by Schmitt *et al.* In this compound the central Mn ion adopts the oxidation state +II and is coordinated by eight μ_4 -O²⁻ oxo ligands. The remaining twelve Mn^{III} atoms adopt tetragonally distorted octahedral coordination environments, and the peripheral ligation is provided by six Cl⁻ ligands and eight t-BuPO₃²⁻ ligands.⁴⁸ Structurally related compounds were also reported by Christou *et al.*⁵³ and Murrie *et al.*⁵⁴ in which the metal centred cuboctahedral atom arrangement is stabilised by carboxylate ligands. The core structures of these reported mixed valent species comprise of one central Mn^{IV} ion, six Mn^{III} ions forming the triangular units and six Mn^{II} ions forming the hexagonal unit. In his paper, Christou reports the structure and properties of the following {Mn₁₃} complexes: [Mn^{IV}Mn^{III}₆Mn^{II}₆O₈(OH)₆(ndc)₆], [Mn^{IV}Mn^{III}₆Mn^{II}₆O₈(OEt)₅(OH)(ndc)₆], [Mn^{IV}Mn^{III}₆Mn^{II}₆O₈(OMe)₆(ndc)₆] and [Mn₁₃O₈(O₂CPh)₁₂(OEt)₆] (ndcH₂ = 1,8-naphthalenedicarboxylic acid). All the Mn atoms in these compounds adopt a near-octahedral coordination geometry and are connected by six μ_5 -O²⁻ and two μ_3 -O²⁻ ligands. Additional bridging and peripheral ligation is provided by μ_3 -OH⁻, μ_3 -EtO⁻ or μ_3 -MeO⁻ ions, and ndc²⁻ or benzoate ligands, respectively. The {Mn₁₃} core in Murrie's compound [Mn₁₃O₈(OEt)₆(O₂CC₆H₄OPh)₁₂] is stabilised by six μ_4 -O²⁻, two μ_3 -O²⁻, six μ_3 -EtO⁻ and twelve 2-phenoxybenzoate ligands. The central Mn^{IV} and the six Mn^{III} ions in Murrie's compound display a distorted octahedral coordination environment, whilst the remaining six Mn^{II} ions adopt a distorted square pyramidal geometry.

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

The infrared spectrum of **11** presented in Figure 3.17 is very similar to that of **10**. Characteristic C–C skeletal vibrations of the aromatic rings appear in the 1600 – 1430 cm^{-1} region, while the C–H out-of-plane bending vibrations can be observed in the 800 – 650 cm^{-1} region. Compared with **10** the IR spectrum of **11** displays some extra bands in the 1200 – 900 cm^{-1} region due to C–C stretching vibrations of the pyridine rings, along with the different P–O stretching vibrations of the phosphonate groups present in this region. Some O–H stretching vibrations appear as a broad band at *ca.* 3500 cm^{-1} .^{36-40, 56, 57}

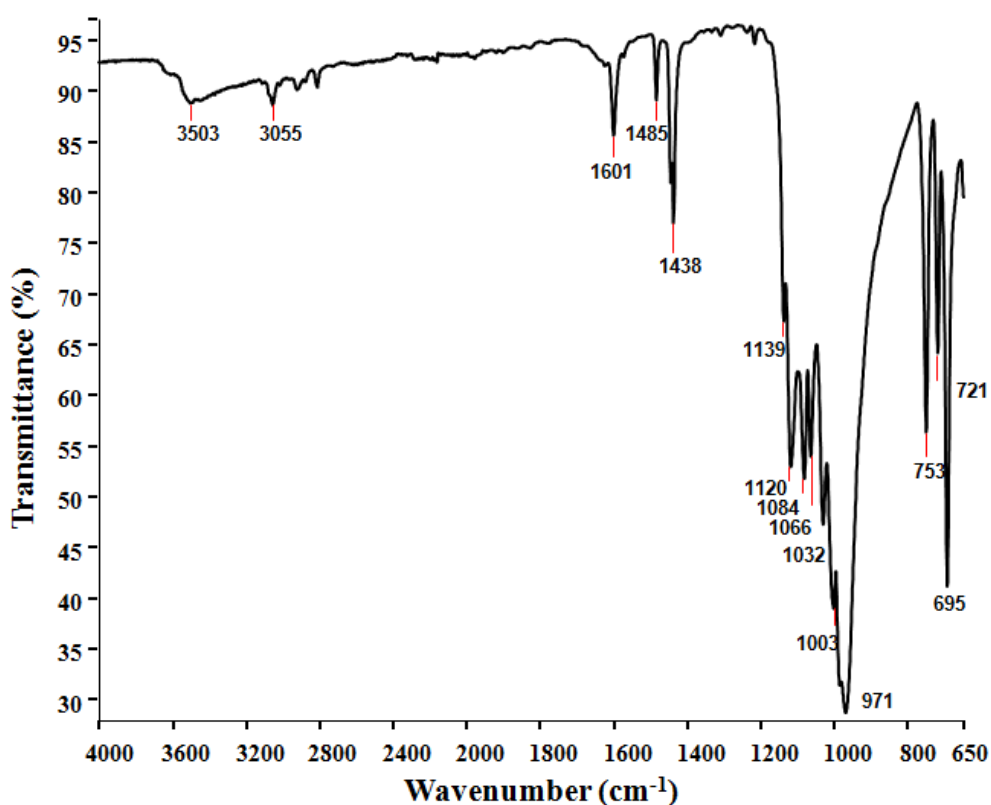


Figure 3.17 – Infrared spectrum of **11**.

- *Thermogravimetric analysis*

The thermogravimetric analysis for compound **11** was performed using a freshly prepared crystalline sample, in the temperature range 30 – 900 °C, in a N₂ atmosphere (Figure 3.18). Upon thermolysis **11** undergoes a weight loss of 6.8 % in the temperature range 30 – 200 °C which may be assigned to the loss of three crystallization H₂O molecules and four coordination CH₃OH molecules (calcd: 6.1 %). This assignment is in agreement with composition determined by elemental analysis. The next step in the TGA curve that corresponds to a weight loss of 12.7 % between 200 – 300 °C can be attributed to the loss of five pyridine molecules (calcd: 13.1 %). A further weight loss that occurs in two distinct steps can be observed above 300 °C. This can be associated with the degradation of the organic ligands within **11** and cluster degradation processes resulting in the probable formation of metal oxide materials.

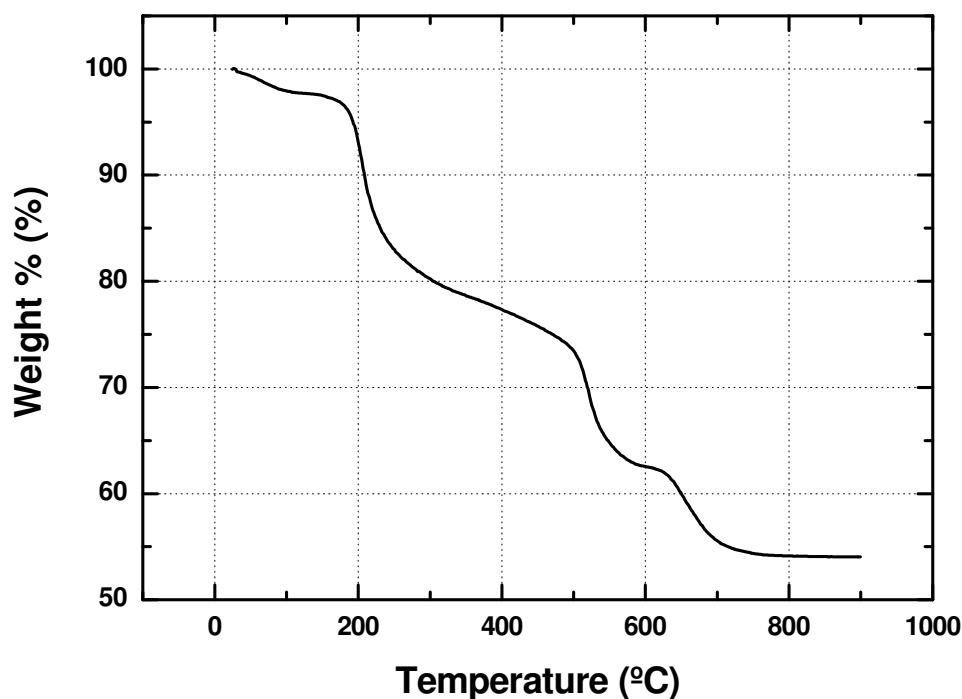


Figure 3.18 – Thermogravimetric analysis of **11**.

- Magnetism

The temperature dependence of the magnetic susceptibility of **11** was measured between 298 and 1.8 K (Figure 3.19). The χT value of $30.7 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature is significantly lower than the expected value of $39 \text{ cm}^3 \text{ K mol}^{-1}$ for the presence of thirteen $S = 2 \text{ Mn}^{\text{III}}$ carriers ($C = \frac{Ng^2\mu_B^2}{3k_B} S(S+1)$ with $\frac{Ng^2\mu_B^2}{3k_B} = 0.12505 \text{ cm}^3 \text{ K mol}^{-1}$ and $g = 2$).⁴¹ This result highlights dominant antiferromagnetic (AF) couplings between spin carriers. Upon lowering the temperature, the χT product decreases down to a minimum of *ca.* $18.3 \text{ cm}^3 \text{ K mol}^{-1}$ at about 20 K. This thermal behavior confirms the presence of dominant AF interactions between spin carriers. The result does not exclude the presence of ferromagnetic interactions but only suggests that the AF interactions are dominant. Experimental data can be fitted to a Curie-Weiss law for a temperature above 120 K, with $C = 38.3(5) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -68(2) \text{ K}$. The Curie constant is in good agreement with the expected value ($39 \text{ cm}^3 \text{ K/mol}$) arising from thirteen Mn^{III} $S = 2$ spins. Below 20 K, at 1000 Oe the χT product increases to reach $19.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. This value suggests an $S_T = 6$ ground state. At 1 T, below 10 K, the χT product decreases to reach $7.9 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K due to field saturation effects of the magnetisation.

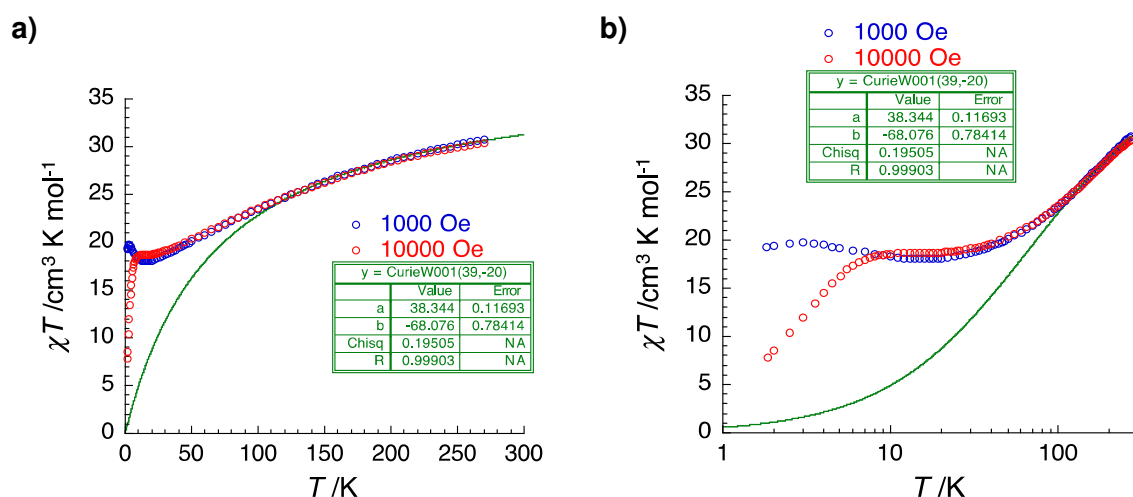


Figure 3.19 – (a) Temperature dependence of the χT product of **11** at 0.1 and 1 T. (b) A magnified view of the χT product in (a) between 1 and 100 K. The green solid line corresponds to the best fit of the experimental data with the Curie-Weiss law ($C = 38.3(5) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -68(2) \text{ K}$).

The field dependence of the magnetisation for this compound has been measured at low temperatures between 1.8 and 8 K (Figure 3.20, a). The magnetisation at low field displays a rapid increase without inflexion point confirming the absence of weak antiferromagnetic interactions and the presence of a well-defined ground state. The high

field behavior that displays a non-linear increase without clear saturation even at 1.8 K at 7 T, suggests the presence of magnetic anisotropy. It is worth noting that the presence of low-lying excited states and also inter-complex magnetic interactions could contribute to this M vs H data even if these two effects are not reflected in χT vs T data at 0.1 T. The data represented in M vs H/T plots at different temperatures (Figure 3.20, b) confirm the presence of anisotropy intrinsic to Mn^{III} metal ions as the data are not superposed on a single master-curve as expected for an isotropic system with a well defined spin ground state. At 1.8 K, the magnetisation reaches $12.2 \mu_{\text{B}}$ at 7 T which is in agreement with an $S_{\text{T}} = 6$ ground state.

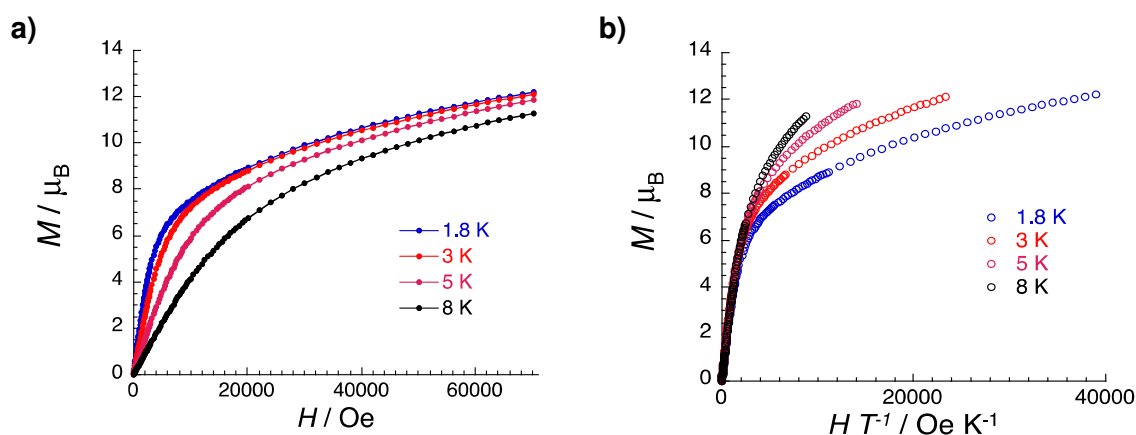


Figure 3.20 – (a) M vs H and (b) M vs H/T data at and below 8 K.

Both measurements, the field dependence of the magnetisation at 1.8 K and the temperature dependence of the χT product at 1000 Oe, are coherent with an $S_{\text{T}} = 6$ ground state. This experimental value can be explained with a configuration of eight Mn^{III} centres whose spin vectors are oriented in an opposite direction to those of the five remaining Mn centres, as a possible result of competing interactions between spin carriers.

The M vs H data at 1.8 K do not show any sign of slow relaxation i.e. hysteresis effects. Nevertheless, the ac susceptibility in zero dc field has been measured to probe possible slow dynamics of the magnetisation for this compound. Clearly at temperatures below 4 K (for frequency around 10000 Hz), slow relaxation of the magnetisation is observed based on the appearance of an out-of-phase signal.

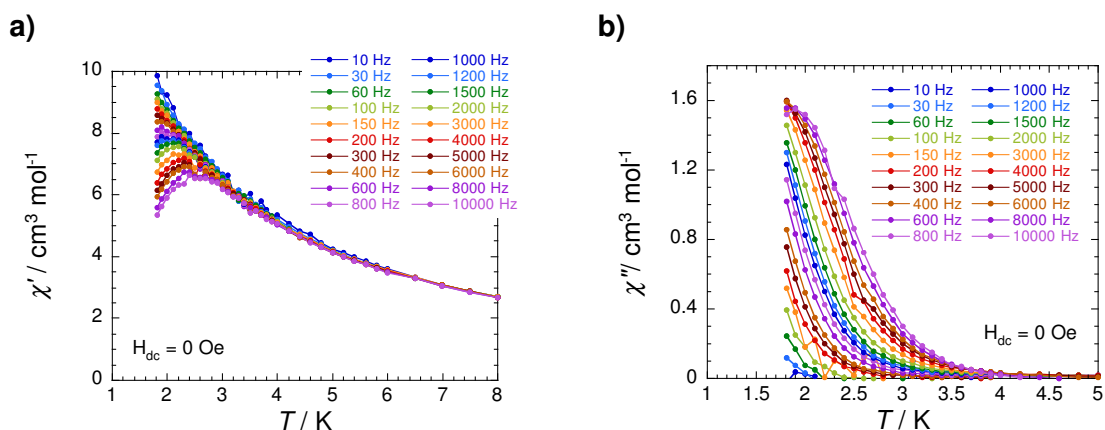


Figure 3.21 – Temperature dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') ac susceptibility under zero dc field for **11**.

In consecutive experiments we measured the ac susceptibility as a function of the frequency at different temperatures. This measurement was performed in zero dc field with the objective to more accurately estimate the relaxation time. The observed frequency dependence and resulting shape of the curve almost by itself demonstrates that this compound is consistent with an SMM.⁷

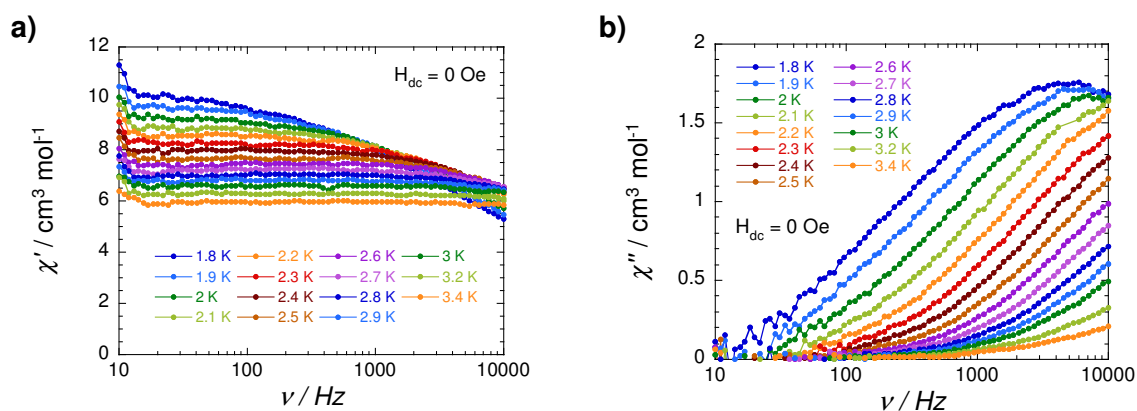


Figure 3.22 – Frequency dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') ac susceptibility from 1.8 to 3.4 K under zero dc field for **11**.

Using a scaling technique, the relaxation time of the compound was determined up to 3.4 K.

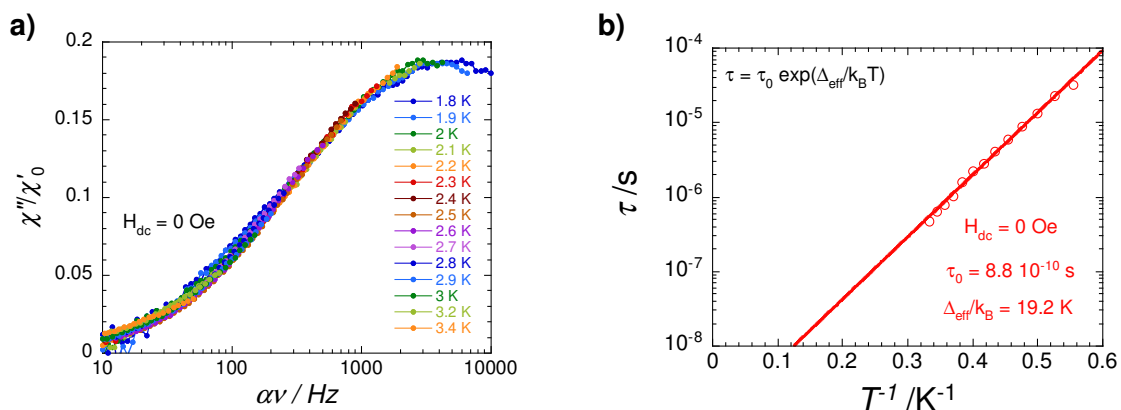


Figure 3.23 – (a) χ''/χ' vs ν from 1.8 to 3.4 K under zero dc field; (b) Magnetisation relaxation time (τ) vs T^{-1} plot for **11** under zero dc field (the solid line corresponds to the Arrhenius law).

From these data, the relaxation time can be deduced between 1.9 and 3 K and fitted to an Arrhenius law. The exponential increase of the relaxation time allowed us to determine the energy barrier of 19.2 K of the thermally activated regime while τ_0 is about 8.8×10^{-10} s.

The ac susceptibility has been measured at dc fields at 1.8 K in order to induce possible quantum relaxation pathways in zero-field and to probe the quantum contribution to the observed relaxation above 1.8 K.

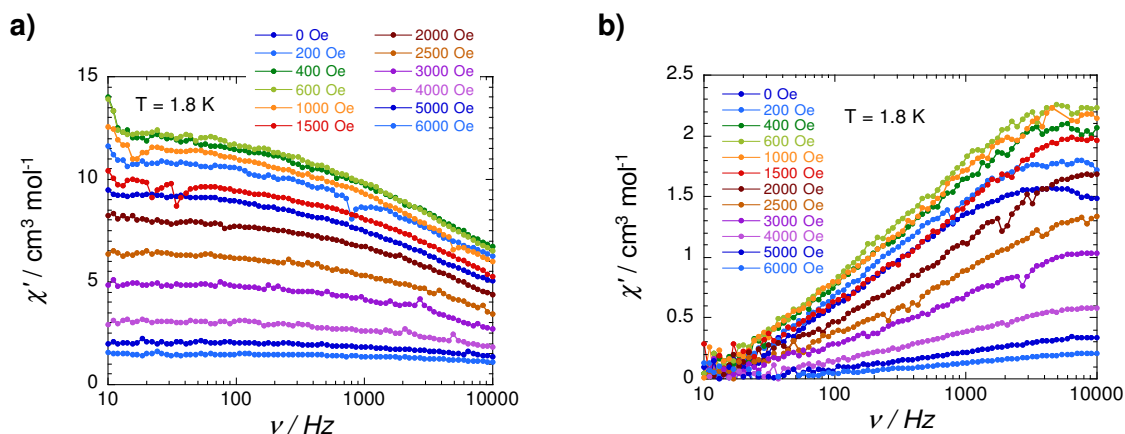


Figure 3.24 – Frequency dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') ac susceptibility with dc fields at 1.8 K for **11**.

With a small dc field, the characteristic frequency increases which demonstrate that the quantum pathway of magnetisation relaxation is only negligible above 1.8 K. Therefore, the ac susceptibility measurements under dc field have not been performed.

- *Mass spectrometry*

Negative mode ESI-MS spectra of compound **11** dissolved in a suitable solvent have been recorded (Table 3.8, Figure 3.25) in order to investigate the stability of the tridecanuclear manganese cluster in solution.⁴²⁻⁴⁸ The mass spectra of **11** dissolved in DMF and DMSO reveal the presence of two isotopic envelopes centered at $m/z = 1279.1$ a.m.u and $m/z = 2559.1$ a.m.u. These signals were attributed to a -2 charged and a -1 charged $\{\text{Mn}_{13}\}$ species as shown in Table 3.8. The mass spectrum of **11** in CH_3CN exhibits a major signal centered at $m/z = 1278.5$ a.m.u which corresponds to the doubly charged species $\{\text{H}[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_{11}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^{2-}$. The ESI-MS studies using the crystalline material confirmed the stability of the $\{\text{Mn}_{13}\}$ cluster in solution. The signals of the identified species were modelled and good fits between the experimental and simulated isotopic envelopes confirm the assignments.

Table 3.8 – ESI-MS assignment for compound **11**.

	Solvent	m/z	Species attributed
Crystals of 11 in:	CH_3CN	1278.5	$\{\text{H}[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_{11}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^{2-} \rightarrow \{\text{Mn}_{13}\}$
	DMF	1279.1	$\{\text{H}_2[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_{12}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^{2-} \rightarrow \{\text{Mn}_{13}\}$
		2559.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$
	DMSO	1279.1	$\{\text{H}_2[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_{12}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^{2-} \rightarrow \{\text{Mn}_{13}\}$
		2559.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$

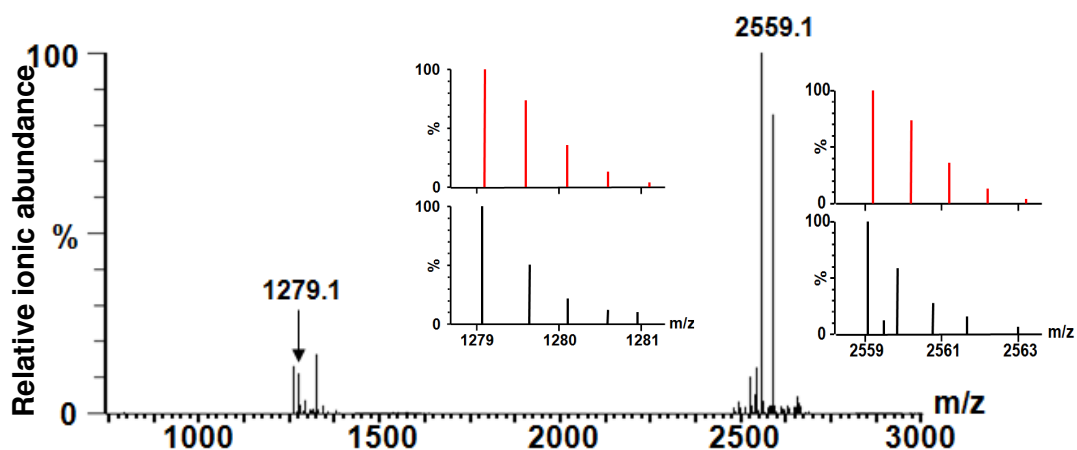


Figure 3.25 – Negative-mode ESI-MS spectra for crystals of **11** dissolved in DMF. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_2[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_{12}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^{2-}$ and $\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_{10}]\}^-$ centered at $m/z = 1279.1$ a.m.u. and $m/z = 2559.1$ a.m.u., respectively (cone voltage: 30 V).

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **11** recorded in CH₃CN is presented in Figure 3.26. The $\pi - \pi^*$ transitions of the organic ligands can be observed by a band centred at *ca.* 270 nm ($\epsilon = 162000 \text{ L mol}^{-1} \text{ cm}^{-1}$), while the d – d transition of the octahedrally coordinated Mn^{III} ions is displayed as a weaker band at *ca.* 446 nm ($\epsilon = 3400 \text{ L mol}^{-1} \text{ cm}^{-1}$). The signal corresponds to a ${}^5\text{T}_{2g} \leftarrow {}^5\text{E}_g$ transition for the octahedrally coordinated Mn^{III} ions within **11**.⁴⁹⁻⁵²

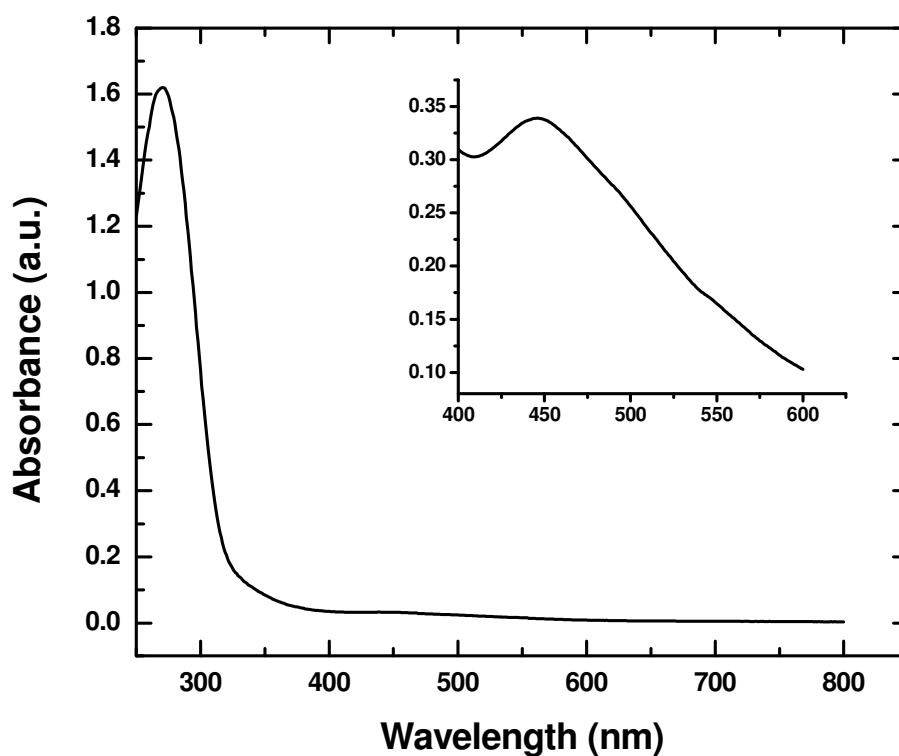


Figure 3.26 – UV-Vis spectrum of a 10^{-5} M solution of **11** in CH₃CN. Inset: A section of the UV-Vis spectrum of a 10^{-4} M solution of **11** in CH₃CN.

Table 3.9 – Crystal data and structural refinement parameters for 11.

Compound 11	
Empirical formula ^a	C ₈₉ H ₈₉ ClMn ₁₃ N ₅ O ₄₂ P ₁₀
Molecular mass/g mol ⁻¹ ^a	2960.05
Crystal colour/shape	Red brown / rhombic
Crystal size/mm ³	0.30×0.30×0.15
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	18.8873(6)
<i>b</i> / Å	23.1480(7)
<i>c</i> / Å	25.3591(7)
α /°	90
β /°	90
γ /°	90
<i>V</i> / Å ³	11087(6)
<i>Z</i>	4
Temperature (K)	100(2)
Density/Mg m ⁻³	1.778
Absorp. coef./mm ⁻¹	13.959
<i>F</i> (000)	5920
$2\theta_{\text{max}}$ /°	100
Reflections collected	42875
Independent reflections	11337 [R(int)=0.1006]
Data / restraints / parameters	11337 / 0 / 1075
<i>S</i> on <i>F</i> ²	1.028
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0753, 0.1869
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0989, 0.2047
Largest diff. peak and hole/e.Å ⁻³	1.353 and -0.712

^aExcluding solvate molecules

3.3.2.2 $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$ (**12**)

Compound **12**, $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$ was obtained by the replacement of the phenylphosphonic acid ligand with benzylphosphonic acid during the preparation procedure that led to the formation of **11**. Rectangular brown crystals of **12** separate from the reaction mixture in a time period of about four days and were characterized by single crystal X-ray diffraction measurements.

12 crystallises in the triclinic crystal system in the space group $P\bar{1}$ and is structurally related with **11**. The core structure within **12** is centrosymmetric, revealing a similar metal-centred, distorted cuboctahedral arrangement as observed in **11**. However, here the atom positions are slightly displaced leading to a lower symmetry compared to **11** (Figure 3.27). The triangular units **A** in **12** appear slightly moved and are not centrally located above and below the hexagonal plane.

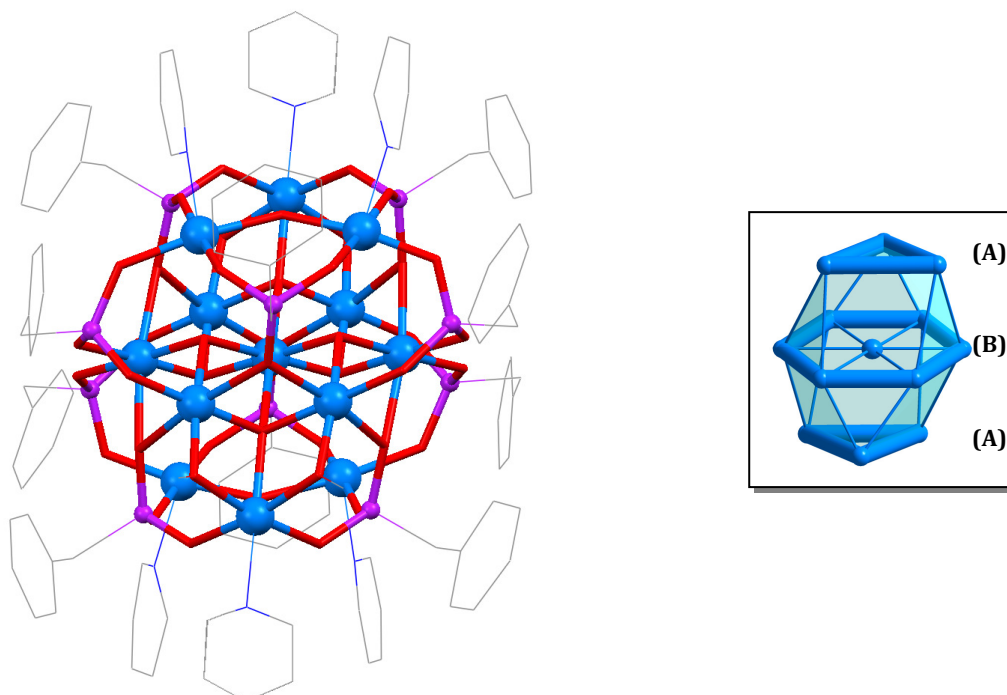


Figure 3.27 – Crystal structure of the tridecanuclear manganese complex in **12**. Colour code: Mn^{III} blue, P purple, O red, C grey (hydrogen atoms have been omitted for clarity).

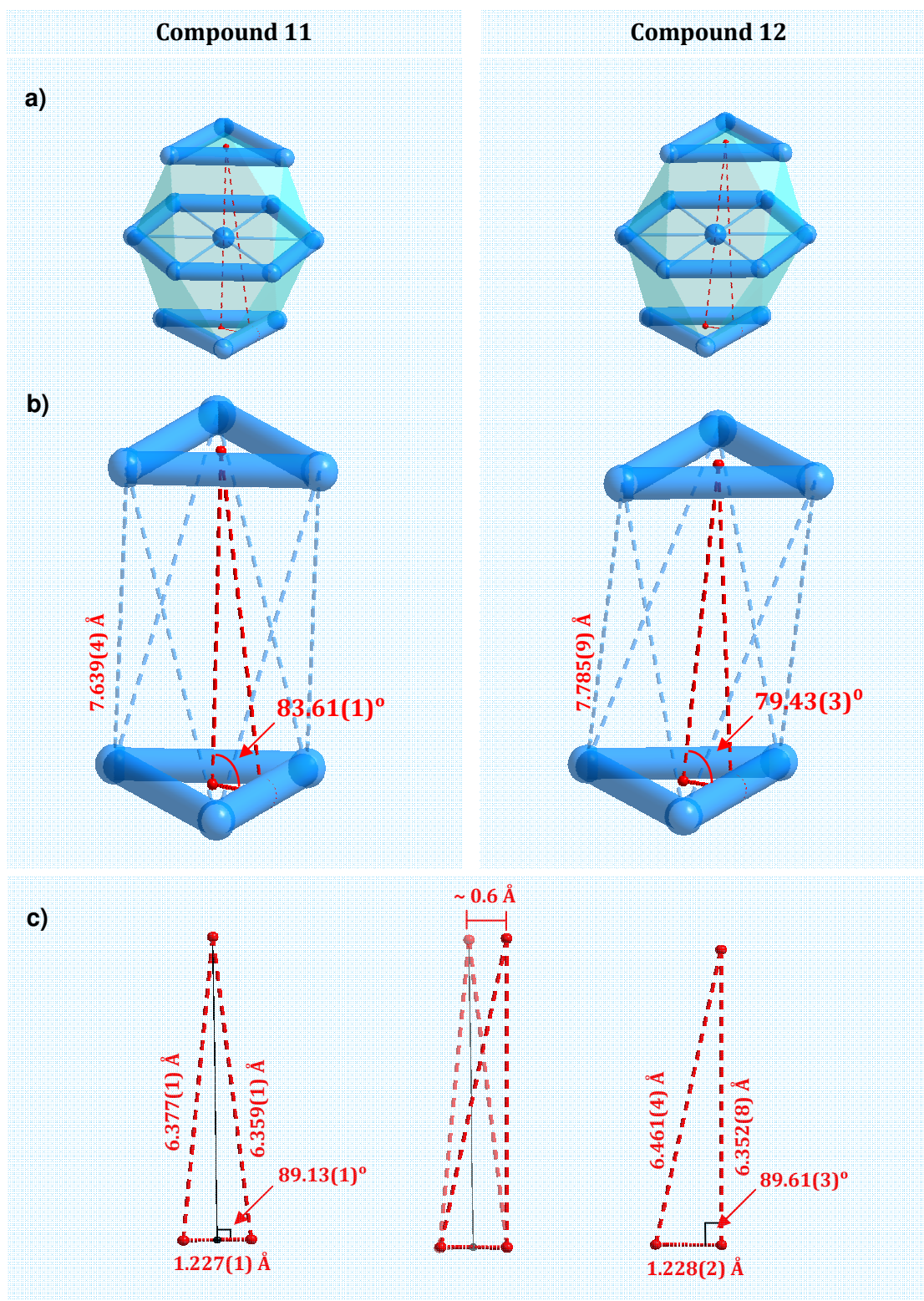


Figure 3.28 – (a) Comparison of the metal-centred distorted cuboctahedral arrangement of the $\{\text{Mn}_{13}\}$ clusters in **11** and **12**; (b) The oblique triangular antiprisms constructed using the two triangular units **A** within **11** and **12**, respectively; (c) Schematic representation showing the position of the centroid of one base relative to the other base in the triangular antiprism representation of units **A** within **11** and **12**, respectively.

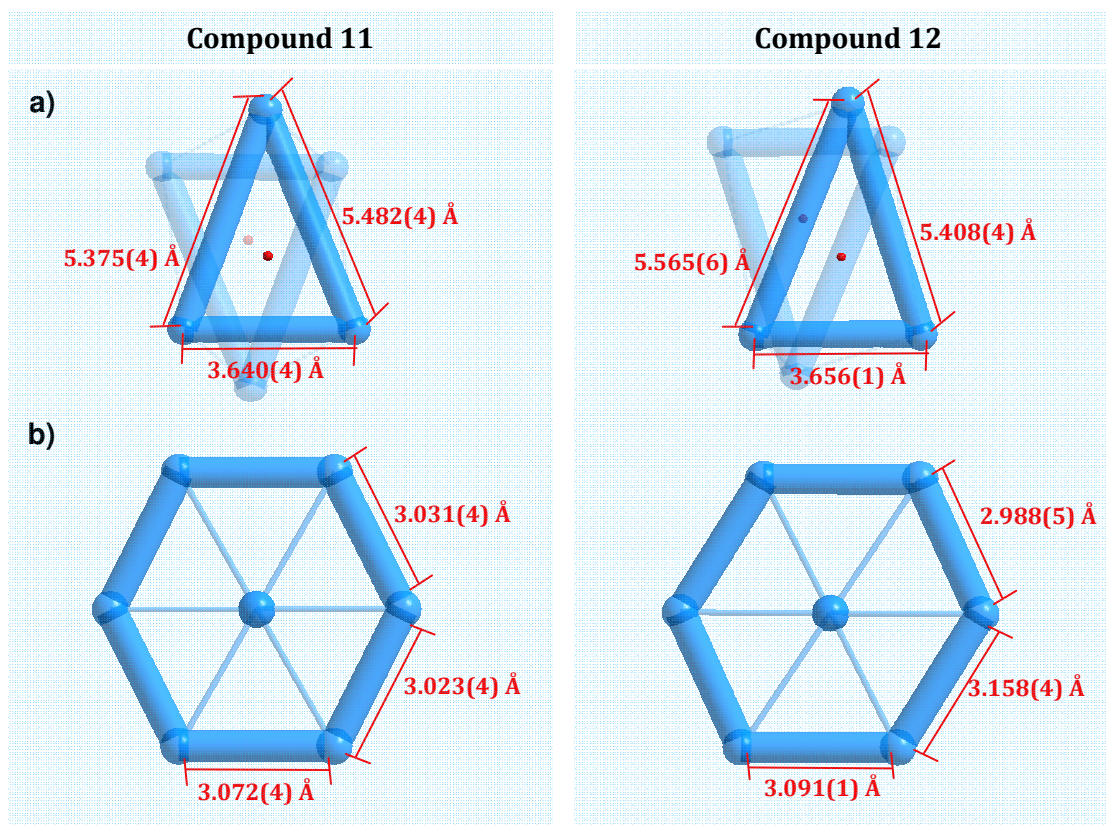


Figure 3.29 – Comparison of the structural parameters of the triangular units **A** and hexagonal unit **B** within **11** and **12**. (a) Top view of the oblique triangular antiprisms constructed using the two triangular units **A** within **11** and **12**, respectively; (b) Hexagonal unit **B** within **11** and **12**, respectively.

A close examination of complexes **11** and **12** reveals the structural differences between the compounds (Figure 3.28, Figure 3.29). The first one is represented by the peripheral ligation which is accomplished by ten phenylphosphonates, five pyridine molecules and a chloride ion for **11** and ten benzylphosphonates and six pyridine molecules for **12**. Then, the two triangular units in **11** and **12** form oblique triangular antiprisms that have edges of 7.639(4) Å and 7.785(9) Å (distances measured between Mn(8) ... Mn(9) in **11** and Mn(5) ... Mn(7) in **12**), respectively and show an angle of 83.61(1)° and 79.43(3)°, respectively between one base and the centroid of the other triangular base (Figure 3.28). Thus, the triangular units **A** in **12** appear moved aside with about 0.6 Å compared to those in **11**. Also, the structural parameters within the triangular and hexagonal units in **12** differ slightly from those in **11**. The geometry of the units in **12** are characterised by interatomic Mn-Mn distances of 3.656(1) Å for Mn(5) ... Mn(7), 5.408(4) Å for Mn(5) ... Mn(6) and 5.565(6) Å for Mn(6) ... Mn(7), compared with 3.640(4) Å for Mn(9) ... Mn(10), 5.375(4) Å for Mn(9) ... Mn(11) and 5.482(4) Å for Mn(10) ... Mn(11) in **11** (Figure 3.29).

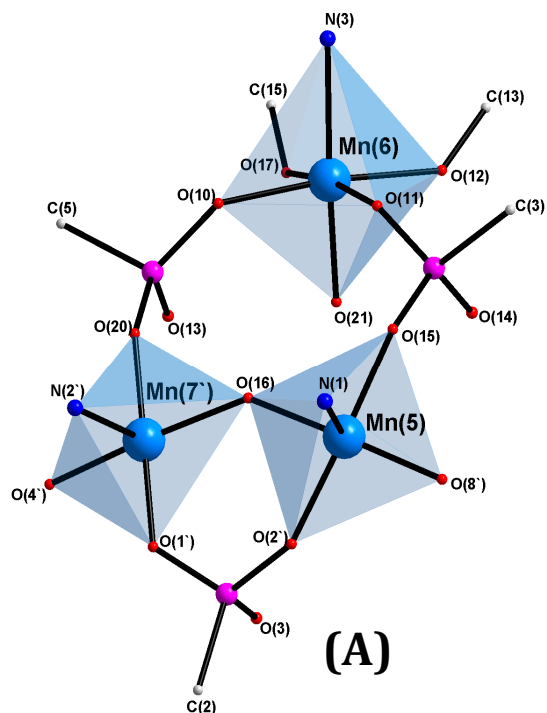


Figure 3.30 – Polyhedral representation of the triangular unit **A** in **12**. Colour code: Mn^{III} blue, P purple, O red, C grey.

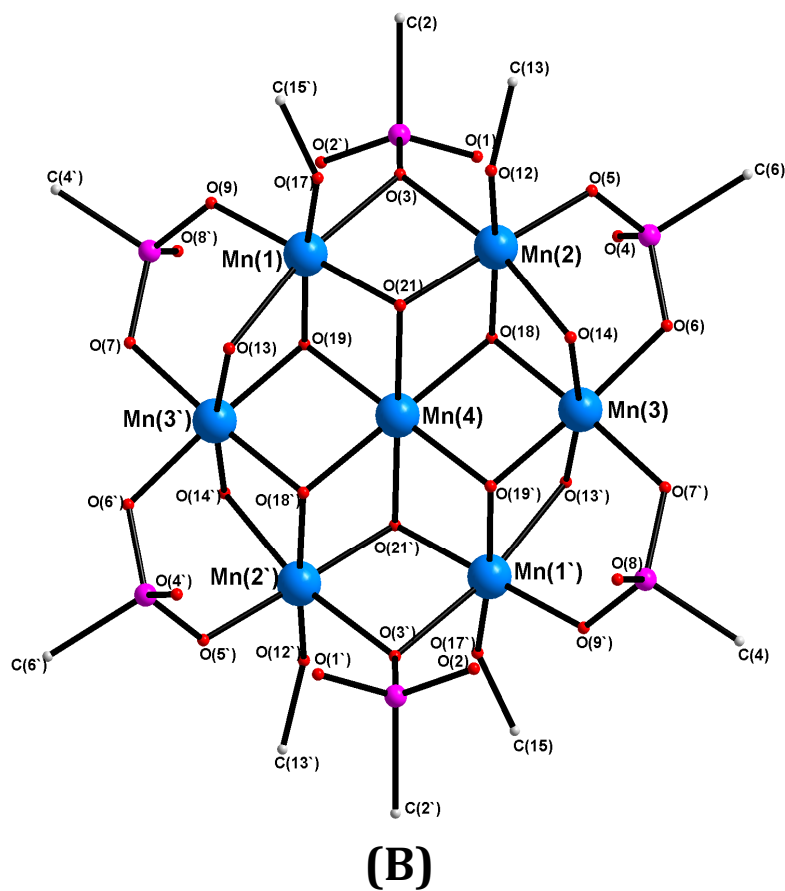


Figure 3.31 – Ball-and-stick representation of the hexagonal unit **B** in **12**. Colour code: Mn^{III} blue, P purple, O red, C grey.

Table 3.10 – Selected bond lengths [$\text{\AA}$] and bond valence sum (BVS) for compound **12**.

Atom	Bond	Bond distances ($\text{\AA}$)	BVS	Assigned oxidation state
Mn(1)	Mn(1)-O(19)	1.947(4)	2.939	+3
	Mn(1)-O(21)	1.962(4)		
	Mn(1)-O(17)	1.961(5)		
	Mn(1)-O(9)	1.963(4)		
	Mn(1)-O(3)	2.174(4)		
	Mn(1)-O(13)	2.239(4)		
Mn(2)	Mn(2)-O(5)	1.898(4)	3.069	+3
	Mn(2)-O(12)	1.918(5)		
	Mn(2)-O(21)	1.911(4)		
	Mn(2)-O(18)	1.960(4)		
	Mn(2)-O(3)	2.273(4)		
	Mn(2)-O(14)	2.299(4)		
Mn(3)	Mn(3)-O(19')	1.948(4)	2.849	+3
	Mn(3)-O(18)	1.965(4)		
	Mn(3)-O(6)	1.964(5)		
	Mn(3)-O(7')	1.964(4)		
	Mn(3)-O(14)	2.237(4)		
	Mn(3)-O(13')	2.276(4)		
Mn(4)	Mn(4)-O(18)	2.008(5)	2.494	+3
	Mn(4)-O(18')	2.008(5)		
	Mn(4)-O(19)	2.017(4)		
	Mn(4)-O(19')	2.017(4)		
	Mn(4)-O(21')	2.292(5)		
	Mn(4)-O(21)	2.292(5)		
Mn(5)	Mn(5)-O(8')	1.819(5)	3.067	+3
	Mn(5)-O(16)	1.890(5)		
	Mn(5)-O(15)	1.942(5)		
	Mn(5)-O(2')	1.949(4)		
	Mn(5)-N(1)	2.303(6)		
Mn(6)	Mn(6)-O(11)	1.975(5)	2.685	+3
	Mn(6)-O(10)	1.985(6)		
	Mn(6)-O(12)	2.032(5)		
	Mn(6)-O(17)	2.023(5)		
	Mn(6)-O(21)	2.107(5)		
	Mn(6)-N(3)	2.419(4)		
Mn(7)	Mn(7)-O(20')	1.852(5)	2.967	+3
	Mn(7)-O(1)	1.873(4)		
	Mn(7)-O(4)	1.970(6)		
	Mn(7)-O(16')	1.988(5)		
	Mn(7)-N(2)	2.253(6)		
Mn(1) ... Mn(2)	3.0913(14)		Mn(2) ... Mn(3)	2.9877(16)
Mn(1) ... Mn(3')	3.1575(16)		Mn(2) ... Mn(6)	2.8701(18)
Mn(1) ... Mn(4)	3.0260(13)		Mn(4) ... Mn(2)	3.2364(13)
Mn(1) ... Mn(6)	3.1309(15)		Mn(4) ... Mn(3)	2.9675(11)

The angles within each triangular unit in **12** measure $38.9(1)^\circ$ for Mn(5)-Mn(6)-Mn(7'), $68.20(1)^\circ$ for Mn(5)-Mn(7')-Mn(6) and $72.90(1)^\circ$ for Mn(6)-Mn(5)-Mn(7'), while for **11** the corresponding angles are $39.64(5)^\circ$ for Mn(8)-Mn(4)-Mn(12), $66.73(7)^\circ$ for

Mn(4)-Mn(12)-Mn(8) and $73.63(8)^\circ$ for Mn(4)-Mn(8)-Mn(12). The interatomic distances within the hexagonal brucite plane in **12**, Mn(1) $\cdots$ Mn(2), Mn(2) $\cdots$ Mn(3) and Mn(3) $\cdots$ Mn(1') are 3.091(1) Å, 2.988(5) Å and 3.158(4) Å, respectively, whereas in **11** the corresponding interatomic distances Mn(1) $\cdots$ Mn(3), Mn(3) $\cdots$ Mn(5) and Mn(5) $\cdots$ Mn(7) are 3.023(4) Å, 3.031(4) Å and 3.072(4) Å, respectively. The hexagonal unit in **12** displays angles of $113.83(1)^\circ$, $121.19(1)^\circ$ and $124.98(1)^\circ$ for Mn(1)-Mn(2)-Mn(3), Mn(2)-Mn(1)-Mn(3') and Mn(1')-Mn(3)-Mn(2), respectively, whereas the hexagonal unit in **11** displays corresponding angles of $116.16(11)^\circ$, $117.22(11)^\circ$ and $126.07(12)^\circ$ for Mn(5)-Mn(7)-Mn(6), Mn(3)-Mn(5)-Mn(7) and Mn(1)-Mn(3)-Mn(5), respectively.

However, despite the slight differences, the bond distances and bond angles within **12** are comparable with those found in **11**. Selected bond lengths and bond angles for compound **12** are listed in Table 3.10 and Table 3.11.

Table 3.11 – Selected bond angles [$^\circ$] for compound **12.**

Bond Angle ($^\circ$)		Bond Angle ($^\circ$)	
O(5)-Mn(2)-O(21)	178.5(2)	O(18)-Mn(3)-O(7')	176.10(19)
O(12)-Mn(2)-O(18)	170.3(2)	O(19')-Mn(3)-O(6)	175.94(18)
O(3)-Mn(2)-O(14)	168.03(15)	O(14)-Mn(3)-O(13')	169.83(15)
O(5)-Mn(2)-O(3)	97.89(18)	O(6)-Mn(3)-O(13')	104.22(18)
O(5)-Mn(2)-O(12)	89.9(2)	O(7')-Mn(3)-O(14)	95.01(18)
O(12)-Mn(2)-O(3)	93.5(2)	O(19')-Mn(3)-O(14)	93.92(17)
O(21)-Mn(2)-O(12)	91.6(2)	O(6)-Mn(3)-O(18)	92.93(19)
O(18)-Mn(2)-O(3)	89.91(17)	O(6)-Mn(3)-O(7')	89.93(19)
O(12)-Mn(2)-O(14)	88.44(19)	O(18)-Mn(3)-O(14)	87.99(16)
O(21)-Mn(2)-O(3)	82.27(16)	O(6)-Mn(3)-O(14)	82.72(18)
O(18)-Mn(4)-O(18')	180.000(1)	N(3)-Mn(6)-O(21)	172.65(15)
O(19)-Mn(4)-O(19')	180.000(1)	O(10)-Mn(6)-O(12)	171.8(2)
O(21')-Mn(4)-O(21)	180.000(1)	O(11)-Mn(6)-O(17)	170.41(19)
O(18')-Mn(4)-O(21)	109.66(15)	N(3)-Mn(6)-O(17)	102.21(16)
O(19')-Mn(4)-O(21)	100.23(16)	N(3)-Mn(6)-O(10)	97.8(2)
O(18')-Mn(4)-O(19')	98.19(17)	O(11)-Mn(6)-O(10)	93.6(3)
O(18)-Mn(4)-O(19')	81.81(17)	N(3)-Mn(6)-O(12)	90.18(17)
O(19')-Mn(4)-O(21')	79.77(16)	O(10)-Mn(6)-O(21)	88.9(2)
O(19)-Mn(4)-O(21)	79.77(16)	N(3)-Mn(6)-O(11)	86.92(19)
O(18)-Mn(4)-O(21)	70.34(15)	O(10)-Mn(6)-O(17)	88.1(2)

The phosphonate ligands within **12** adopt two different bridging modes $\eta^1:\eta^1:\eta^1:\mu_3$ and $\eta^1:\eta^1:\eta^2:\mu_4$, similar as in **11**. The oxidation states of the Mn and O ions in **12** were established by bond valence sum analysis and charge considerations (Table 3.10 and Table 3.12).

Table 3.12 – Bond valence sum (BVS) calculations for some O atoms in **12**.

Atom	BVS	Assignment ^a
O(21)	1.871	μ_4 -O ²⁻
O(19)	1.677	μ_3 -O ²⁻
O(18)	1.667	μ_3 -O ²⁻
O(16)	1.242	μ_2 -OH ⁻

^a An oxygen BVS in the ~1.8-2.0, ~1.0-1.2, and ~0.2-0.4 ranges is indicative of non-, single- and double protonation, respectively.^{7, 53}

The packing arrangement of the {Mn₁₃} clusters in **12** displays small channels that extend in the direction of the crystallographic *b*-axis (Figure 3.32). These channels are filled with constitutional solvent molecules.

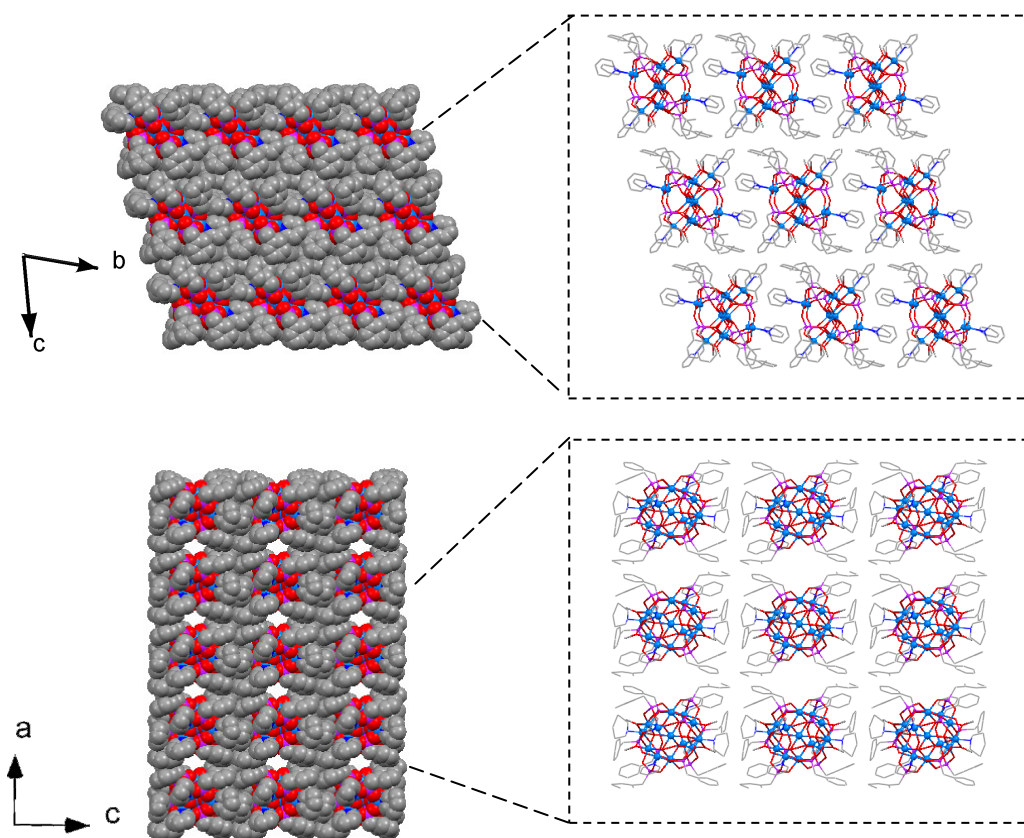


Figure 3.32 – Packing arrangement of the tridecanuclear manganese clusters in **12** viewed in the direction of the crystallographic *a*- and *b*-axis. Colour code: Mn blue, P purple, O red, C grey, (crystallization solvent molecules and hydrogen atoms have been omitted for clarity).

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

In comparison to **11**, the IR spectrum of **12** presented in Figure 3.33 displays some extra bands in the $1500 - 1150\text{ cm}^{-1}$ and $850 - 690\text{ cm}^{-1}$ region due to the C–H bending and rocking vibrations of the $-\text{CH}_2$ groups of the benzylphosphonic acid ligands. The bands located in the $3040 - 2800\text{ cm}^{-1}$ region are more intense due to the overlapping C–H stretching vibrations of the aromatic rings and aliphatic $-\text{CH}_2$ groups.^{36-40, 56, 57}

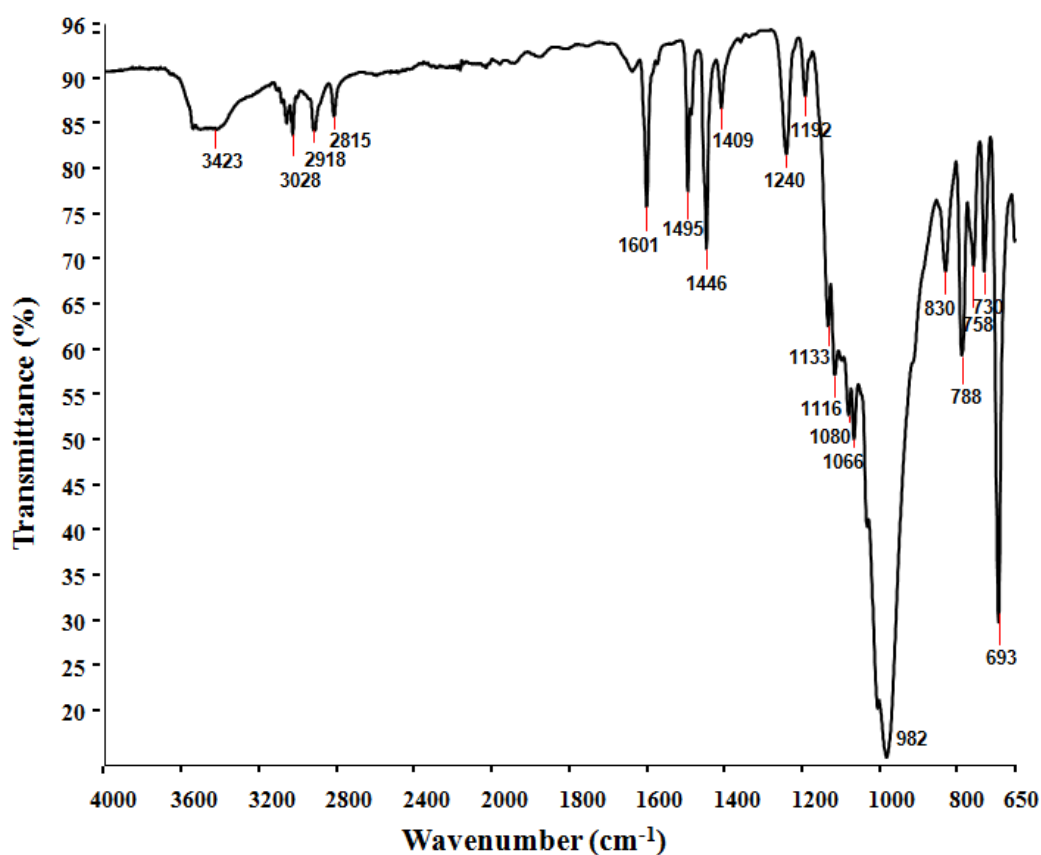


Figure 3.33 – Infrared spectrum of **12**.

- *Thermogravimetric analysis*

Thermogravimetric analysis was performed using a freshly prepared crystalline sample of **12**, in the temperature range 30 – 900 °C, in an N₂ atmosphere. The compound reveals a similar decomposition behaviour as **11**. The first thermogravimetric step of about 6.5 % occurs in a temperature range between 30 – 195 °C as a result of the proposed loss of five crystallization H₂O molecules and four coordinated CH₃OH molecules (calcd: 6.7 %). This constitutional assignment is in agreement with the elemental analysis of **12**. The next step in the TGA curve corresponds to a weight loss of 14.3 % between 195 – 270 °C, which is associated with the loss of six pyridine molecules (calcd: 14.5 %). Further cluster degradation and decomposition of the organic ligands can be observed above 270 °C.

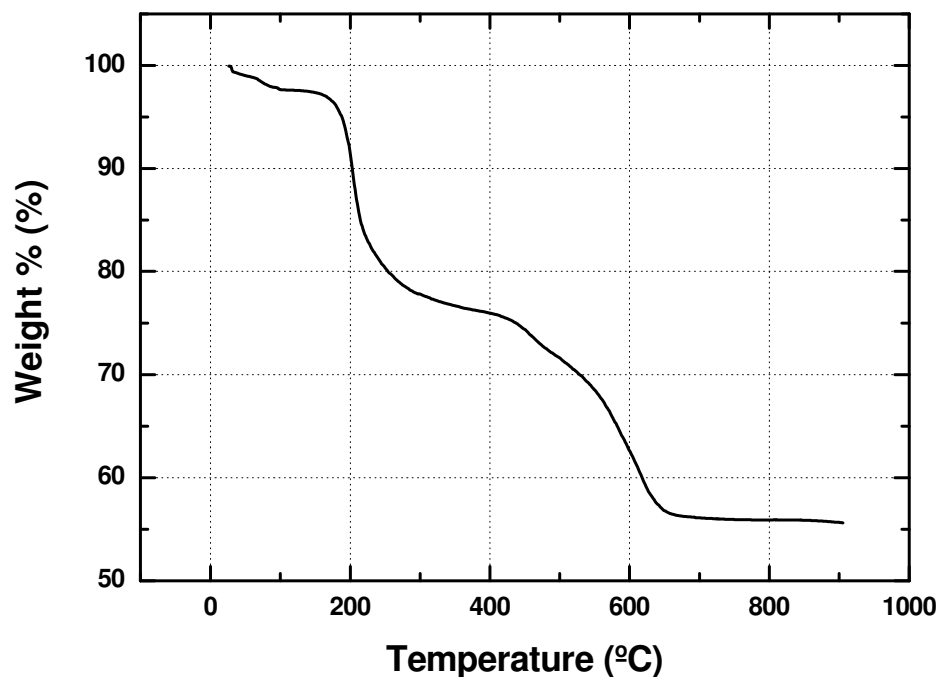


Figure 3.34 – Thermogravimetric analysis of **12**.

- Magnetism

The temperature dependence of the magnetic susceptibility of **12** was measured between 298 and 1.8 K (Figure 3.35). At room temperature, the experimental χT product reaches $38.1 \text{ cm}^3 \text{ K mol}^{-1}$. That is approximately in agreement with the expected value of $39 \text{ cm}^3 \text{ K mol}^{-1}$ for the presence of thirteen $S = 2 \text{ Mn}^{\text{III}}$ metal ions ($C = 3 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2$). Upon lowering the temperature, the χT product decreases down to 34.7 at 100 K, then increases to $35.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 K and then finally decreases down to $32.6 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. This thermal behavior suggests the presence of dominant antiferromagnetic (AF) interactions between the spin carriers. This result does not exclude the presence of ferromagnetic interactions but only suggests that the AF exchange pathways are dominant. It is worth mentioning that this magnetic behavior is significantly different from that observed for **11** showing that the intra-complex magnetic interactions must be different. Despite the fact that the spin ground state is very difficult to establish only based on the χT vs T data. The value of about $35 \text{ cm}^3 \text{ K mol}^{-1}$ at low temperature suggests a spin ground state of 8.

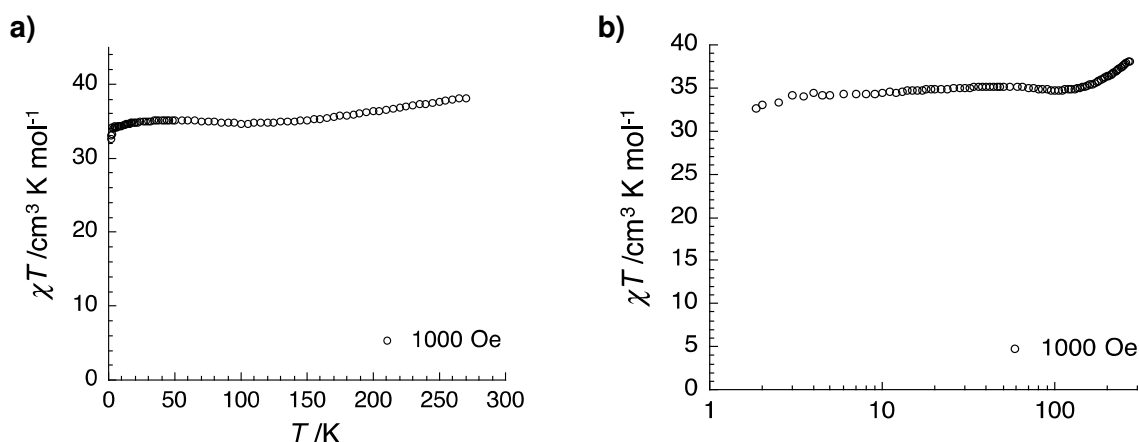


Figure 3.35 – (a) Temperature dependence of the χT product of **12** at 0.1 T. (b) A magnified view of the χT product in (a) between 1 and 100 K.

The field dependence of magnetisation for this compound has been measured at low temperatures between 1.8 and 8 K (Figure 3.36, a). The magnetisation at low field displays a rapid increase without inflexion point confirming the absence of weak antiferromagnetic interactions. The high field behavior displays a non-linear and non-monotone increase without clear saturation even at 1.8 K at 7 T, suggesting the presence of magnetic anisotropy and also low lying excited states. The data shown as a M vs H/T plot (Figure 3.36, b) confirms the presence of both magnetic anisotropy intrinsic to Mn^{III} metal ions and low-lying excited states as the data are not superposed on a single master-curve as

expected for an isotropic system with a well defined spin ground state. At 1.8 K, the magnetisation reaches $18.9 \mu_B$ at 7 T which is above the $16 \mu_B$ expected for an $S_T = 8$ ground state confirming the field induce population of low lying excited states.

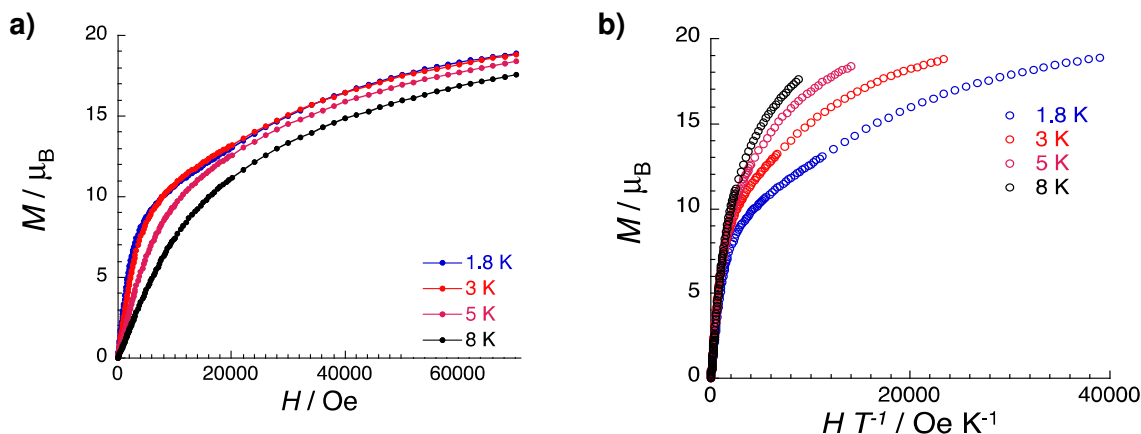


Figure 3.36 – (a) M vs H and (b) M vs H/T data at and below 8 K.

Both measurements, the field dependence of the magnetisation at 1.8 K and the temperature dependence of the χT product at 1000 Oe, are coherent with an $S_T = 8$ ground state even if this conclusion is not as clear as for **11**.

The M vs H data at 1.8 K do not show any sign of slow relaxation i.e. hysteresis effects. Nevertheless, the ac susceptibility in zero dc field has been measured to probe possible slow dynamics of the magnetisation in this compound. Clearly at temperatures below 4 K (for frequency around 10000 Hz), slow relaxation of the magnetisation is observed in agreement with the appearance of an out-of-phase signal.

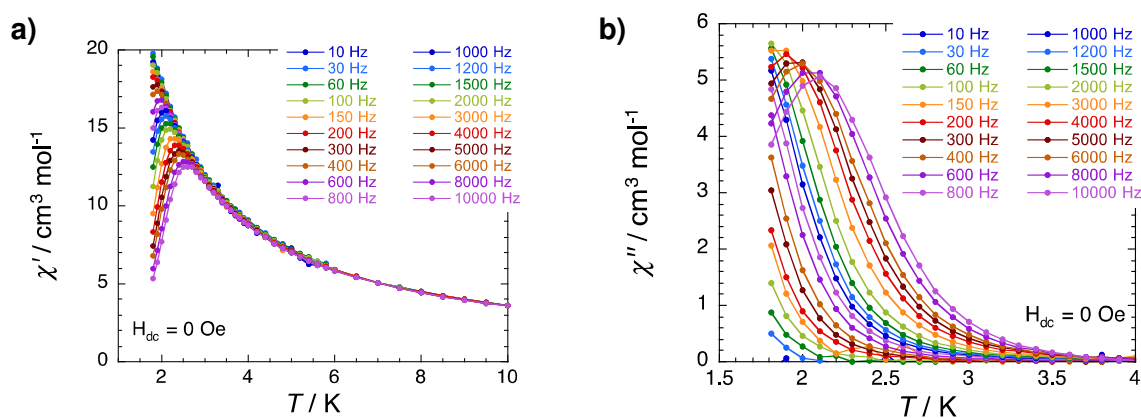


Figure 3.37 – Temperature dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') ac susceptibility under zero dc field for **12**.

Cosecutively, we measured the ac susceptibility as a function of the frequency at different temperatures in zero dc field in order to estimate the relaxation time. The observed frequency dependence and shape of the curve idicates that this compound is consistent with an SMM.⁷

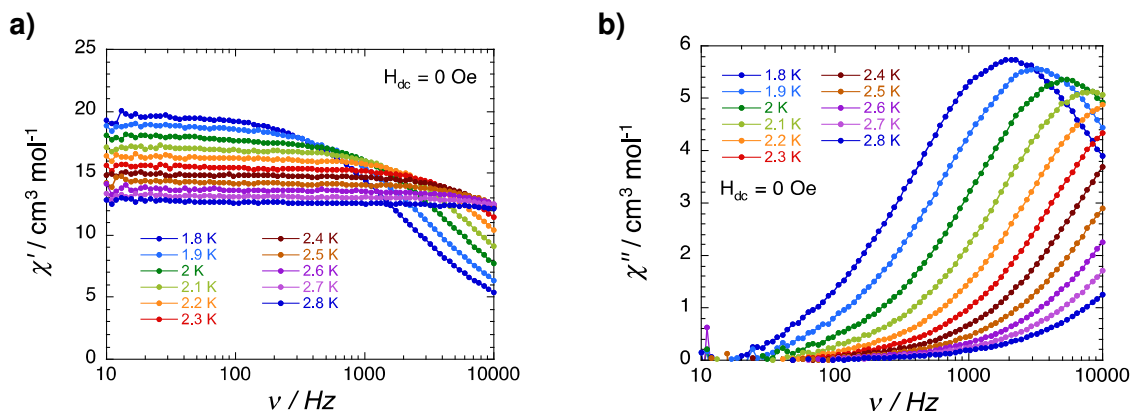


Figure 3.38 – Frequency dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') ac susceptibility from 1.8 to 2.8 K under zero dc field for **12**.

Using a scaling technique, the relaxation time of the compound was determined up to 2.8 K.

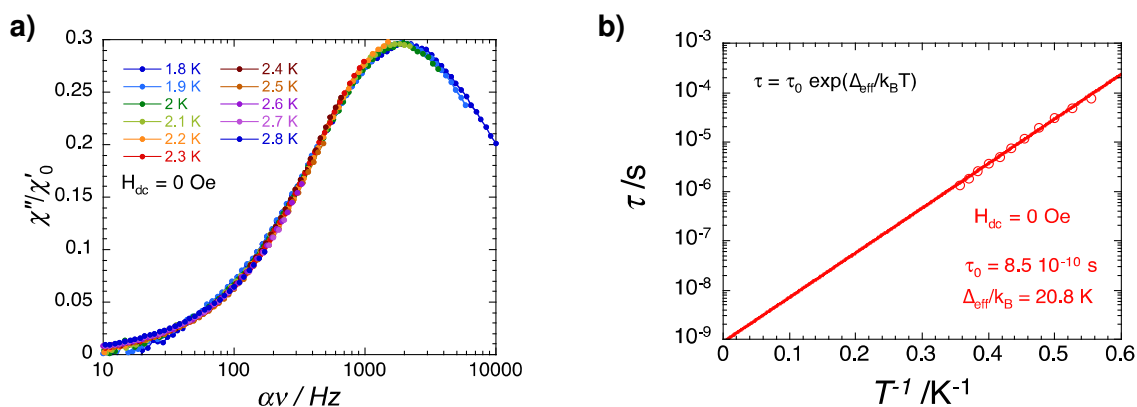


Figure 3.39 – (a) χ''/χ_0 vs $\alpha\nu$ from 1.8 to 2.8 K under zero dc field; (b) Magnetisation relaxation time (τ) vs T^{-1} plot for **12** under zero dc field (the solid line correspond to the Arrhenius law).

From these data, the relaxation time can be deduced between 1.9 and 2.8 K and fitted to an Arrhenius law. The exponential increase of the relaxation allowed us to determine the energy barrier of 20.8 K of the thermally activated regime while τ_0 is about 8.5×10^{-10} s.

The ac susceptibility has been measured in dc fields at 1.8 K in order to investigate possible quantum relaxation pathways in zero-field and to probe the quantum contribution to the observed relaxation above 1.8 K.

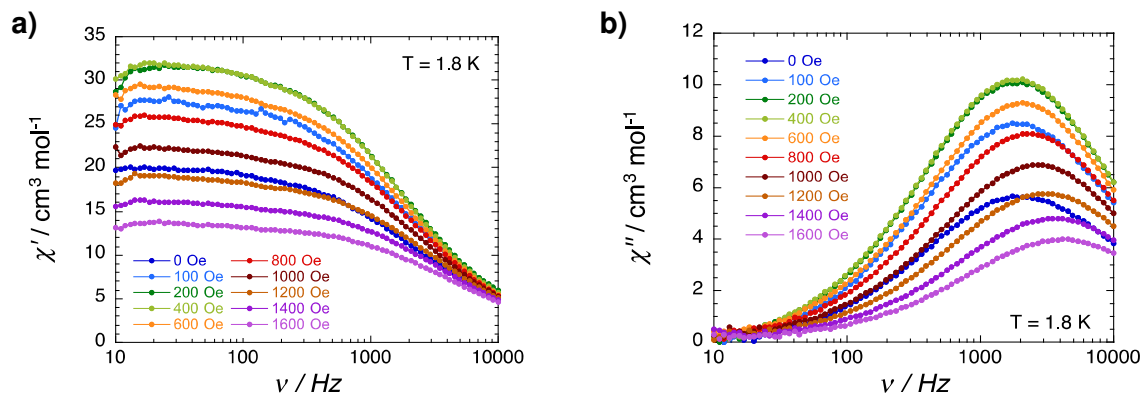


Figure 3.40 – Frequency dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') ac susceptibility with dc fields at 1.8 K for **12**.

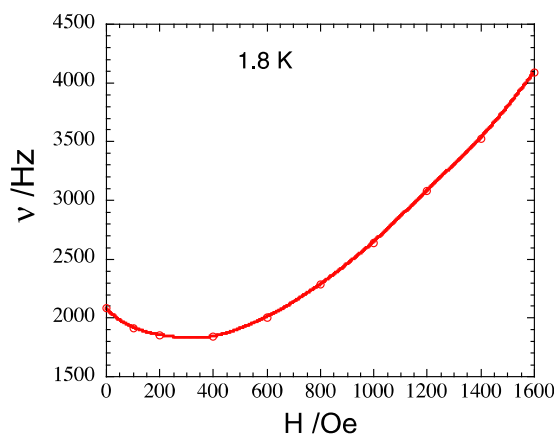


Figure 3.41 – ν vs H plot at 1.8 K.

The shift of the characteristic frequency (with an optimum field of 300 Oe) is very small highlighting that the quantum pathway only provides a minor contribution to the relaxation of the magnetisation at 1.8 K. Therefore, the ac susceptibility measurements at 300 Oe have not been performed as the resulting data would be extremely similar to that obtained at zero-dc field.

- *Mass spectrometry*

The stability of the $\{\text{Mn}_{13}\}$ cluster in solution was investigated by electrospray ionisation mass spectrometry. Negative mode ESI-MS spectra of **12** in CH_3CN , DMF (Figure 3.42) and DMSO reveal the presence of an isotopic envelope centred at $m/z = 2699.1$ a.m.u. (Table 3.13). This signal can be attributed to the $\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^-$ species, confirming that the cluster is stable in CH_3CN , DMF or DMSO environments.

Table 3.13 – ESI-MS assignment for compound **12**.

	Solvent	m/z	Species attributed
Crystals of 12 in:	CH_3CN	2699.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$
	DMF	2699.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$
	DMSO	2699.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$

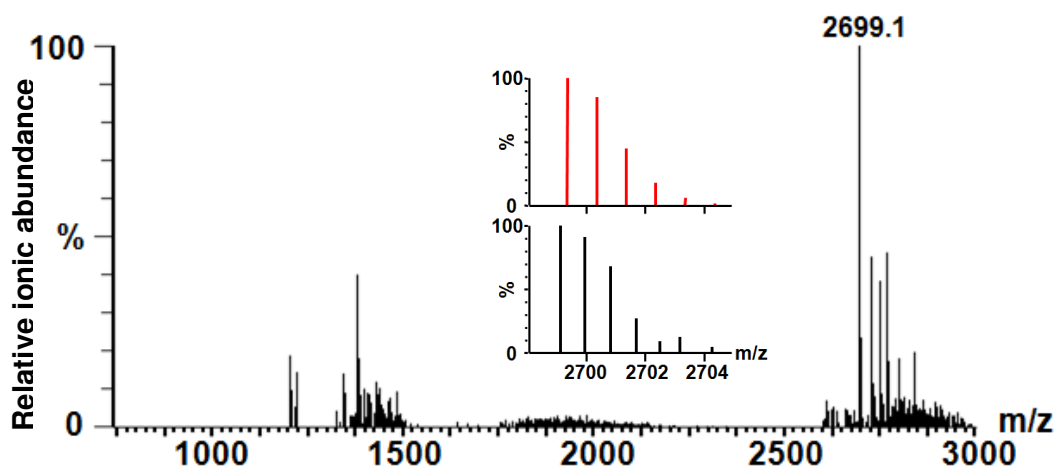


Figure 3.42 – Negative-mode ESI-MS spectra for crystals of **12** dissolved in DMF. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^-$ centered at $m/z = 2699.1$ a.m.u. (cone voltage: 30 V).

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **12** recorded in CH₃CN (Figure 3.43) displays a shoulder at *ca.* 257 nm ($\epsilon = 61000 \text{ L mol}^{-1} \text{ cm}^{-1}$) attributed to $\pi - \pi^*$ transitions of the organic ligands. A very weak absorption band is also displayed at *ca.* 443 nm ($\epsilon = 4500 \text{ L mol}^{-1} \text{ cm}^{-1}$) which corresponds to a $^5\text{T}_{2g} \leftarrow ^5\text{E}_g$ transition within the octahedrally coordinated Mn^{III} ions.⁴⁹⁻⁵²

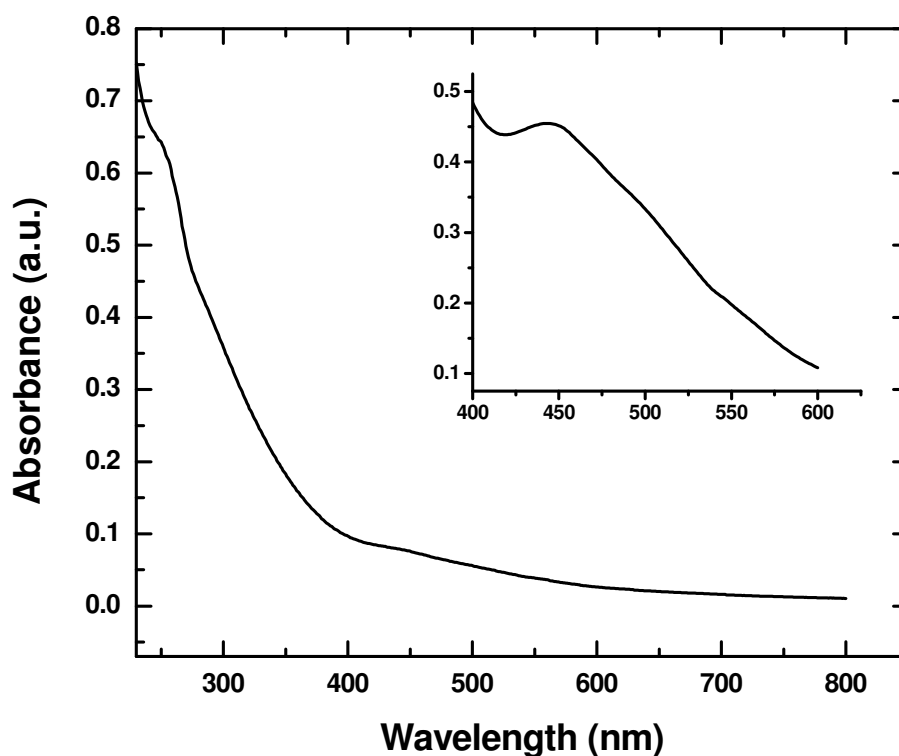


Figure 3.43 – UV-Vis spectrum of a 10^{-5} M solution of **12** in CH₃CN. Inset: A section of the UV-Vis spectrum of a 10^{-4} M solution of **12** in CH₃CN.

Table 3.14 – Crystal data and structural refinement parameters for 12.

Compound 12	
Empirical formula ^a	C ₁₀₄ H ₁₁₄ ClMn ₁₃ N ₆ O ₄₂ P ₁₀
Molecular mass/g mol ⁻¹ ^a	3179.41
Crystal colour/shape	Brown / rectangular block
Crystal size/mm ³	0.50×0.15×0.10
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	14.990(3)
b/ Å	15.833(3)
c/ Å	16.410(3)
α /°	73.19(3)
β /°	83.00(3)
γ /°	64.78(3)
V/ Å ³	3372.9(11)
Z	1
Temperature (K)	150(2)
Density/Mg m ⁻³	1.530
Absorp. coef./mm ⁻¹	1.366
F(000)	1555
2 θ_{max} /°	60
Reflections collected	44311
Independent reflections	15941 [R(int)=0.0527]
Data / restraints / parameters	15941 / 6 / 751
S on <i>F</i> ²	1.035
R ₁ , wR ₂ [I>2 σ (I)]	0.0814, 0.2364
R ₁ , wR ₂ (all data)	0.1200, 0.2619
Largest diff. peak and hole/e.Å ⁻³	3.320 and -0.925

^aExcluding solvate molecules

3.3.2.3 $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_6\text{H}_5\text{-C}_3\text{H}_6\text{-C}_5\text{H}_4\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$ (13**)**

Compound **13**, $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_6\text{H}_5\text{-C}_3\text{H}_6\text{-C}_5\text{H}_4\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$ was the result of replacing the pyridine ligands in the reaction mixture of **12** with 4-(3-phenylpropyl)pyridine ligands. The crystallisation process that occurs over a week affords rectangular brown crystals of **13** which were characterized by single crystal X-ray diffraction measurements.

13 crystallises in the triclinic crystal system in the space group $P\bar{1}$ and is structurally related to **11** and **12**. The metal-centered, distorted cuboctahedral arrangement of the $\{\text{Mn}_{13}\}$ cluster in **13** is very similar to the highly symmetric arrangement in **11** (Figure 3.44). The bond distances and bond angles within **13** are comparable with those found in **11** and **12** as can be seen in Table 3.15 and Table 3.16.

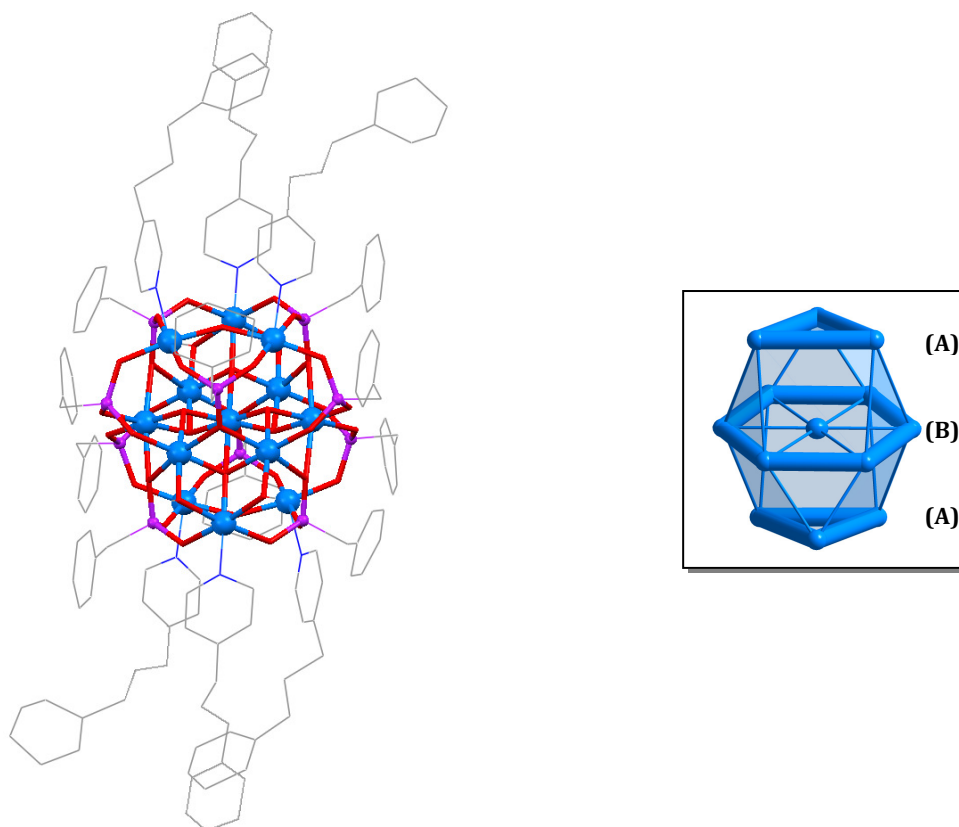


Figure 3.44 – Crystal structure of the tridecanuclear manganese complex in **13**. Colour code: Mn^{III} blue, P purple, O red, C grey (hydrogen atoms have been omitted for clarity).

Table 3.15 – Selected bond lengths [$\text{\AA}$] and bond valence sum (BVS) for compound 13.

Atom	Bond	Bond distances ($\text{\AA}$)	BVS	Assigned oxidation state
Mn(1)	Mn(1)-O(17)	1.947(4)	2.738	+3
	Mn(1)-O(17')	1.947(4)		
	Mn(1)-O(16)	1.954(5)		
	Mn(1)-O(16')	1.954(5)		
	Mn(1)-O(10)	2.404(5)		
	Mn(1)-O(10')	2.404(5)		
Mn(2)	Mn(2)-O(21)	1.909(5)	3.156	+3
	Mn(2)-O(10')	1.926(5)		
	Mn(2)-O(19)	1.926(5)		
	Mn(2)-O(17)	1.944(5)		
	Mn(2)-O(8')	2.185(5)		
	Mn(2)-O(20)	2.220(5)		
Mn(3)	Mn(3)-O(11)	1.925(5)	3.105	+3
	Mn(3)-O(18)	1.926(5)		
	Mn(3)-O(16)	1.929(5)		
	Mn(3)-O(17)	1.929(5)		
	Mn(3)-O(3)	2.228(5)		
	Mn(3)-O(20)	2.228(5)		
Mn(4)	Mn(4)-O(9)	1.878(6)	3.162	+3
	Mn(4)-O(5)	1.915(5)		
	Mn(4)-O(16)	1.946(5)		
	Mn(4)-O(10)	1.957(5)		
	Mn(4)-O(8)	2.195(5)		
	Mn(4)-O(3)	2.229(5)		
Mn(5)	Mn(5)-O(10)	1.902(5)	3.215	+3
	Mn(5)-O(2)	1.958(5)		
	Mn(5)-O(19)	1.992(5)		
	Mn(5)-N(1)	2.033(6)		
	Mn(5)-O(1)	2.079(6)		
	Mn(5)-O(9)	2.132(6)		
Mn(6)	Mn(6)-O(23)	1.873(6)	3.138	+3
	Mn(6)-O(7)	1.887(5)		
	Mn(6)-O(6)	1.898(6)		
	Mn(6)-O(12)	1.928(5)		
	Mn(6)-N(3)	2.229(7)		
Mn(7)	Mn(7)-O(22)	1.871(6)	3.234	+3
	Mn(7)-O(4)	1.871(6)		
	Mn(7)-O(14)	1.891(5)		
	Mn(7)-O(12)	1.908(6)		
	Mn(7)-N(2)	2.216(8)		
Mn(1)-Mn(3)	2.9125(11)		Mn(2)-Mn(3)	3.0407(15)
Mn(1)-Mn(2)	3.1145(11)		Mn(2)-Mn(4')	3.1115(15)
Mn(1)-Mn(4)	3.1551(11)		Mn(3)-Mn(4)	3.0415(15)
Mn(2)-Mn(5')	2.8865(16)		Mn(4)-Mn(5)	2.9452(17)

Table 3.16 – Selected bond angles [°] for compound **13.**

Bond Angle (°)		Bond Angle (°)	
O(17 ⁻)-Mn(1)-O(17)	180.000(1)	O(21)-Mn(2)-O(10 ⁻)	179.9(2)
O(16 ⁻)-Mn(1)-O(16)	180.000(1)	O(19)-Mn(2)-O(17)	169.5(2)
O(10 ⁻)-Mn(1)-O(10)	180.000(1)	O(8 ⁻)-Mn(2)-O(20)	167.82(19)
O(16 ⁻)-Mn(1)-O(10)	105.82(18)	O(21)-Mn(2)-O(8 ⁻)	98.1(2)
O(17)-Mn(1)-O(10)	105.04(17)	O(21)-Mn(2)-O(19)	96.2(2)
O(17)-Mn(1)-O(16 ⁻)	97.87(19)	O(21)-Mn(2)-O(20)	93.6(2)
O(17)-Mn(1)-O(16)	82.13(19)	O(21)-Mn(2)-O(17)	92.8(2)
O(17)-Mn(1)-O(10 ⁻)	74.96(17)	O(19)-Mn(2)-O(20)	91.3(2)
O(17 ⁻)-Mn(1)-O(10)	74.95(17)	O(19)-Mn(2)-O(8 ⁻)	90.6(2)
O(16)-Mn(1)-O(10)	74.18(18)	O(10 ⁻)-Mn(2)-O(19)	83.7(2)
O(11)-Mn(3)-O(17)	177.7(2)	O(10)-Mn(5)-N(1)	175.7(2)
O(18)-Mn(3)-O(16)	177.5(2)	O(2)-Mn(5)-O(19)	175.2(2)
O(3)-Mn(3)-O(20)	170.45(18)	O(1)-Mn(5)-O(9)	174.9(2)
O(18)-Mn(3)-O(3)	98.5(2)	N(1)-Mn(5)-O(9)	97.4(2)
O(18)-Mn(3)-O(17)	94.5(2)	O(10)-Mn(5)-O(1)	95.0(2)
O(17)-Mn(3)-O(3)	89.8(2)	O(19)-Mn(5)-N(1)	94.2(2)
O(11)-Mn(3)-O(3)	89.7(2)	O(2)-Mn(5)-O(1)	94.5(2)
O(16)-Mn(3)-O(17)	83.3(2)	O(2)-Mn(5)-N(1)	90.3(2)
O(17)-Mn(3)-O(20)	82.87(19)	O(19)-Mn(5)-O(1)	87.1(2)
O(16)-Mn(3)-O(3)	82.59(19)	N(1)-Mn(5)-O(1)	87.6(2)

A close inspection of the three complexes **11**, **12** and **13** reveals only a few structural differences, the most important ones being the peripheral ligation and the symmetry of the core structure. The structural parameters within **13** are closer to that of **11** than **12**. In accordance to this observation the triangular units in **13** display lateral Mn-Mn distances of 3.616(3) Å for Mn(6) $\cdots$ Mn(7), 5.387(3) Å for Mn(5) $\cdots$ Mn(6) and 5.408(4) Å for Mn(5) $\cdots$ Mn(7), and angles of 39.15(2)° for Mn(6)-Mn(5)-Mn(7), 70.11(3)° for Mn(5)-Mn(7)-Mn(6) and 70.75(3)° for Mn(5)-Mn(6)-Mn(7). Further, the interatomic distances in the hexagonal unit in **13** are 3.041(3) Å, 3.042(3) Å and 3.111(3) Å for Mn(2) $\cdots$ Mn(3), Mn(3) $\cdots$ Mn(4) and Mn(4) $\cdots$ Mn(2), respectively. Also, the angles within the hexagonal unit in **13** are closer to those in **11**. The Mn(2)-Mn(4)-Mn(3), Mn(3)-Mn(2)-Mn(4), and Mn(2)-Mn(3)-Mn(4) angles measure 115.63(5)°, 117.36(5)° and 127.00(5)°, respectively.

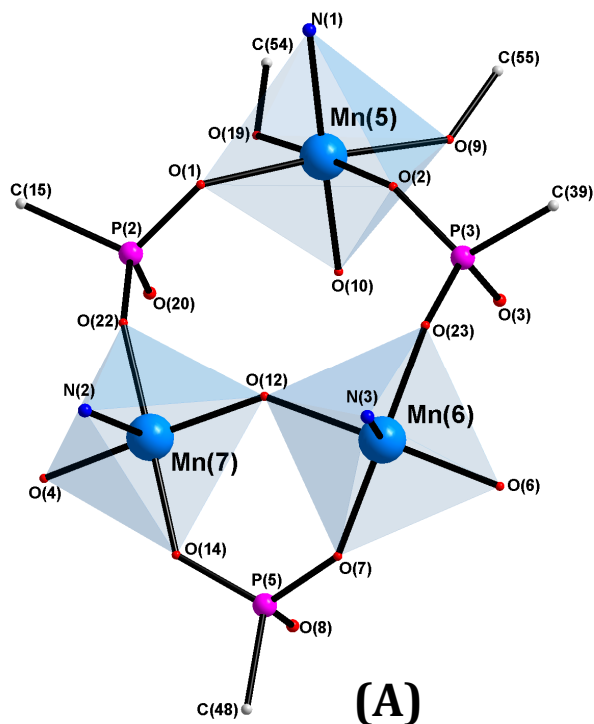


Figure 3.45 – Polyhedral representation of the triangular unit **A** in **13**. Colour code: Mn^{III} blue, P purple, O red, C grey.

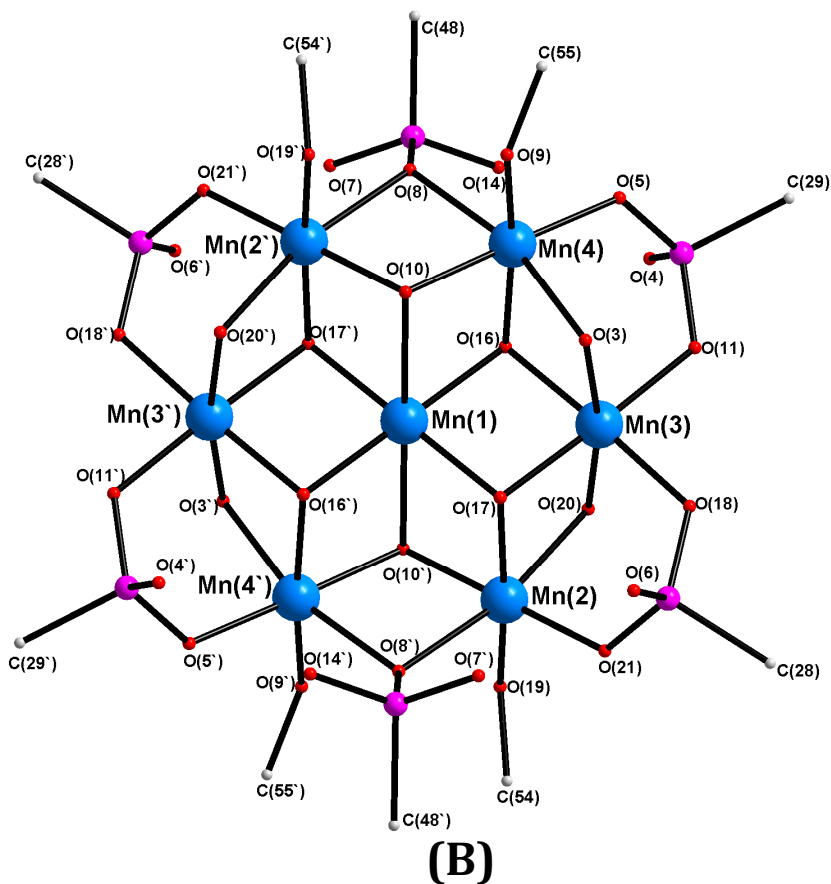


Figure 3.46 – Ball-and-stick representation of the hexagonal unit **B** in **13**. Colour code: Mn^{III} blue, P purple, O red, C grey.

All phosphonate ligands within **13** bridge between three Mn^{III} ions in a $\eta^1:\eta^1:\eta^1:\mu_3$ and $\eta^1:\eta^1:\eta^2:\mu_4$ bridging modes. The oxidation states of the Mn and O ions in **13** were established by bond valence sum analysis and charge considerations (Table 3.15 and Table 3.17).

Table 3.17 – Bond valence sum (BVS) calculations for some O atoms in 13.

Atom	BVS	Assignment ^a
O(10)	2.079	$\mu_4\text{-O}^{2-}$
O(16)	1.827	$\mu_3\text{-O}^{2-}$
O(17)	1.842	$\mu_3\text{-O}^{2-}$
O(12)	1.270	$\mu_2\text{-OH}^-$

^a An oxygen BVS in the ~1.8-2.0, ~1.0-1.2, and ~0.2-0.4 ranges is indicative of non-, single- and double protonation, respectively.^{7, 53}

In the solid state the tridecanuclear manganese clusters are linked by weak hydrogen bonds between the Mn clusters and constitutional solvent molecules resulting in a lamellar arrangement with alternating organic hydrophobic and polar inorganic areas (Figure 3.47). In addition dispersion forces between the peripheral, hydrophobic 4-(3-phenylpropyl)pyridine ligands stabilise the observed packing arrangement. The coordination clusters arrange in the *ac*-plane and the latter forces involving the hydrophobic moieties stabilise the packing in [010].

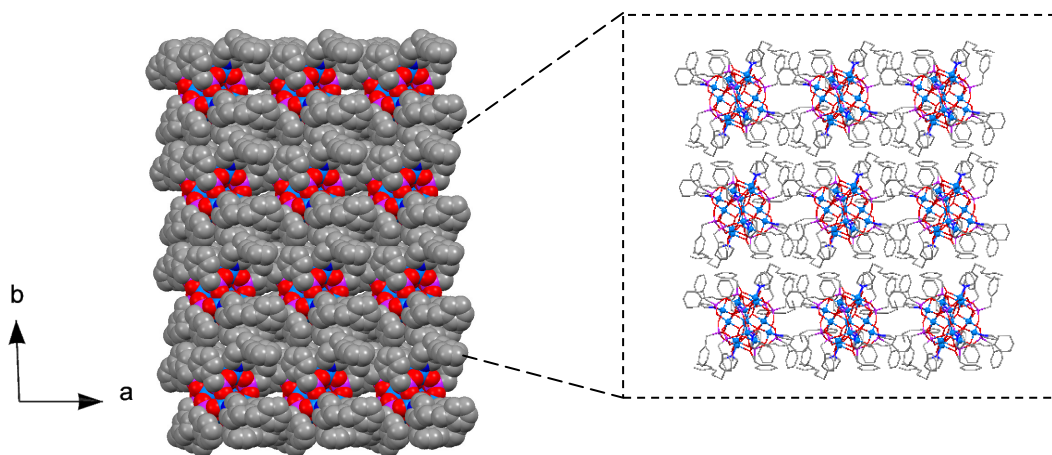


Figure 3.47 – Packing arrangement of the tridecanuclear manganese clusters in **13** viewed in the direction of the crystallographic *c*-axis. Colour code: Mn blue, P purple, O red, C grey, (crystallization solvent molecules and hydrogen atoms have been omitted for clarity).

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

The IR spectrum of **13** (Figure 3.48) is comparable with that of **12**. Some dissimilarities can be observed due to the contribution of the C–H vibrations of the –CH₂ groups of the 4-(3-phenylpropyl)pyridine ligands. This has an effect on the C–H vibration bands which appear in the spectrum as more intense and better resolved bands compared with those of **12**.^{36-40, 56, 57}

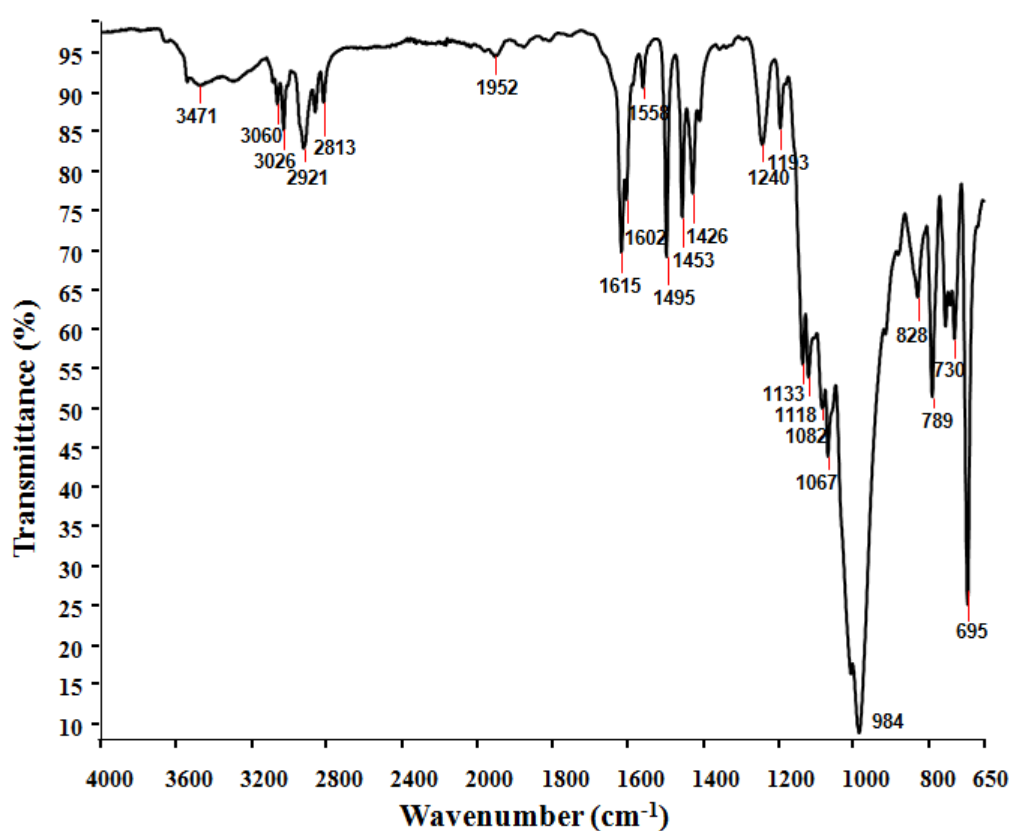


Figure 3.48 – Infrared spectrum of **13**.

- *Thermogravimetric analysis*

13 displays a similar thermal decomposition behaviour in N₂ as **11** and **12** (Figure 3.49). An initial weight loss of 5.6 % occurs between 30 – 150 °C as a possible result of the loss of five crystallization H₂O molecules and four coordinated CH₃OH molecules (calcd: 5.3 %). This assignment is also in agreement with the elemental analysis of the **13**. The following step in the TGA curve corresponds to a weight loss of 27.3 % between 150 – 550 °C, which is associated with the loss of six 4-(3-phenylpropyl)pyridine molecules (calcd: 29.7 %). Further degradation of the organic ligands occurs above 550 °C.

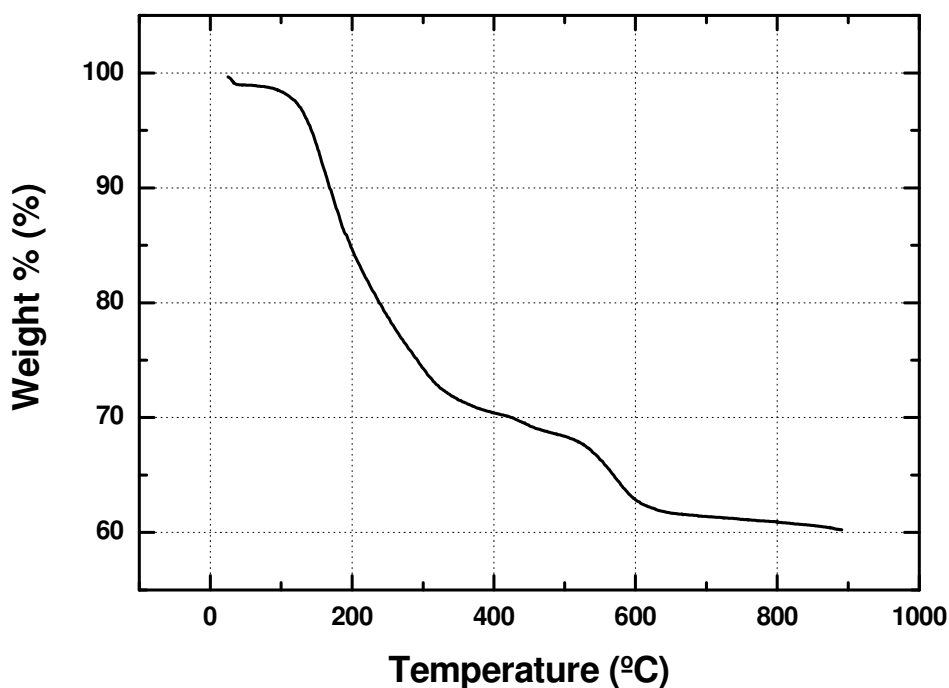


Figure 3.49 – Thermogravimetric analysis of **13**.

- Magnetism

Compound **13** shows similar magnetic behaviour as **11**. The room temperature χT value of $30.3 \text{ cm}^3 \text{ K mol}^{-1}$ (Figure 3.50) is significantly lower than the expected value of $39 \text{ cm}^3 \text{ K mol}^{-1}$ for the presence of thirteen $S = 2 \text{ Mn}^{\text{III}}$ carriers ($C = 3 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2$). This result indicates dominant antiferromagnetic (AF) exchange couplings between spins carriers. Upon lowering the temperature, the χT product decreases down to a minimum of *ca.* $16.5 \text{ cm}^3 \text{ K mol}^{-1}$ at about 20 K. The experimental data can be fitted to a Curie-Weiss law for temperatures above 70 K, with $C = 39.3(9) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -84(5) \text{ K}$. The Curie constant is in good agreement with the expected value ($39 \text{ cm}^3 \text{ K/mol}$) agreeing well with the presence of the thirteen Mn^{III} $S = 2$ spin centres. Below 20 K, at 1000 Oe the χT product increases to reach $17.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. This value suggests an $S_T = 6$ ground state as for **11**. At 1 T, below 10 K, the χT product decreases to reach $7.2 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K due to field saturation effects.

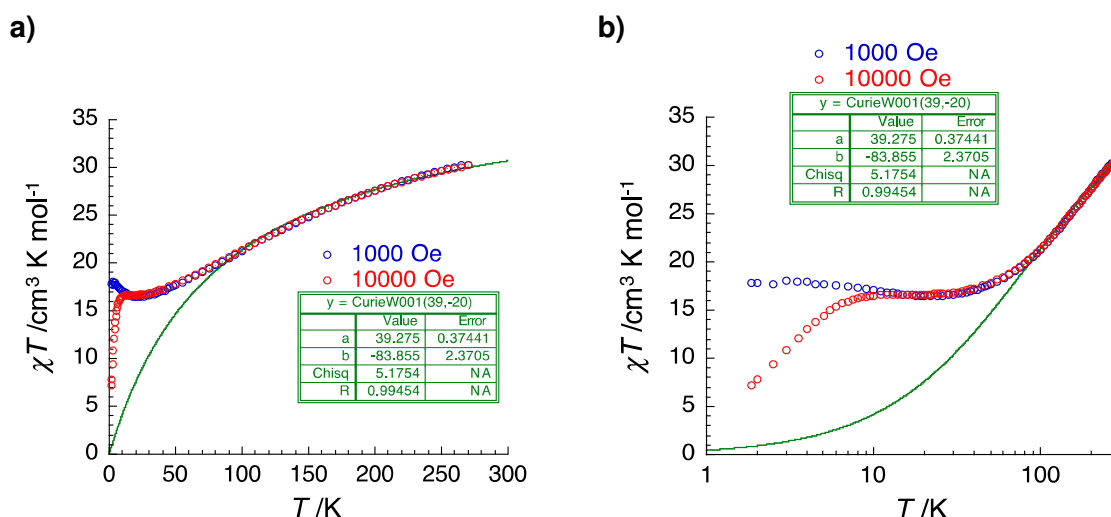


Figure 3.50 – (a) Temperature dependence of the χT product of **13** at 0.1 and 1 T. (b) A magnified view of the χT product in (a) between 1 and 100 K. The green solid line corresponds to the best fit of the experimental data with the Curie-Weiss law ($C = 39.3(9) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -84(5) \text{ K}$).

The field dependence of magnetisation for this compound has also been measured below 8 K (Figure 3.51, a). The magnetisation at low field displays a rapid increase without inflexion point confirming the absence of weak antiferromagnetic interactions and the presence of a well-defined ground state. The high field behavior that displays no clear saturation even at 1.8 K at 7 T, suggests the presence of magnetic anisotropy. It is worth noting that the presence of low-lying excited states and inter-complex magnetic interactions could contribute to this M vs H data even if these two effects have not been

observed for χT vs T data at 0.1 T. The data presented as a M vs H/T plot (Figure 3.51, b) confirms the presence of magnetic anisotropy intrinsic to Mn^{III} metal ions and the cluster as the data are not superposed on a single master-curve as expected for an isotropic system with a well defined spin ground state. At 1.8 K, the magnetisation reaches $11.3 \mu_{\text{B}}$ at 7 T in agreement with an $S_{\text{T}} = 6$ ground state.

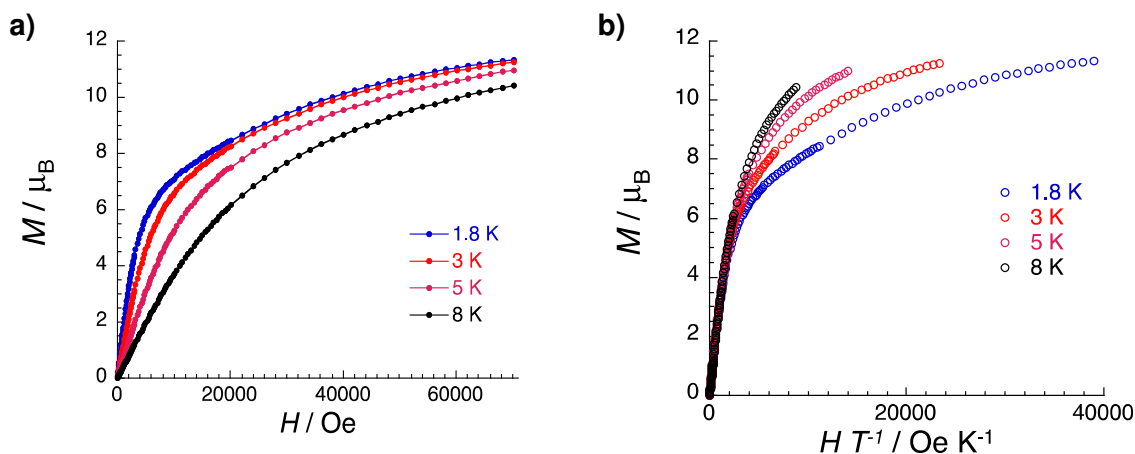


Figure 3.51 – (a) M vs H and (b) M vs H/T data at and below 8 K.

Both measurements, the field dependence of the magnetisation at 1.8 K and the temperature dependence of the χT product at 1000 Oe, are coherent with a ground state $S_{\text{T}} = 6$. This experimental value can be explained by a configuration in which the spin vectors of eight Mn^{III} centres are oriented in opposite direction than those of the five remaining centre, due to probable competing interactions between spin carriers.

The M vs H data at 1.8 K do not show any sign of slow relaxation i.e. hysteresis effects. Nevertheless as for **11** and **12**, the ac susceptibility in zero dc field has been measured to probe possible slow dynamics of the magnetisation. Clearly below 4 K (for frequency around 10000 Hz), slow relaxation of the magnetisation is observed in agreement with the appearance of an out-of-phase signal.

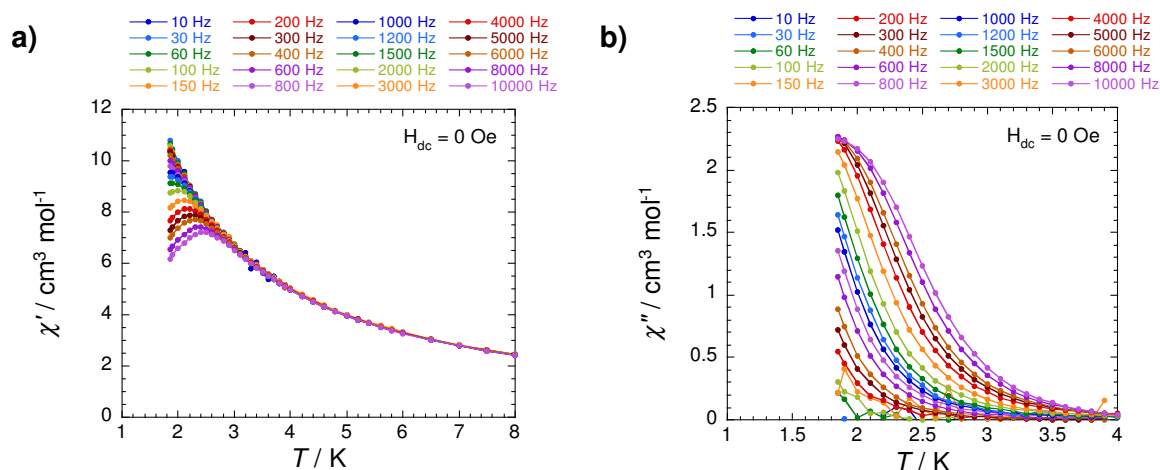


Figure 3.52 – Temperature dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') ac susceptibility under zero dc field for **13**.

Frequency-dependent out-of-phase (χ'') ac susceptibility signals were also observed at temperatures below 3.2 K, suggesting that **13** is consistent with an SMM.⁷

For this compound the relaxation time can be deduced between 1.9 and 3.2 K and fitted to an Arrhenius law. The fit of the thermally activated region gives the energy barrier of 17.8 K while τ_0 is about 2.3×10^{-9} s.

- *Mass spectrometry*

The $\{\text{Mn}_{13}\}$ cluster in **13** was also found to be stable in CH_3CN , DMF and DMSO environments. The $\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^-$ species could be identified in the ESI-MS spectrum of pristine crystals dissolved in CH_3CN , DMF or DMSO (Table 3.18, Figure 3.53) as a signal centered at $m/z = 2699.1$ a.m.u. Furthermore, the ESI-MS spectrum of **13** dissolved in CH_3CN reveals the presence of a signal centered at $m/z = 2753.4$ a.m.u. that was assigned to $\{\text{H}_7[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{13}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^-$. This latter species is related to the former identified species but has three additional H_2O molecules associated with the coordination cluster. Both species were modelled and good fits between the experimental and simulated isotopic envelopes could be found.

Table 3.18 – ESI-MS assignment for compound **13**.

	Solvent	m/z	Species attributed
Crystals of 13 in:	CH_3CN	2699.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$
		2753.4	$\{\text{H}_7[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{13}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$
	DMF	2699.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$
	DMSO	2699.1	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^- \rightarrow \{\text{Mn}_{13}\}$

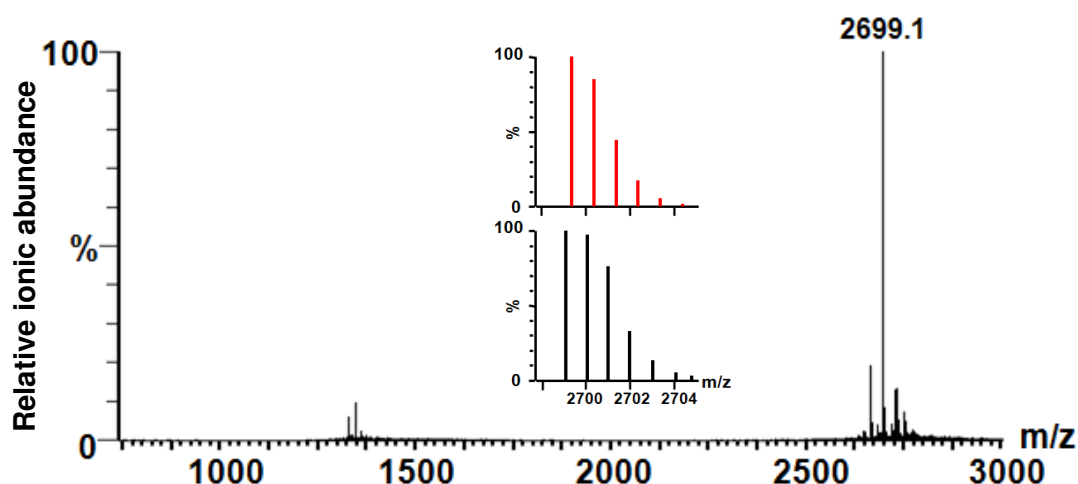


Figure 3.53 – Negative-mode ESI-MS spectra for crystals of **13** dissolved in DMF. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}_{10}\text{O}_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}]\}^-$ centered at $m/z = 2699.1$ a.m.u. (cone voltage: 30 V).

- *UV-Vis spectroscopy*

Similar to the previous three compounds the UV-Vis absorption spectrum of **13** recorded in CH₃CN (Figure 3.54) displays two absorption bands, an intense band at *ca.* 256 nm ($\epsilon = 41000 \text{ L mol}^{-1} \text{ cm}^{-1}$) and a weak band at *ca.* 446 nm ($\epsilon = 3600 \text{ L mol}^{-1} \text{ cm}^{-1}$). These corresponds to a $\pi - \pi^*$ transition of the organic ligands and a ${}^5\text{T}_{2g} \leftarrow {}^5\text{E}_g$ transition within the octahedrally coordinated Mn^{III} ions.⁴⁹⁻⁵²

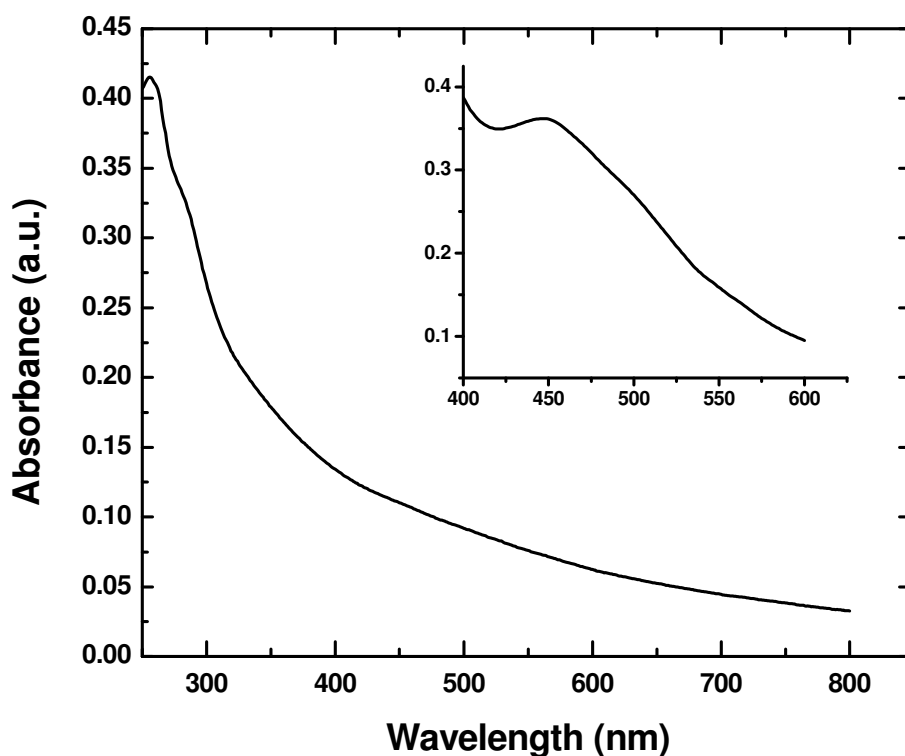


Figure 3.54 – UV-Vis spectrum of a 10^{-5} M solution of **13** in CH₃CN. Inset: A section of the UV-Vis spectrum of a 10^{-4} M solution of **13** in CH₃CN.

Table 3.19 – Crystal data and structural refinement parameters for 13.

Compound 13	
Empirical formula ^a	C ₁₅₈ H ₁₇₄ ClMn ₁₃ N ₆ O ₄₂ P ₁₀
Molecular mass/g mol ⁻¹ ^a	3888.47
Crystal colour/shape	Brown / rectangular block
Crystal size/mm ³	0.11×0.06×0.05
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	14.8581(5)
b/ Å	16.0216(6)
c/ Å	19.3531(7)
α /°	102.721(2)
β /°	97.439(2)
γ /°	90.847(2)
V/ Å ³	4451.6(3)
Z	1
Temperature (K)	100(2)
Density/Mg m ⁻³	1.498
Absorp. coef./mm ⁻¹	8.863
F(000)	2064
2 $\theta_{\max}$ /°	60
Reflections collected	25996
Independent reflections	12843 [R(int)=0.0571]
Data / restraints / parameters	12843 / 2151 / 1012
S on <i>F</i> ²	0.981
R ₁ , wR ₂ [I>2 σ (I)]	0.0960, 0.2609
R ₁ , wR ₂ (all data)	0.1120, 0.2775
Largest diff. peak and hole/e.Å ⁻³	2.005 and -1.021

^aExcluding solvate molecules

3.3.3 Synthesis and characterisation of dodecanuclear manganese complexes

3.3.3.1 $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Cl}_2 \cdot 3\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ (**14**)

The labile nature of the pyridine ligands in Jahn-Teller sites in **12** allowed the replacement of these ligands with 4-(3-phenylpropyl)pyridine in **13**. This observation prompted us to investigate if we could use a bipyridine ligand to connect the polynuclear manganese complexes into polymers. Therefore, 4,4'-trimethylenedipyridine and 4,4'-bipyridine were used as organic bases in similar reaction mixtures that led to the formation of the tridecanuclear manganese complexes. Unfortunately, no crystalline material was obtained when 4,4'-trimethylenedipyridine was used. However, when 4,4'-bipyridine was employed, rectangular brown crystals of $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Cl}_2 \cdot 3\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ (**14**) separated from the reaction mixture within a time period of a week.

Single crystal X-ray diffraction measurements revealed that **14** contains a dodecanuclear manganese complex. **14** crystallises in the orthorhombic crystal system in the space group *Pbca*. The exceptional ring-shaped cluster core in **14** possesses some structural features that resemble those of the complexes in **11-13**. The cluster core can be visualised as constructed of two triangular units **A** and three dinuclear units **B** (Figure 3.55). However, in this case the triangular units **A** are structurally different to those in **11-13**. They adopt an eclipsed arrangement, are directly linked through O-donor atoms, and are further stabilised by three dimer moieties **B**. The two triangular units **A** in **14** each consist of three Mn^{III} ions (Mn(2), Mn(3) and Mn(5), and Mn(1), Mn(4) and Mn(6), respectively) connected through three deprotonated, bridging phosphonate ligands to form a ring motif (Figure 3.56). Each Mn ion in the each triangular unit adopts a square pyramidal geometry that shares a common edge with its partner from the second triangular unit to generate a $\{\text{Mn}_2\text{O}_8\}^{10-}$ subunit (Figure 3.56). The coordination environments of the Mn^{III} ions in **A** comprise of two bridging $\mu_3\text{-O}^{2-}$ oxo ligands involved in the $\{\text{Mn}_2\text{O}_8\}^{10-}$ subunits and three phosphonate O donors that derive from three deprotonated organophosphonate ligands. The short Mn ... Mn contact in the $\{\text{Mn}_2\text{O}_8\}^{10-}$ subunit (2.8043(14) Å – 2.8281(14) Å) is a result of the short Mn – ($\mu_3\text{-O}^{2-}$) distances (1.871(4) Å

– 1.891(4) Å. The other three Mn–O bond lengths involving the phosphonate ligands vary between 1.873(4) Å – 2.114(4) Å (Table 3.20).

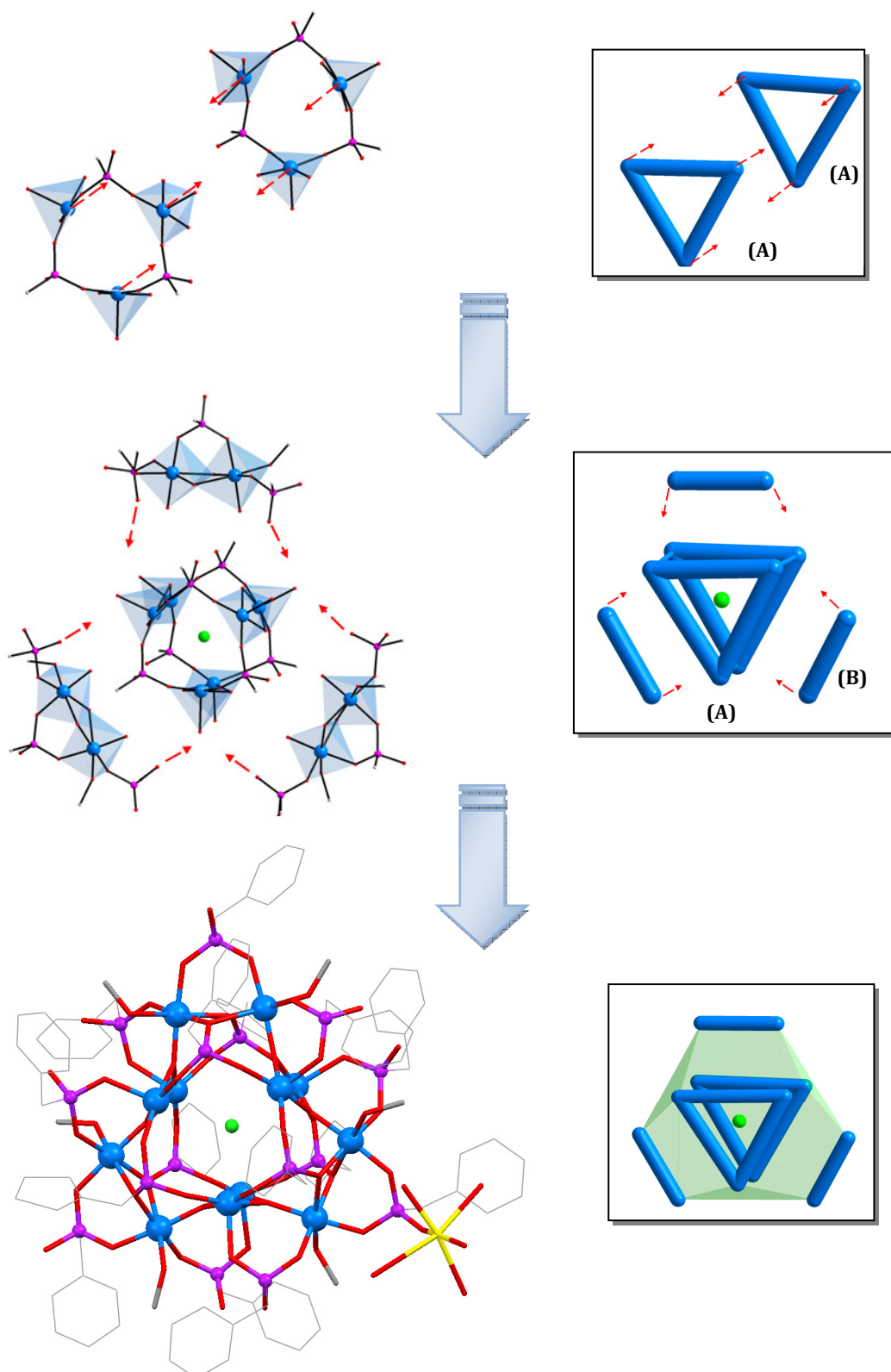


Figure 3.55 – Crystal structure of the dodecanuclear manganese complex in **14** showing the triangular units **A** and the dinuclear units **B**. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green, K yellow (hydrogen atoms have been omitted for clarity).

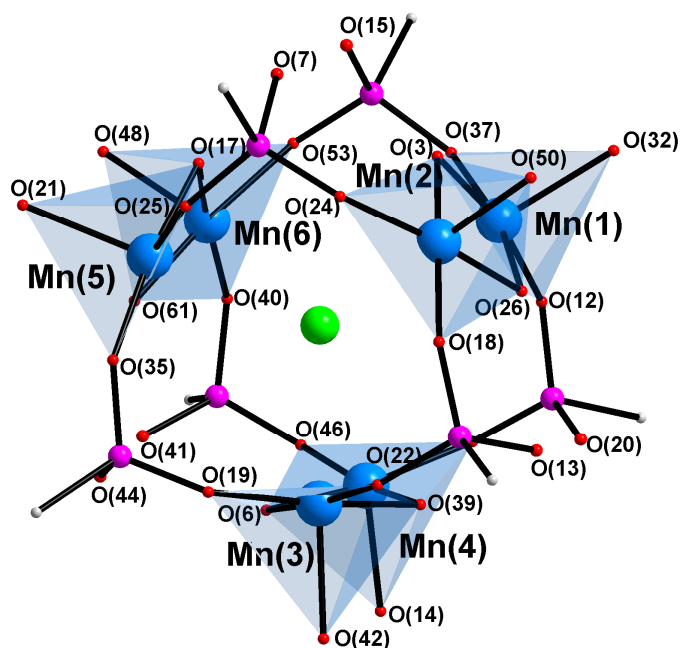
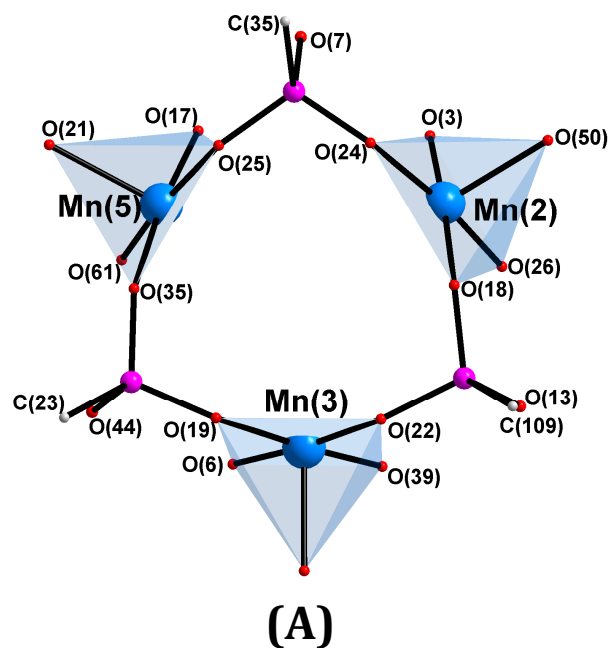


Figure 3.56 – Polyhedral representation of the triangular units **A** in **14**. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green.

The remaining six Mn^{III} ions in **14** (Mn(7) – Mn(12)) are organised into three {Mn₂O₁₀}¹⁴⁻ dimer units (**B**) (Figure 3.57). In these dinuclear units the Mn ions display slightly distorted octahedral coordination environments. The polyhedra in the dimeric subunit share a common edge that involves two phosphonate O donors. The remaining coordination sites of the polyhedra are occupied by two other phosphonate O donors (Mn – O_{phosphonate} distances 1.885(4) Å – 2.374(4) Å), one terminal methanol O-donor (Mn – O_{methanol} distances 2.185(4) Å – 2.220(5) Å) and a μ₃-O²⁻ oxo ligand (Mn – (μ₃-O) distances 1.857(4) Å – 1.870(4) Å). The μ₃-O²⁻ oxo ligands bridge between the three {Mn₂O₁₀}¹⁴⁻

dimer units **B** and the triangular units **A** to give the $\{\text{Mn}_{12}\}$ core structure. The distorted nature of the octahedral coordination environment of the Mn ions in **B** arises from the JT axial elongation and sterical restraints. The distortion is reflected in various bond lengths and angles that deviate from the ideal octahedral geometrical parameters. Thus, the atoms in the elongated JT axes show bond lengths to the Mn centres that range between 2.185(4) Å – 2.374(4) Å and employ one terminal methanol O-donor and one phosphonate O donor. The bond angle O(38)-Mn(11)-O(41) of 165.74(16)° shows the greatest deviation from the ideal octahedral angle of 180°, while the bond angle O(43)-Mn(9)-O(49) of 96.44(18)° shows the greatest deviation from the ideal octahedral angle of 90°. Selected bond angles for the Mn ions in **B** are listed in Table 3.21.

The cluster is stabilized by altogether fifteen phosphonate ligands that bridge between the **A** and **B** units. Nine ligands are situated on the periphery of the $\{\text{Mn}_{12}\}$ ring, with six of them bridging between an octahedron and a square pyramidal polyhedron in a $\eta^1:\eta^1:\mu_2$ mode (P(8), P(9), P(10), P(12), P(14), P(15)). The other three peripheral organic ligands bridge between two octahedra: one phosphonate moiety adopts a $\eta^1:\eta^1:\mu_2$ mode (P(11)) and the two other phosphonate groups act as $\eta^1:\eta^1:\eta^1:\mu_3$ ligands, (P(6), P(7)). The remaining six stabilising organophosphonate ligands can be visualised as pairs of three, situated on opposite sides of the ring moiety. Each of these ligands bridge between two square pyramidal polyhedra and a common vertex of two octahedra in a $\eta^1:\eta^1:\eta^1:\mu_3$ mode (P(1) – P(5) and P(13)) (Figure 3.58). The $\{\text{Mn}_{12}\}$ cluster in **14** is further stabilised by intramolecular hydrogen bonding between the protonated phosphonate ligands, giving rise to O-O distances of 2.447(0) Å – 2.564(0) Å (Figure 3.58).

All Mn atoms in **14** adopt the oxidation state +III. The assignment of the oxidation states was confirmed by BVS calculations (Table 3.20). The cluster is surrounded by two Cl^- counterions, one situated in the central cavity of the ring. The ion is located 2.835(2) Å, 2.8124(19) Å and 2.830(2) Å from Mn(2), Mn(3) and Mn(5), respectively. The other Cl^- counterion, Cl(2), resides in the vicinity of the cluster core, being situated at 3.612(0) Å from the Cl(1) atom of a neighbouring cluster. The charge of the cluster and the Cl^- ions is further compensated by partially hydrated potassium ions $\{\text{K}(\text{H}_2\text{O})_4\}^+$ that link the cluster entities into 1D zigzag chains. The resulting packing arrangement with views in the direction of the crystallographic *a*- and *c*- axes is shown in Figure 3.59.

Intermolecular hydrogen bonding between the crystallisation solvent molecules and the core structure within **14**, together with weak π - π interactions (shortest contact 3.6 Å)

involving the aromatic ring moieties of phosphonate ligands further contribute to the stability of **14** in the solid state.

Table 3.20 – Selected bond lengths [Å] and bond valence sum (BVS) for compound 14.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mn(1)	Mn(1)-O(37)	1.873(4)	3.244	+3
	Mn(1)-O(26)	1.883(4)		
	Mn(1)-O(3)	1.887(4)		
	Mn(1)-O(12)	1.916(4)		
	Mn(1)-O(32)	2.074(4)		
Mn(2)	Mn(2)-O(3)	1.879(4)	3.114	+3
	Mn(2)-O(26)	1.879(4)		
	Mn(2)-O(18)	1.919(4)		
	Mn(2)-O(24)	1.936(4)		
	Mn(2)-O(50)	2.103(4)		
Mn(3)	Mn(3)-O(39)	1.871(4)	3.125	+3
	Mn(3)-O(6)	1.885(4)		
	Mn(3)-O(22)	1.921(4)		
	Mn(3)-O(19)	1.931(4)		
	Mn(3)-O(42)	2.101(4)		
Mn(4)	Mn(4)-O(6)	1.875(4)	3.044	+3
	Mn(4)-O(39)	1.888(4)		
	Mn(4)-O(27)	1.900(4)		
	Mn(4)-O(46)	1.919(4)		
	Mn(4)-O(14)	2.060(4)		
Mn(5)	Mn(5)-O(61)	1.882(4)	3.106	+3
	Mn(5)-O(17)	1.891(4)		
	Mn(5)-O(25)	1.915(4)		
	Mn(5)-O(35)	1.921(4)		
	Mn(5)-O(21)	2.114(4)		
Mn(6)	Mn(6)-O(17)	1.877(4)	3.434	+3
	Mn(6)-O(61)	1.884(4)		
	Mn(6)-O(40)	1.891(4)		
	Mn(6)-O(53)	1.922(4)		
	Mn(6)-O(48)	2.078(4)		
Mn(7)	Mn(7)-O(17)	1.858(4)	2.886	+3
	Mn(7)-O(51)	1.895(4)		
	Mn(7)-O(28)	1.903(4)		
	Mn(7)-O(7)	1.963(4)		
	Mn(7)-O(45)	2.211(5)		
	Mn(7)-O(15)	2.324(4)		
Mn(8)	Mn(8)-O(3)	1.862(4)	2.670	+3
	Mn(8)-O(60)	1.893(4)		
	Mn(8)-O(31)	1.921(4)		
	Mn(8)-O(15)	1.986(4)		
	Mn(8)-O(30)	2.186(4)		
	Mn(8)-O(7)	2.293(4)		
Mn(9)	Mn(9)-O(26)	1.858(4)	3.232	+3
	Mn(9)-O(52)	1.894(4)		
	Mn(9)-O(43)	1.899(4)		
	Mn(9)-O(13)	1.975(4)		
	Mn(9)-O(49)	2.202(5)		
	Mn(9)-O(20)	2.313(4)		

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mn(10)	Mn(10)-O(39)	1.870(4)	3.148	+3
	Mn(10)-O(16)	1.913(4)		
	Mn(10)-O(29)	1.914(4)		
	Mn(10)-O(20)	1.970(4)		
	Mn(10)-O(11)	2.210(4)		
	Mn(10)-O(13)	2.313(4)		
Mn(11)	Mn(11)-O(6)	1.857(4)	3.155	+3
	Mn(11)-O(33)	1.885(4)		
	Mn(11)-O(59)	1.919(5)		
	Mn(11)-O(44)	1.984(4)		
	Mn(11)-O(38)	2.220(5)		
	Mn(11)-O(41)	2.374(4)		
Mn(12)	Mn(12)-O(61)	1.861(4)	3.212	+3
	Mn(12)-O(34)	1.906(4)		
	Mn(12)-O(47)	1.916(4)		
	Mn(12)-O(41)	1.965(4)		
	Mn(12)-O(54)	2.185(4)		
	Mn(12)-O(44)	2.298(4)		
Mn(1) ... Mn(2)	2.8135(14)		Mn(2) ... Cl(1)	2.835(2)
Mn(3) ... Mn(4)	2.8281(14)		Mn(3) ... Cl(1)	2.8124(19)
Mn(5) ... Mn(6)	2.8043(14)		Mn(5) ... Cl(1)	2.830(2)
			Cl(1) ... Cl(2)	3.612(0)

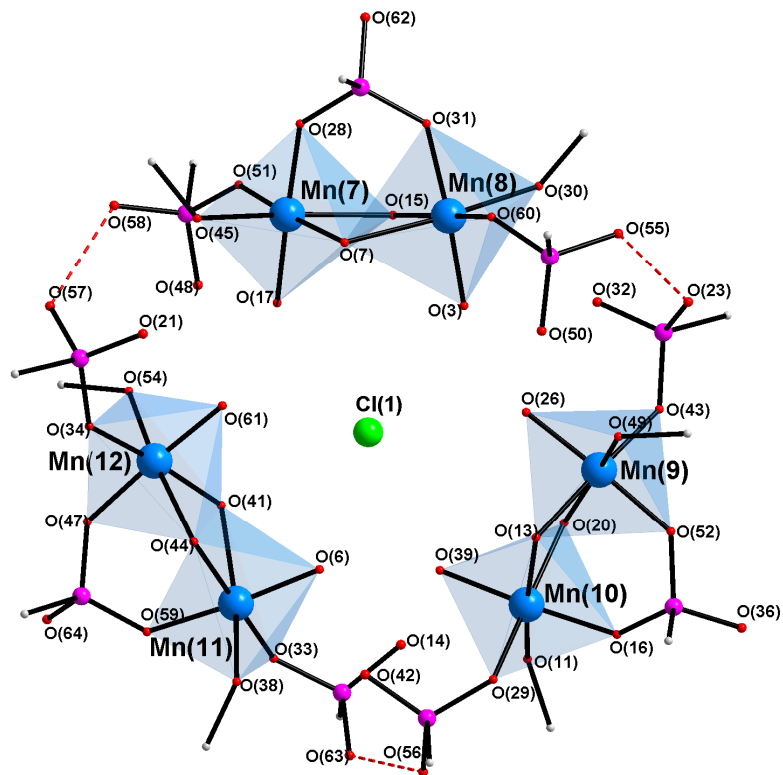


Figure 3.57 – Polyhedral representation of the $\{\text{Mn}_2\text{O}_{10}\}^{14-}$ units in **14**. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green.

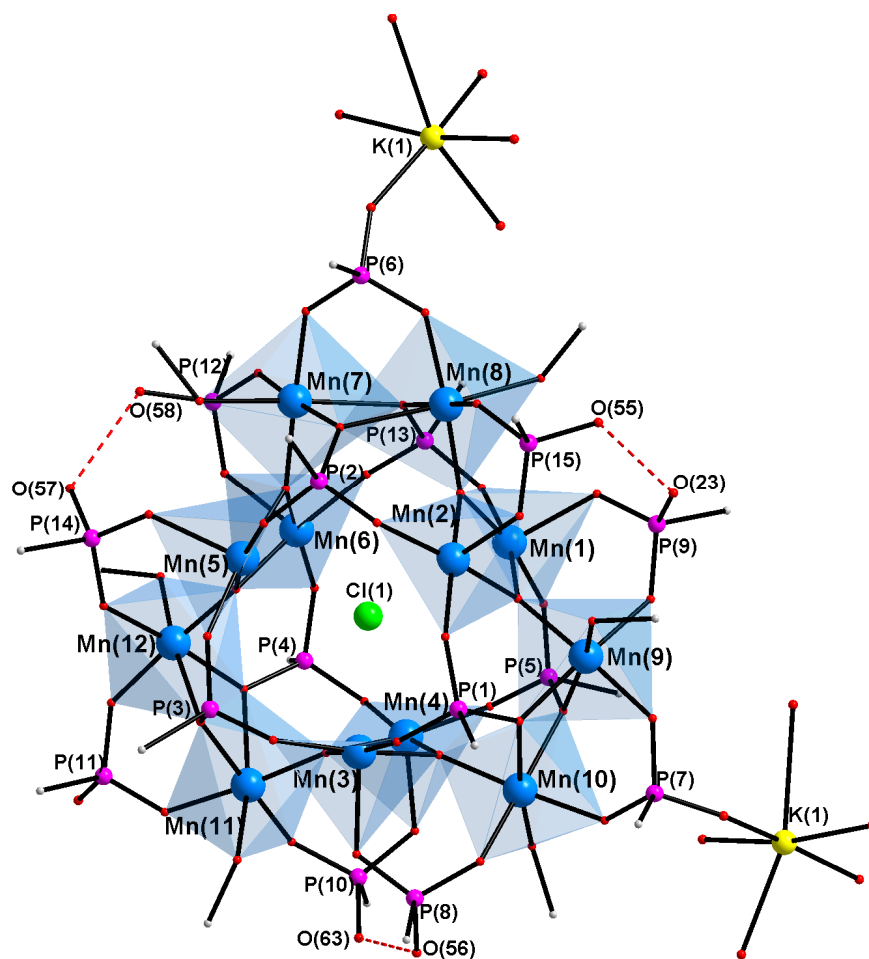


Figure 3.58 – Polyhedral representation of the {Mn₁₂} core structure in **14** showing the intramolecular hydrogen bonding. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green, K yellow.

Table 3.21 – Selected bond angles [°] for compound 14.

Bond Angle (°)		Bond Angle (°)	
O(17)-Mn(7)-O(28)	177.8(2)	O(3)-Mn(8)-O(31)	176.06(19)
O(51)-Mn(7)-O(7)	174.97(19)	O(60)-Mn(8)-O(15)	172.88(19)
O(45)-Mn(7)-O(15)	169.03(17)	O(30)-Mn(8)-O(7)	170.59(16)
O(51)-Mn(7)-O(45)	94.40(19)	O(60)-Mn(8)-O(30)	95.09(19)
O(17)-Mn(7)-O(51)	92.81(18)	O(3)-Mn(8)-O(30)	93.78(17)
O(17)-Mn(7)-O(45)	91.61(17)	O(3)-Mn(8)-O(60)	92.01(18)
O(7)-Mn(7)-O(45)	90.41(17)	O(15)-Mn(8)-O(30)	91.86(17)
O(28)-Mn(7)-O(45)	88.96(17)	O(31)-Mn(8)-O(30)	89.69(17)
O(17)-Mn(7)-O(15)	88.93(16)	O(3)-Mn(8)-O(15)	89.08(17)
O(17)-Mn(7)-O(7)	88.52(17)	O(3)-Mn(8)-O(7)	88.19(16)
O(26)-Mn(9)-O(52)	177.48(19)	O(39)-Mn(10)-O(16)	176.30(18)
O(43)-Mn(9)-O(13)	174.67(18)	O(29)-Mn(10)-O(20)	172.45(19)
O(49)-Mn(9)-O(20)	166.69(16)	O(11)-Mn(10)-O(13)	171.53(16)
O(43)-Mn(9)-O(49)	96.44(18)	O(39)-Mn(10)-O(11)	94.00(17)
O(26)-Mn(9)-O(43)	92.75(18)	O(20)-Mn(10)-O(11)	93.77(17)
O(26)-Mn(9)-O(49)	91.90(17)	O(29)-Mn(10)-O(11)	93.51(18)
O(52)-Mn(9)-O(49)	89.15(18)	O(39)-Mn(10)-O(29)	92.34(18)
O(13)-Mn(9)-O(49)	88.65(17)	O(39)-Mn(10)-O(20)	89.16(17)
O(26)-Mn(9)-O(13)	88.64(17)	O(16)-Mn(10)-O(11)	88.87(18)
O(26)-Mn(9)-O(20)	88.77(16)	O(39)-Mn(10)-O(13)	88.50(16)
O(33)-Mn(11)-O(44)	176.0(2)	O(61)-Mn(12)-O(47)	176.62(19)
O(6)-Mn(11)-O(59)	175.65(19)	O(34)-Mn(12)-O(41)	174.30(19)
O(38)-Mn(11)-O(41)	165.74(16)	O(54)-Mn(12)-O(44)	169.67(17)
O(33)-Mn(11)-O(38)	94.84(19)	O(34)-Mn(12)-O(54)	94.58(19)
O(6)-Mn(11)-O(38)	93.76(17)	O(61)-Mn(12)-O(54)	92.97(18)
O(6)-Mn(11)-O(33)	93.07(18)	O(61)-Mn(12)-O(34)	92.57(19)
O(44)-Mn(11)-O(38)	88.92(17)	O(41)-Mn(12)-O(54)	90.64(18)
O(59)-Mn(11)-O(38)	88.91(19)	O(47)-Mn(12)-O(54)	90.04(18)
O(6)-Mn(11)-O(44)	88.14(18)	O(61)-Mn(12)-O(41)	89.46(18)
O(6)-Mn(11)-O(41)	86.79(16)	O(61)-Mn(12)-O(44)	87.53(17)

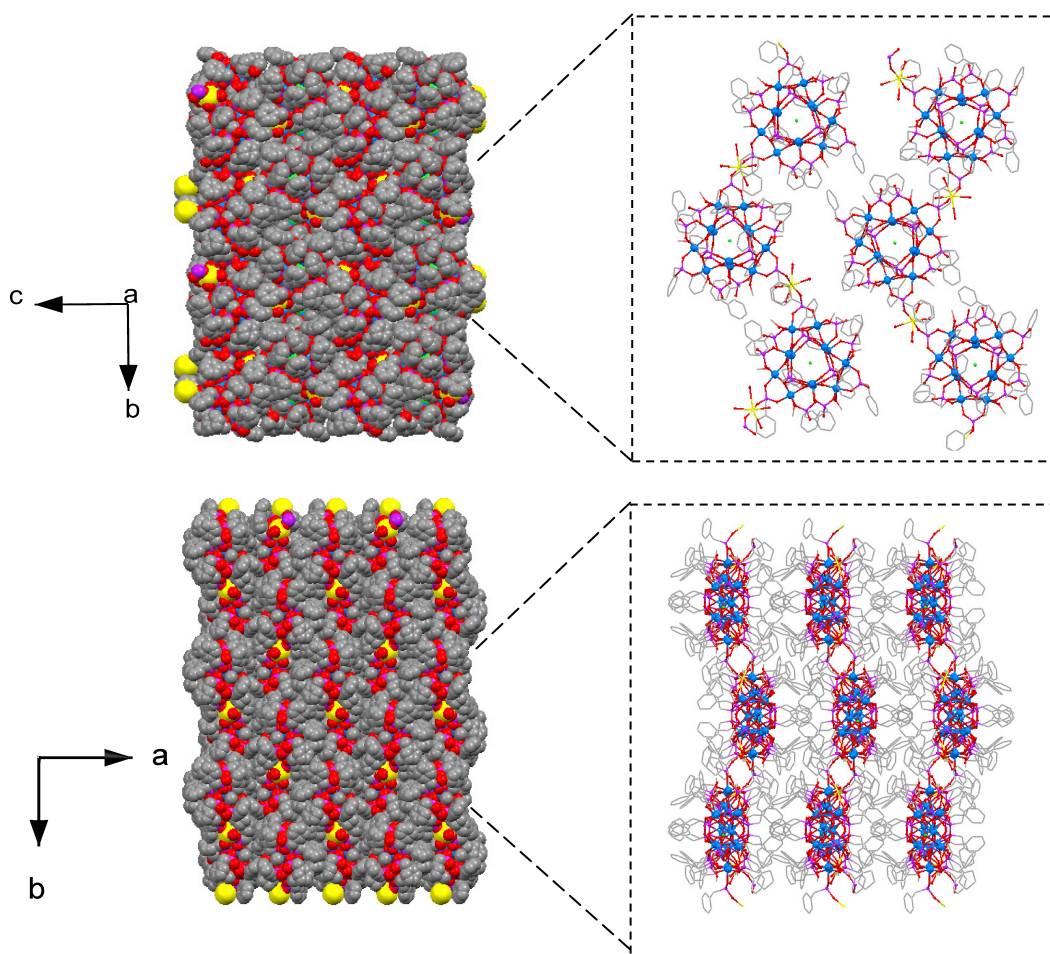


Figure 3.59 – Packing arrangement of the dodecanuclear manganese clusters in **14** viewed in the direction of the crystallographic *a*- and *c*-axis. Colour code: Mn blue, P purple, O red, C grey, Cl green, (crystallization solvent molecules and hydrogen atoms have been omitted for clarity).

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

The IR spectrum of **14** is presented in Figure 3.60. Characteristic C–H out-of-plane bending vibrations of the benzylphosphonic acid ligands can be found in the range 800 – 650 cm^{-1} . C–C skeletal vibrations of the phenyl rings and C–H bending and rocking vibrations of the $-\text{CH}_2$ groups of the benzylphosphonic acid ligands appear in the 1500 – 1200 cm^{-1} region. Different P–O stretching vibrations of the phosphonate groups can be observed in the range 1200 – 900 cm^{-1} . In addition, the corresponding O–H stretching vibrations and H–O–H bending vibrations of the crystallization water molecules engaged in H-bonds appear as broad bands at *ca.* 3200 cm^{-1} and *ca.* 1600 cm^{-1} , respectively.³⁶⁻⁴⁰

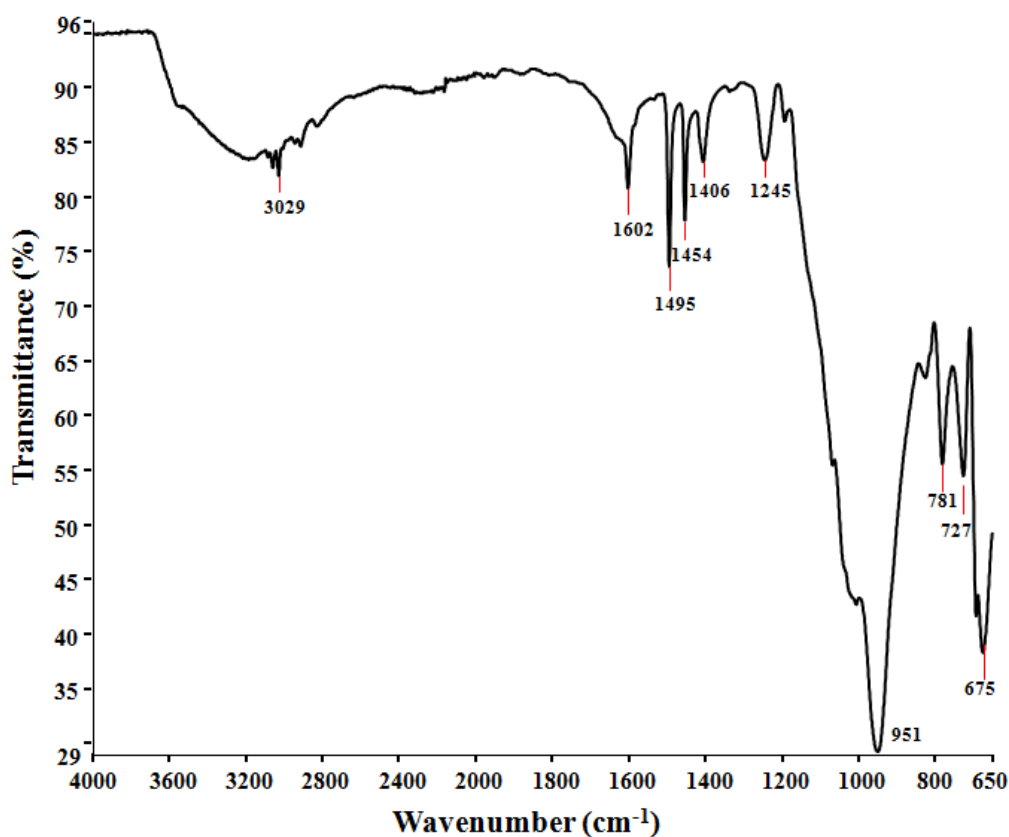


Figure 3.60 – Infrared spectrum of **14**.

- *Thermogravimetric analysis*

The thermal stability of a freshly prepared crystalline sample of **14** was investigated, in an N₂ atmosphere, in the temperature range 30 – 900 °C (Figure 3.61). The first thermogravimetric step observed in the TGA curve of **14** corresponds to a weight loss of 4.7 % and occurs in the temperature range between 30 – 100 °C. This event corresponds to the loss of three crystallization CH₃OH molecules and four crystallization H₂O molecules (calcd: 4.4 %). The following step in the TGA curve corresponds to a weight loss of 6.9 % between 100 – 210 °C, which is associated with the loss of six coordinated CH₃OH molecules and four coordinated H₂O molecules (calcd: 6.8 %). The compound then undergoes a gradual decomposition between 210 – 500 °C involving the organic ligands. The final thermogravimetric step is centered at 550 °C .

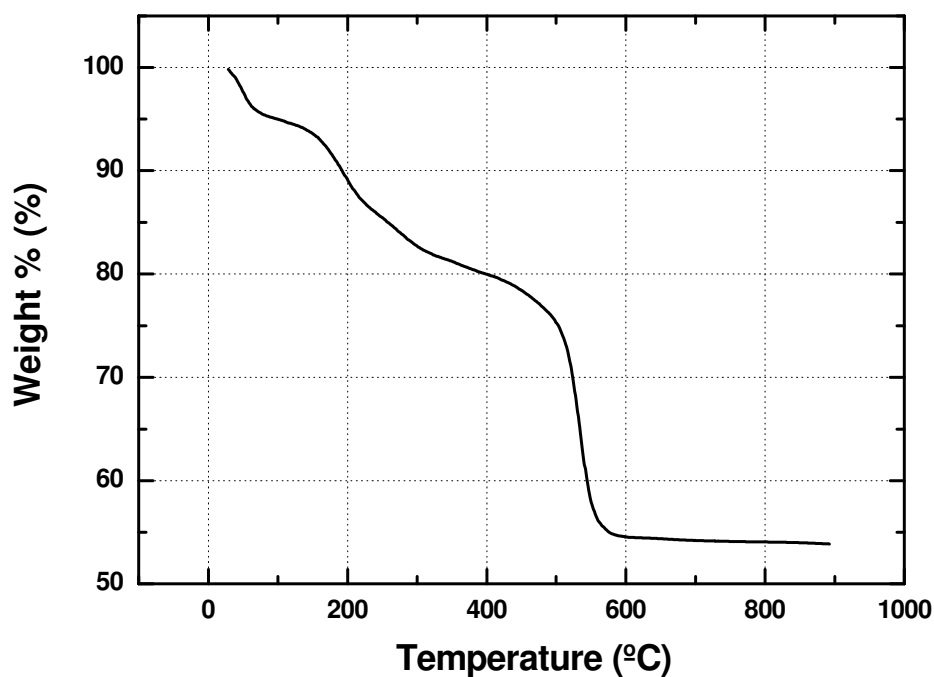


Figure 3.61 – Thermogravimetric analysis of **14**.

- Magnetism

The temperature dependence of the magnetic susceptibility of **14** was measured between 298 and 1.8 K (Figure 3.62). The χT value of $29.5 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature is significantly lower than the expected value of $36 \text{ cm}^3 \text{ K mol}^{-1}$ of twelve $S = 2$ Mn^{III} spin carriers ($C = \frac{Ng^2\mu_B^2}{3k_B} S(S+1)$ with $\frac{Ng^2\mu_B^2}{3k_B} = 0.12505 \text{ cm}^3 \text{ K mol}^{-1}$ and $g = 2$).⁴¹ This result indicates that antiferromagnetic interactions dominate between the spin centres. The gradual decrease of the χT product down to a minimum of *ca.* $18.5 \text{ cm}^3 \text{ K mol}^{-1}$ at *ca.* 40 K further confirm the presence of AF interactions. Below 40 K, at 1000 Oe the χT product decreases rapidly down to $6 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K suggesting an $S_T = 3$ spin ground state.

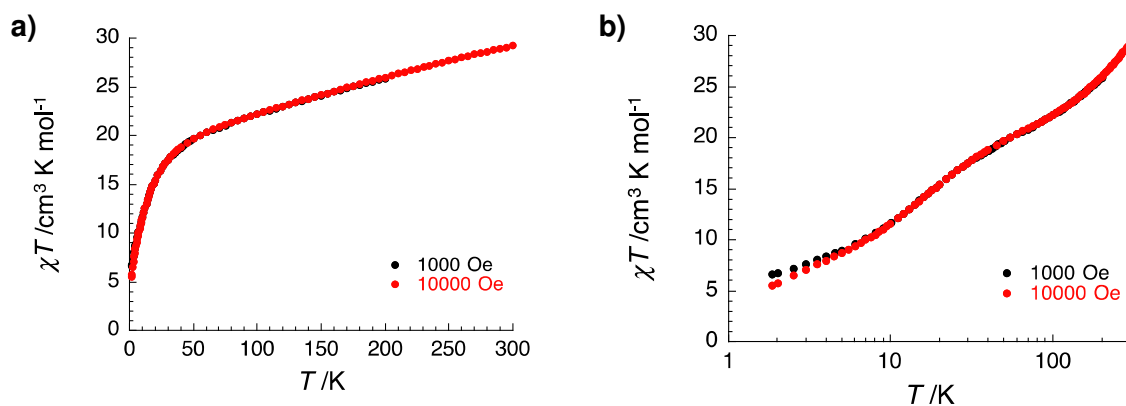


Figure 3.62 – (a) Temperature dependence of the χT product of **14** at 0.1 and 1 T. (b) A magnified view of the χT product in (a) between 1 and 100 K.

The field dependence of the magnetisation measured at temperatures between 1.84 and 8 K is shown in Figure 3.63, a. The M vs H plot reveals a continuous increase of the magnetisation without clear saturation even at 1.84 K at 7 T. This observation suggests the presence of magnetic anisotropy. The data represented as a M vs H/T plot (Figure 3.63, b) confirms the presence of anisotropy intrinsic to Mn^{III} metal ions and the cluster as the data are not superposed on a single master-curve as expected for isotropic systems. However, the complex is not expected to have a significant anisotropy as the Mn^{III} Jahn-Teller axes are approximately aligned with the plane of the $\{\text{Mn}_{12}\}$ ring (see crystal structure in Figure 3.58).

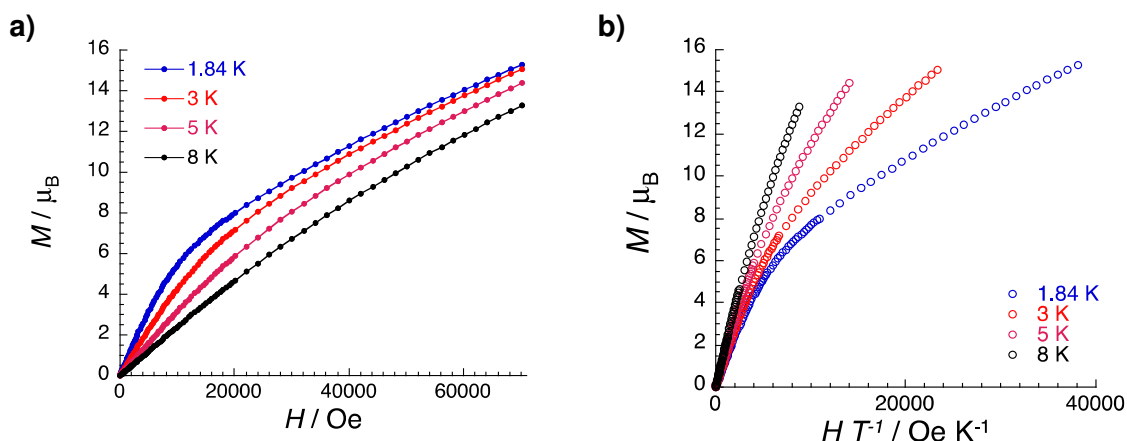


Figure 3.63 – (a) M vs H and (b) M vs H/T data at and below 8 K.

- Mass spectrometry

ESI-MS studies on the crystalline material revealed that the $\{\text{Mn}_{12}\}$ cluster in **14** is stable in CH_3CN , DMF and DMSO environments (Table 3.22). The mass spectrum of **14** dissolved in DMSO is presented in Figure 3.64 and reveals the presence of one major isotopic envelop in the high molecular mass region. This signal is centered at $m/z = 1673.4$ a.m.u. and was assigned to a doubly charged species $\{\text{H}_7[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\text{Cl}\}^{2-}$. A summary of the ESI-MS assignment is given in Table 3.22. The envelopes of all assigned species were modelled.

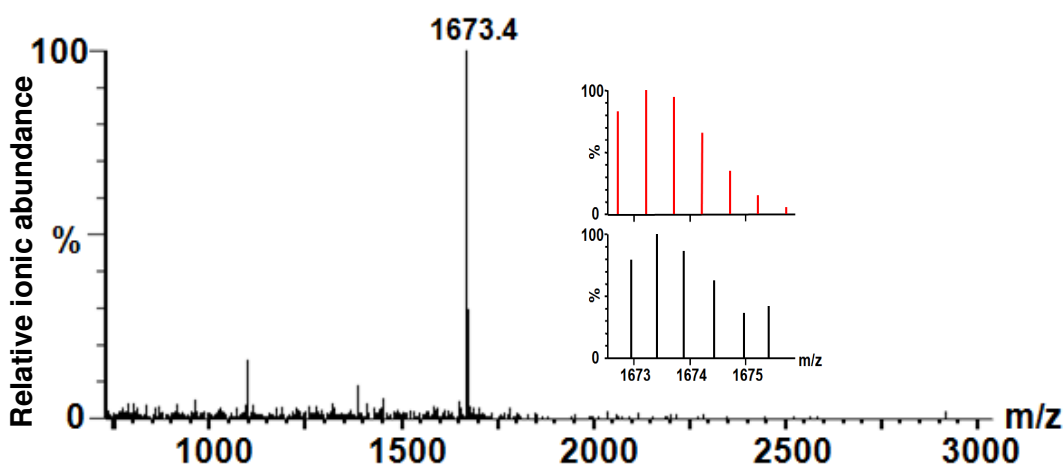


Figure 3.64 – Negative-mode ESI-MS spectra for crystals of **14** dissolved in DMSO. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_7[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\text{Cl}\}^{2-}$ centered at $m/z = 1673.4$ a.m.u. (cone voltage: 30 V).

Table 3.22 – ESI-MS assignment for compound **14**.

	Solvent	m/z	Species attributed
Crystals of 14 in:	CH ₃ CN	1673.4	$\{H_7[Mn^{III}_{10}Mn^{II}_2O_6(C_6H_5CH_2PO_3)_{15}]Cl\}^{2-} \rightarrow \{Mn_{12}\}$
	DMF	1673.4	$\{H_7[Mn^{III}_{10}Mn^{II}_2O_6(C_6H_5CH_2PO_3)_{15}]Cl\}^{2-} \rightarrow \{Mn_{12}\}$
	DMSO	1673.4	$\{H_7[Mn^{III}_{10}Mn^{II}_2O_6(C_6H_5CH_2PO_3)_{15}]Cl\}^{2-} \rightarrow \{Mn_{12}\}$

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **14** recorded in CH₃CN (Figure 3.65) displays an intense absorption band at *ca.* 257 nm ($\epsilon = 36000 \text{ L mol}^{-1} \text{ cm}^{-1}$) which can be attributed to $\pi - \pi^*$ transitions of the aromatic phosphonate ligands. The weak band observed at *ca.* 488 nm ($\epsilon = 3200 \text{ L mol}^{-1} \text{ cm}^{-1}$) may arise from d – d transitions that can be assigned to $^5T_{2g} \leftarrow ^5E_g$ transitions of octahedrally coordinated Mn^{III} ions within **14**.⁴⁹⁻⁵²

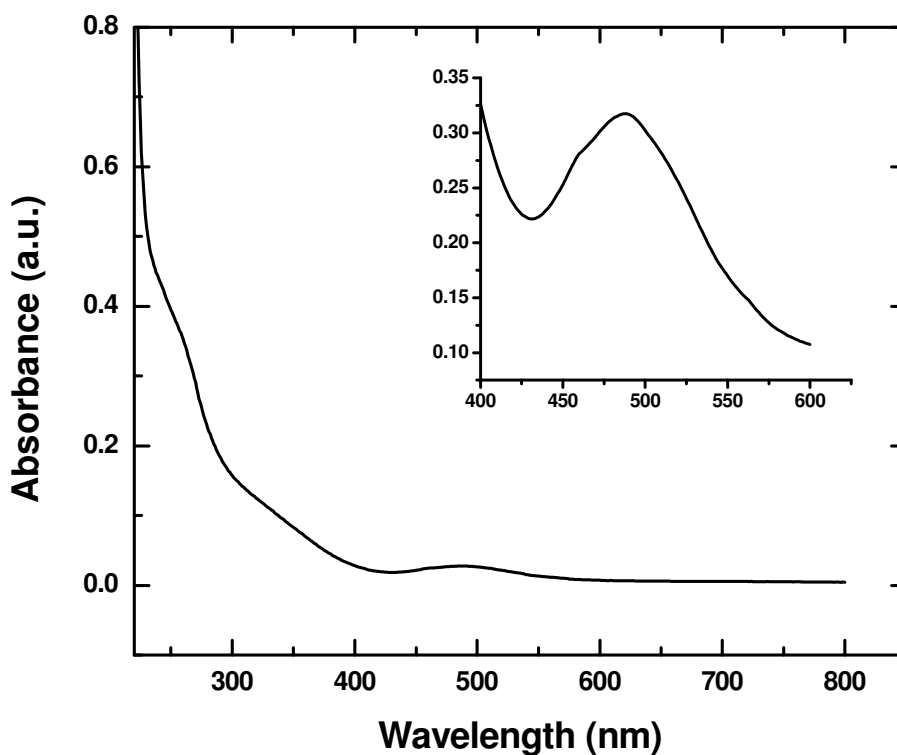


Figure 3.65 – UV-Vis spectrum of a 10^{-5} M solution of **14** in CH₃CN. Inset: A section of the UV-Vis spectrum of a 10^{-4} M solution of **14** in CH₃CN.

Table 3.23 – Crystal data and structural refinement parameters for 14.

Compound 14	
Empirical formula ^a	C ₁₁₁ H ₁₄₄ Cl ₂ KMn ₁₂ O ₆₁ P ₁₅
Molecular mass/g mol ⁻¹ ^a	3688.16
Crystal colour/shape	Dark brown / rectangular block
Crystal size/mm ³	0.50×0.20×0.15
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> / Å	27.2527(17)
<i>b</i> / Å	29.947(2)
<i>c</i> / Å	41.980(3)
α /°	90
β /°	90
γ /°	90
<i>V</i> / Å ³	34261(4)
<i>Z</i>	1
Temperature (K)	150(2)
Density/Mg m ⁻³	1.402
Absorp. coef./mm ⁻¹	1.125
<i>F</i> (000)	14144
$2\theta_{\text{max}}$ /°	50
Reflections collected	198099
Independent reflections	30136 [R(int)=0.1519]
Data / restraints / parameters	30136 / 0 / 1880
<i>S</i> on <i>F</i> ²	1.024
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0602, 0.1412
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1146, 0.1514
Largest diff. peak and hole/e.Å ⁻³	2.299 and -1.597

^aExcluding solvate molecules

3.3.3.2 $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Br}_2 \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**15**)

Compound **15**, $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Br}_2 \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ was prepared in a similar manner to **14** using $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ instead of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, in order to investigate the role of the halide ion as a potential templating agent. X-ray structural analysis revealed that **15** (Figure 3.66) is almost isostructural to **14**, having only slightly different structural and geometrical parameters. Selected interatomic distances and angles for compound **15** are given in Table 3.24 and Table 3.25, and agree very well with those observed for **14**. Bond valence sum analysis confirms again that all the Mn ions in **15** are in the oxidation state +III; the overall charge of the cluster is compensated by one K^+ ion and two Br^- ions. As before, one Br^- ion is situated in the central cavity of the ring, at 2.954(1) Å, 2.973(1) Å and 2.981(1) Å to Mn(1), Mn(3) and Mn(5) respectively. The other Br^- ion, Br(2) is situated just above the cavity of the ring, residing 3.879(2) Å from Br(1). As for **14**, the potassium ions link the cluster entities into 1D zigzag chains.

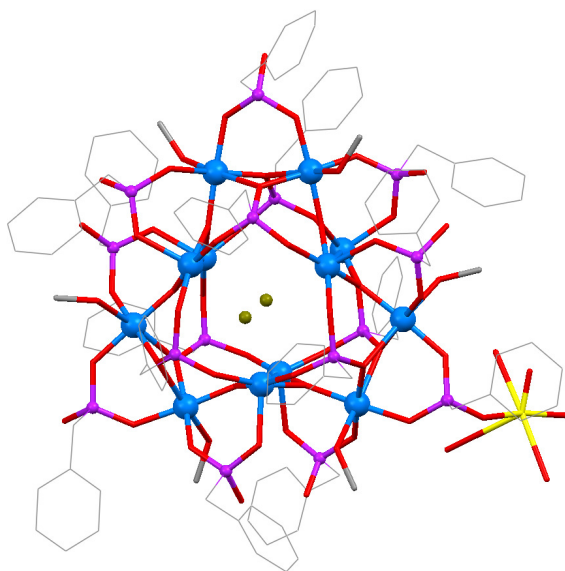


Figure 3.66 – Crystal structure of the dodecanuclear manganese complex in **15**. Colour code: Mn^{III} blue, P purple, O red, C grey, Br dark green, K yellow (hydrogen atoms have been omitted for clarity).

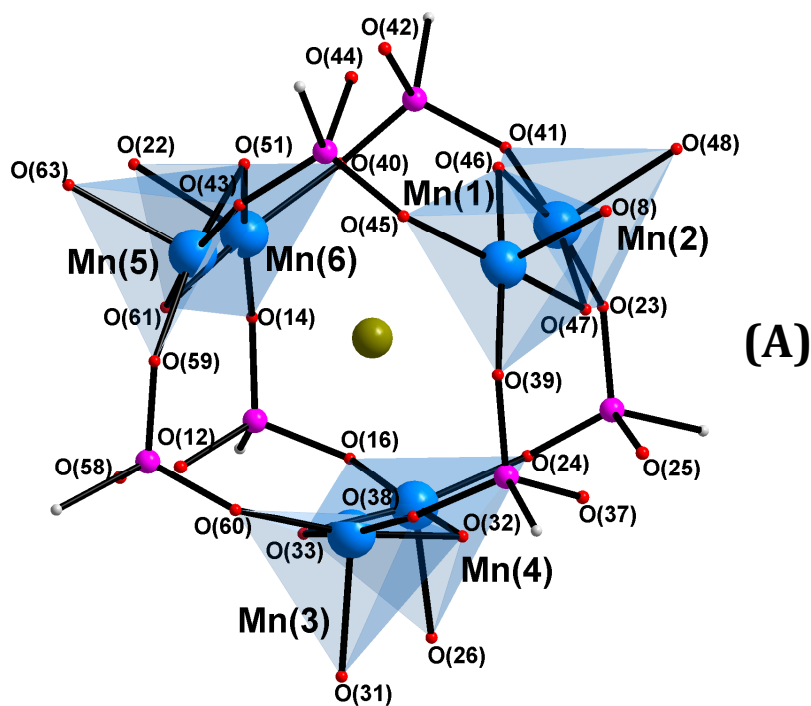


Figure 3.67 – Polyhedral representation of the triangular units **A** found in **15**. Colour code: Mn^{III} blue, P purple, O red, C grey, Br dark green.

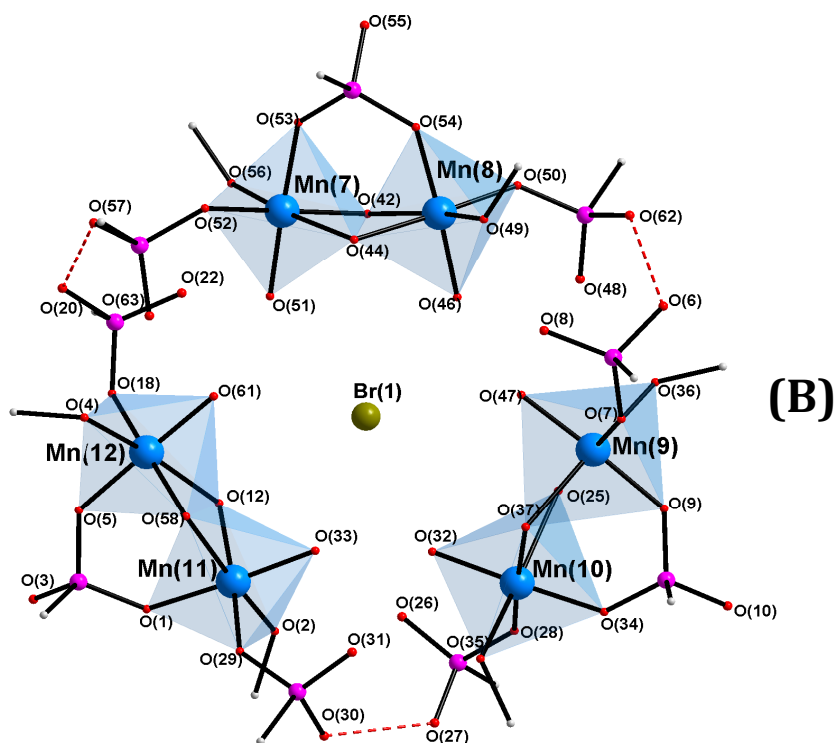


Figure 3.68 – Polyhedral representation of the {Mn₂O₁₀}¹⁴⁻ units in **15**. Colour code: Mn^{III} blue, P purple, O red, C grey, Br dark green.

Table 3.24 – Selected bond lengths [$\text{\AA}$] and bond valence sum (BVS) for compound 15.

Atom	Bond	Bond distances ($\text{\AA}$)	BVS	Assigned oxidation state
Mn(1)	Mn(1)-O(46)	1.871(5)	3.135	+3
	Mn(1)-O(47)	1.877(5)		
	Mn(1)-O(39)	1.916(5)		
	Mn(1)-O(45)	1.938(5)		
	Mn(1)-O(8)	2.104(5)		
Mn(2)	Mn(2)-O(46)	1.874(5)	3.198	+3
	Mn(2)-O(47)	1.891(5)		
	Mn(2)-O(23)	1.899(5)		
	Mn(2)-O(41)	1.914(5)		
	Mn(2)-O(48)	2.084(5)		
Mn(3)	Mn(3)-O(33)	1.873(5)	3.161	+3
	Mn(3)-O(32)	1.877(5)		
	Mn(3)-O(38)	1.911(5)		
	Mn(3)-O(60)	1.943(5)		
	Mn(3)-O(31)	2.077(5)		
Mn(4)	Mn(4)-O(32)	1.873(5)	3.224	+3
	Mn(4)-O(16)	1.884(5)		
	Mn(4)-O(33)	1.891(4)		
	Mn(4)-O(24)	1.920(5)		
	Mn(4)-O(26)	2.076(5)		
Mn(5)	Mn(5)-O(51)	1.879(5)	3.125	+3
	Mn(5)-O(61)	1.893(5)		
	Mn(5)-O(59)	1.909(5)		
	Mn(5)-O(43)	1.930(5)		
	Mn(5)-O(63)	2.094(5)		
Mn(6)	Mn(6)-O(61)	1.873(5)	3.204	+3
	Mn(6)-O(51)	1.882(5)		
	Mn(6)-O(40)	1.897(5)		
	Mn(6)-O(14)	1.925(5)		
	Mn(6)-O(22)	2.080(5)		
Mn(7)	Mn(7)-O(51)	1.863(4)	3.127	+3
	Mn(7)-O(52)	1.911(5)		
	Mn(7)-O(53)	1.939(5)		
	Mn(7)-O(42)	1.974(5)		
	Mn(7)-O(56)	2.188(5)		
	Mn(7)-O(44)	2.324(5)		
Mn(8)	Mn(8)-O(46)	1.865(4)	3.135	+3
	Mn(8)-O(50)	1.892(5)		
	Mn(8)-O(54)	1.912(5)		
	Mn(8)-O(44)	1.989(5)		
	Mn(8)-O(49)	2.218(5)		
	Mn(8)-O(42)	2.366(5)		
Mn(9)	Mn(9)-O(47)	1.862(4)	3.166	+3
	Mn(9)-O(9)	1.903(5)		
	Mn(9)-O(7)	1.923(5)		
	Mn(9)-O(25)	1.968(5)		
	Mn(9)-O(36)	2.214(5)		
	Mn(9)-O(37)	2.313(5)		

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mn(10)	Mn(10)-O(32)	1.866(4)	3.178	+3
	Mn(10)-O(34)	1.890(5)		
	Mn(10)-O(28)	1.902(5)		
	Mn(10)-O(37)	1.992(5)		
	Mn(10)-O(35)	2.217(5)		
	Mn(10)-O(25)	2.316(5)		
Mn(11)	Mn(11)-O(33)	1.863(4)	3.161	+3
	Mn(11)-O(29)	1.903(5)		
	Mn(11)-O(1)	1.917(4)		
	Mn(11)-O(12)	1.991(5)		
	Mn(11)-O(2W)	2.197(5)		
	Mn(11)-O(58)	2.303(5)		
Mn(12)	Mn(12)-O(61)	1.861(5)	3.185	+3
	Mn(12)-O(18)	1.895(5)		
	Mn(12)-O(5)	1.907(5)		
	Mn(12)-O(58)	1.978(5)		
	Mn(12)-O(4W)	2.212(5)		
	Mn(12)-O(12)	2.332(5)		
Mn(1) ... Mn(2)	2.8232(15)		Mn(1) ... Br(1)	2.954(1)
Mn(3) ... Mn(4)	2.8098(15)		Mn(3) ... Br(1)	2.973(1)
Mn(5) ... Mn(6)	2.8029(16)		Mn(5) ... Br(1)	2.981(1)
			Br(1) ... Br(2)	3.879(2)

Table 3.25 – Selected bond angles [°] for compound 15.

Bond Angle (°)		Bond Angle (°)	
O(51)-Mn(7)-O(53)	177.3(2)	O(46)-Mn(8)-O(54)	176.6(2)
O(52)-Mn(7)-O(42)	173.5(2)	O(50)-Mn(8)-O(44)	175.8(2)
O(56)-Mn(7)-O(44)	169.23(19)	O(49)-Mn(8)-O(42)	165.46(19)
O(52)-Mn(7)-O(56)	94.9(2)	O(50)-Mn(8)-O(49)	95.0(2)
O(51)-Mn(7)-O(56)	91.9(2)	O(46)-Mn(8)-O(50)	92.6(2)
O(51)-Mn(7)-O(52)	91.8(2)	O(46)-Mn(8)-O(49)	92.5(2)
O(42)-Mn(7)-O(56)	91.4(2)	O(44)-Mn(8)-O(49)	88.9(2)
O(53)-Mn(7)-O(56)	90.4(2)	O(54)-Mn(8)-O(49)	88.7(2)
O(51)-Mn(7)-O(42)	89.8(2)	O(46)-Mn(8)-O(44)	88.6(2)
O(51)-Mn(7)-O(44)	88.27(19)	O(46)-Mn(8)-O(42)	87.76(19)
O(47)-Mn(9)-O(9)	177.2(2)	O(32)-Mn(10)-O(34)	178.0(2)
O(7)-Mn(9)-O(25)	171.8(2)	O(28)-Mn(10)-O(37)	174.5(2)
O(36)-Mn(9)-O(37)	171.41(19)	O(35)-Mn(10)-O(25)	165.67(18)
O(7)-Mn(9)-O(36)	94.1(2)	O(28)-Mn(10)-O(35)	96.6(2)
O(25)-Mn(9)-O(36)	94.0(2)	O(32)-Mn(10)-O(28)	92.7(2)
O(47)-Mn(9)-O(36)	92.8(2)	O(32)-Mn(10)-O(35)	91.51(19)
O(47)-Mn(9)-O(7)	91.8(2)	O(34)-Mn(10)-O(35)	89.3(2)
O(9)-Mn(9)-O(36)	89.3(2)	O(32)-Mn(10)-O(25)	88.90(18)
O(47)-Mn(9)-O(25)	89.05(19)	O(32)-Mn(10)-O(37)	88.82(19)
O(47)-Mn(9)-O(37)	88.64(18)	O(37)-Mn(10)-O(35)	88.63(19)
O(33)-Mn(11)-O(1)	176.7(2)	O(61)-Mn(12)-O(5)	178.8(2)
O(29)-Mn(11)-O(12)	172.1(2)	O(18)-Mn(12)-O(58)	175.0(2)
O(2)-Mn(11)-O(58)	170.60(19)	O(4)-Mn(12)-O(12)	168.66(19)
O(29)-Mn(11)-O(2)	95.8(2)	O(18)-Mn(12)-O(4)	94.4(2)
O(33)-Mn(11)-O(2)	92.83(19)	O(61)-Mn(12)-O(18)	92.3(2)
O(12)-Mn(11)-O(2)	91.95(19)	O(61)-Mn(12)-O(4)	91.13(19)
O(33)-Mn(11)-O(29)	91.7(2)	O(58)-Mn(12)-O(4)	90.4(2)
O(1)-Mn(11)-O(2)	90.09(19)	O(61)-Mn(12)-O(12)	89.52(18)
O(33)-Mn(11)-O(12)	89.46(19)	O(5)-Mn(12)-O(4)	89.37(19)
O(33)-Mn(11)-O(58)	88.39(18)	O(61)-Mn(12)-O(58)	88.9(2)

- PHYSICOCHEMICAL CHARACTERISATION

The IR spectrum of compound **15** exhibits the same general characteristics than that of **14**. The UV-Vis absorption spectrum of **15** in CH₃CN also displays identical features to the spectrum of **14**, showing an intense absorption band at *ca.* 258 nm ($\epsilon = 52000 \text{ L mol}^{-1} \text{ cm}^{-1}$) ($\pi - \pi^*$ transitions of the phosphonate ligands), and a weak absorption band at *ca.* 489 nm ($\epsilon = 4000 \text{ L mol}^{-1} \text{ cm}^{-1}$) ($^5\text{T}_{2g} \leftarrow ^5\text{E}_g$ most likely resulting from d-d transitions of octahedrally coordinated Mn^{III} centers).

- Thermogravimetric analysis

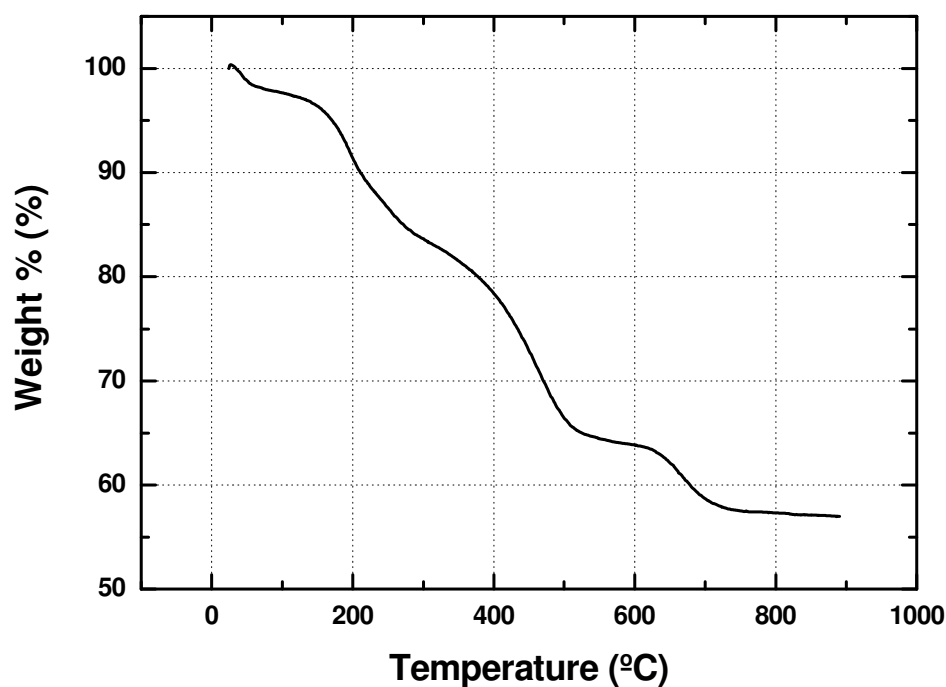


Figure 3.69 – Thermogravimetric analysis of **15**.

The TGA analysis in an N₂ atmosphere reveals that **15** also undergoes a similar decomposition behaviour as **14**. The first thermogravimetric step observed in the TGA curve of **15** (Figure 3.69) corresponds to a weight loss of 2.6 % between 30 – 100 °C. This step was attributed to the loss of two crystallization CH₃OH molecules and two crystallization H₂O molecules (calcd: 2.6 %). The next thermogravimetric step observed in the TGA occurs in the temperature range between 100 – 200 °C and corresponds to a weight loss of 6.3 %.

This weight loss can be associated with the loss of six coordinated CH_3OH molecules and four coordinated H_2O molecules (calcd: 6.8 %). Decompositions of the organic ligands and thermolysis processes between 200 – 600 °C destroy the cluster entities.

- *Magnetism*

Magnetisation data for compound **15** were collected at high magnetic field strengths and low temperatures. The magnetic properties of **15** are almost identical with those of **14**, being characterised by dominant antiferromagnetic interactions between the spin centres and an $S_T = 3$ ground state. As expected, exchange of the halide ions has no significant effect on the structure and thus on magnetic properties of the cluster core.

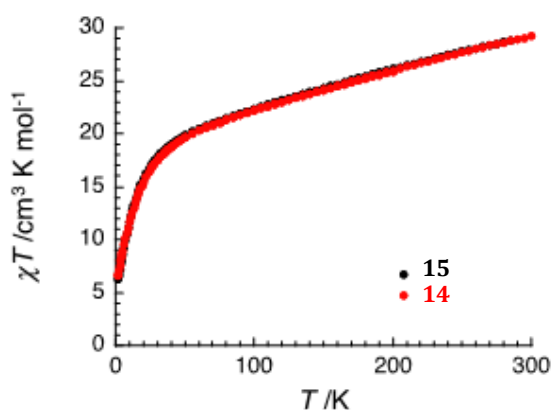


Figure 3.70 – Comparison of the χT vs T plot of **14** and **15** at 0.1 T.

- *Mass spectrometry*

The solution stability of the $\{\text{Mn}_{12}\}$ cluster in **15** was again investigated by electrospray ionisation mass spectrometry. The ESI-MS spectrum of pristine crystals of **15** dissolved in CH_3CN is presented in Figure 3.71 and reveals the presence of three major isotopic envelopes in the high mass region of the spectrum. Two of the signals were assigned to $\{\text{H}_6[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\}^{2-}$ centered at $m/z = 1655.0$ a.m.u. and $\{\text{H}_6[\text{Mn}^{\text{III}}_{11}\text{Mn}^{\text{II}}\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\text{Br}\}^{2-}$ centered at $m/z = 1695.4$ a.m.u., while the third signal could not be assigned, most likely due to overlapping species. ESI-MS studies revealed that the $\{\text{Mn}_{12}\}$ cluster in **15** is stable in CH_3CN , DMF and DMSO environments. A summary of the ESI-MS assignment is presented in Table 3.26. The isotopic envelopes of all assigned species were modelled.

Table 3.26 – ESI-MS assignment for compound **15**.

	Solvent	m/z	Species attributed
Crystals of 15 in:	CH_3CN	1655.0	$\{\text{H}_6[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\}^{2-} \rightarrow \{\text{Mn}_{12}\}$
		1695.4	$\{\text{H}_6[\text{Mn}^{\text{III}}_{11}\text{Mn}^{\text{II}}\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\text{Br}\}^{2-} \rightarrow \{\text{Mn}_{12}\}$
	DMF	1655.0	$\{\text{H}_6[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\}^{2-} \rightarrow \{\text{Mn}_{12}\}$
		1655.0	$\{\text{H}_6[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\}^{2-} \rightarrow \{\text{Mn}_{12}\}$
	DMSO	1655.0	$\{\text{H}_6[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\}^{2-} \rightarrow \{\text{Mn}_{12}\}$
		1695.4	$\{\text{H}_6[\text{Mn}^{\text{III}}_{11}\text{Mn}^{\text{II}}\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\text{Br}\}^{2-} \rightarrow \{\text{Mn}_{12}\}$

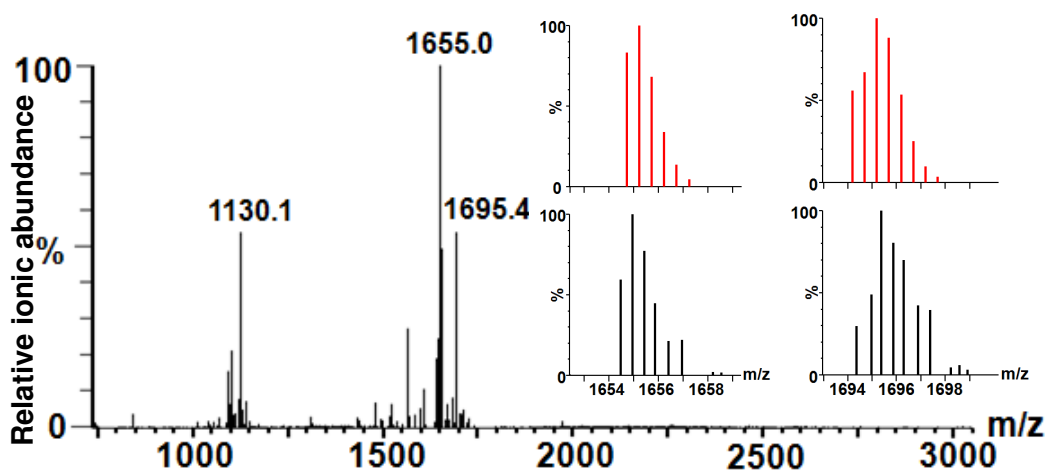


Figure 3.71 – Negative-mode ESI-MS spectra for crystals of **15** dissolved in CH_3CN . Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_6[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\}^{2-}$ centered at $m/z = 1655.0$ a.m.u. and $\{\text{H}_6[\text{Mn}^{\text{III}}_{11}\text{Mn}^{\text{II}}\text{O}_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{15}]\text{Br}\}^{2-}$ centered at $m/z = 1695.4$ a.m.u. (cone voltage: 30 V).

Table 3.27 – Crystal data and structural refinement parameters for 15.

Compound 15	
Empirical formula ^a	C ₁₁₁ H ₁₄₄ Br ₂ KMn ₁₂ O ₆₁ P ₁₅
Molecular mass/g mol ⁻¹ ^a	3777.06
Crystal colour/shape	Brown / rectangular block
Crystal size/mm ³	0.50×0.10×0.10
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> / Å	27.112(2)
<i>b</i> / Å	29.957(2)
<i>c</i> / Å	41.972(3)
α /°	90
β /°	90
γ /°	90
<i>V</i> / Å ³	34089(4)
<i>Z</i>	1
Temperature (K)	150(2)
Density/Mg m ⁻³	1.458
Absorp. coef./mm ⁻¹	1.569
<i>F</i> (000)	14584
$2\theta_{\text{max}}$ /°	50
Reflections collected	194198
Independent reflections	29987 [R(int)=0.1221]
Data / restraints / parameters	29987 / 0 / 1859
<i>S</i> on <i>F</i> ²	0.965
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0708, 0.2030
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1095, 0.2196
Largest diff. peak and hole/e.Å ⁻³	2.661 and -3.278

^aExcluding solvate molecules

3.3.4 Synthesis and characterisation of a hexanuclear manganese complex

3.3.4.1 $(\text{H}_3\text{O})_4[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_4\text{-O})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2\{(\text{C}_6\text{H}_5)_3\text{CPO}_3\}_6]\text{Cl}_2 \cdot 2\text{CH}_3\text{CN} \cdot 4\text{H}_2\text{O}$ (**16**)

Compound **16**, $(\text{H}_3\text{O})_4[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_4\text{-O})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2\{(\text{C}_6\text{H}_5)_3\text{CPO}_3\}_6]\text{Cl}_2 \cdot 2\text{CH}_3\text{CN} \cdot 4\text{H}_2\text{O}$, (Figure 3.72) was prepared by a comproportionation reaction between $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 , using triphenylmethylphosphonic acid as a stabilising ligand and triethylamine as an organic base. The reaction mixture was stirred for five hours, filtered and kept undisturbed at 25 °C for slow evaporation of the solvent. Rectangular red-brown crystals of **16** separated from the reaction mixture within a time period of five days. These were characterised by single crystal X-ray diffraction measurements.

16 crystallises in the monoclinic crystal system in the space group $C2/c$. This compound contains a mixed-valent, hexanuclear manganese cluster in which the six Mn ions are arranged to form two edge-sharing tetrahedra, with a $\mu_4\text{-O}^{2-}$ ion at the center of each tetrahedron (Figure 3.73). The symmetry of the cluster core is characterised by an inversion centre located at the mid-point of the common edge of the two tetrahedra.

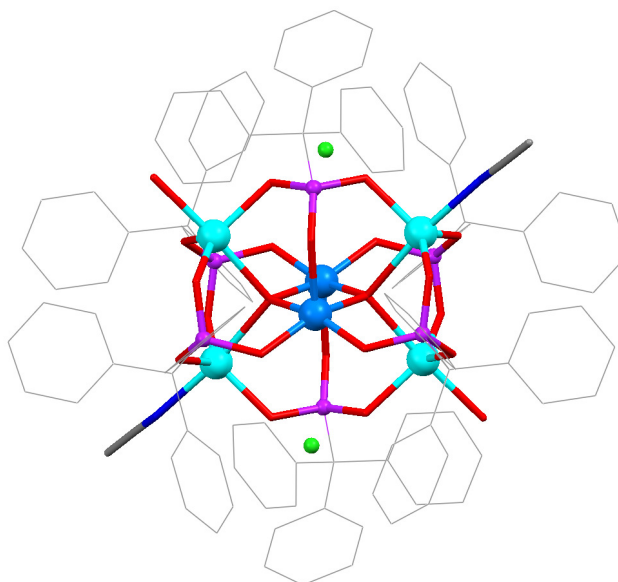


Figure 3.72 – Crystal structure of the hexanuclear manganese complex in **16**. Colour code: Mn^{III} blue, Mn^{II} cyan, P purple, O red, C grey, N dark blue, Cl green (hydrogen atoms have been omitted for clarity).

The resultant $\{\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2\}^{10+}$ core structure is related to previously reported coordination clusters that are stabilised by carboxylate ligands.⁵⁸⁻⁶⁴ However, in **16**, the

two edge-sharing tetrahedra are further connected by six fully deprotonated phosphonate ligands, that bridge between three Mn atoms in a $\eta^1:\eta^1:\eta^1:\mu_3$ bridging mode. The cluster is further stabilised by two CH₃CN and two H₂O molecules that complete the trigonal bipyramidal environments of the four peripheral Mn^{II} ions (Mn(3) – O(6) bond length 2.250(4) Å and Mn(2) – N(1) bond length 2.312(5) Å). The $\mu_4\text{-O}^{2-}$ oxo ligand and its symmetry equivalent are situated in *trans* positions to the H₂O/CH₃CN ligands giving rise to Mn(2) – O(3) and Mn(3) – O(3) distances of 2.347(3) Å and 2.319(4) Å, respectively. The remaining coordination sites of the trigonal bipyramidal coordination environments of these outer Mn centres, Mn(2), Mn(3) and symmetry equivalents, are occupied by three phosphonate O donors. The resulting Mn – O distances range between 2.034(4) Å – 2.073(4) Å.

The two central Mn ions, Mn(1) and Mn(1'), adopt square pyramidal coordination environments, with the polyhedra facing in opposite directions with respect to each other. The square pyramidal polyhedra consist of two $\mu_4\text{-O}^{2-}$ oxo ligands (Mn(1) – O(3) and Mn(1) – O(3') distances 1.896(3) Å and 1.880(3) Å, respectively), and three phosphonate O donors (Mn – O distances range between 1.952(3) Å – 2.143(4) Å).

Bond valence sum analysis (Table 3.28) confirms that the two Mn ions Mn(1) and Mn(1') are in the oxidation state +III. The remaining four Mn ions are in the oxidation state +II. The short Mn(1) ... Mn(1') contact of 2.7950(16) Å is in agreement with the assigned +III oxidation state of the Mn ions, and compares well with bond distances observed in structurally related compounds [Mn₆O₂(O₂CPh)₁₀(py)₂(MeCN)₂]·2MeCN (2.820(3) Å), [Mn₆O₂(O₂CPh)₁₀(4hmpH)₃(MeCN)] (2.817(19) Å) and [Mn₆O₂(O₂CPh)₁₀(pym)₂(MeCN)₂] (2.823(3) Å) previously reported in the literature.^{58, 59}

16 is further stabilised by two symmetry equivalent chloride counterions that reside in the vicinity of the cluster core. Four H₃O⁺ ions were assigned in order to balance the overall charge of the cluster. Hydronium counterions have previously been reported to stabilise related Mn coordination clusters, e.g. in {(H₃O)₂[Mn₄-(4-Haba)₂(4-aba)₆(SCN)₄(H₂O)₂]} (4-Haba = 4-aminobenzoic acid), (H₃O)[Na₂Mn^{III}₆Mn^{II}₂($\mu_4\text{-O}$)₂($\mu_{1,1}\text{-N}_3$)₇($\mu_{1,3}\text{-N}_3$)(H₂L)₆Cl]·3H₂O, (H₃O)[Na₄Mn^{III}₁₂Mn^{II}₄($\mu_4\text{-O}$)₄($\mu_{1,1}\text{-N}_3$)₉($\mu_{1,1,3}\text{-N}_3$)₂(H₂L)₁₂(CH₃O)₄(H₂O)₄]·2ClO₄·2(CH₃OH)₂·4H₂O, (H₄L = 2-[(2-hydroxy-3-methoxyphenyl)methylene]amino}-2-(hydroxymethyl)-1,3-propanediol).^{65, 66}

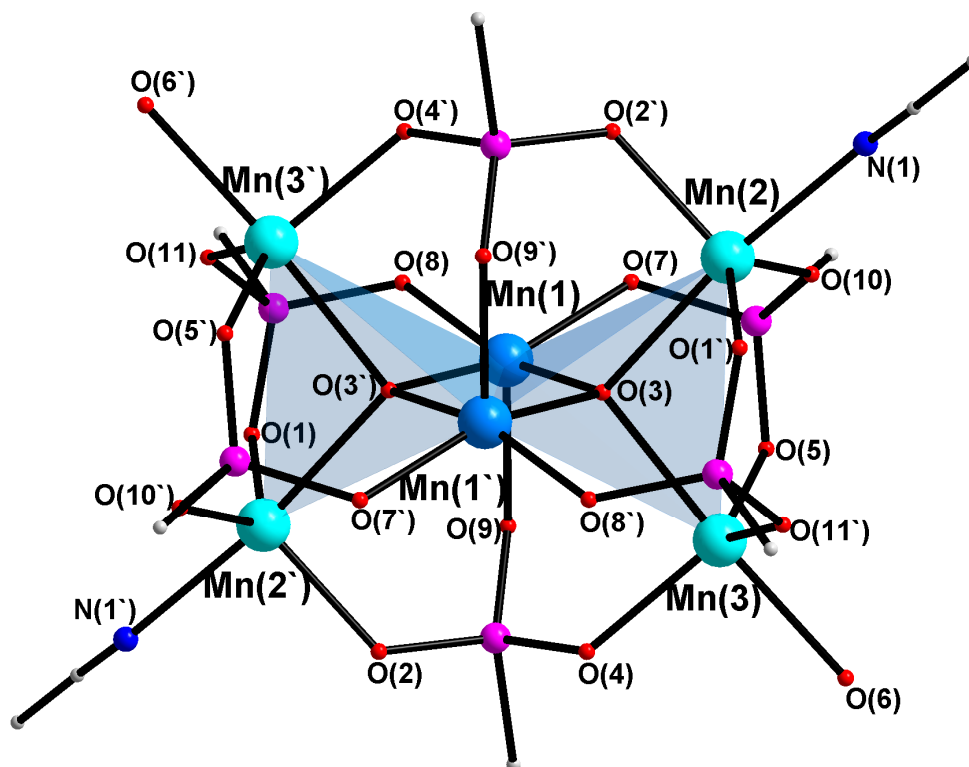


Figure 3.73 – Polyhedral representation of the {Mn₆} core structure in **16**. Colour code: Mn^{III} blue, Mn^{II} cyan, P purple, O red, C grey.

Table 3.28 – Selected bond lengths [Å] and bond valence sum (BVS) for compound **16**.

Atom	Bond	Bond distances (Å)	BVS	Assigned oxidation state
Mn(1)	Mn(1)-O(3')	1.880(3)	2.955	+3
	Mn(1)-O(3)	1.896(3)		
	Mn(1)-O(8)	1.952(4)		
	Mn(1)-O(7)	1.954(4)		
	Mn(1)-O(9)	2.143(4)		
Mn(2)	Mn(2)-O(2')	2.034(4)	1.971	+2
	Mn(2)-O(10)	2.037(4)		
	Mn(2)-O(1')	2.064(4)		
	Mn(2)-N(1)	2.312(5)		
	Mn(2)-O(3)	2.347(3)		
Mn(3)	Mn(3)-O(11')	2.048(4)	1.977	+2
	Mn(3)-O(4)	2.055(4)		
	Mn(3)-O(5)	2.073(4)		
	Mn(3)-O(6)	2.250(4)		
	Mn(3)-O(3)	2.319(4)		
Mn(1) ... Mn(1')		2.7950(16)		

The $\{\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2\}^{10+}$ core structure in **16** can alternatively be described as consisting of two triangular units with Mn(1), Mn(2) and Mn(3), and Mn(1'), Mn(2') and Mn(3') as vertices (Mn(1) $\cdots$ Mn(2), Mn(2) $\cdots$ Mn(3) and Mn(3) $\cdots$ Mn(1) are 3.499(55) Å, 3.664(3) Å and 3.598(2) Å, respectively). These triangular units are connected to each other by four phosphonate ligands and two $\mu_4\text{-O}^{2-}$ ions.

The crystal structure of **16** is stabilized by weak intermolecular hydrogen bonds and π - π interactions, resulting in a grid-like packing arrangement that can be seen in the direction of the crystallographic *b*-axis. A number of hydrogen bonds involve the two coordinated H_2O molecules of the Mn cluster and the N atoms of the CH_3CN solvent molecules (O(6) – N(2) distance 2.764(31) Å).

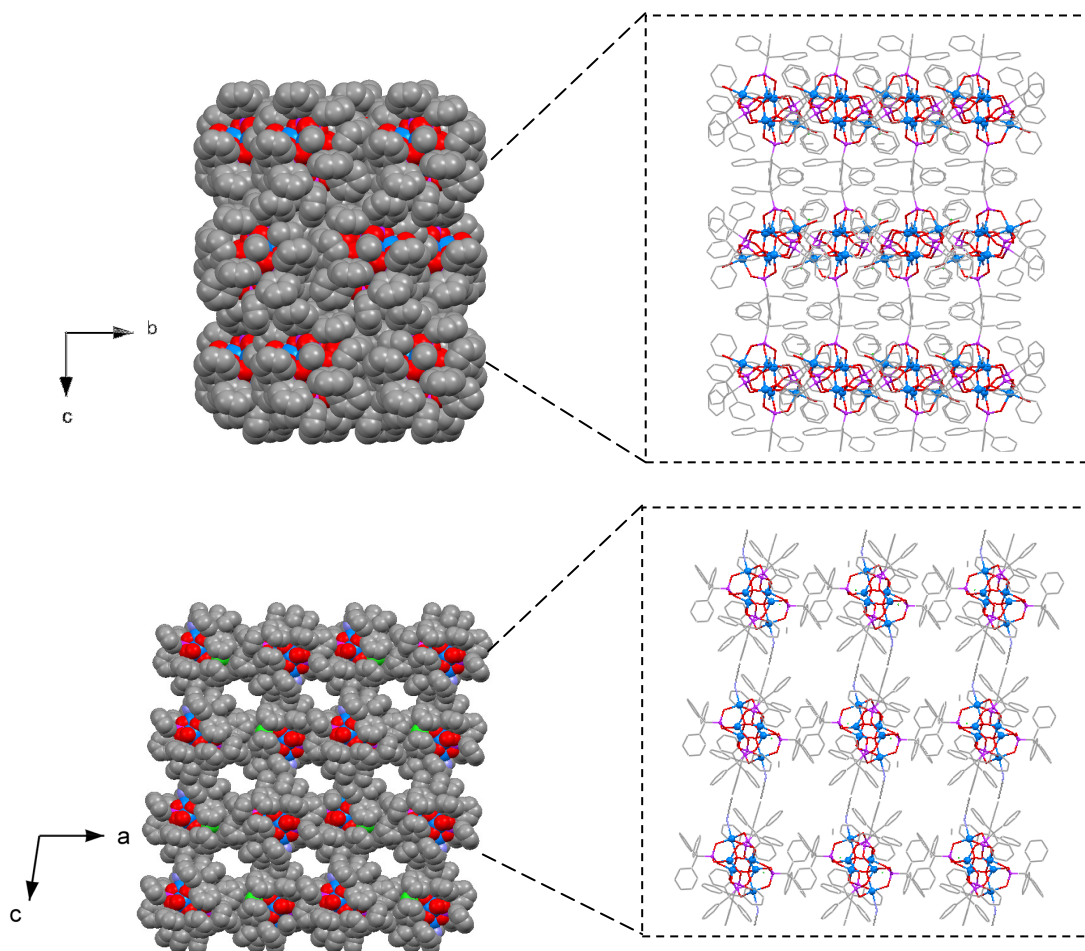


Figure 3.74 – Packing arrangement of the hexanuclear manganese clusters in **16** viewed in the direction of the crystallographic *a*- and *b*-axis. Colour code: Mn blue, P purple, O red, C grey, Cl green, (crystallization solvent molecules and hydrogen atoms have been omitted for clarity).

- PHYSICOCHEMICAL CHARACTERISATION

- FT-IR spectroscopy

The IR spectrum of **16** presented in Figure 3.75 displays some characteristic bands of the aromatic rings of the phosphoate ligands, such as C–C skeletal vibrations ($1600 - 1400\text{ cm}^{-1}$) and C–H out-of-plane bending vibrations ($900 - 650\text{ cm}^{-1}$). Different P–O stretching vibrations of the phosphonate groups can be observed in the range $1200 - 900\text{ cm}^{-1}$, while the corresponding O–H stretching vibrations and H–O–H bending vibrations of the crystallization water molecules engaged in H-bonds appear as broad bands at *ca.* 3200 cm^{-1} and *ca.* 1600 cm^{-1} , respectively.³⁶⁻⁴⁰

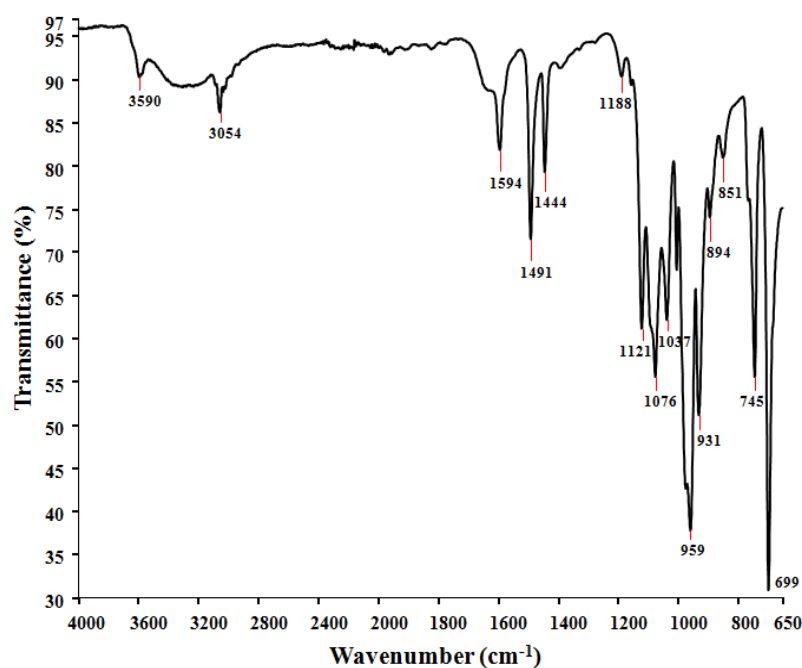


Figure 3.75 – Infrared spectrum of **16**.

- *Thermogravimetric analysis*

The thermal stability of the compound in an N₂ atmosphere in the temperature range 30 – 900 °C was investigated using a freshly prepared crystalline sample of **16** (Figure 3.76). The compound exhibits a weight loss of 6.3 % in the temperature range between 30 – 150 °C that can be attributed to the loss of two crystallization CH₃CN molecules and four crystallization H₂O molecules (calcd: 5.7 %). A further temperature increase results in a gradual weight loss of 4.8 % between 150 – 280 °C, which could be associated with the loss of two coordinated CH₃CN molecules and two coordinated H₂O molecules (calcd: 4.4 %). Between 280 – 600 °C the oxidative degradation of the organic ligands takes place and further thermolysis processes result in the cluster degradation.

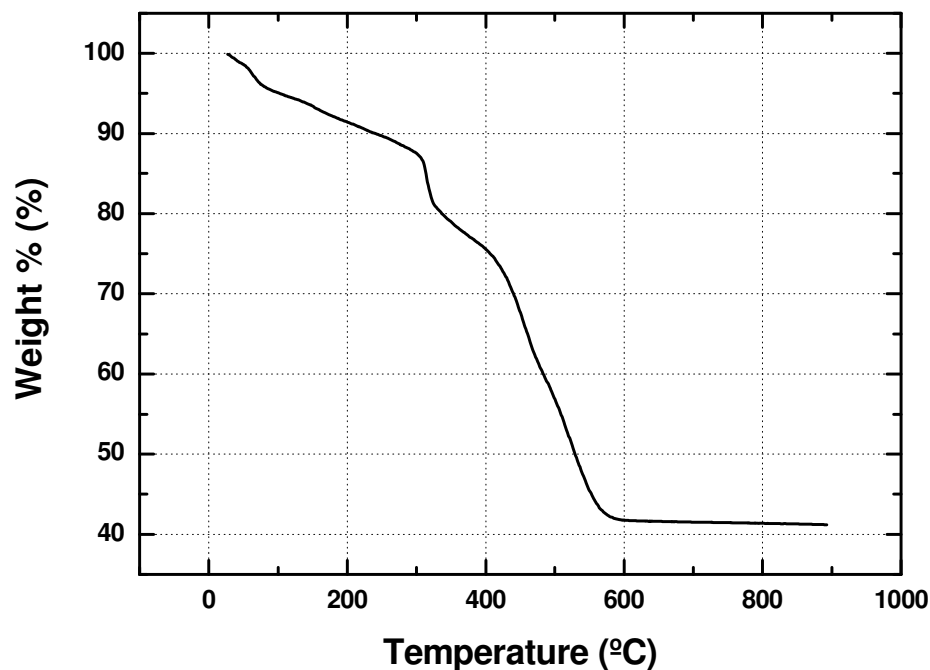


Figure 3.76 – Thermogravimetric analysis of **16**.

- *Magnetism*

The magnetic studies for compound **16** were carried out on a polycrystalline sample at high magnetic field strengths and low temperatures. The temperature dependence of the χT product (Figure 3.77) reveals dominant AF interactions between the spin centres; a Curie-Weiss fit was applied to analyse the data. The Curie constant of $23.2 \text{ cm}^3 \text{ K mol}^{-1}$ is comparable to the expected value of $23.5 \text{ cm}^3 \text{ K mol}^{-1}$ of two $S = 2 \text{ Mn}^{\text{III}}$ and four $S = 5/2 \text{ Mn}^{\text{II}}$ spin carriers ($C = \frac{Ng^2\mu_B^2}{3k_B} S(S+1)$ with $\frac{N\mu_B^2}{3k_B} = 0.12505 \text{ cm}^3 \text{ K mol}^{-1}$ and $g = 2$).⁴¹ The extrapolation of the χT vs T data at low temperature implies that the ground state of **16** is $S_T = 0$.

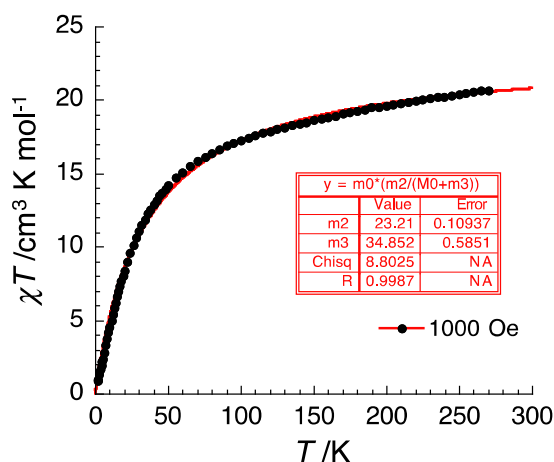


Figure 3.77 – Temperature dependence of the χT product of **16** at 0.1 T. The red solid line corresponds to the best fit of the experimental data with the Curie-Weiss law ($C = 23.2 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = 34 \text{ K}$).

- *Mass spectrometry*

The stability of the $\{\text{Mn}_6\}$ cluster in solution was investigated by electrospray ionisation mass spectrometry. A major isotopic envelop centered at $m/z = 2296.1$ a.m.u is observed in the ESI-MS spectrum of the pristine crystals dissolved in CH_3CN and DMF and it can be assigned to a $\{\text{HMn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$ species. The corresponding doubly charged species could also be identified in the ESI-MS spectrum of the pristine crystals dissolved in CH_3CN ($m/z = 1147.4$, $\{\text{H}_2\text{Mn}^{\text{II}}_6\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^{2-}$). A summary of the ESI-MS signal assignment for compound **16** is presented in Table 3.29. The mass spectrum of **16** dissolved in DMSO does not show any signals in the high molecular mass region, suggesting that **16** is not stable in DMSO.

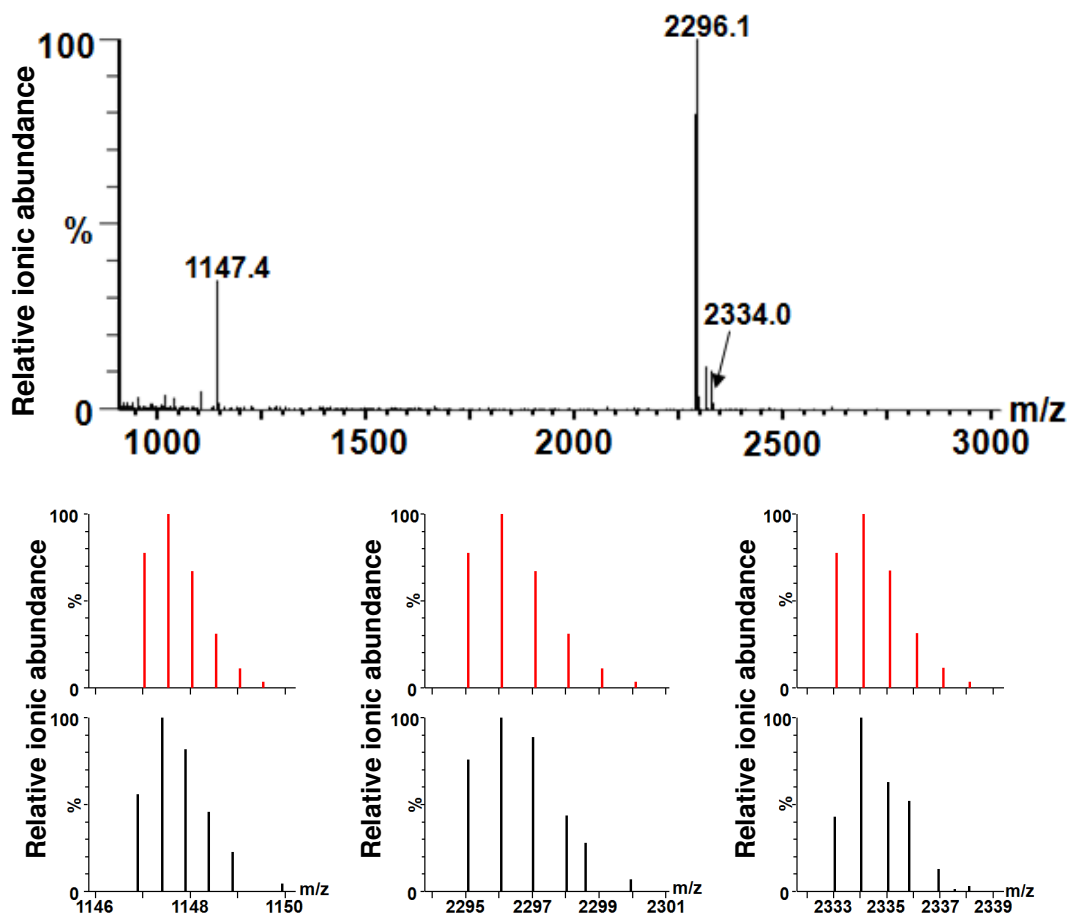


Figure 3.78 – Negative-mode ESI-MS spectra for crystals of **16** dissolved in CH_3CN . Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_2\text{Mn}^{\text{II}}_6\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^{2-}$ centered at $m/z = 1147.4$ a.m.u., $\{\text{HMn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$ centered at $m/z = 2296.1$ a.m.u. and $\{\text{H}_7\text{Mn}^{\text{II}}_6\text{O}_4[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$ centered at $m/z = 2334.0$ a.m.u., (cone voltage: 30 V).

Table 3.29 – ESI-MS assignment for compound **16**.

Solvent		m/z	Species attributed	
Crystals of 16 in:	CH ₃ CN	1147.4	$\{\text{H}_2\text{Mn}^{\text{II}}_6\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^{2-}$	$\rightarrow \{\text{Mn}_6\}$
		2296.1	$\{\text{HMn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$	$\rightarrow \{\text{Mn}_6\}$
		2334.0	$\{\text{H}_7\text{Mn}^{\text{II}}_6\text{O}_4[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$	$\rightarrow \{\text{Mn}_6\}$
	DMF	2296.1	$\{\text{HMn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$	$\rightarrow \{\text{Mn}_6\}$

- *UV-Vis spectroscopy*

The UV-Vis absorption spectrum of **16** recorded in CH₃CN is presented in Figure 3.79. The intense absorption band observed at *ca.* 263 nm ($\epsilon = 87000 \text{ L mol}^{-1} \text{ cm}^{-1}$) can be attributed to $\pi - \pi^*$ transitions of the phosphonate ligands, while the weak band observed at *ca.* 487 nm ($\epsilon = 900 \text{ L mol}^{-1} \text{ cm}^{-1}$) involves d – d transitions.⁴⁹⁻⁵²

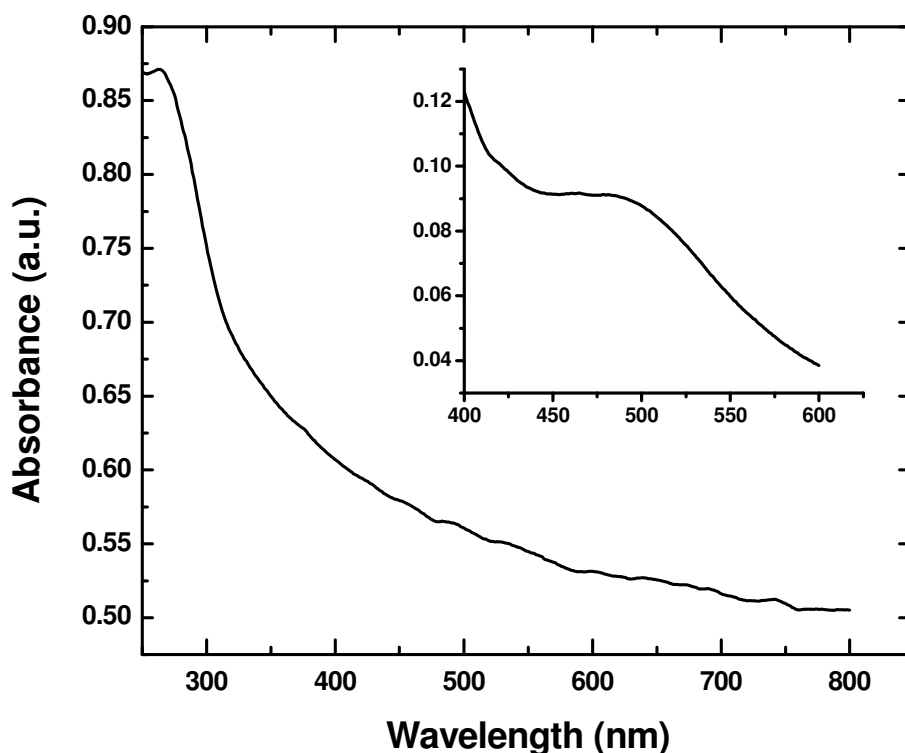


Figure 3.79 – UV-Vis spectrum of a 10^{-5} M solution of **16** in CH₃CN. Inset: A section of the UV-Vis spectrum of a 10^{-4} M solution of **16** in CH₃CN.

Table 3.30 – Crystal data and structural refinement parameters for 16.

Compound 16	
Empirical formula ^a	C ₁₁₈ H ₁₁₂ Cl ₂ Mn ₆ N ₂ O ₂₆ P ₆
Molecular mass/g mol ⁻¹ ^a	2560.52
Crystal colour/shape	Red brown / rectangular block
Crystal size/mm ³	0.60×0.20×0.10
Crystal system	Monoclinic
Space group	<i>C</i> 2/c
<i>a</i> / Å	31.374(6)
<i>b</i> / Å	14.709(3)
<i>c</i> / Å	28.425(6)
α /°	90
β /°	93.46(3)
γ /°	90
<i>V</i> / Å ³	13094(5)
<i>Z</i>	1
Temperature (K)	150(2)
Density/Mg m ⁻³	1.336
Absorp. coef./mm ⁻¹	0.743
<i>F</i> (000)	5385
$2\theta_{\text{max}}$ /°	50
Reflections collected	49746
Independent reflections	11477 [R(int)=0.0473]
Data / restraints / parameters	11477/ 0 / 743
<i>S</i> on <i>F</i> ²	1.081
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0804, 0.2205
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0832, 0.2233
Largest diff. peak and hole/e.Å ⁻³	1.834 and -0.714

^aExcluding solvate molecules

3.4 ESI-MS STUDIES OF COMPLEX REACTION MIXTURES TO INVESTIGATE THE FORMATION OF POLYNUCLEAR MANGANESE COORDINATION COMPLEXES

3.4.1 Investigation of the reaction system that led to the formation of the {Mn₁₅} complex in **10**

The comproportionation reaction between MnCl₂·4H₂O and KMnO₄, in MeOH, in the presence of phenylphosphonic acid resulted in a deep brown solution, from which red-brown crystals of **10**, [Mn^{III}₁₅(μ₂-H₂O)₂(CH₃OH)₁₆(C₆H₅PO₃)₂₀]Cl₅·22CH₃OH·8H₂O, separate within a time period of approximately one week (Figure 3.80).

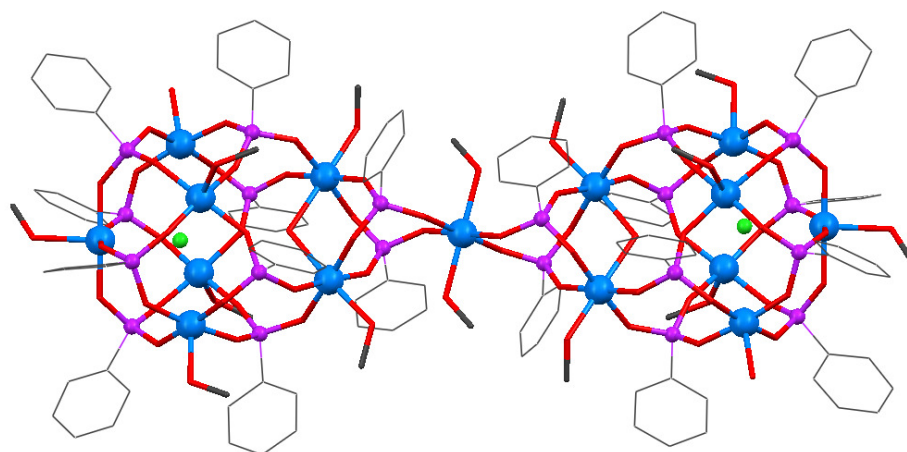


Figure 3.80 – Crystal structure of the pentadecanuclear manganese complex in **10**. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green (hydrogen atoms have been omitted for clarity).

The initial reaction mixture was examined by ESI-MS and a rather complex mass spectrum was obtained (Figure 3.82). The spectrum revealed to be very interesting as three different species, {Mn₇}, {Mn₈} and {Mn₁₃}, could be identified in the high molecular mass region of the spectrum (Table 3.31).

The most intense signal in the high molecular mass region of the spectrum is centered at $m/z = 1684.3$ a.m.u. and corresponds to a {Mn₇} species, {H₁₇[Mn^{IV}₆Mn^{III}O₁₅(C₆H₅PO₃)₆]Cl₃}⁻. The signals centered at $m/z = 1016.7$ a.m.u. and $m/z = 2034.3$ a.m.u. can be attributed to a {Mn₈} species, the {H₅[Mn^{III}₈O₅(C₆H₅PO₃)₉]Cl₃}²⁻ and {H₄[Mn^{IV}₂Mn^{III}₆O₅(C₆H₅PO₃)₉]Cl₃}⁻, respectively. The fourth isotopic envelope that

can be assigned in the mass spectrum of the reaction mixture of **10** is centered at $m/z = 2122.0$ a.m.u. and corresponds to the formula of a tridecanuclear manganese complex, $\{H[Mn^{IV}_8Mn^{III}_5O_{15}(CH_3O)_4(C_6H_5PO_3)_6]Cl_3\}^-$. The $\{Mn_{15}\}$ complex itself could not be identified in the mass spectrum of the reaction mixture that led to the crystallisation of **10** as there is no signal present in the spectrum above 3000 a.m.u. The species could also not be identified in the low molecular mass region of the spectrum as this part of the spectrum contains crowded large number of signals due to fragmentation and arising from multiple charged species. All species identified in the mass spectrum were modelled and good fits between the experimental and simulated isotopic envelopes confirm the assignments (Figure 3.82).

Table 3.31 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **10**.

		m/z	Species attributed	
Reaction mixture of 10		1016.7	$\{H_5[Mn^{III}_8O_5(C_6H_5PO_3)_9]Cl_3\}^{2-}$	$\rightarrow \{Mn_8\}$
		1684.3	$\{H_{17}[Mn^{IV}_6Mn^{III}_6O_{15}(C_6H_5PO_3)_6]Cl_3\}^-$	$\rightarrow \{Mn_7\}$
		2034.3	$\{H_4[Mn^{IV}_2Mn^{III}_6O_5(C_6H_5PO_3)_9]Cl_3\}^-$	$\rightarrow \{Mn_8\}$
		2122.0	$\{H[Mn^{IV}_8Mn^{III}_5O_{15}(CH_3O)_4(C_6H_5PO_3)_6]Cl_3\}^-$	$\rightarrow \{Mn_{13}\}$

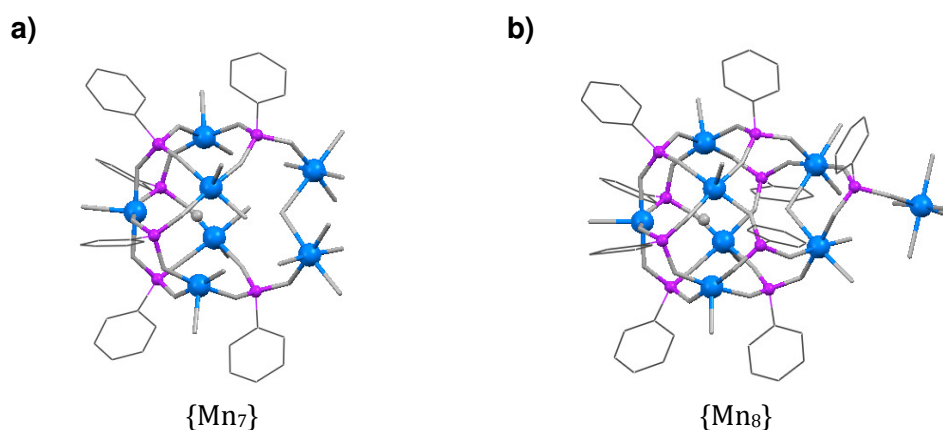


Figure 3.81 – Representation of structural motifs that agree with the constitutional assignment: (a) $\{Mn_7\}$ and (b) $\{Mn_8\}$ species identified in the mass spectrum of the reaction mixture that led to the crystallisation of **10**. Colour code: Mn blue, P purple, C grey, O and Cl light grey.

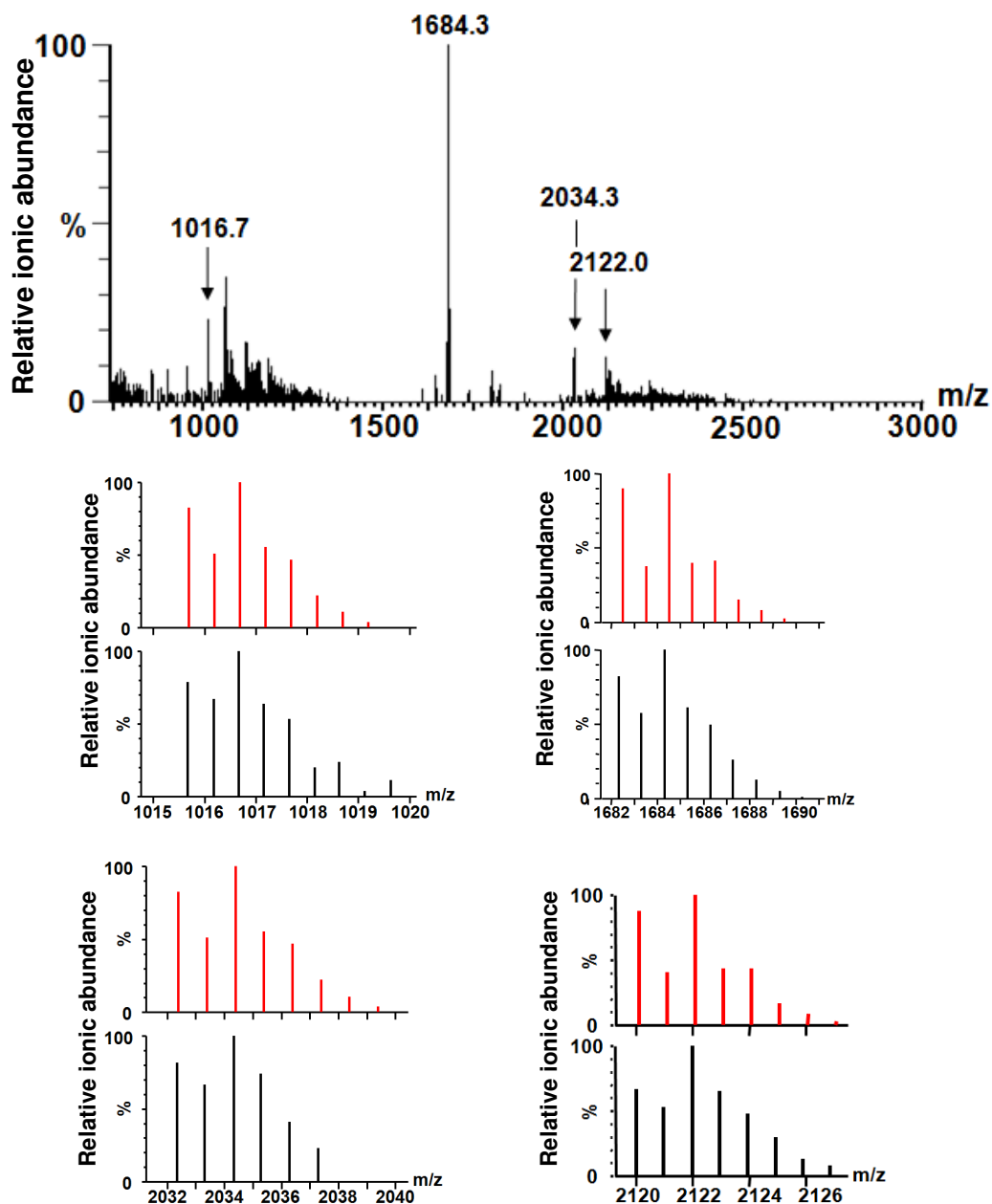


Figure 3.82 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **10** (24 h after preparation). Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_5[\text{Mn}^{\text{III}}_8\text{O}_5(\text{C}_6\text{H}_5\text{PO}_3)_9]\text{Cl}_3\}^{2-}$ centered at $m/z = 1016.7$ a.m.u., $\{\text{H}_{17}[\text{Mn}^{\text{IV}}_6\text{Mn}^{\text{III}}_{15}\text{O}_{15}(\text{C}_6\text{H}_5\text{PO}_3)_6]\text{Cl}_3\}^-$ centered at $m/z = 1684.3$ a.m.u., $\{\text{H}_4[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_6\text{O}_5(\text{C}_6\text{H}_5\text{PO}_3)_9]\text{Cl}_3\}^-$ centered at $m/z = 2034.3$ a.m.u. and $\{\text{H}[\text{Mn}^{\text{IV}}_8\text{Mn}^{\text{III}}_5\text{O}_{15}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{PO}_3)_6]\text{Cl}_3\}^-$ centered at $m/z = 2122.0$ a.m.u. (cone voltage: 30 V).

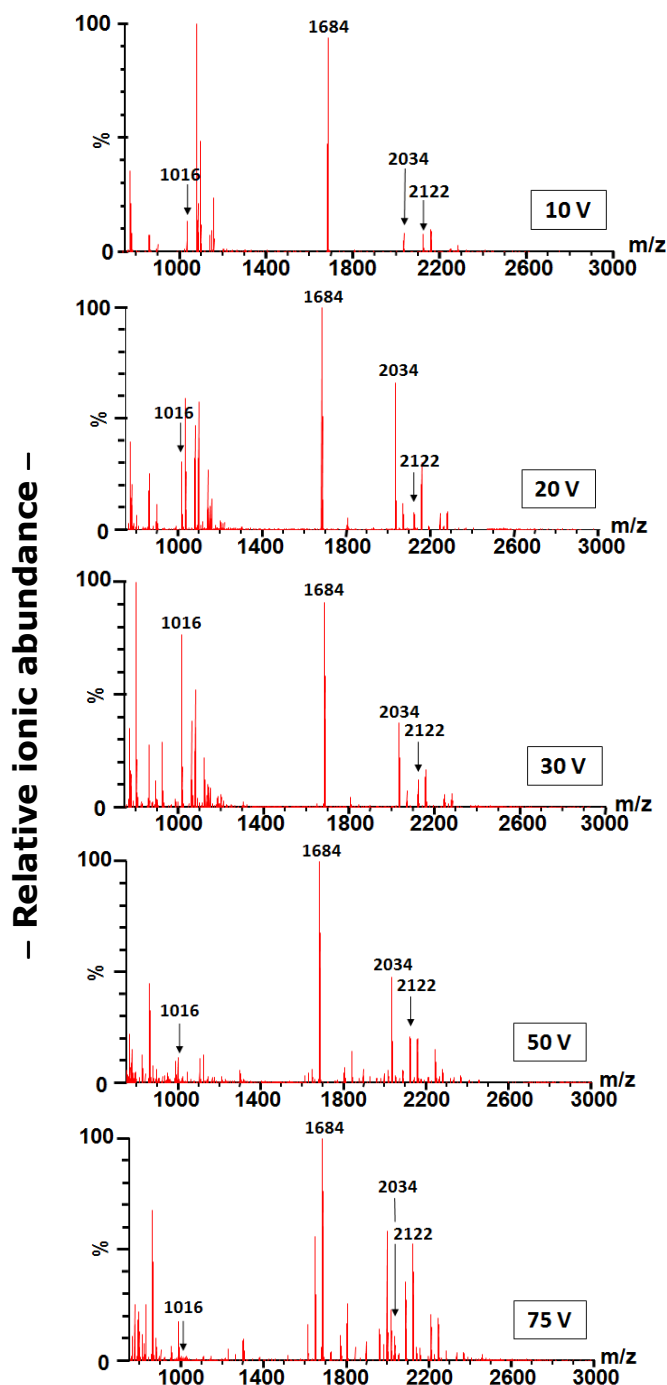


Figure 3.83 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **10** at different cone voltages: 10V, 20V, 30V, 50V and 75V, respectively.

In an effort to confirm that the assigned species coexist in solution and that they are not a result of a primary processes occurring in the spraying chamber, we set out to investigate the effect of cone voltage (CV) variations on the obtained ESI-MS spectrum (Figure 3.83). Usually the species observed in the gas phase are closely related to the actual species in solution, and lower CV values favour preservation of these species. In addition, it was observed in the literature that the ionic abundances of the fragment ions

produced in the gas phase grow with increasing CV values, while the abundance of the parent ions decreases with increasing CV values.^{67, 68}

The signal attributed to the {Mn₇} species in the mass spectrum of the reaction mixture that led to the crystallisation of **10** is independent on CV variations up to 75 V (Figure 3.83), and the relative ionic abundance of the species start to decrease in intensity at CV greater than 100 V. The signal attributed to the {Mn₈} species shows similar behaviour and the relative ionic abundance of this species starts to decrease in intensity at 75 V, due to the induced defragmentation processes. These suggests that {Mn₇}, and {Mn₈} species exist in solution, and we believe that these species represent building units of the pentadecanuclear manganese complex which crystallises out from this reaction mixture. The most probable structural arrangement for {Mn₇} and {Mn₈} species are represented in Figure 3.81. These structural motifs that agree with the constitutional assignment correspond to subunits of the {Mn₁₅} cluster, and are further supported by the experimental observation of the same {Mn₇} species in the mass spectra of pristine crystals of **10** dissolved in CH₃CN, DMF and DMSO. As earlier mentioned in section 3.3.1 of this chapter the {Mn₁₅} cluster is not stable in solution and break into two {Mn₇} units as a consequence of the labile methanol groups from the JT sites of the central Mn(8) ion, (see section 3.3.1, Figure 3.3).

Another remarkable feature observed in the mass spectrum of the reaction mixture of **10** are signals that are undoubtedly attributable to a {Mn₁₃} species. Surprisingly CV variations experiments show that the ionic abundance of this species increases when CV values were increased from 10 to 75 V. This behaviour suggests that this species could indeed form in the spraying chamber and may not be structurally related to the {Mn₁₅} structure in **10**. Alternatively, it could be related to the {Mn₁₃} clusters that crystallise from other reaction mixtures, such those of compounds **11**, **12** and **13**. Considerable fragmentation can be observed at higher cone voltages. The {Mn₇}, {Mn₈} and {Mn₁₃} species cannot be identified at CV greater than 150 V, suggesting that the species no longer retain their integrity under these harsh ionisation conditions.

3.4.2 Investigation of the reaction system that led to the formation of {Mn₁₃} complexes observed in 11-13

Using a similar synthetic procedure as for **10** and adding pyridine as an organic base, a dark brown solution was obtained. The ESI-MS spectrum of this reaction mixture is much simpler (Figure 3.85) than the original mixture that led to the crystallisation of **10**. It reveals the presence of only one major isotopic envelope in the high mass region centered at $m/z = 2594.0$ a.m.u. This signal was assigned to the phenylphosphonic acid-stabilised $\{H_2[Mn^{IV}_4Mn^{III}_9O_{11}(C_6H_5PO_3)_{10}]Cl_4\}^-$ species, which corresponds to the tridecanuclear manganese complex characterised in **11**, $[Mn^{III}_{13}(\mu_4-O)_2(\mu_3-O)_4(\mu_2-OH)_2(\mu_2-CH_3O)_4(C_6H_5PO_3)_{10}(C_5H_5N)_5Cl] \cdot 3H_2O$, that indeed crystallizes out from this reaction mixture (Table 3.32).

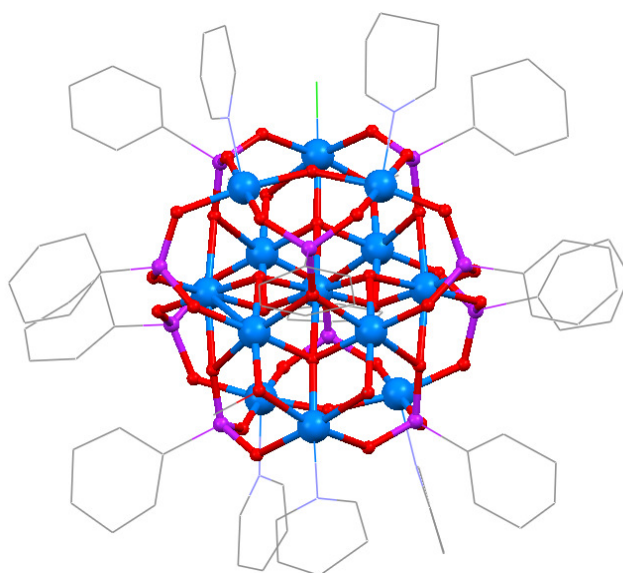


Figure 3.84 – Crystal structure of the tridecanuclear manganese complex in **11**. Colour code: Mn^{III} blue, P purple, O red, Cl green, C grey (hydrogen atoms have been omitted for clarity).

Table 3.32 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **11**.

	m/z	Species attributed	
Reaction mixture of 11	2594.0	$\{H_2[Mn^{IV}_4Mn^{III}_9O_{11}(C_6H_5PO_3)_{10}]Cl_4\}^-$	$\rightarrow \{Mn_{13}\}$

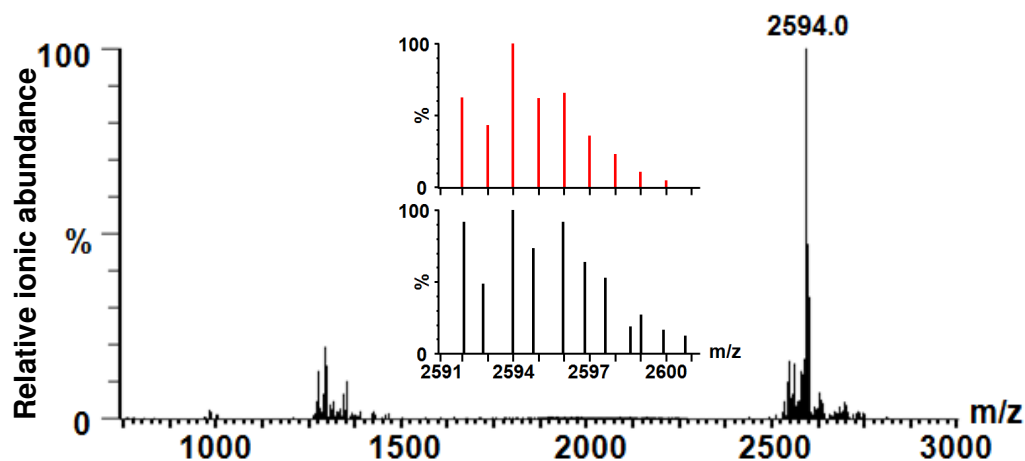


Figure 3.85 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **11** (24 h after preparation). Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{H_2[Mn^{IV}_4Mn^{III}_9O_{11}(C_6H_5PO_3)_{10}]Cl_4\}^-$ centered at $m/z = 2594.0$ a.m.u. (cone voltage: 30 V).

The ESI-MS technique proved to be very efficient in identifying new polynuclear manganese species that form under certain conditions in the reaction mixture, and therefore we decided to exploit the analytic screening technique further and investigate the influence of different ligands on the formation of manganese coordination clusters.

When benzylphosphonic acid was used instead of phenylphosphonic acid under the same reaction conditions that led to **11**, we obtained a reaction mixture from which compound **12**, $[Mn^{III}_{13}(\mu_4-O)_2(\mu_3-O)_4(\mu_2-OH)_2(\mu_2-CH_3O)_4(C_6H_5CH_2PO_3)_{10}(C_5H_5N)_6]Cl \cdot 5H_2O$ separates over a time period of four days.

Table 3.33 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **12**.

	<i>m/z</i>	Species attributed
Reaction mixture of 12	1086.6	$\{H_2[Mn^{IV}_2Mn^{III}_{11}O_{13}(CH_3O)_4(C_6H_5CH_2PO_3)_6]Cl_3\}^{2-} \rightarrow \{Mn_{13}\}$
	1348.6	$\{H[Mn^{IV}_2Mn^{III}_{11}O_{10}(CH_3O)_4(C_6H_5CH_2PO_3)_{10}]\}^{2-} \rightarrow \{Mn_{13}\}$
	2138.3	$\{H_9[Mn^{IV}_2Mn^{III}_{11}O_{18}(C_6H_5CH_2PO_3)_6]Cl_3\}^- \rightarrow \{Mn_{13}\}$
	2212.3	$\{H_7[Mn^{IV}_2Mn^{III}_{11}O_{15}(CH_3O)_4(C_6H_5CH_2PO_3)_6]Cl_3\}^- \rightarrow \{Mn_{13}\}$
	2699.1	$\{H[Mn^{IV}_3Mn^{III}_{10}O_{10}(CH_3O)_4(C_6H_5CH_2PO_3)_{10}]\}^- \rightarrow \{Mn_{13}\}$

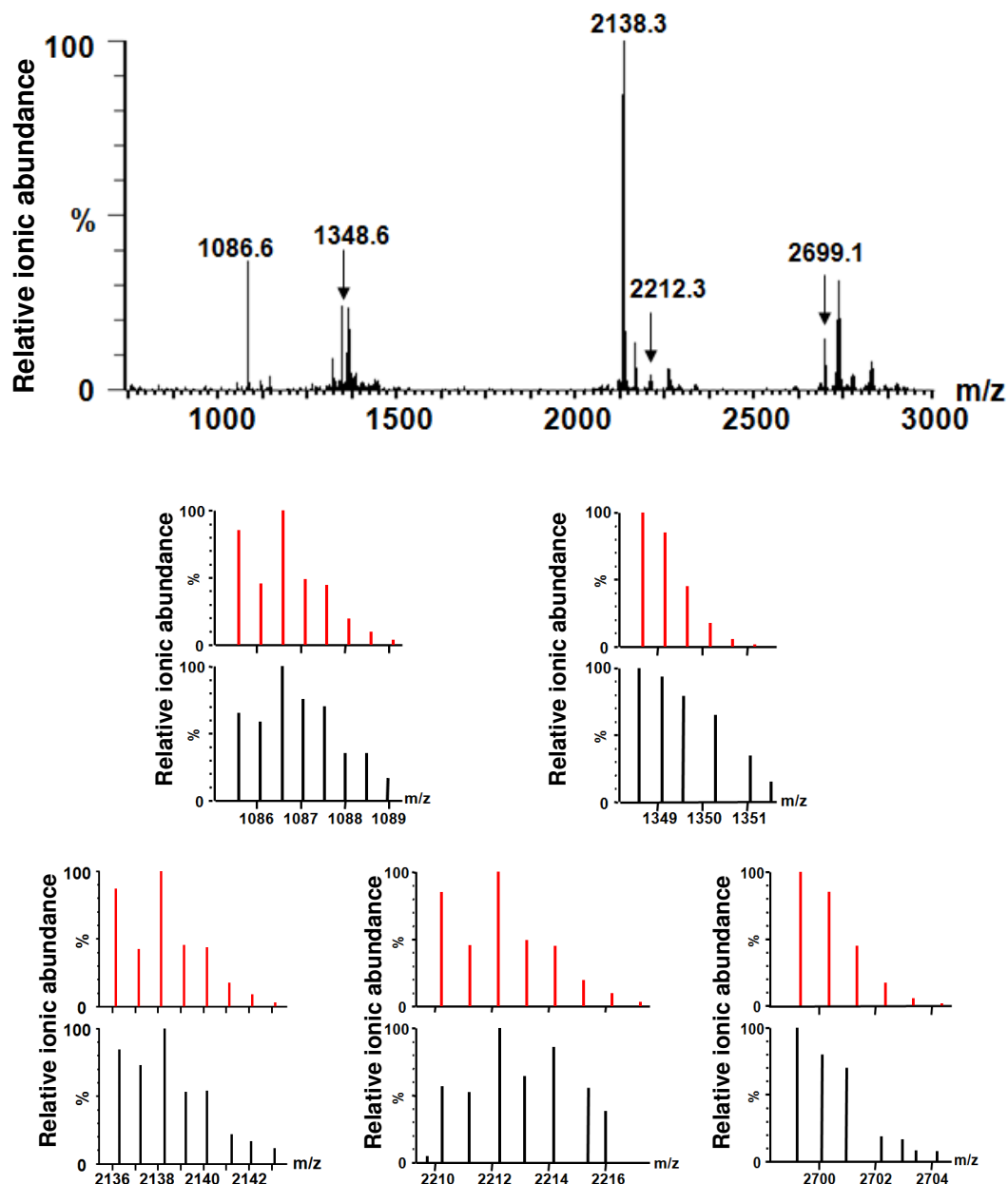


Figure 3.86 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **12** (24 h after preparation). Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{H_2[Mn^{IV}_2Mn^{III}_{11}O_{13}(CH_3O)_4(C_6H_5CH_2PO_3)_6]Cl_3\}^{2-}$ centered at $m/z = 1086.6$ a.m.u., $\{H[Mn^{IV}_2Mn^{III}_{11}O_{10}(CH_3O)_4(C_6H_5CH_2PO_3)_{10}]\}^{2-}$ centered at $m/z = 1348.6$ a.m.u., $\{H_9[Mn^{IV}_2Mn^{III}_{11}O_{18}(C_6H_5CH_2PO_3)_6]Cl_3\}^-$ centered at $m/z = 2138.3$ a.m.u., $\{H_7[Mn^{IV}_2Mn^{III}_{11}O_{15}(CH_3O)_4(C_6H_5CH_2PO_3)_6]Cl_3\}^-$ centered at $m/z = 2212.3$ a.m.u. and $\{H[Mn^{IV}_3Mn^{III}_{10}O_{10}(CH_3O)_4(C_6H_5CH_2PO_3)_{10}]\}^-$ centered at $m/z = 2699.1$ a.m.u. (cone voltage: 30 V).

The ESI-MS spectrum of this reaction mixture is presented in Figure 3.86 showing an intense peak centered at $m/z = 2138.3$ a.m.u. which corresponds to the parent $\{H_9[Mn^{IV}_2Mn^{III}_{11}O_{18}(C_6H_5CH_2PO_3)_6]Cl_3\}^-$ species. Two other singly charged and two other doubly charged $\{Mn_{13}\}$ species stabilized by a different number of phosphonate ligands, water molecules and chloride ions could be identified in the high mass region of the spectrum (Table 3.33). We successfully simulated the isotopic envelopes for these

identified species and good fits between experimental and theoretical data further substantiate our assignments (Figure 3.86).

The same reaction conditions as for **12** but replacing the pyridine ligands with 4-(3-phenylpropyl)pyridine gave a dark brown solution from which compound **13**, $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_6\text{H}_5\text{-C}_3\text{H}_6\text{-C}_5\text{H}_4\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$, was obtained. The mass spectrum of this reaction mixture recorded in negative mode is simple (Figure 3.87). It reveals the presence of an intense signal corresponding to a singly charged $\{\text{Mn}_{13}\}$ species and a much lower intensity signal arising from a doubly charged species. The ESI-MS peak assignment for the reaction mixture of **13** is presented in Table 3.34.

Table 3.34 – ESI-MS assignment for the reaction mixture that led to the crystallisation of 13.

	<i>m/z</i>	Species attributed
Reaction mixture of 13	1086.6	$\{\text{H}_2[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_{11}\text{O}_{13}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Cl}_3\}^{2-} \rightarrow \{\text{Mn}_{13}\}$
	2138.3	$\{\text{H}_9[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_{11}\text{O}_{18}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Cl}_3\}^- \rightarrow \{\text{Mn}_{13}\}$

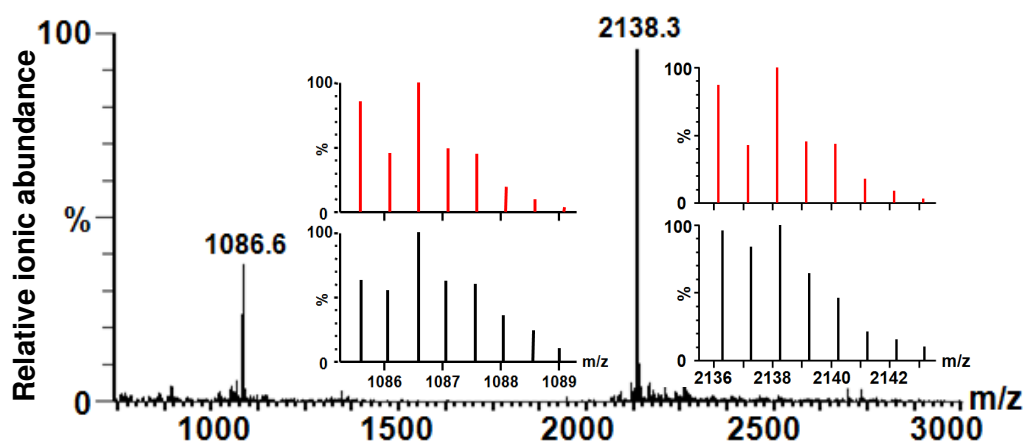


Figure 3.87 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **13** (24 h after preparation). Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}_2[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_{11}\text{O}_{13}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Cl}_3\}^{2-}$ centered at $m/z = 1086.6$ a.m.u. and $\{\text{H}_9[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}_{11}\text{O}_{18}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Cl}_3\}^-$ centered at $m/z = 2138.3$ a.m.u. (cone voltage: 30 V).

3.4.3 Investigation of the reaction system that led to the formation of {Mn₁₂} complexes observed in 14-15

Preliminary studies on the coordination clusters **11** – **13** demonstrate that the ligands in apical position of the Mn^{III} Jahn Teller sites are labile and can be successively replaced. This observation prompted us to explore if the tridecanuclear manganese clusters could be connected using bifunctional pyridine ligands. Therefore, 4,4'-bipyridine was employed as an organic base in a similar reaction to that used for the synthesis of the tridecanuclear manganese complexes. However, this approach did not result in the linkage of the tridecanuclear manganese clusters. However, under these conditions a {Mn₁₂} coordination cluster was obtained instead. The ESI-MS spectrum of the reaction mixture that led to the crystallisation of **14**, K(H₂O)₄[Mn^{III}₁₂(μ₃-O)₆(CH₃OH)₆(C₆H₅CH₂PO₃H)₇(C₆H₅CH₂PO₃)₈]Cl₂·3CH₃OH·4H₂O (Figure 3.88), is relatively simple. Nevertheless, the resulting spectrum is interesting, as we were able to identify three different species that exist in the same reaction mixture: a {Mn₇}, a {Mn₁₂} and a {Mn₁₃} species (Table 3.35, Figure 3.89).

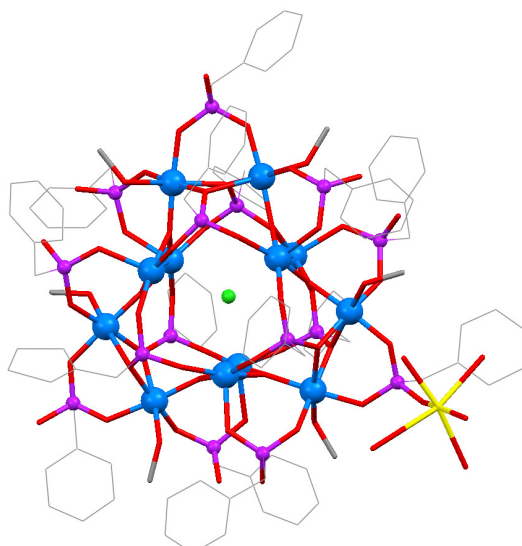


Figure 3.88 – Crystal structure of the dodecanuclear manganese complex in **14**. Colour code: Mn^{III} blue, P purple, O red, C grey, Cl green, K yellow (hydrogen atoms have been omitted for clarity).

The most intense isotopic envelope in the high molecular mass region of the spectrum is centered at $m/z = 1796.4$ a.m.u. and corresponds to the {Mn₇} species {H₂₉[Mn^{III}₃Mn^{II}₄O₁₆(C₆H₅CH₂PO₃)₆]Cl₃}⁻. Two other significantly less intensive signals centered at $m/z = 915.7$ a.m.u. and $m/z = 1920.1$ a.m.u. could be observed in the high molecular mass region of the spectrum. These signals were attributed to a {Mn₁₂} species,

$\{H_6[Mn^{III}_4Mn^{II}_8O_{11}(C_6H_5CH_2PO_3)_5]Cl_4\}^{2-}$ and a $\{Mn_{13}\}$ species, $\{H_6[Mn^{III}_7Mn^{II}_6O_{13}(C_6H_5CH_2PO_3)_5]Cl_4\}^-$, respectively. The former species relates to the cluster of **14** that crystallises under these conditions, the latter is expected to be related to the cluster core structures of **11-13**.

Table 3.35 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **14**.

	m/z	Species attributed
Reaction mixture of 14	915.7	$\{H_6[Mn^{III}_4Mn^{II}_8O_{11}(C_6H_5CH_2PO_3)_5]Cl_4\}^{2-} \rightarrow \{Mn_{12}\}$
	1796.4	$\{H_{29}[Mn^{III}_3Mn^{II}_4O_{16}(C_6H_5CH_2PO_3)_6]Cl_3\}^- \rightarrow \{Mn_7\}$
	1920.1	$\{H_6[Mn^{III}_7Mn^{II}_6O_{13}(C_6H_5CH_2PO_3)_5]Cl_4\}^- \rightarrow \{Mn_{13}\}$

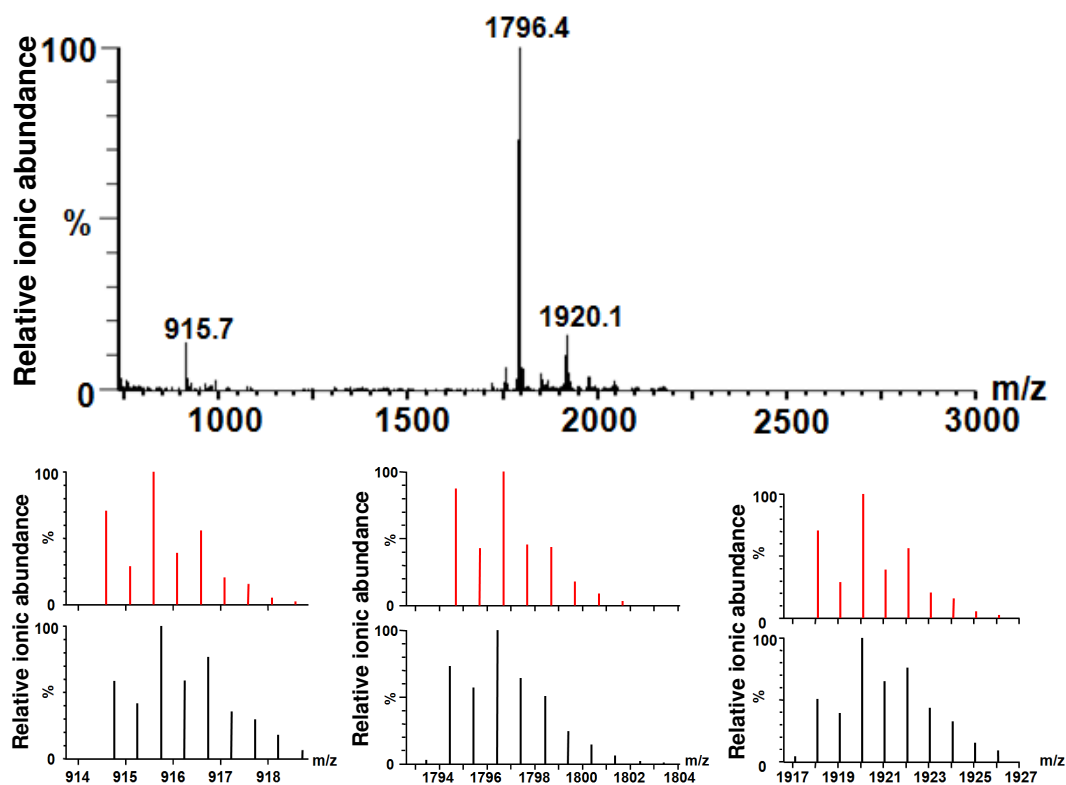


Figure 3.89 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **14** (24 h after preparation). Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{H_6[Mn^{III}_4Mn^{II}_8O_{11}(C_6H_5CH_2PO_3)_5]Cl_4\}^{2-}$ centered at $m/z = 915.7$ a.m.u., $\{H_{29}[Mn^{III}_3Mn^{II}_4O_{16}(C_6H_5CH_2PO_3)_6]Cl_3\}^-$ centered at $m/z = 1796.4$ a.m.u. and $\{H_6[Mn^{III}_7Mn^{II}_6O_{13}(C_6H_5CH_2PO_3)_5]Cl_4\}^-$ centered at $m/z = 1920.1$ a.m.u. (cone voltage: 30 V).

A summary of the ESI-MS assignment for the reaction mixture that led to the crystallisation of **14** is presented in Table 3.35, and a comparison of the experimental isotopic envelopes together with the simulated patterns for all identified species can be found in Figure 3.89.

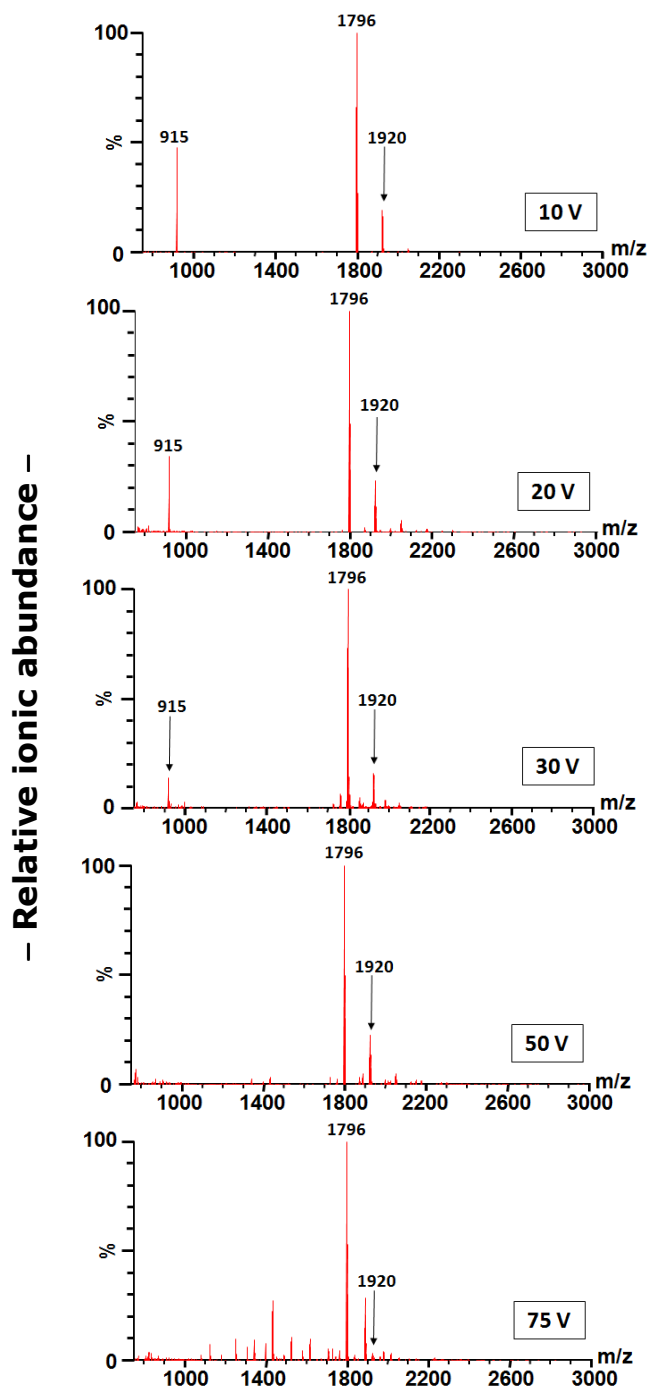


Figure 3.90 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **14** at different cone voltages: 10V, 20V, 30V, 50V and 75V, respectively.

Cone voltage variations experiments show that the relative ionic abundance of $\{\text{Mn}_7\}$, $\{\text{Mn}_{12}\}$ and $\{\text{Mn}_{13}\}$ species decreases with increasing CV values. These experimental observations indicating that the assigned species form in solution in the same reaction mixture (Figure 3.90). Furthermore, we believe that the $\{\text{Mn}_7\}$ species is structurally related to the $\{\text{Mn}_{13}\}$ core structure, adopting a hexagonal brucite arrangement as shown in Figure 3.91.

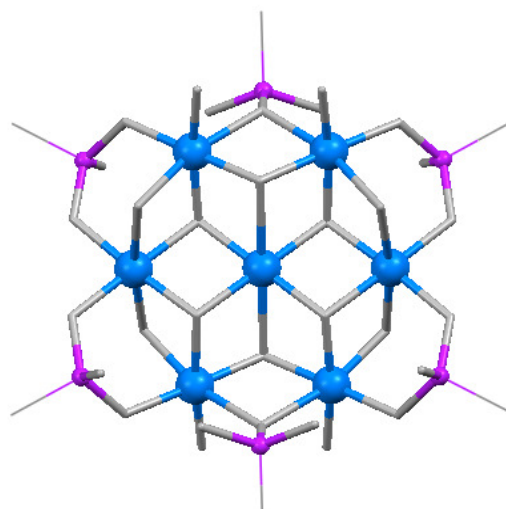


Figure 3.91 – Representation of a structural motif that agrees with the constitutional assignment for the $\{\text{Mn}_7\}$ species identified in the mass spectrum of the reaction mixture that led to the crystallisation of **14**. Colour code: Mn blue, P purple, C grey, O light grey.

Compound **15**, $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Br}_2 \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ was obtained by replacing the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ in the reaction mixture of **14** in order to investigate the role of the halide ions as a potential templating agent.

The ESI-MS study on the reaction mixture that led to the crystallisation of **15** is essentially analogous to that of **14**. The mass spectrum displays characteristic signals at $m/z = 740.0$ a.m.u. and $m/z = 1930.3$ a.m.u. which correspond to $\{\text{Mn}_3\}$ and $\{\text{Mn}_7\}$ species, $\{\text{HMn}^{\text{IV}}_3\text{O}_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_3\}^-$ and $\{\text{H}_{29}[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{II}}_4\text{O}_{16}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Br}_3\}^-$, respectively. Two other significantly less intense isotopic envelopes centered at $m/z = 2032.3$ a.m.u. and $m/z = 2062.9$ a.m.u. were attributed to the $\{\text{Mn}_{12}\}$ and $\{\text{Mn}_{13}\}$ species, $\{\text{H}[\text{Mn}^{\text{III}}_{12}\text{O}_{12}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Br}_2\}^-$ and $\{\text{H}_3[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_7\text{O}_{11}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_5]\text{Br}_4\}^-$ (Table 3.36, Figure 3.92).

Table 3.36 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **15**.

	m/z	Species attributed	
Reaction mixture of 15	740.0	$\{\text{H}[\text{Mn}^{\text{IV}}_3\text{O}_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_3]\}^-$	$\rightarrow \{\text{Mn}_3\}$
	1930.3	$\{\text{H}_{29}[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{II}}_4\text{O}_{16}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Br}_3\}^-$	$\rightarrow \{\text{Mn}_7\}$
	2032.3	$\{\text{H}[\text{Mn}^{\text{III}}_{12}\text{O}_{12}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Br}_2\}^-$	$\rightarrow \{\text{Mn}_{12}\}$
	2062.9	$\{\text{H}_3[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_7\text{O}_{11}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_5]\text{Br}_4\}^-$	$\rightarrow \{\text{Mn}_{13}\}$

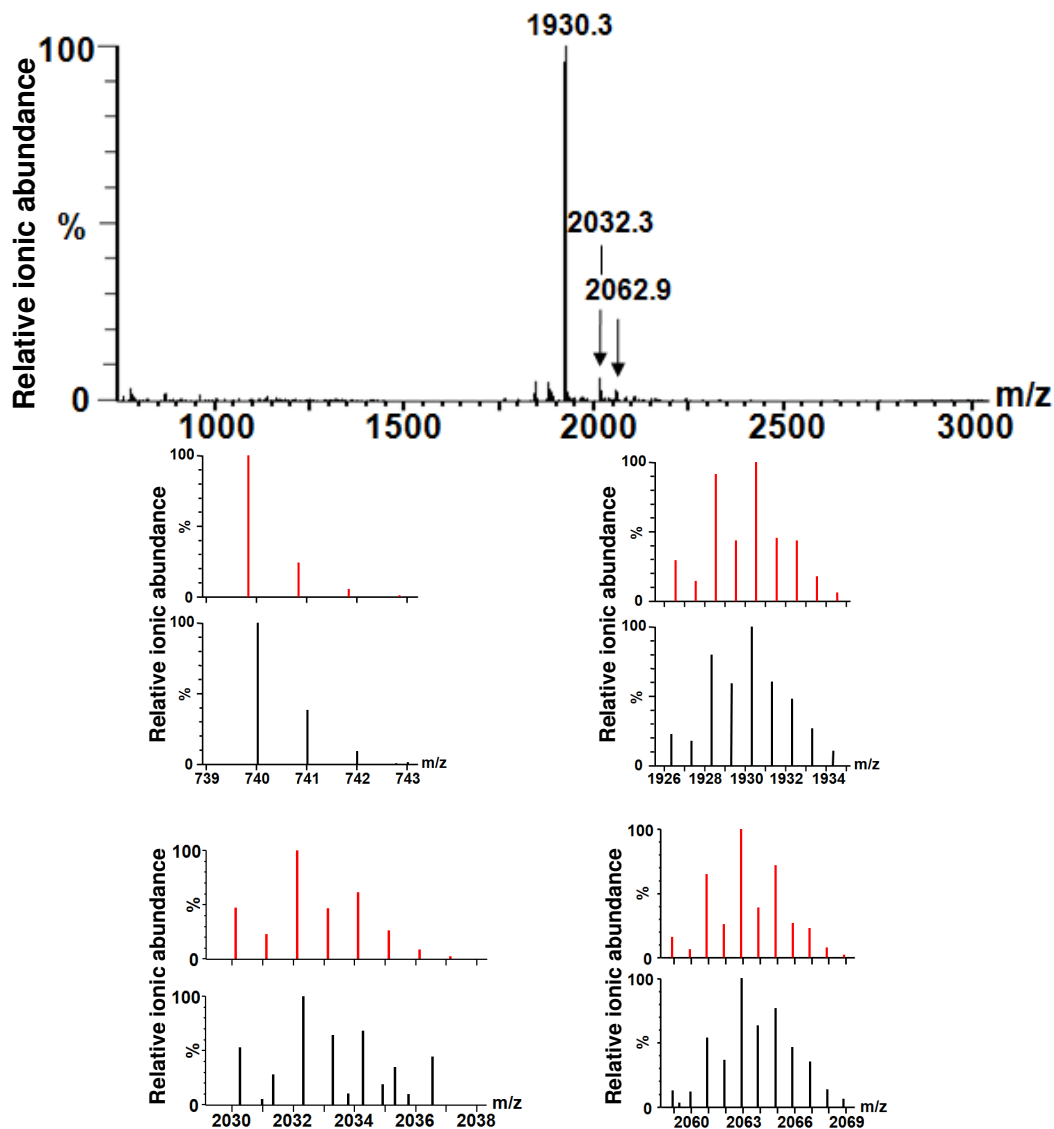


Figure 3.92 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **15** (24 h after preparation). Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{H}[\text{Mn}^{\text{IV}}_3\text{O}_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_3]\}^-$ centered at $m/z = 740.0$ a.m.u., $\{\text{H}_{29}[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{II}}_4\text{O}_{16}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Br}_3\}^-$ centered at $m/z = 1930.3$ a.m.u., $\{\text{H}[\text{Mn}^{\text{III}}_{12}\text{O}_{12}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_6]\text{Br}_2\}^-$ centered at $m/z = 2032.3$ a.m.u. and $\{\text{H}_3[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_7\text{O}_{11}(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_5]\text{Br}_4\}^-$ centered at $m/z = 2062.9$ a.m.u. (cone voltage: 30 V).

3.4.4 Investigation of the reaction system that led to the formation of the {Mn₆} complex in **16**

When the reaction mixture of compound **16**, $(\text{H}_3\text{O})_4\{\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_4\text{-O})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}\text{Cl}_2 \cdot 2\text{CH}_3\text{CN} \cdot 4\text{H}_2\text{O}$, was examined by ESI-MS we obtained a spectrum in which one major isotopic isotope could be observed. Unfortunately, we were not able to assign this signal, but we succeeded to identify a {Mn₆} species which relates to a considerably less intense signal centered at $m/z = 2296.1$ a.m.u. The signal corresponds to the hexanuclear complex in **16** which crystallizes from this reaction mixture (Table 3.37, Figure 3.94).

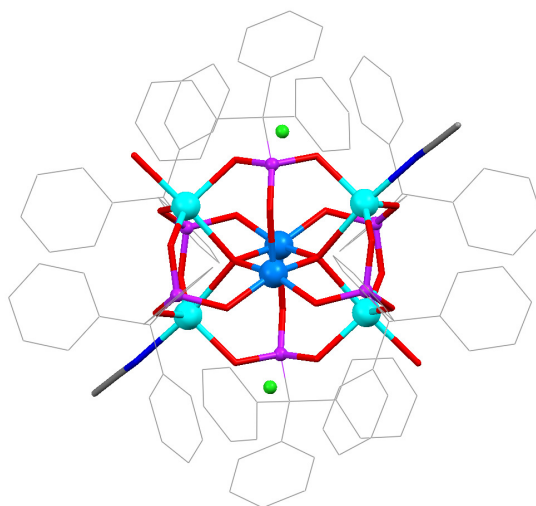


Figure 3.93 – Crystal structure of the hexanuclear manganese complex in **16**. Colour code: Mn^{III} blue, Mn^{II} cyan, P purple, O red, C grey, N dark blue, Cl green (hydrogen atoms have been omitted for clarity).

Table 3.37 – ESI-MS assignment for the reaction mixture that led to the crystallisation of **16**.

	m/z	Species attributed	
Reaction mixture of 16	2296.1	$\{\text{HMn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$	$\rightarrow \{\text{Mn}_6\}$

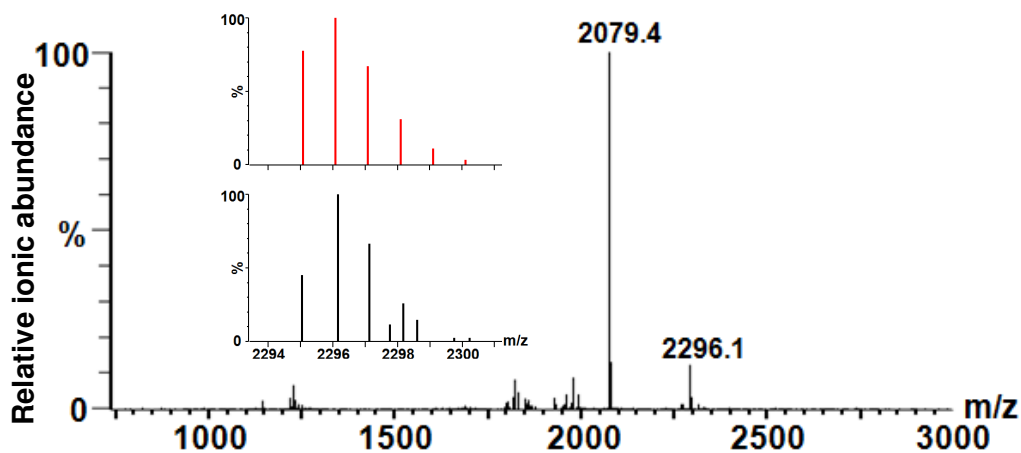


Figure 3.94 – Negative-mode ESI-MS spectra for the reaction mixture that led to the crystallisation of **16** (24 h after preparation). Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for $\{\text{HMn}^{\text{III}}_2\text{Mn}^{\text{II}}_4\text{O}_2[(\text{C}_6\text{H}_5)_3\text{CPO}_3]_6\}^-$ centered at $m/z = 2296.1$ a.m.u. (cone voltage: 30 V).

3.5 CONCLUSION AND FUTURE WORK

A facile synthetic approach to polynuclear manganese coordination complexes that involves comproportionation reactions between Mn^{II} and Mn^{VII} salts in the presence of organophosphonate ligands was developed. This synthetic approach led to the formation of three types of unprecedented manganese cluster compounds in **10**, **14** and **15**, three structurally related compounds **11**, **12** and **13** that belong to a family of $\{\text{Mn}_{13}\}$ complexes containing a metal-centered cuboctahedral core structures and a hexanuclear, mixed valent coordination complex (**16**).

We found that small changes to the reaction conditions result in drastic changes of the cluster nuclearity and topology. The nature of the phosphonate ligand and organic base are most influential and determine the product formation. Our approach allowed us to utilize organophosphonate as organic, stabilizing ligands. In comparison to carboxylate ligands, there are only a few polynuclear manganese complexes stabilized by phenylphosphonic acid ligands reported in the literature, which makes the here reported class of compounds interesting. **10** contains a remarkable $\{\text{Mn}_{15}\}$ oxo-cluster with characteristic dunbell-type arrangement of its sub-units. Compound **11** was the result of adding pyridine to the reaction mixture of **10**, while compound **12** was obtained by replacing the phenylphosphonic acid ligands in **11** with benzylphosphonic acid ligands.

We noticed that the $\{\text{Mn}_{13}\}$ clusters contain active sites provided by ligands that reside in tetragonally elongated positions of the Jahn-Teller distorted, octahedral coordination environments. The kinetic lability of these sites gives rise to ligand exchange reactions and functionalisation of the compounds (e.g. introduction of organic moieties in these positions). In consecutive experiments, we further aimed to exploit this feature and connect the $\{\text{Mn}_{13}\}$ clusters using bi-functional ligands, e.g. bipyridine-type ligands, however, our attempts were unsuccessful.

Studies of the magnetic properties reveal dominant antiferromagnetic interactions between the spin centres and a ground state spin values of $S_{\text{T}} = 0$ for **10** and **16**, $S_{\text{T}} = 3$ for **14** and **15**, $S_{\text{T}} = 6$ for **11** and **13** and $S_{\text{T}} = 8$ for **12**. The ac susceptibility studies in zero dc field for compounds **11-13** reveal slow relaxation of the magnetisation highlighted by appearance of out-of-phase signals below 4 K (for frequency around 10000 Hz), indicating that these compounds are SMMs.

The thermal stability of the compounds was investigated by thermogravimetric analysis. Solution stability studies for **10** – **16** were performed using ESI-MS and UV-Vis spectroscopy. In particular, the ESI-MS technique proved to be highly valuable to characterise the stability of the complexes. It is surprising that this technique has not previously been utilized to investigate the solution behavior of larger, polynuclear Mn complexes. Indeed we also applied ESI-MS to screen reaction mixtures prior crystallisation attempts of **10-16**. These approaches aimed to investigate the real-time growth reactions of polynuclear Mn complexes and analyses of the magnetic properties of **10-16**.

The {Mn₇} and the {Mn₁₃} species were observed in the ESI-MS spectra of the reaction mixture that led to the crystallisation of **10**, **14** and **15**. The {Mn₇} species may be a brucite-type, disk-like building unit which appears in several clusters reported in the literature and in tridecanuclear clusters in **11** - **13**.⁶⁹⁻⁷² The {Mn₁₃} species identified by ESI-MS relates to the latter family of tridecanuclear manganese complexes which contain a metal-centered cuboctahedral topology. Another noticeable feature observed in the mass spectra of the reaction mixture that led to the crystallisation of **10**, **14** and **15** is that the signals attributed to the {Mn₇} species appear as the most intense signals in the high mass region of the spectra. This observation in combination with cone voltage variations suggest that this {Mn₇} species is the predominant high molecular mass species present in these reaction mixtures. Consequently, one expects several cluster topologies to incorporate this building unit and forming larger assemblies involving for instance hydroxo- and oxo-groups or donor atoms of multidentate ligands. This observation is substantiated by the crystal structures of **11-13** and several structures reported in the literature that contain the said brucite-type core.^{12, 48, 53-55} In addition the identification of trinuclear Mn species support this proposal. The {Mn₁₂} species identified in the reaction mixture that led to the crystallisation of **14** and **15** seems to be in equilibrium with the {Mn₁₃} species. This equilibrium can be manipulated in order to crystallise either the {Mn₁₂} or the {Mn₁₃} species by slight changes of the reaction conditions. In the case of the pentadecanuclear manganese complex in **10**, we found that the {Mn₁₅} cluster is not stable in solution since this species could not be identified by ESI-MS studies. Moreover, we were able to identify building units of the {Mn₁₅} cluster as {Mn₇} and {Mn₈} species present in the reaction mixture that led to the crystallisation of **10**. The fact that the {Mn₇} species was also present in the mass spectra of pristine crystals of **10** dissolved in CH₃CN, DMF and DMSO suggest that the {Mn₁₅} cluster break into two {Mn₇} units, most likely due to the labile methanol groups from the JT sites of the central Mn ion.

A summary of the ESI-MS assignment for the reaction mixtures of the $\{\text{Mn}_{15}\}$, $\{\text{Mn}_{13}\}$ and $\{\text{Mn}_{12}\}$ systems, highlighting related structural motifs and possible building units, is presented in Figure 3.95.

Future work aims to exploit the kinetic lability of the Jahn-Teller sites of the $\{\text{Mn}_{13}\}$ clusters for further functionalisation of these compounds. It could also be possible to connect the $\{\text{Mn}_{13}\}$ clusters using bi-functional ligands, which could lead to the formation of porous structures. Additionally, ESI-MS technique will be further exploited to characterise new polynuclear manganese coordination complexes.

The extensive research in the field of molecular magnetism is not only concerned with the understanding of the magnetic properties of these materials, and providing structure-property relationships but also with the real need for the development of rational synthetic approaches to complex polynuclear species.

Currently it is rather challenging to predict what kind of cluster topologies will be obtained and which would be desired to achieve exciting magnetic properties. Under this prevue mass spectrometry analyses might provide a step towards more rational approaches to more predictable, structurally related materials that will help to understand and improve the properties of molecule magnetic materials.

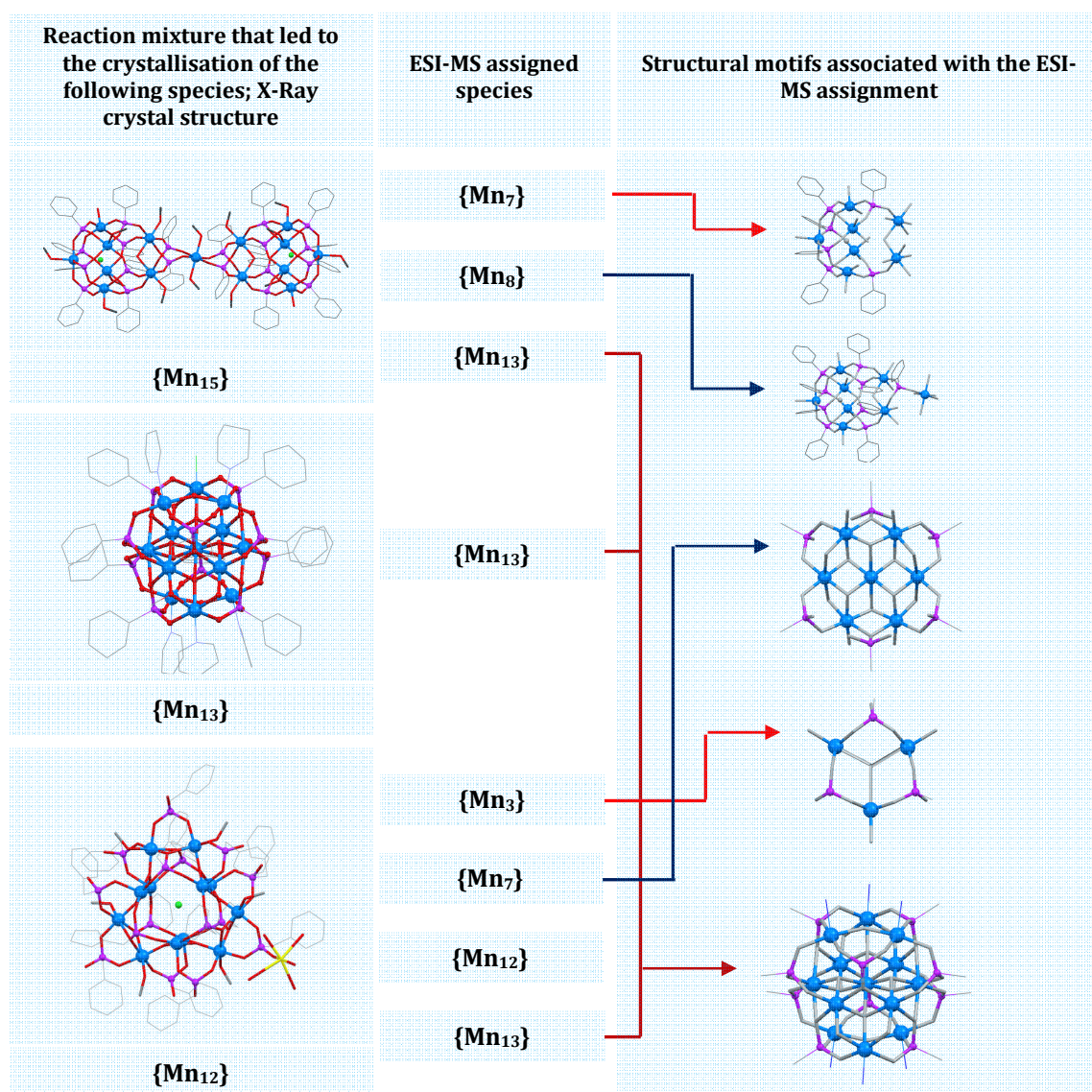


Figure 3.95 – Summary of the ESI-MS assignment for the reaction mixture of the {Mn₁₅}, {Mn₁₃} and {Mn₁₂} systems, showing some related structures and possible building units.

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4. SUPRAMOLECULAR COORDINATION NETWORKS EMPLOYING TRIPHOSPHONATE LINKERS

4.1 INTRODUCTION

The massive increase in energy demand, the depletion of the world's fossil fuels combined with the undesired products of burning fossil fuels, such as carbon dioxide, has led to a need for alternative energy sources. A promising alternative fuel which has attracted much attention in the last few years is hydrogen, which is a clean energy carrier having the highest energy content per unit of weight of any known fuel.^{1, 2} Thus, hydrogen is shown to be the fuel of the future. But, before being used at large scale there are a few problems that need to be solved, such as finding a safe and cost effective storage medium for hydrogen.³⁻⁵

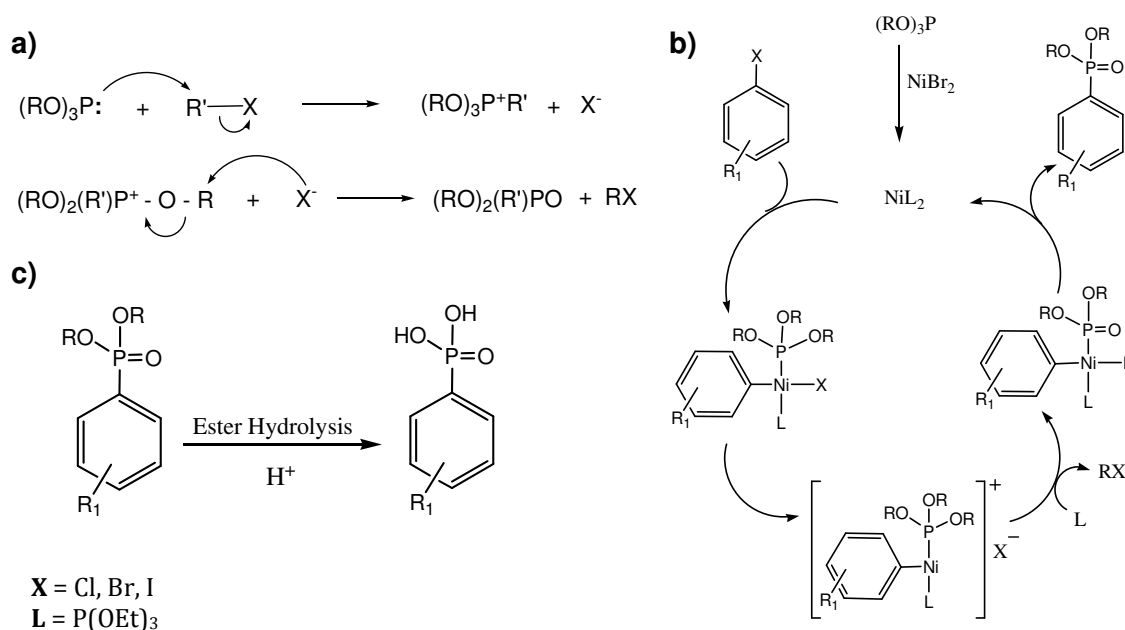
Considerable research efforts have been devoted to the development of innovative materials including high surface area adsorbents such as metal-organic frameworks for reversible hydrogen storage and carbon dioxide capture.⁶⁻⁸

Metal-organic frameworks (MOFs) represent a new class of porous materials with high surface areas and tunable pore sizes, which can result in the selective uptake of small molecules. These unique properties make MOFs interesting materials for potential applications in catalysis, gas storage and separation.^{7, 9-11} The most studied class of MOFs is represented by the carboxylate-based compounds, while the use of phosphonate ligands for the formation of framework structures is less common. The reason for this is that many metal phosphonates tend to form densely packed layered structures that are not porous; growth of single crystals with phosphonates represents a real challenge as they often precipitate rapidly as less ordered, insoluble phases; phosphonates have more possible ligating modes compared to carboxylates, making the coordination chemistry of phosphonates less predictable. Even though, carboxylate-based MOFs have high surface area and uniform pore size distribution, the large scale applications are hampered by their lack of stability. Phosphonates have shown to form stronger bonds with metal ions than carboxylates and therefore have great potential to form robust porous solids.¹²⁻¹⁴

In this chapter we describe the synthesis and characterisation of coordination networks employing mononuclear SBUs and triphosphonate linkers.

4.2 EXTENDED TRIPHOSPHONATE LIGANDS

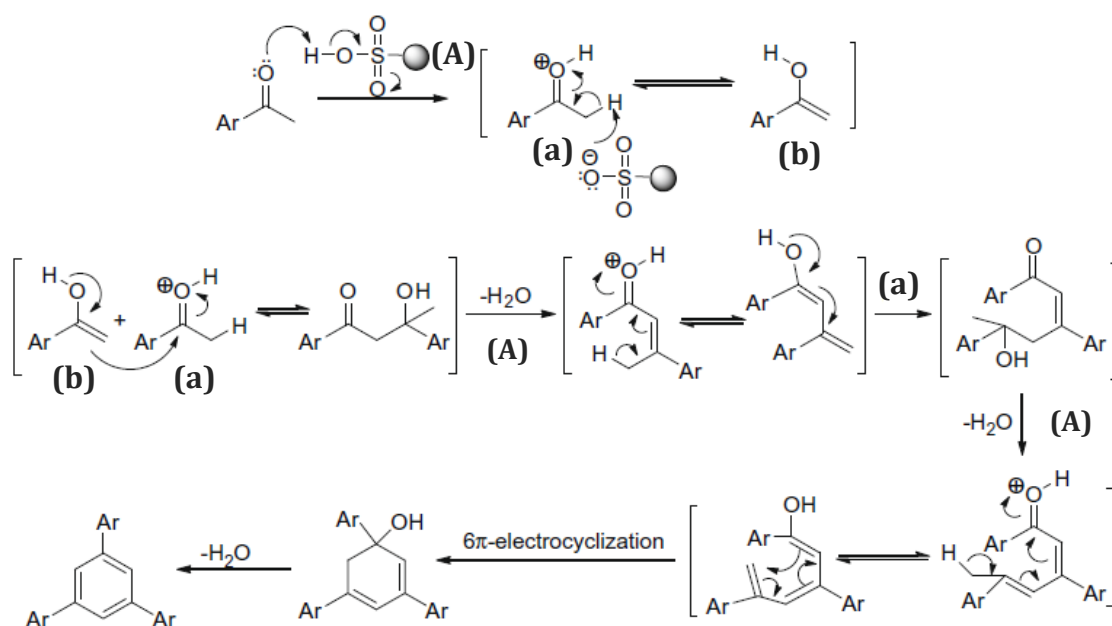
The triphosphonate ligands were synthesised by a modified Michaelis-Arbuzov reaction (Scheme 4.1, b).^{15, 16} The synthetic procedure involves a catalyzed phosphonylation of aryl halides by trialkyl phosphites in the presence of 1,3-diisopropylbenzene as a solvent and at high temperature. Nickel(II) salts are usually used as catalysts.¹⁷



Scheme 4.1 – a) Mechanism of the Michaelis – Arbuzov reaction for the preparation of alkylphosphonates (R' = alkyl); b) Modified Michaelis – Arbuzov reaction for the preparation of arylphosphonates; c) Ester hydrolysis under acidic conditions.¹⁵⁻¹⁷

The reaction mechanism involves *in situ* reduction of the nickel(II) halide to a nickel(0) phosphite complex, followed by the formation of an aryl nickel(II) intermediate. This intermediate is formed by an oxidative insertion of the nickel(0) phosphite complex into the carbon-halogen bond of the aryl halide. Then, an aryl(alkoxy)phosphonium salt is formed which rearranges to give the desired phosphonate ester. The major by-product of the reaction is an alkyl halide. It was observed that in order to obtain better yields one needs to remove the generated alkyl halide continuously from the reaction mixture until the reaction is complete. The phosphonate ester is then converted to the corresponding phosphonic acid by ester hydrolysis under acidic conditions.^{15, 16} The synthetic approach used to obtain phosphonic acids is presented in Scheme 4.1, a - c.

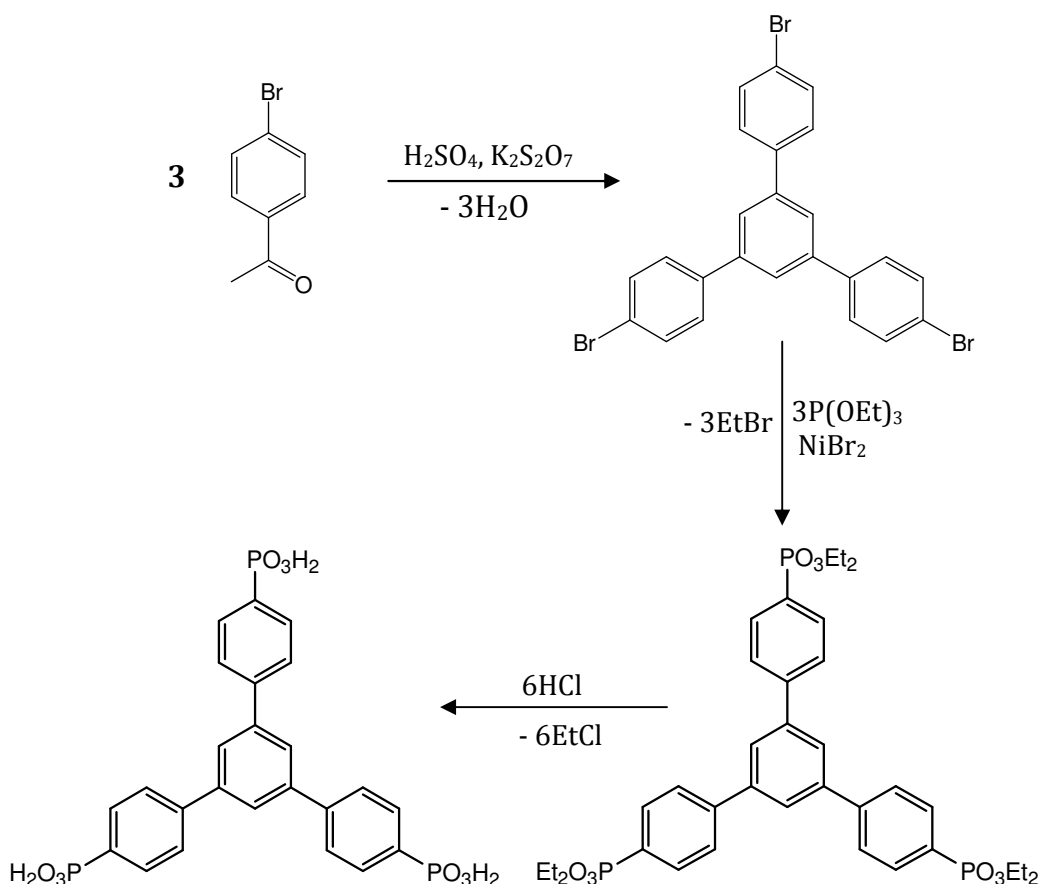
The halogenated triarylbenzenes, used as starting materials for the preparation of the triphosphonate ligands, were synthesised through a triple condensation reaction according to literature procedures.^{18, 19} A reaction mechanism for the formation of triarylbenzenes was proposed by A. Goel et al.²⁰ As shown in Scheme 4.2, the protonation of acetophenone results in the formation of intermediates (a) and (b). Then subsequent reactions between the intermediates, and further dehydration and 6 π -electrocyclisation processes afford the desired triarylbenzene ligand.



Scheme 4.2 – Plausible reaction mechanism for the formation of triarylbenzene.²⁰

4.2.1 Synthesis of 1,3,5-Tris(4-phosphonophenyl)benzene (P-TPB)

1,3,5-Tris(4-phosphonophenyl)benzene (P-TPB) was prepared by a modified Arbuzov reaction using the aryl halide tris(4-bromophenyl)benzene (Br-TPB) as an intermediate.¹⁷ The synthetic route to Br-TPB involves a triple condensation reaction using 4-bromoacetophenone as the starting material, in the presence of H_2SO_4 and $\text{K}_2\text{S}_2\text{O}_7$ (Scheme 4.3).¹⁸



Scheme 4.3 – Schematic representation for the formation of **P-TPB**.

Br-TPB formed in high yields (80%), while the P-TPB ligand formed in a lower yield of 58%. The ligands were characterised by FT-IR and NMR spectroscopy, and mass spectrometry. The ^1H NMR spectra of the Br-TPB and P-TPB ligands, including the assignment of the aromatic H-atoms of the triphenyl-benzene backbone moieties, can be seen in Figure 4.1 and Figure 4.2. The conversion of Br-TPB into P-TPB was confirmed by the presence of an intense absorption band at 1139 cm^{-1} in the IR spectrum, due to P-O

stretching vibrations. In addition the signal at 13.7 ppm in the ^{31}P NMR spectrum is characteristic for the desired phosphonate ligand. A detailed description of the preparation procedures together with the analytical data of the ligands is presented in the experimental section of chapter 8.

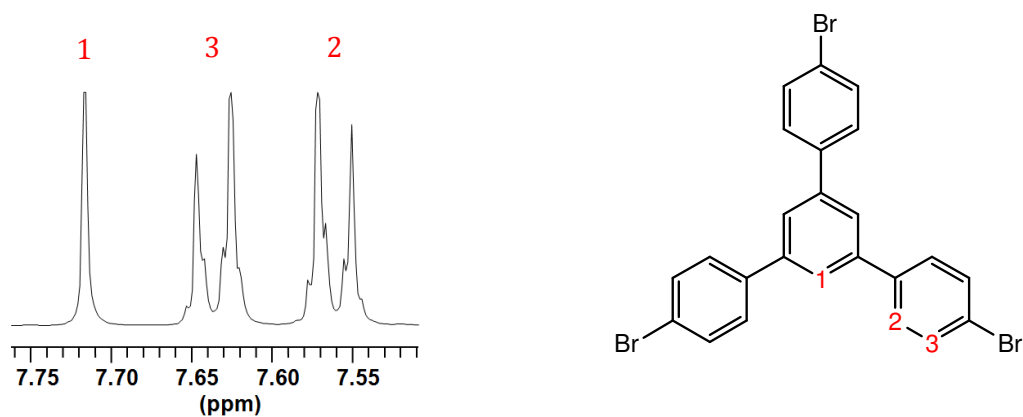


Figure 4.1 – A section of the ^1H NMR (400MHz, CDCl_3) spectrum showing the assignment for **Br-TPB**.

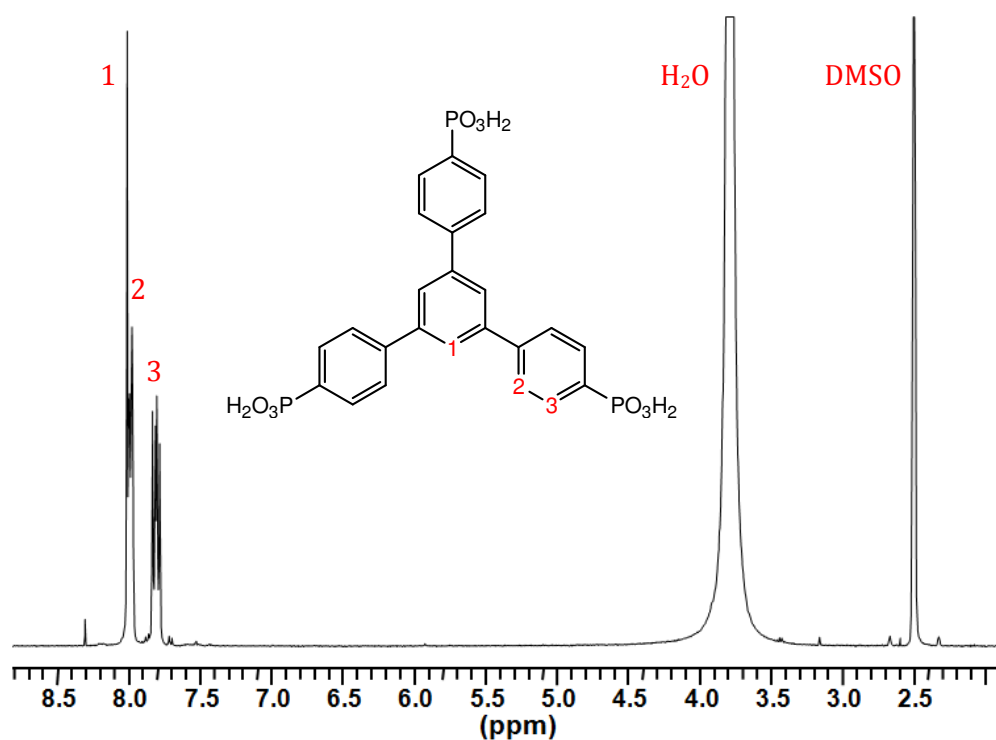
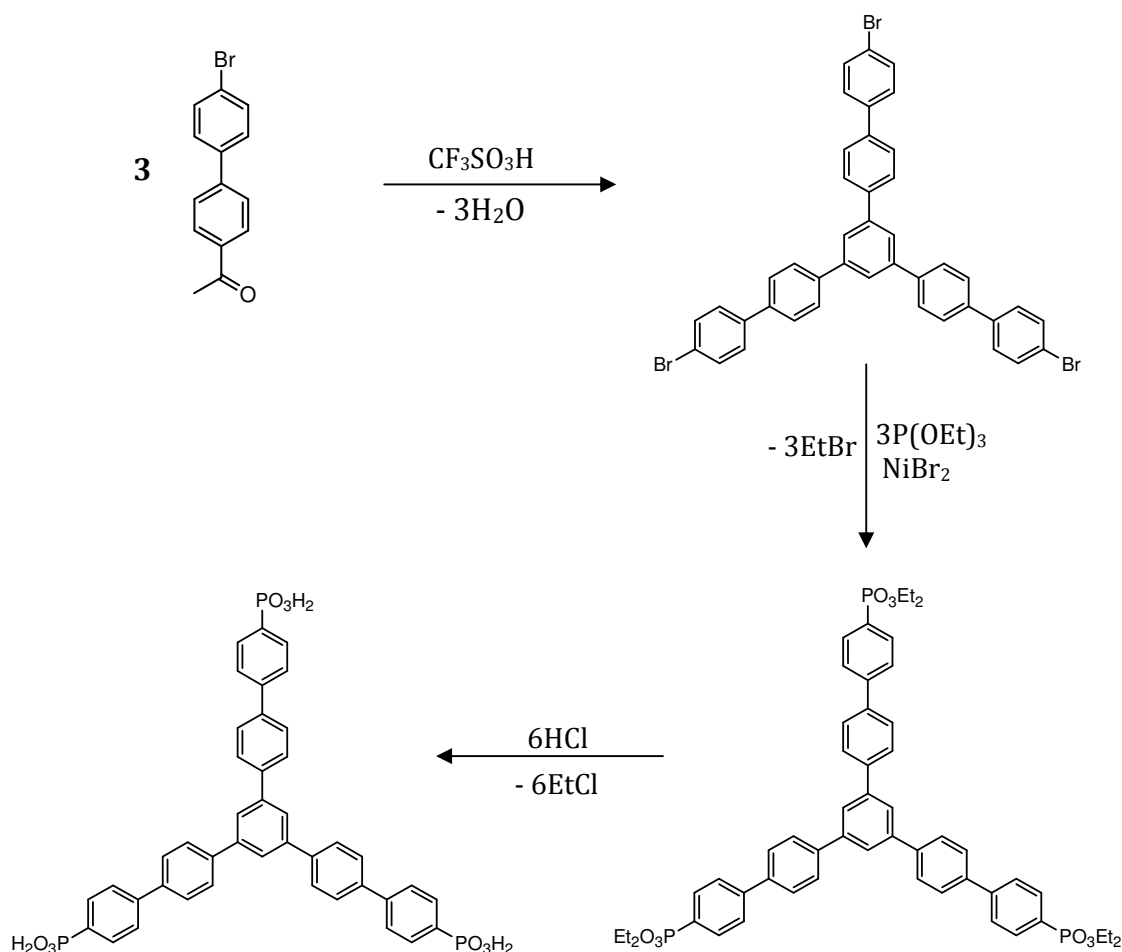


Figure 4.2 – The ^1H NMR (400MHz, CDCl_3) spectrum and assignment for **P-TPB**.

4.2.2 Synthesis of 1,3,5-Tris(4'-phosphonobiphenyl-4-yl)benzene (P-TBB)

1,3,5-Tris(4'-phosphonobiphenyl-4-yl)benzene (P-TBB) is a novel triphosphonate ligand which was prepared by a similar method to that that led to P-TPB. In this case, 1,3,5-tris(4'-bromobiphenyl-4-yl)benzene (Br-TBB) was used as aryl halide reactant. It was synthesised from commercially available 4-acetyl-4'-bromobiphenyl *via* a triple condensation reaction.¹⁹ Br-TBB formed in about 50% yield, while in the next synthetic step P-TBB ligand formed in a yield of 66%. The synthetic route used for the preparation of the P-TBB ligand is presented in Scheme 4.4.



Scheme 4.4 – Schematic representation for the formation of **P-TBB**.

The Br-TBB and P-TBB ligands were characterised by FT-IR and NMR spectroscopy, and mass spectrometry. The conversion of Br-TBB into P-TBB was

confirmed by FT-IR and ^{31}P NMR spectroscopy. The IR spectrum of the P-TBB ligand displays an intense absorption band at 1137 cm^{-1} due to P-O stretching vibrations, while the ^{31}P NMR spectrum reveals a characteristic signal at 12.6 ppm. The identity and structure of the P-TBB ligand was further characterised by X-ray diffraction measurements. Colourless crystals were obtained after re-crystallisation, upon dissolving the P-TBB ligand in DMF and layering the resulting solution with CH_3CN (43% yield).

The ligand crystallises in the monoclinic crystal system in the space group $C 2/c$. The crystal structure of the ligand is presented in Figure 4.3. The benzene rings of the P-TBB molecule are tilted with respect to each other. The tilt angles of the aryl rings denoted as **2**, **3**, and **4** to the central benzene ring **1** (Figure 4.3) are $37.21(99)^\circ$, $42.59(99)^\circ$ and $28.76(87)^\circ$, respectively, while the tilt angles of the aryl rings **5**, **6**, and **7** to the central benzene ring **1** are $86.85(94)^\circ$, $6.51(78)^\circ$, $57.86(77)^\circ$, respectively.

In the solid state the P-TBB molecules are linked by weak π - π stacking interactions and hydrogen bonding to generate a honeycomb-like supramolecular structure that supports voids of about 2.5 nm in diameter. The solvent molecules within these voids were highly disordered and could not be modelled properly, thus the SQUEEZE routine of the PLATON program was applied to remove the contributions to the scattering from the solvent molecules. The honeycomb-like structure can be seen in the direction of the crystallographic c -axis and is presented in Figure 4.4. In the crystal structure the unit cell comprises of eight P-TBB molecules organised into dimers. The molecules in these dimer assemblies exhibit a face-to-face (**A**) and a head-to-tail (**B**) arrangement, creating an interdigitating packing arrangement which can be seen in the direction of the crystallographic a -axis (Figure 4.5). The dimers are stabilised by hydrogen bonding and π - π interactions. Strong intermolecular H-bonding between O(1) and O(2) of two adjacent molecules of the dimer unit **A** are characterised by an interatomic distance of $2.466(16)\text{ \AA}$.²¹ Face-to-face π - π interactions between rings **1**, **3**, **6** of two adjacent molecules in dimer **A** range from $3.722(12)\text{ \AA}$ to $3.891(12)\text{ \AA}$ and off-set π - π interactions of $3.663(10)\text{ \AA}$ and $3.828(13)\text{ \AA}$ can also be observed in dimer **A**.²² Dimer **B** is stabilised by off-set π - π interactions of $3.958(12)\text{ \AA}$ and $3.977(13)\text{ \AA}$.

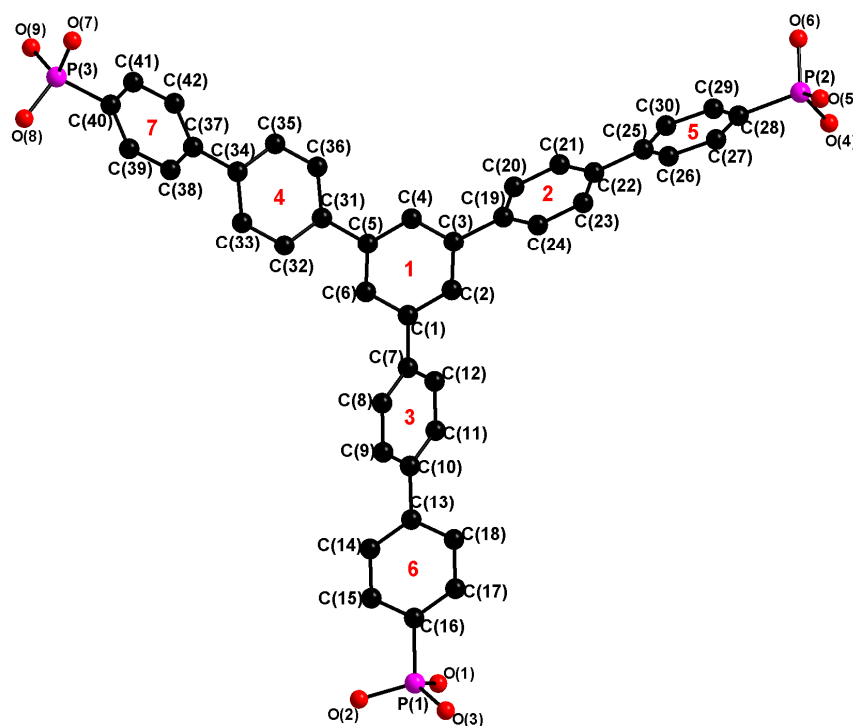


Figure 4.3 – The crystal structure of the **P-TBB** ligand. Colour code: P purple, O red, C black (H atoms have been removed for clarity).

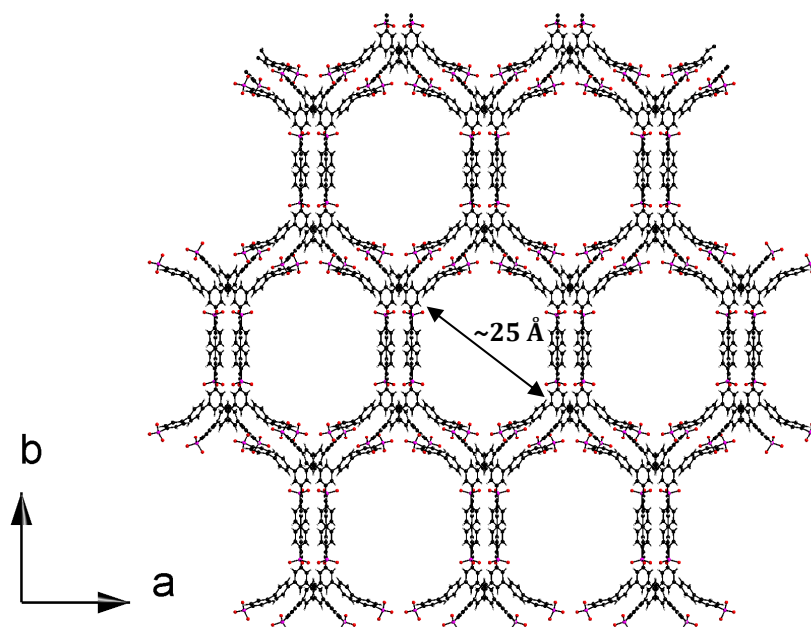


Figure 4.4 – The packing arrangement of the **P-TBB** ligand viewed in the direction of the crystallographic *c*-axis. Colour code: P purple, O red, C black, H grey.

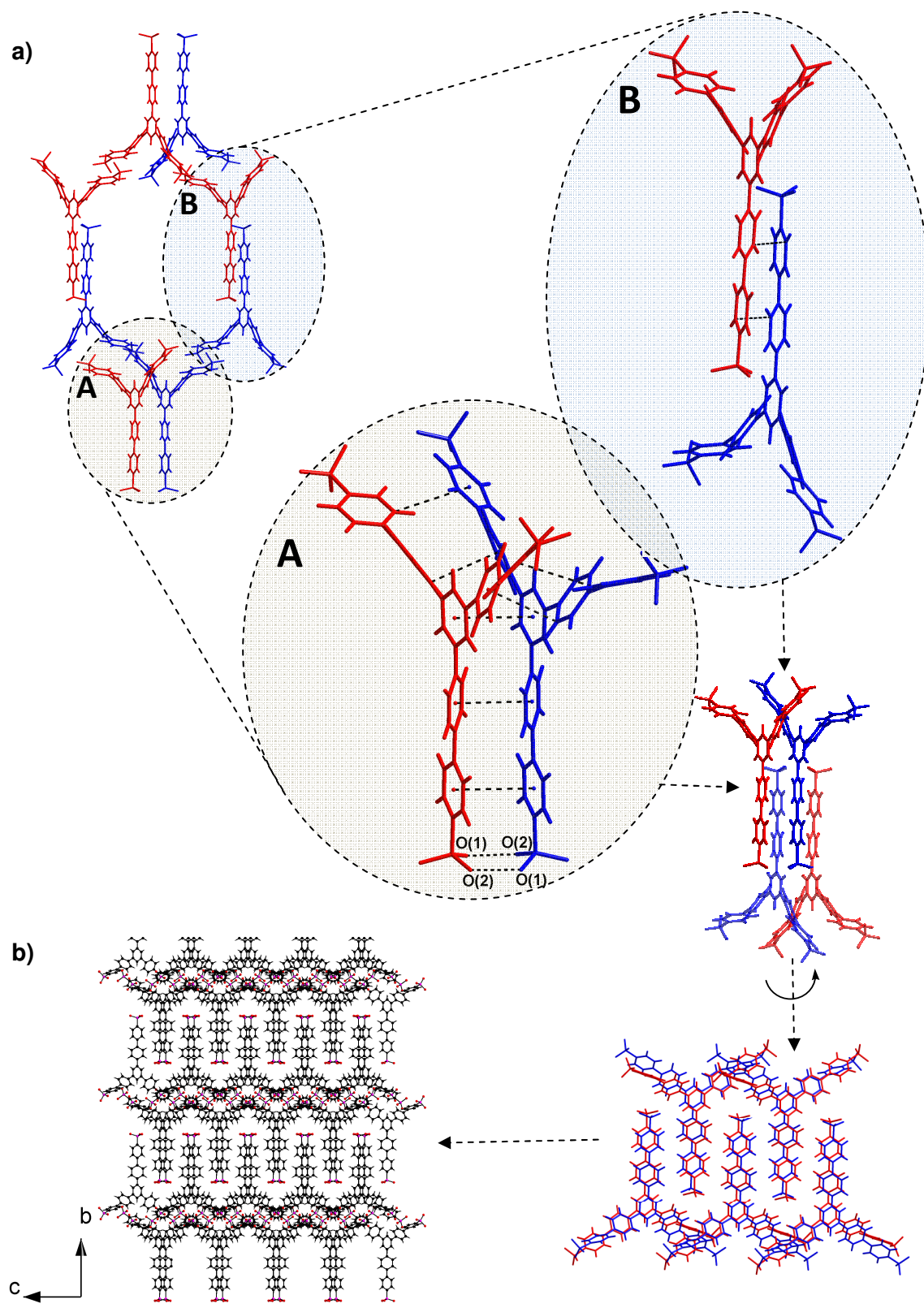


Figure 4.5 – (a) The unit cell content showing the face-to-face (A) and head-to-tail (B) arrangement of the molecules; (b) The packing arrangement of the **P-TBB** ligand viewed in the direction of the crystallographic *a*-axis. Colour code: P purple, O red, C black, H grey.

Table 4.1 – Crystal data and structural refinement parameters for P-TBB.

P-TBB Ligand	
Empirical formula ^a	C ₄₂ H ₃₃ O ₉ P ₃
Molecular mass/g mol ⁻¹ ^a	774.62
Crystal colour/shape	Colourless / needle
Crystal size/mm ³	0.30×0.15×0.15
Crystal system	Monoclinic
Space group	<i>C</i> 2/c
<i>a</i> / Å	24.378(14)
<i>b</i> / Å	50.24(3)
<i>c</i> / Å	12.132(7)
α /°	90
β /°	90.761(10)
γ /°	90
<i>V</i> / Å ³	14856(14)
<i>Z</i>	8
Temperature (K)	150(2)
Density/Mg m ⁻³	0.693
Absorp. coef./mm ⁻¹	0.109
<i>F</i> (000)	3216
$2\theta_{\text{max}}$ /°	40
Reflections collected	17967
Independent reflections	6933 [R(int) = 0.1149]
Data / restraints / parameters	6933 / 27 / 328
<i>S</i> on <i>F</i> ²	0.809
<i>R</i> ₁ , <i>wR</i> ₂ [I>2σ(I)]	0.1303, 0.3031
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.2345, 0.3528
Largest diff. peak and hole/e.Å ⁻³	0.590 and -0.431

^a Excluding solvate molecules

4.3 SYNTHESIS AND CHARACTERISATION OF COORDINATION NETWORKS EMPLOYING MONONUCLEAR INORGANIC SBUS AND TRIPHOSPHONATE LINKERS

4.3.1 $(\text{H}_3\text{O})\{\text{Mn}^{\text{II}}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_2[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ (**17**)

Compound **17**, $(\text{H}_3\text{O})\{\text{Mn}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_2[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ was prepared by the reaction of 1,3,5-tris(4-phosphonophenyl)benzene (P-TPB) with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in MeOH. Rectangular yellow crystals of **17** were obtained during a time period of four days and characterised by single crystal X-ray diffraction measurements.

17 crystallises in the triclinic crystal system in the space group $P\bar{1}$, and consists of a coordination network containing a mononuclear Mn^{II} SBU. The Mn ion in **17** displays a distorted octahedral coordination environment formed by one oxygen atom from a coordinating water molecule, two oxygen donors arising from two CH_3OH ligands and the remaining coordination sites are occupied by oxygen donors originating from three distinct phosphonate ligands (Figure 4.6). The bond distances between the Mn ion and the O donors originating from the organic phosphonate ligands vary between 2.105(4) Å – 2.185(4) Å, the Mn- $\text{O}_{\text{methanol}}$ bond lengths for Mn(1)-O(2) and Mn(1)-O(6) are 2.216(4) Å and 2.225(4) Å, respectively, while the bond distance between the Mn ion and the O atom of the water molecule, Mn(1)-O(1), is 2.222(4) Å.

The distorted nature of the octahedral coordination geometry of the Mn^{II} ion can be observed from the bond angles involving the metal centre. Indeed, the bond angles, O(3)-Mn(1)-O(6), O(5)-Mn(1)-O(2) and O(4)-Mn(1)-O(1) of 174.53(16)°, 170.51(16)° and 165.38(16)°, respectively, deviate significantly from the ideal octahedral angle of 180°, whilst the bond angles O(3)-Mn(1)-O(1) and O(4)-Mn(1)-O(6), of 98.07(16)° and 81.57(16)°, respectively, show the greatest deviation from the ideal angle of 90°.

Selected bond distances and bond angles for compound **17** are summarised in Table 4.2 and Table 4.3, respectively.

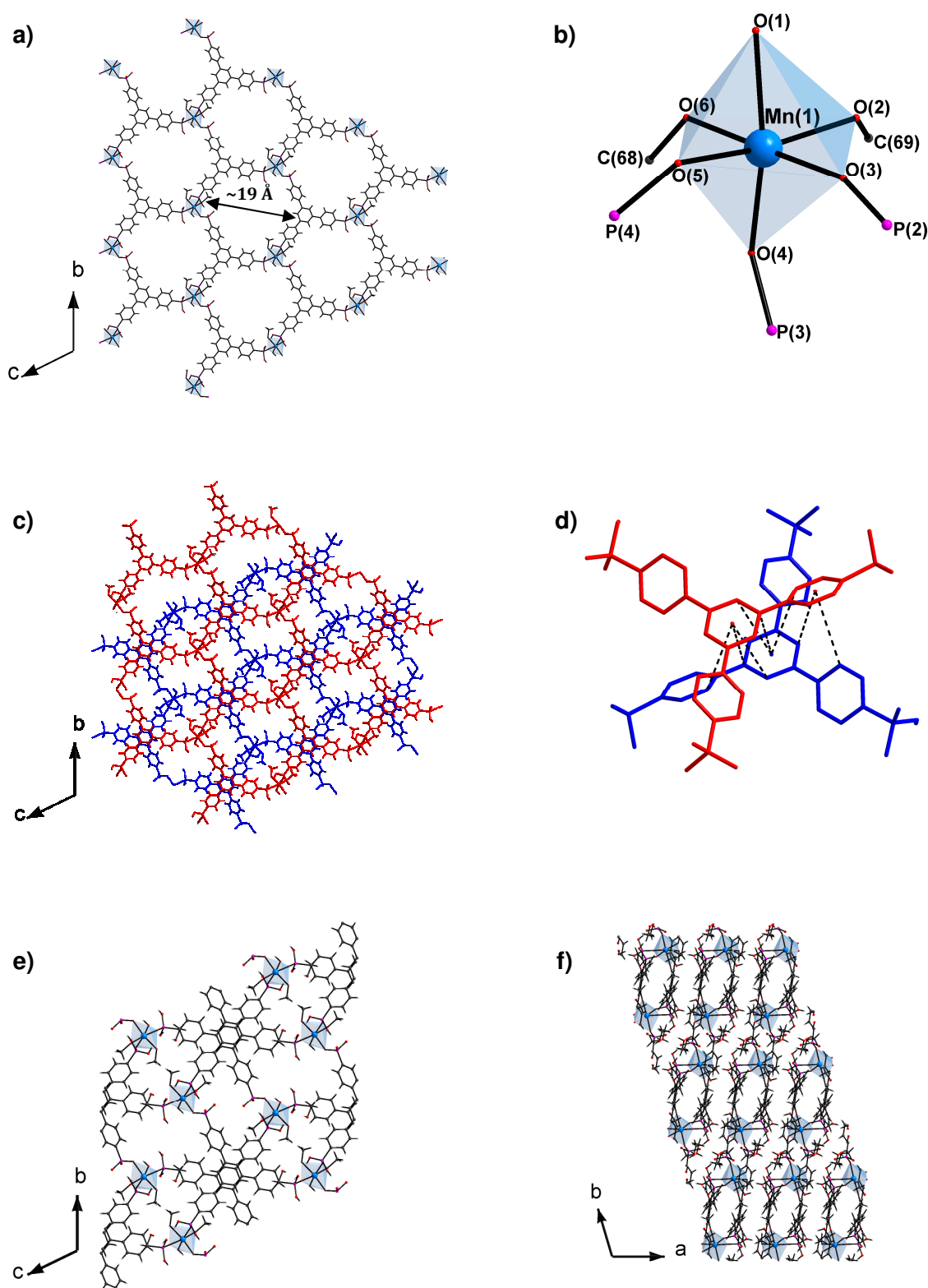


Figure 4.6 – (a) The hexagonal packing arrangement of the mononuclear Mn^{II} SBUs in **17** as seen in the direction of the crystallographic a -axis; (b) The coordination environment of the Mn^{II} ion; (c) Packing arrangement showing two layers with hexagonal motif viewed in the direction of the crystallographic a -axis; (d) π - π stacking of the organic moieties; (e) and (f) Packing arrangement of the 2D networks in **17** viewed in the direction of the crystallographic a - and c -axis, respectively. Colour code: Mn blue, P purple, O red, C dark grey, H light grey (crystallization solvent molecules have been omitted for clarity).

Table 4.2 – Selected bond lengths [Å] for compound 17.

Bond	Bond distances (Å)
Mn(1)-O(3)	2.105(4)
Mn(1)-O(4)	2.136(4)
Mn(1)-O(5)	2.185(4)
Mn(1)-O(2)	2.216(4)
Mn(1)-O(1)	2.222(4)
Mn(1)-O(6)	2.225(4)
P(2)-O(3)	1.490(4)
P(2)-O(9)	1.522(4)
P(2)-O(10)	1.575(4)
P(3)-O(4)	1.488(4)
P(3)-O(11)	1.542(4)
P(3)-O(12)	1.575(4)
P(4)-O(8)	1.516(5)
P(4)-O(5)	1.519(4)
P(4)-O(7)	1.578(5)

Table 4.3 – Selected bond angles [°] for compound 17.

Bond Angle (°)		Bond Angle (°)	
O(3)-Mn(1)-O(6)	174.53(16)	O(3)-Mn(1)-O(5)	90.72(15)
O(5)-Mn(1)-O(2)	170.51(16)	O(2)-Mn(1)-O(6)	89.50(18)
O(4)-Mn(1)-O(1)	165.38(16)	O(2)-Mn(1)-O(1)	86.95(16)
O(3)-Mn(1)-O(1)	98.07(16)	O(3)-Mn(1)-O(2)	85.48(18)
O(3)-Mn(1)-O(4)	96.52(16)	O(5)-Mn(1)-O(1)	84.97(15)
O(4)-Mn(1)-O(5)	95.82(15)	O(1)-Mn(1)-O(6)	83.82(16)
O(5)-Mn(1)-O(6)	94.57(17)	O(4)-Mn(1)-O(6)	81.57(16)
O(4)-Mn(1)-O(2)	93.26(16)		

All three phosphonate groups of the P-TPB ligand are monodentate and singly protonated. The protonation state of the phosphonate groups was established by examining the P-O bond lengths (Table 4.2). Each phosphonate group of the organic ligands display an elongated P-O bond that range between 1.575(4) Å – 1.578(5) Å, and which is consistent with the values found in the literature for P-OH bonds.²³⁻²⁵ Thus each anionic ligand carries three negative charges which are compensated by one Mn^{II} ion and a H₃O⁺ ion. Several coordination networks stabilised by hydronium counterions have previously been reported, e.g. in [M^{II}₆(C₄O₇)(C₃HO₅)₃(H₂O)₆(H₃O)]·8H₂O (M = Zn or Mn), {(H₃O)₂[Mn₄(4-Haba)₂(4-aba)₆(SCN)₄(H₂O)₂]} (4-Haba = 4-aminobenzoic acid),

$[\text{H}_3\text{O}]_{2x}[\text{M}(\text{pyzdc})_2]_x$ ($\text{M} = \text{Mn}, \text{Cd}$; $\text{pyzdcH}_2 = 2,3\text{-pyrazinedicarboxylic acid}$),
 $(\text{H}_3\text{O})_2[\text{Cu}_3(\text{tbip})_{3.5}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ($\text{H}_2\text{tbip} = 5\text{-tert-butyl isophthalic acid}$).²⁶⁻²⁹

The connectivity of the organic ligands and the mononuclear Mn^{II} SBUs in **17** results a layered architecture, whereby the hexagonal topology extends parallel to the (011) plane (Figure 4.6, a). The layers stack in an *ABAB* fashion and can be described using the Schläfli symbols as having a honeycomb {6,3} topology.³⁰ The two-dimensional honeycomb-like net results voids of almost 2 nm in diameter and is stabilised in the crystal structure by weak hydrogen bonding and π - π interactions between different layers that stack off-set in the direction of the crystallographic *a*-axis. The hydrogen bonding interactions involve the coordinating and constitutional solvent molecules, but a detailed analysis of these interactions was not possible due to the disordered nature of the constitutional solvent molecules and the low quality of the obtained data-set of the crystal structure analysis. The π - π interactions observed in the crystal structure of **17** involve the organic moieties of different layers and range between 3.795(25) Å – 4.095(54) Å. The packing arrangement of the mononuclear Mn^{II} SBUs in **17** and the network topology viewed in the direction of the crystallographic *a*- and *c*-axis are shown in Figure 4.6.

- **PHYSICOCHEMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

The IR spectrum of **17** shown in Figure 4.7 reveals some characteristic stretches of the organophosphonate ligands. The set of bands in the region $1600 - 1350\text{ cm}^{-1}$ arise from C–C skeletal vibrations of the phenyl rings, while the bands in the region $1200 - 900\text{ cm}^{-1}$ are attributed to different P–O stretching vibrations of the phosphonate groups. The two sharp bands observed between $820 - 650\text{ cm}^{-1}$ arise from C–H out-of-plane bending vibrations of the aromatic rings. Then, the corresponding O–H stretching vibrations and H–O–H bending vibrations of the crystallization water molecules engaged in H-bonds appear as broad bands at *ca.* 3200 cm^{-1} and *ca.* 1650 cm^{-1} , respectively.³¹⁻³⁵

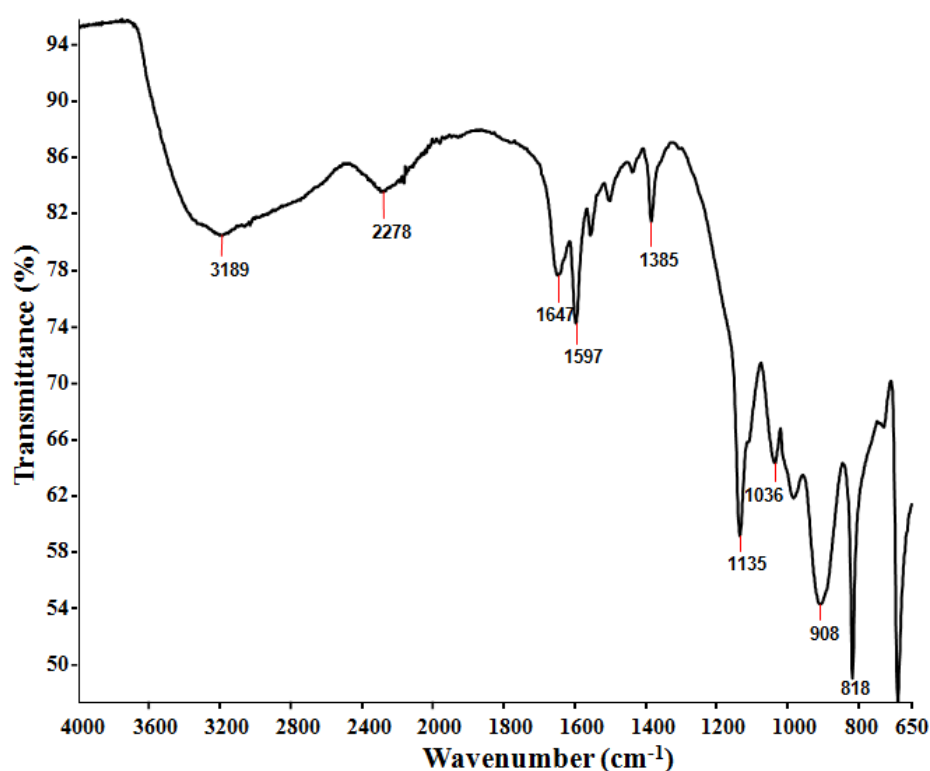


Figure 4.7 – Infrared spectrum of **17**.

- *Thermogravimetric analysis*

The thermal stability of compound **17** was investigated by thermogravimetric analysis (TGA) using a freshly prepared crystalline sample. The analysis was carried out in the temperature range between 30 and 900 °C, in an N₂ atmosphere. Upon heating **17** undergoes a weight loss of 25.1 % below 200 °C. This weight loss can be attributed to the loss of two crystallization CH₃OH molecules, three crystallization H₂O molecules, two coordinating CH₃OH molecules and one coordinating H₂O molecule (calcd: 24.5 %). Other crystallization solvent molecules of **17** may have been lost prior to the TGA. The compound then undergoes a gradual thermal decomposition between 200 – 500 °C that can be associated with the degradation of the organic ligands. The thermogravimetric step centered at 550 °C is, most likely, being associated with the formation of a metal oxide material. In addition it is expected that under the applied N₂ atmosphere, amorphous carbon is formed.

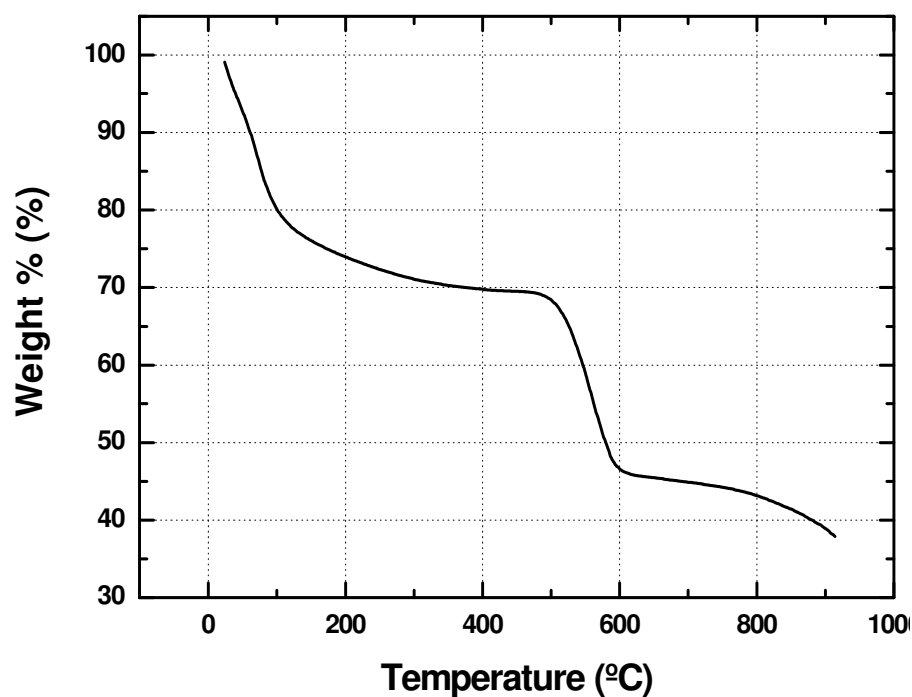


Figure 4.8 – Thermogravimetric analysis of **17**.

Table 4.4 – Crystal data and structural refinement parameters for 17.

Compound 17	
Empirical formula ^a	C ₂₆ H ₃₁ MnO ₁₃ P ₃
Molecular mass/g mol ⁻¹ ^a	699.37
Crystal colour/shape	Yellow / rectangular
Crystal size/mm ³	0.50×0.20×0.10
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	7.7458(15)
b/ Å	16.352(3)
c/ Å	16.975(5)
α /°	112.58(3)
β /°	100.65(3)
γ /°	100.90(3)
V/ Å ³	1869.2(7)
Z	1
Temperature (K)	150(2)
Density/Mg m ⁻³	1.358
Absorp. coef./mm ⁻¹	0.547
F(000)	756
$2\theta_{\text{max}}$ /°	50
Reflections collected	28825
Independent reflections	6578 [R(int) = 0.2102]
Data / restraints / parameters	6578 / 0 / 464
S on F^2	1.027
R ₁ , wR ₂ [I>2 σ (I)]	0.0802, 0.1962
R ₁ , wR ₂ (all data)	0.1260, 0.2678
Largest diff. peak and hole/e.Å ⁻³	0.948 and -1.329

^a Excluding solvate molecules

4.3.2 $(\text{H}_3\text{O})\{\text{Cu}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ (**18**)

Compound **18**, $(\text{H}_3\text{O})\{\text{Cu}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ was prepared by the reaction of P-TPB with $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ in MeOH. Needle-like green crystals of **18** were obtained during a time period of five days and characterised by single crystal X-ray diffraction measurements.

18 crystallises in the triclinic crystal system in the space group $P\bar{1}$, and is structurally closely related to **17**. It consists of a coordination network containing mononuclear Cu^{II} SBUs, in which the Cu^{II} ion displays a distorted octahedral coordination environment. The coordination sphere of the Cu ion consists of two oxygen atoms originating from two coordinating water molecules, one oxygen donor arising from a CH_3OH ligand and the remaining coordination sites are occupied by monodentate oxygen donors originating from three distinct phosphonate ligands (Figure 4.9). The deviation of the Cu^{II} ion from the ideal octahedral coordination geometry can be visualised by examining the bond angles and bond lengths of the Cu(II) centre. The bond distances between the Cu ion and the O donors originating from the organic phosphonate ligands vary between 1.897(6) Å – 1.962(5) Å. The three O donors originating from the organic ligands are located in the equatorial plane of the octahedra, along with a fourth O donor of a water molecule (Cu(1)-O(1') of 1.961(6) Å). The apical binding sites of the octahedral coordination polyhedron are occupied by one O atom from a water molecule and one O atom from a methanol molecule. The bond distance between the Cu ion and the O atom of the water molecule Cu(1)-O(8') is 2.201(15) Å, and the Cu-O_{methanol} bond length, Cu(1)-O(7') is 2.209(11) Å. These two bonds involving the O atoms located in the apical position of the octahedra are slightly elongated when compared to those in the equatorial plane and which might be explained by the Jahn-Teller (JT) effect of d^9 ion in octahedral coordination environment. The bond angles of the Cu ion also deviate slightly from those expected of an ideal octahedral geometry. The bond angles O(8')-Cu(1)-O(7'), O(1')-Cu(1)-O(4) and O(1)-Cu(1)-O(7) of 178.1(7)°, 171.5(3)° and 168.5(3)°, respectively, deviate from the ideal octahedral angle of 180°, whilst the bond angles O(4)-Cu(1)-O(8') and O(4)-Cu(1)-O(7') of 101.9(5)° and 79.3(3)°, respectively, show the greatest deviation from the ideal angle of 90°. Selected bond distances and bond angles for compound **18** are summarised in Table 4.5 and Table 4.6, respectively.

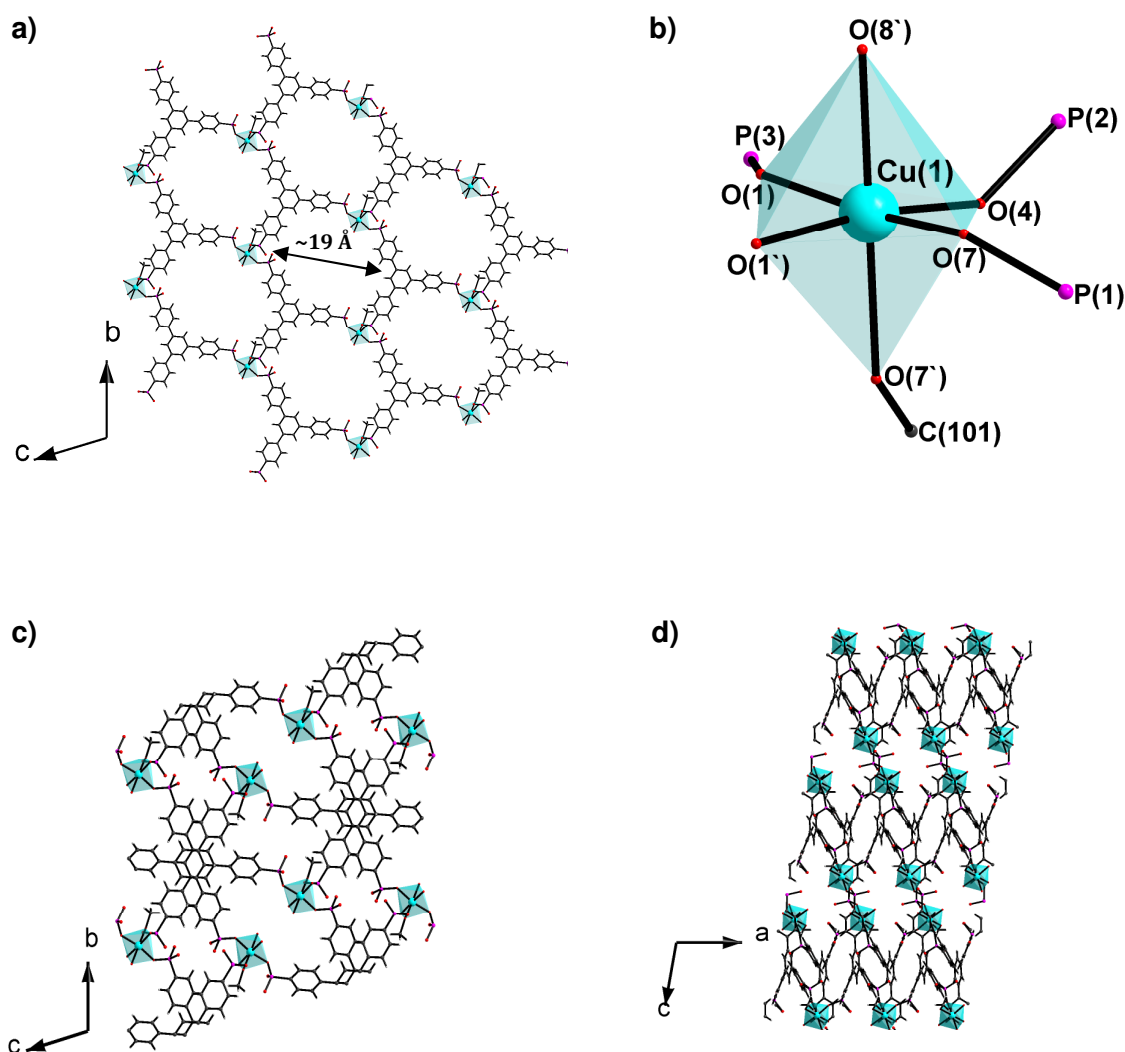


Figure 4.9 – (a) The hexagonal packing arrangement of the mononuclear Cu^{II} SBUs in **18** as seen in the direction of the crystallographic a -axis; (b) The coordination environment of the Cu^{II} ion; (c) and (d) Packing arrangement of the 2D networks in **18** viewed in the direction of the crystallographic a - and b -axis, respectively. Colour code: Mn blue, P purple, O red, C dark grey, H light grey (crystallization solvent molecules have been omitted for clarity).

Table 4.5 – Selected bond lengths [$\text{\AA}$] for compound **18**.

Bond	Bond distances ($\text{\AA}$)
Cu(1)-O(1)	1.897(6)
Cu(1)-O(7)	1.926(6)
Cu(1)-O(1')	1.961(6)
Cu(1)-O(4)	1.962(5)
Cu(1)-O(8')	2.201(15)
Cu(1)-O(7')	2.209(11)
P(1)-O(7)	1.505(7)
P(1)-O(9)	1.510(9)
P(1)-O(8)	1.559(11)

Table 4.6 – Selected bond angles [°] for compound 18.

Bond Angle (°)		Bond Angle (°)	
O(8')-Cu(1)-O(7')	178.1(7)	O(1')-Cu(1)-O(7')	92.2(4)
O(1')-Cu(1)-O(4)	171.5(3)	O(1)-Cu(1)-O(8')	87.0(6)
O(1)-Cu(1)-O(7)	168.5(3)	O(1')-Cu(1)-O(8')	86.6(6)
O(4)-Cu(1)-O(8')	101.9(5)	O(7)-Cu(1)-O(1')	86.3(3)
O(7)-Cu(1)-O(4)	94.8(3)	O(1)-Cu(1)-O(1')	86.2(3)
O(7)-Cu(1)-O(7')	94.5(7)	O(7)-Cu(1)-O(8')	83.9(7)
O(1)-Cu(1)-O(7')	94.4(7)	O(4)-Cu(1)-O(7')	79.3(3)
O(1)-Cu(1)-O(7')	93.9(2)		

Similar with **17**, all three phosphonate groups of the organic ligands in **18** are monodentate and singly protonated, and the overall charge of the network is compensated by one H_3O^+ ion. In the solid state **18** displays a similar packing arrangement with **17**, and builds up into a two-dimensional honeycomb-like net that adopts a {6,3} topology, to form a layered structure. The packing arrangement of the mononuclear Cu^{II} complexes in **18** viewed in the direction of the crystallographic *a*- and *b*-axis is shown in Figure 4.9.

- **PHYSICOCHMICAL CHARACTERISATION**

- *FT-IR spectroscopy*

The IR spectrum of **18** shown in Figure 4.10 is almost identical with that of **17**. Characteristic C–C skeletal vibrations and C–H out-of-plane bending vibrations of the phenyl rings can be observed in the IR spectrum between $1600 - 1350\text{ cm}^{-1}$ and $850 - 650\text{ cm}^{-1}$, respectively. Different P–O stretching vibrations of the phosphonate groups can be observed in the range $1200 - 900\text{ cm}^{-1}$, while the O–H stretching vibrations and H–O–H bending vibrations of the crystallization water molecules engaged in H-bonds appear as broad bands at ca. 3200 cm^{-1} and ca. 1650 cm^{-1} , respectively.³¹⁻³⁵

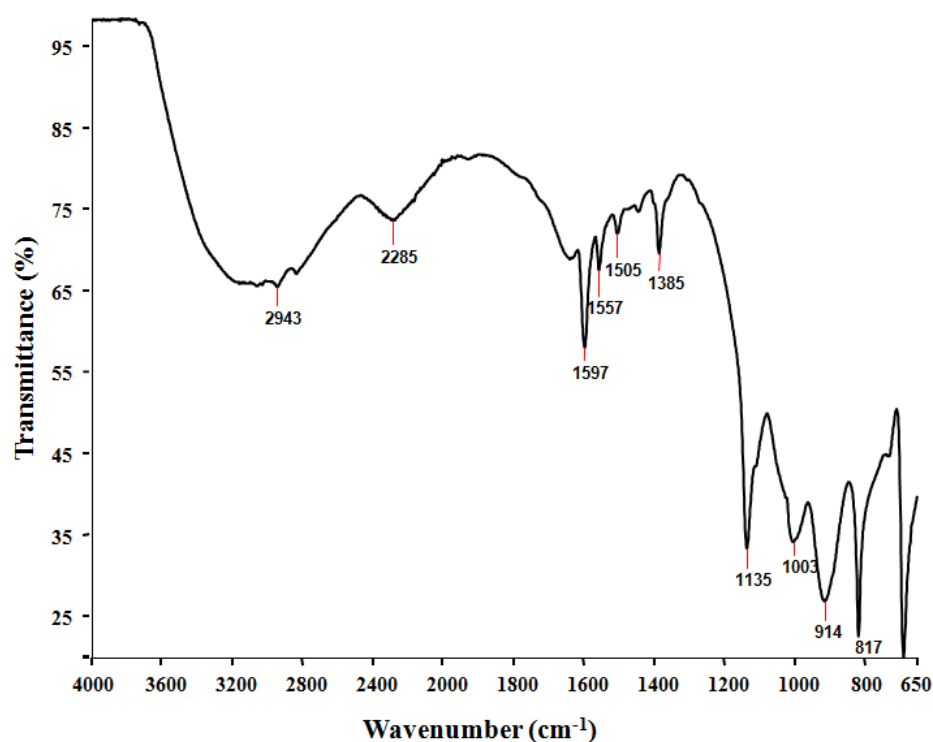


Figure 4.10 – Infrared spectrum of **18**.

- *Thermogravimetric analysis*

The thermal stability of a freshly prepared crystalline sample of **18** was investigated in an N₂ atmosphere, in the temperature range 30 – 900 °C (Figure 4.11). TGA reveals that **18** undergoes a similar decomposition pathway as **17**. The first thermogravimetric step corresponding to 18.9 % is observed in the temperature range between 30 – 200 °C. This weight loss can be attributed to the loss of four crystallization H₂O molecules, one coordinating CH₃OH molecule and two coordinating H₂O molecules (calcd: 18.3 %). Other crystallization solvent molecules of **18** may have been lost prior to the TGA. The oxidation of the organic ligands can be observed above 200 °C resulting, most likely, in the formation of a metal oxide material and amorphous carbon.

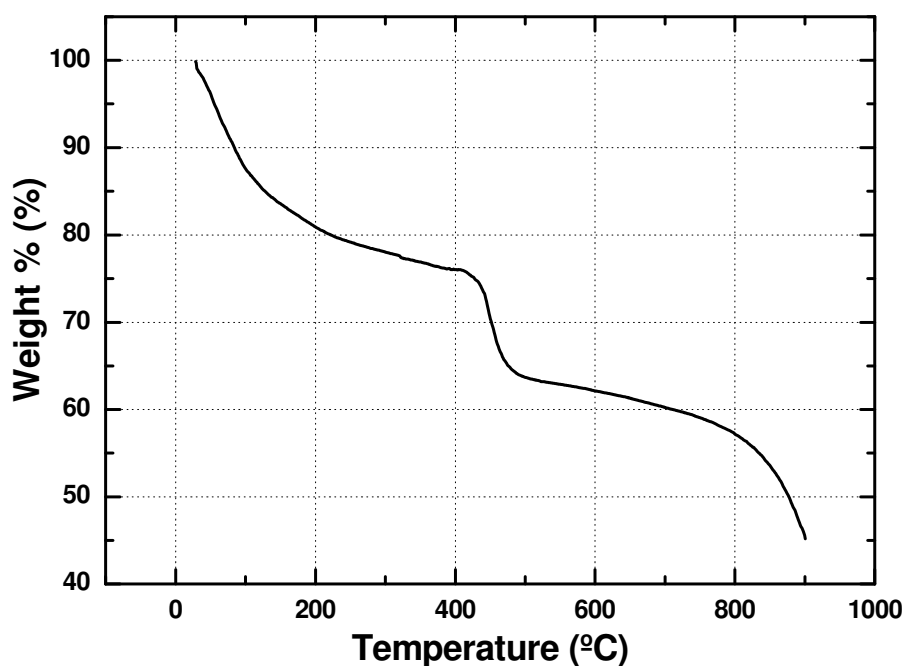


Figure 4.11 – Thermogravimetric analysis of **18**.

Table 4.7 – Crystal data and structural refinement parameters for 18.

Compound 18	
Empirical formula ^a	C ₂₅ H ₂₉ CuO ₁₃ P ₃
Molecular mass/g mol ⁻¹ ^a	693.95
Crystal colour/shape	Light green / needle
Crystal size/mm ³	0.60×0.20×0.20
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a/ Å	7.4116(15)
b/ Å	15.240(3)
c/ Å	15.942(3)
α /°	105.45(3)
β /°	98.15(3)
γ /°	95.68(3)
V/ Å ³	1700.4(6)
Z	2
Temperature (K)	150(2)
Density/Mg m ⁻³	1.443
Absorp. coef./mm ⁻¹	0.849
F(000)	748
2 θ_{max} /°	50
Reflections collected	18080
Independent reflections	5964 [R(int) = 0.0287]
Data / restraints / parameters	5964 / 0 / 409
S on <i>F</i> ²	1.029
R ₁ , wR ₂ [I>2 σ (I)]	0.1171, 0.4288
R ₁ , wR ₂ (all data)	0.1237, 0.4555
Largest diff. peak and hole/e.Å ⁻³	1.749 and -1.129

^a Excluding solvate molecules

4.4 CONCLUSION AND FUTURE WORK

In this chapter we describe that room temperature synthetic methods can be used to produce coordination networks that employ mononuclear, partially solvated SBUs and triphosphonate ligands as linkers.

One of the aims of this project was to synthesise organophosphonate-based open-frameworks. To accomplish this, extended triphosphonate ligands, 1,3,5-tris(4-phosphonophenyl)benzene (P-TPB) and 1,3,5-tris(4'-phosphonobiphenyl-4-yl)benzene (P-TBB) were employed.

Metal organic frameworks in **17** and **18**, containing mononuclear Mn(II) and Cu(II) SBUs assemble in the presence of the P-TPB ligand. The two structurally related compounds exhibit a 2D layered architecture with hexagonal topologies. These 2D nets pack in the solid state in an *ABAB* fashion. Due to the fact that the metal complexes are partially solvated one expects that the stability of the two-dimensional honeycomb-like net is limited. This is substantiated by the thermogravimetric analysis of the compounds. The packing structure of **17** and **18** is further characterised by weak hydrogen bonding and π - π interactions. BET analyses of **17** and **18** revealed almost negligible surface areas of samples that were treated under vacuum. The materials did not show any permanent porosity.

During the course of the project, we designed an even more extended tri-functional phosphonate ligand, P-TBB. The ligand crystallises to generate a honeycomb-like supramolecular structure that has cross-sectional diameters of about 2.5 nm. We believe that this ligand has the potential to generate MOFs. However, up to now we were not able to unambiguously characterise new coordination compounds using this ligand. The low solubility of this ligand severely hampered the isolation of crystalline materials. In addition, synthetic approaches often resulted in precipitations.

Future research efforts will be devoted to the construction of rigid three-dimensional networks using this rather unique ligand and solvothermal synthesis approaches in less polar solutions might allow the crystallisation of the MOFs.

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5. EXPERIMENTAL

5.1 MATERIALS AND METHODS

5.1.1 Reagents

All chemicals and solvents were of reagent grade and purchased from Sigma-Aldrich Ltd., Fluka Chemica-Biochemica (U.K.), ABCR GmbH & Co. KG (Germany) or local solvent suppliers and used as received, unless otherwise stated. Water was deionised before use.

5.1.2 Elemental Analysis

Elemental analyses were performed using an Exeter Analytical CE 440 housed at the analytical laboratory, UCD Belfield.

5.1.3 Infrared Spectroscopy

Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using a universal Attenuated Total Reflectance (ATR) sampling accessory. Data were collected and processed using Spectrum v5.0.1 (2002 PerkinElmer Instrument LLC) software. The scan rate was 16 scans per minute with a resolution of 4 scans in the range 4000-600 cm^{-1} . The following abbreviations were used to describe the intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad and vbr, very broad.

5.1.4 Nuclear Magnetic Resonance Spectroscopy

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 400.13 MHz, 100.14 MHz and 161.98 MHz, respectively, by either Dr. John O'Brien or Dr. Manuel Rüther. Samples were carried out in deuterated solvents and are listed for each spectrum. Chemical shifts are reported in ppm and coupling constants in Hertz. Standard abbreviations for spectra: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; qt quartet; q, quaternary; m, multiplet; br broad, J, coupling constant.

5.1.5 Ultraviolet – Visible Spectroscopy

UV/vis spectra were recorded in the range 200-800 nm on a Cary 300 Scan spectrophotometer at 20 °C using quartz cells of 1 cm path length.

5.1.6 Thermogravimetric Analysis

Thermogravimetric analysis was carried out using a Perkin Elmer Pyris 1TGA, in an N₂ atmosphere, using a ceramic crucible (*ca.* 2 mg sample; heating rate of 10 °C/min; range 25-900 °C). The instrument was calibrated to Ni and Fe standards in N₂ atmosphere.

5.1.7 Single Crystal X-ray Diffraction

X-ray analyses for crystals described in this report were performed by Dr. Tom McCabe, Dr. Lei Zhang, Dr. Nianying Zhu or Dr. Wolfgang Schmitt with a Bruker SMART APEX CCD diffractometer, a Rigaku Saturn-724 diffractometer or a Bruker APEX2 Duo diffractometer.

The Bruker SMART APEX CCD and the Rigaku Saturn-724 diffractometers utilise a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) source, while the Bruker APEX2 Duo utilises two radiation sources, a Mo-K α source and a high intensity Cu-K α source ($\lambda = 1.5418 \text{ \AA}$) generated from a microfocus anode. This Cu source was especially useful for the analysis of small crystal samples. The omega and phi scans method was used to collect either a full sphere or hemisphere of data for each crystal with a detector to crystal distance of either 5 or 6 cm. The data sets collected from the Bruker SMART APEX CCD diffractometer were processed and corrected for Lorentz and polarisation effects using SMART¹ and SAINT-PLUS² software. The structures were solved using direct methods with the SHELXTL³ program package. The data sets from the Rigaku Saturn-724 diffractometer were collected using Crystalclear-SM 1.4.0 software. Data integration, reduction and correction for absorption and polarisation effects were all performed using the Crystalclear-SM 1.4.0 software.⁴ Space group determination, structure solution and refinement were obtained using the Crystalstructure ver.3.8 and the Bruker SHELXTL³ software. Datasets collected on the Bruker APEX2 Duo were processed and the structures solved using Bruker APEX v2011.8-0 software.⁵

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms (excluding water) were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters. The SQUEEZE/PLATON program was used in the structural refinement in the case where there were a large number of solvent molecules disordered within the structure.⁶

5.1.8 X-Ray Powder Diffraction

X-ray powder diffraction was performed using a Siemens D500 diffractometer with Cu-K α_1 radiation with a wavelength of $\lambda = 1.54056 \text{ \AA}$.

5.1.9 Magnetic Measurements

All magnetic measurements were performed and modelled by Prof. Rodolphe Cl  rac at the Centre de Recherche Paul Pascal (CRPP), Pessac, France. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL and susceptometer PPMS-9. The MPMS-XL magnetometer operates between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on polycrystalline samples. ac-Susceptibility measurements were performed with an oscillating ac field of 3 Oe with a frequency between 1 to 1500 Hz or 1 Oe with a frequency between 10 to 10000 Hz (PPMS-9). The magnetic data were corrected for the sample holder and the diamagnetic contributions.

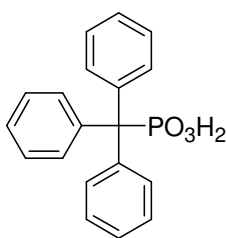
5.1.10 Mass Spectrometry

Electrospray ionization (ESI) mass spectra were collected by Dr. J. Bernard Jean-Denis and Dr. Martin Feeney, using a TOF-MS (Time-of-Flight – Mass Spectrometer, LCT Premier) instrument supplied by Waters Corp. All data, including simulated isotope patterns and molecular weight calculations, were processed using Masslynx v 4.0 (Waters Corp.) data analysis software.⁷ An injection of a standard sodium formate (Na[CHO₂Na]_n, 10% formic acid/0.1M NaOH/acetonitrile, 1:1:8, v/v/v) solution was used, for a mass calibration between m/z 100-3000. Samples were introduced into the MS *via* a waters alliance 2690 HPLC at a solvent flow rate of 200 $\mu\text{L min}^{-1}$, whilst a Leu-Enk solution (10 $\mu\text{g mL}^{-1}$ in acetonitrile/0.1 TFA in water, 50:50, v/v) was co-injected *via* a micropump at 2

$\mu\text{L min}^{-1}$ and used as an internal lock mass. The ESI settings were set with the nebuliser gas and desolvation gas at 60 and 500 L h^{-1} , respectively. The ESI gas used was nitrogen. Source and desolvation gas temperature were set at 100 and 200 $^{\circ}\text{C}$, respectively. The ion polarity for all MS scans were recorded in negative mode with voltage of the capillary tip set between 2.5-3 kV, sample cone at 30 V, extraction cone at 3 V, RF value set between 100-1000, m/z range set between 100-3000, scan time at 0.9 sec and inter-scan delay set at 0.1 sec.

5.2 LIGAND SYNTHESIS

5.2.1 Synthesis of Triphenylmethylphosphonic acid (P-TPM)

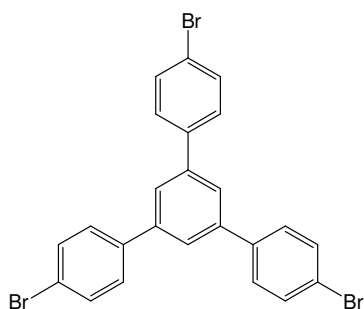


Triphenylmethylphosphonic acid was prepared according to literature procedures.⁸⁻¹⁰ Triphenylcarbinol (10 g, 38 mmol) and phosphorus trichloride (10 g, 74 mmol) were added to an ice-cooled flask and kept in the ice bath for 30 min. After removal from the ice bath the reaction mixture was refluxed for one hour. A small quantity of diethyl ether was added to the resulting pale-yellow solid, followed by the addition of some ice-cooled deionised H_2O . The formed product was collected by filtration, washed with aqueous ammonia and water and dried in a vacuum desiccator. In order to remove the triphenylchloromethane, which is produced along with triphenylmethoxyphosphorus dichloride, the crude product was boiled for 2 min in ethanol. The triphenylmethoxyphosphorus dichloride was further purified by recrystallizing from chloroform to which acetone was added (2:1 v:v mixture).

Triphenylmethoxyphosphorus dichloride (4 g, 11 mmol) and 60 mL of 8% potassium hydroxide solution in ethanol was heated under reflux for 45 min. The reaction mixture was treated with 30 mL of water and the mixture was evaporated to dryness on a water bath. The solid residue was treated with 1 L of water and the mixture was made alkaline by the addition of a small quantity of potassium hydroxide. After this, the mixture was boiled, cooled and filtered. Then, some hydrochloric acid was added to the clear filtrate (till the solution became slightly acidic) and a white precipitate of

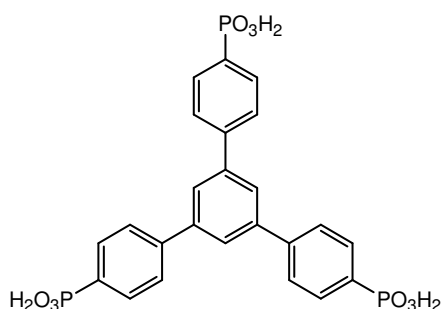
triphenylmethylphosphonic acid formed. After standing for 2 h, the precipitate was filtered, washed with 100 mL of water containing 1 mL of HCl and dried in a vacuum desiccator. The product was recrystallized from ethanol. Yield: ~ 55%. Mp: 235 °C. FT-IR (cm^{-1}) ν_{max} : 1597(w), 1492(m), 1445(m), 1178(m), 1158(m), 1086(w), 1031(s), 988(s), 968(s), 930(sh), 880(w), 758(s), 743(s), 698(s). ^1H NMR (400 MHz, DMSO): δ (ppm) = 7.28 (m, 15H, C_6H_5). ^{13}C NMR (100 MHz, DMSO): δ (ppm) = 142.5 (3Cq, C_6H_5), 130.1 (6C, C_6H_5), 127.6 (6C, C_6H_5), 126.5 (3C, C_6H_5), 61.8 (Cq, C- Ph_3). ^{31}P NMR (162 MHz, DMSO): δ (ppm) = 25.1. ESI-MS (DMSO): 347.0 m/z [$\text{C}_{19}\text{H}_{17}\text{O}_3\text{PNa}$] $^+$.

5.2.2 Synthesis of Tris(4-bromophenyl)benzene (Br-TPB)



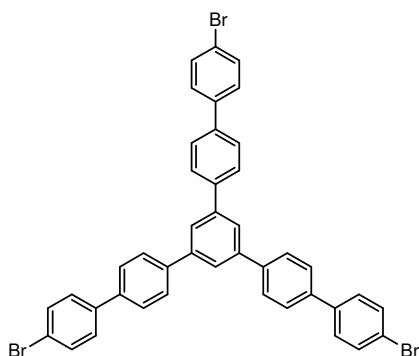
The Br-TPB ligand was prepared by a condensation reaction, according to literature methods.¹¹ 4-Bromoacetophenone (20 g, 10.050 mmol), 1 mL of $\text{H}_2\text{SO}_4(\text{c})$ and $\text{K}_2\text{S}_2\text{O}_7$ (30 g, 118 mmol) were added to a round-bottom flask and heated at 180 °C for 14 h. The resulting crude solid was cooled to room temperature and refluxed in 100 mL of EtOH for 1 h. Then, the yellow solid was collected by filtration and refluxed again in 100 mL of H_2O . The resulting product was dried under vacuum and purified by recrystallizing from chloroform. Yield: ~ 80%. Mp: 260 °C. FT-IR (cm^{-1}) ν_{max} : 3090(w), 1626(m), 1584(m), 1509(m), 1488(s), 1440(m), 1378(m), 1244(m), 1072(s), 1004(s), 885(w), 809(s), 698(m). ^1H -NMR (400 MHz, CDCl_3): δ (ppm) = 7.72 (s, 3H, C_6H_3), 7.63 (d, 6H, $^3J_{\text{HH}} = 8.5$ Hz, C_6H_4), 7.55 (d, 6H, $^3J_{\text{HH}} = 8.5$ Hz, C_6H_4). ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) = 141.0 (3Cq, C_6H_3), 139.1 (3Cq, C_6H_4), 131.6 (6C, C_6H_4), 128.4 (6C, C_6H_4), 124.5 (3C, C_6H_3), 121.6 (3Cq, $\text{C}_6\text{H}_4\text{-Br}$).

5.2.3 Synthesis of 1,3,5-Tris(4-phosphonophenyl)benzene (P-TPB)



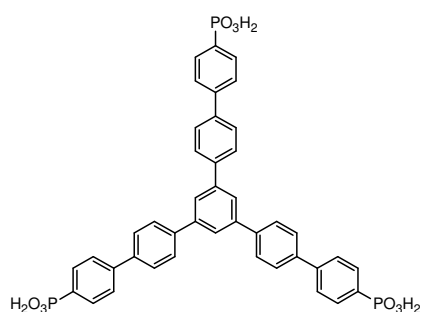
A slightly modified Arbuzov reaction was used for the synthesis of the phosphonate diethylester of the desired acid.¹² Tris(4-bromophenyl)benzene (10.860 g, 20 mmol) in 50 mL of 1,3-diisopropylbenzene was heated to 185 °C in a 250-mL three-necked round-bottom flask, fitted with a Dean Stark apparatus used in combination with a reflux condenser, N₂ inlet, and an additional funnel. The flask was purged with N₂, and 0.50 g of NiBr₂ was added as a catalyst. Then, 10 mL triethyl phosphite was added over a 6 h period under a gentle stream of N₂. The generated ethyl bromide was continuously removed from the reaction mixture until the reaction was complete. The mixture was further refluxed for 24 h followed by the addition of 0.25 g of NiBr₂ and 5 mL of triethyl phosphite. After refluxing for another 24 h, the cooled black solution was distilled under vacuum to remove the solvent and unreacted triethyl phosphite. The resulting black solid was dissolved in CHCl₃, and the product was extracted with petroleum ether to afford a viscous yellow oil after removing the solvent. This phosphonate diethyl ester was then converted to the corresponding triphosphonic acid by refluxing in HCl. The viscous residue resulted from removing the solvent was dried at high vacuum to obtain the product as an off-white, foam-like solid. Yield: ~ 58%. Mp: 300 °C. FT-IR (cm⁻¹) ν_{max}: 2976(vbr), 1600(m), 1558(vw), 1387(w), 1139(s), 1042(s), 1016(s), 923(s), 818(s), 755(m), 680(s). ¹H NMR (400 MHz, DMSO): δ (ppm) = 8.02 (s, 3H, C₆H₃), 7.99 (m, 6H, ³J_{HH} = 8.0 Hz, ⁴J_{PH} = 2.5 Hz, C₆H₄), 7.80 (dd, 6H, ³J_{HH} = 8.0 Hz, ³J_{PH} = 12.5 Hz, C₆H₄-PO₃H₂). ¹³C NMR (100 MHz, DMSO): δ (ppm) = 142.0 (3Cq, C₆H₄), 141.0 (3Cq, C₆H₃), 134.2 (3Cq, C₆H₄-PO₃H₂), 131.1 (6C, C₆H₄), 127.0 (6C, C₆H₄), 125.1 (3C, C₆H₃). ³¹P NMR (162 MHz, DMSO): δ (ppm) = 13.7. ESI-MS (H₂O): 545.0 *m/z* [C₂₄H₂₀O₉P₃]⁻.

5.2.4 Synthesis of 1,3,5-Tris(4'-bromobiphenyl-4-yl)benzene (Br-TBB)



The Br-TBB ligand was prepared by a condensation reaction, according to literature procedure.¹³ 4-Acetyl-4'-bromobiphenyl (4.400 g, 0.016 mol), trifluoromethanesulfonic acid (0.8 mL), and toluene (35 mL) were added to a 100 mL three-necked round-bottom flask fitted with a magnetic stirrer, a condenser, and a nitrogen inlet. The reaction solution was refluxed under nitrogen for 15 h at 120 °C. After cooling, the crude product was collected by filtration, washed with methanol, and purified by recrystallizing twice from chloroform. The product was washed again with plenty of methanol and the off white (slightly orange) powder was dried in the oven at 60 °C. Yield: ~ 48%. Mp: 280 °C. FT-IR (cm⁻¹) ν_{max} : 3033(w), 1650(m), 1584(m), 1479(m), 1441(w), 1386(m), 1274(m), 1219(m), 1195(m), 1075(m), 999(m), 952(w), 848(w), 807(s), 700(w), 669(w). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.89 (s, 3H, C₆H₃), 7.82 (d, 6H, ³J_{HH} = 8.0 Hz, C₆H₄), 7.72 (d, 6H, ³J_{HH} = 8.0 Hz, C₆H₄), 7.62 (d, 6H, ³J_{HH} = 8.0 Hz, C₆H₄), 7.56 (d, 6H, ³J_{HH} = 8.0 Hz, C₆H₄). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 141.4 (3Cq, C₆H₃), 138.8 (9Cq, C₆H₄), 131.5 (6C, C₆H₄-Br), 128.2 (6C, C₆H₄), 127.4 (6C, C₆H₄), 126.9 (6C, C₆H₄), 124.6 (3C, C₆H₃), 121.3 (3Cq, C₆H₄-Br). MALDI-TOF MS (DMSO): 767.9 *m/z* [C₄₂H₂₇Br₃].

5.2.5 Synthesis of 1,3,5-Tris(4'-phosphonobiphenyl-4-yl)benzene (P-TBB)



The phosphonate diethylester of the desired acid was prepared using a slightly modified Arbusov reaction, and then converted to the corresponding triphosphonic acid by ester hydrolysis under acidic conditions.¹² 1,3,5-Tris(4'-bromobiphenyl-4-yl)benzene (7.827 g, 10.104 mmol) and 35 mL of 1,3-diisopropylbenzene were added to a 250 mL three-

necked round-bottom flask, fitted with a Dean-Stark apparatus used in combination with a reflux condenser, N₂ inlet and an addition funnel. The solution was heated to 185°C, and 0.25 g of NiBr₂ was added as a catalyst. The flask was purged with N₂, and 7 mL triethyl phosphite was added over a 4 h period under a gentle stream of N₂. The generated ethyl bromide was continuously removed from the reaction mixture until the reaction was complete. The mixture was further refluxed for 24 h followed by the addition of 0.125 g of NiBr₂ and 3 mL of triethyl phosphite. After refluxing for another 24 h, the cooled black solution was distilled under vacuum to remove the solvent and unreacted triethyl phosphite. The resulted grey solid was then refluxed in HCl to convert the ester into the corresponding triphosphonic acid. CH₃OH was added to aid dissolution. The solvent was then removed under vacuum, and the viscous residue was dried at high vacuum, which afforded the product as a brown solid. Yield: ~ 66%. Mp: 310 °C. FT-IR (cm⁻¹) $\nu_{\max}$: 3334(br), 2247(w), 1599(m), 1492(w), 1441(w), 1387(w), 1139(m), 989(s), 922(s), 810(s), 757(s), 659(s). ¹H NMR (400 MHz, DMSO): δ (ppm) = 8.05 (m, 9H), 7.87 (m, 18H). ¹³C NMR (100 MHz, DMSO): δ (ppm) = 141.6 (3Cq, C₆H₄), 140.9 (3Cq, C₆H₃), 139.5 (6Cq, C₆H₄), 138.5 (3Cq, C₆H₄-PO₃H₂), 131.2 (6C, C₆H₄), 127.7 (12C, C₆H₄), 127.2 (6C, C₆H₄), 126.2 (3C, C₆H₃). ³¹P NMR (162 MHz, DMSO): δ (ppm) = 12.6. ESI-MS (CH₃CN): 773.1 m/z [C₄₂H₃₂O₉P₃]⁻.

1,3,5-Tris(4'-phosphonobiphenyl-4-yl)benzene (P-TBB) (0.116 g, 0.150 mmol) was dissolved under stirring in DMF (5 mL), at room temperature, and 2 mL of CH₃CN were layered to obtain needle-like colourless crystals overnight. Yield: ~ 43%. Anal. Calc. for C₅₀H₆₅N₄O₁₉P₃, Expected: C% 53.67, H% 5.85, N% 5.01. Found: C% 53.40, H% 5.55, N% 5.15. FTIR (cm⁻¹) $\nu_{\max}$: 2929(w), 2321(br), 1655(s), 1596(m), 1493(m), 1437(m), 1410(m), 1386(s), 1253(m), 1137(s), 1092(s), 1000(s), 918(s), 814(s), 757(s), 658(s).

5.3 SYNTHESIS OF THE METAL COMPLEXES

5.3.1 Synthesis of $(\text{NH}_4)_2\text{H}_2[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_5)_4]\cdot 5\text{H}_2\text{O}$ (1)

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.224 g, 0.180 mmol) and $\text{CH}_3\text{COONH}_4$ (0.500 g, 6.488 mmol) were dissolved under stirring in H_2O (10 mL) at room temperature and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ (0.032 g, 0.244 mmol) was added as a reducing agent. Then phenylarsonic acid (0.612 g, 3.030 mmol) was added and the resulting reaction mixture was stirred for 10 minutes. Subsequently, the pH was adjusted to pH = 3.9 (20°C) through the addition of 3.32 mL of aqueous CH_3COOH solution (50%, v/v). After three weeks red-brown crystals were collected from a dark blue solution, and washed with cold water. Yield: ~ 57%. Anal. Calc. for $\text{As}_4\text{C}_{24}\text{H}_{40}\text{Mo}_4\text{N}_2\text{O}_{25}$, Expected: C% 20.01, H% 2.79, N% 1.94. Found: C% 19.65, H% 2.15, N% 1.69. FT-IR (cm^{-1}) ν_{max} : 2981(b), 1641(w), 1439(m), 1092(m), 966(vs), 743(vs). ^1H NMR (400 MHz, DMSO): δ (ppm) = 7.67 (m, 12H, C_6H_5), 7.97 (d, $^3J_{\text{HH}} = 7.0$ Hz, 8H, C_6H_5). UV/Vis (DMF): λ_{max} (ϵ) = 457 nm ($1000 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.2 Synthesis of $(\text{NH}_4)_2\text{H}_2[\text{Mo}^{\text{V}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4]\cdot \text{DMF}\cdot 4\text{H}_2\text{O}$ (2)

$\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ (0.032 g, 0.244 mmol) was added to a mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.224 g, 0.180 mmol), $\text{CH}_3\text{COONH}_4$ (0.500 g, 6.488 mmol), H_2O (5 mL) and DMF (5 mL). The solution was vigorously stirred for 5 min and (4-aminophenyl)arsonic acid (0.659 g, 3.030 mmol) was added. The resulting reaction mixture was further stirred for 10 min and subsequently the pH was adjusted to pH = 4.9 (20°C) through addition of an aqueous CH_3COOH solution (50%, v/v). Red-brown crystals were obtained after 5-7 days. Yield: ~ 53%. Anal. Calc. for $\text{As}_4\text{C}_{27}\text{H}_{49}\text{Mo}_4\text{N}_7\text{O}_{25}$, Expected: C% 20.85, H% 3.17, N% 6.30. Found: C% 21.14, H% 2.61, N% 6.23. FT-IR (cm^{-1}) ν_{max} : 3329(m), 3209(m), 1714(w), 1628(m), 1594(s), 1502(m), 1425(m), 1295(w), 1182(w), 1095(m), 958(s), 768(vs), 692(s). ^1H NMR (400 MHz, DMSO): δ (ppm) = 5.80 (s, 8H, NH_2), 6.73 (d, $^3J_{\text{HH}} = 8.5$ Hz, 8H, C_6H_5), 7.56 (d, $^3J_{\text{HH}} = 8.5$ Hz, 8H, C_6H_5). UV/Vis (DMF): λ_{max} (ϵ) = 460 nm ($1000 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.3 Synthesis of $(\text{NH}_4)_5[\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_3\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]\cdot 9\text{H}_2\text{O}$ (3)

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.224 g, 0.180 mmol) and $\text{CH}_3\text{COONH}_4$ (0.500 g, 6.488 mmol) were dissolved under stirring in H_2O (10 mL) at room temperature and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ (0.032 g, 0.244 mmol) was added as a reducing agent. Then (4-hydroxyphenyl)arsonic acid (0.660 g, 3.030 mmol) was added and the resulting reaction mixture was stirred for 10 minutes. Subsequently the pH was adjusted to pH = 4.0 (20°C) through addition of 3.32 mL of an aqueous CH_3COOH solution (50%, v/v). Dark blue crystals were collected after a week, and washed with cold water. Yield: ~ 53%. Anal. Calc. for $\text{As}_5\text{C}_{30}\text{H}_{63}\text{Mo}_5\text{N}_5\text{O}_{40}$, Expected: C% 18.12, H% 3.19, N% 3.52. Found: C% 19.03, H% 2.70, N% 3.20. FT-IR (cm^{-1}) ν_{max} : 2998(vbr), 1582(m), 1500(w), 1425(s), 1253(m), 1171(w), 1092(s), 944(s), 729(s). UV/Vis (DMF): λ_{max} (ϵ) = 531 nm (2700 L mol⁻¹ cm⁻¹).

5.3.4 Synthesis of $(\text{NH}_4)_4[\text{Mo}^{\text{VI}}_4\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_3\text{NO}_2\text{OH})_4]\cdot 2\text{H}_2\text{O}$ (4)

Synthetic procedure as for **1**, using (4-hydroxy-3-nitrophenyl) arsonic acid (0.797 g, 3.030 mmol) as ligand. The pH was adjusted to pH = 3.9 (20°C) through addition of 3.32 mL of an aqueous CH_3COOH solution (50%, v/v) and orange crystals of $(\text{NH}_4)_4[\text{Mo}_4\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_3\text{NO}_2\text{OH})_4]\cdot 2\text{H}_2\text{O}$ were obtained within three weeks. Yield: ~ 75%. Anal. Calc. for $\text{As}_4\text{C}_{24}\text{H}_{36}\text{Mo}_4\text{N}_8\text{O}_{36}$, Expected: C% 17.00, H% 2.14, N% 6.61. Found: C% 16.52, H% 2.06, N% 5.61. FT-IR (cm^{-1}) ν_{max} : 3189(br), 1614(m), 1570(w), 1532(w), 1407(m), 1355(w), 1327(m), 1247(w), 1158(m), 1099(m), 940(w), 810 (vs), 762(s).

5.3.5 Synthesis of $(\text{NH}_4)_4\cdot\text{H}_4\{\text{Mn}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (5)

MoO_3 (0.135 g, 0.930 mmol), H_3BO_3 (0.096 g, 1.550 mmol) and H_2O (10 mL) were heated to 90°C and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (0.075 mL) were added to obtain a blue clear solution. A second solution of phenylphosphonic acid (0.700 g, 4.420 mmol) in H_2O (10 mL) was heated to 90 °C and added to the first solution. The mixture was then stirred at 70 °C for 10 min, and $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.140 g, 0.700 mmol) was added. After stirring for another 30 min at 70 °C the red brown solution was kept at 45°C and orange crystals were obtained within a time period of three days. Yield: ~ 30%. Anal. Calc. for $\text{C}_{48}\text{H}_{82}\text{MnMo}_{12}\text{N}_4\text{O}_{62}\text{P}_8$, Expected: C% 18.23, H% 2.61, N% 1.77. Found: C% 19.14, H% 2.23, N% 1.50. FT-IR

(cm^{-1}) ν_{max} : 3211(vbr), 1594(m), 1438(m), 1142(m), 1024(s), 937(vs), 741(s), 721(s), 691(s). UV/Vis (CH_3CN): λ_{max} (ϵ) = 305 nm ($11000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 443 nm ($1050 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.6 Synthesis of $(\text{NH}_4)_4\cdot\text{H}_4\{\text{Fe}[\text{Mo}^{\text{V}}\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (6)

Synthetic procedure as for **5**, using $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.189 g, 0.700 mmol). Yield: ~ 40%. Anal. Calc. for $\text{C}_{48}\text{H}_{82}\text{FeMo}_{12}\text{N}_4\text{O}_{62}\text{P}_8$, Expected: C% 18.23, H% 2.61, N% 1.77. Found: C% 18.42, H% 2.02, N% 1.36. FT-IR (cm^{-1}) ν_{max} : 3216(vbr), 1595(w), 1438(m), 1142(s), 1022(s), 960(vs), 744(s), 720(s), 689(vs). UV/Vis (CH_3CN): λ_{max} (ϵ) = 274 nm ($88000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 440 nm ($1300 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.7 Synthesis of $(\text{NH}_4)_4\cdot\text{H}_4\{\text{Co}[\text{Mo}^{\text{V}}\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (7)

Synthetic procedure as for **5**, using $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.166 g, 0.700 mmol). Yield: ~ 20%. Anal. Calc. for $\text{C}_{48}\text{H}_{82}\text{CoMo}_{12}\text{N}_4\text{O}_{62}\text{P}_8$, Expected: C% 18.21, H% 2.61, N% 1.77. Found: C% 18.42, H% 2.13, N% 1.69. FT-IR (cm^{-1}) ν_{max} : 3209(vbr), 1617(m), 1441(w), 1142(m), 1093(w), 1039(s), 930(vs), 761(w), 739(m), 721 (s), 701 (w), 686 (m). UV/Vis (H_2O): λ_{max} (ϵ) = 252 nm ($30000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 450 nm ($2900 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.8 Synthesis of $(\text{NH}_4)_4\cdot\text{H}_4\{\text{Ni}[\text{Mo}^{\text{V}}\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (8)

Synthetic procedure as for **5**, using $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.166 g, 0.700 mmol). Yield: ~ 20%. Anal. Calc. for $\text{C}_{48}\text{H}_{82}\text{NiMo}_{12}\text{N}_4\text{O}_{62}\text{P}_8$, Expected: C% 18.21, H% 2.61, N% 1.77. Found: C% 17.83, H% 1.99, N% 1.52. FT-IR (cm^{-1}) ν_{max} : 3215(vbr), 1618(m), 1439(m), 1142(m), 1093(w), 1038(s), 935(ws), 739(s), 721(s), 700 (w), 687 (s). UV/Vis (H_2O): λ_{max} (ϵ) = 301 nm ($14000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 440 nm ($3900 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.9 Synthesis of $(\text{NH}_4)_4\cdot\text{H}_4\{\text{Mg}[\text{Mo}^{\text{V}}\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]_2\}\cdot 8\text{H}_2\text{O}$ (9)

Synthetic procedure as for **5**, using MgCl_2 (0.028 g, 0.300 mmol). Yield: ~ 22%. Anal. Calc. for $\text{C}_{48}\text{H}_{82}\text{MgMo}_{12}\text{N}_4\text{O}_{62}\text{P}_8$, Expected: C% 18.41, H% 2.64, N% 1.78. Found: C% 17.71, H% 1.99, N% 1.55. FT-IR (cm^{-1}) ν_{max} : 2981(w), 1617(w), 1438(m), 1142(m),

1021(s), 940(vs), 745(s), 718(s), 691(vs). UV/Vis (CH₃CN): $\lambda_{\max}$ (ϵ) = 297 nm (12000 L mol⁻¹ cm⁻¹), 450 nm (800 L mol⁻¹ cm⁻¹).

5.3.10 Synthesis of [Mn^{III}₁₅(μ_2 -H₂O)₂(CH₃OH)₁₆(C₆H₅PO₃)₂₀]Cl₅·22CH₃OH·8H₂O (10)

MnCl₂·4H₂O (0.198 g, 1.000 mmol), KMnO₄ (0.039 g, 0.250 mmol) and phenylphosphonic acid (0.158 g, 1.000 mmol) were dissolved in CH₃OH (10 mL), stirred for 5h, filtered and left undisturbed for four days at room temperature. Then the reaction mixture was kept at *ca.* 2°C in a refrigerator for another four days, to obtain rectangular red-brown crystals. Yield: ~ 30%. Anal. Calc. for a dried sample with the expected formula C₁₂₀H₁₃₆Cl₅Mn₁₅O₇₈P₂₀, Expected: C% 32.41, H% 3.08. Found: C% 32.04, H% 2.68. FT-IR (cm⁻¹) $\nu_{\max}$: 3266(vbr), 2944(w), 2835(w), 1628(br), 1487(w), 1438(m), 1124(s), 1032(s), 983(s), 750(s), 722(s), 693(s). UV/Vis (CH₃CN): $\lambda_{\max}$ (ϵ) = 280 nm (34000 L mol⁻¹ cm⁻¹), 465 nm (6400 L mol⁻¹ cm⁻¹).

5.3.11 Synthesis of [Mn^{III}₁₃(μ_4 -O)₂(μ_3 -O)₄(μ_2 -OH)₂(μ_2 -CH₃O)₄(C₆H₅PO₃)₁₀(C₅H₅N)₅Cl]·3H₂O (11)

MnCl₂·4H₂O (0.198 g, 1.000 mmol), KMnO₄ (0.039 g, 0.250 mmol) and phenylphosphonic acid (0.094 g, 0.600 mmol) were dissolved under stirring in a mixture of CH₃OH/CH₃CN (5/5 mL), at room temperature, and 1.2 mL of pyridine were added. The reaction mixture was stirred for 5h, filtered and left undisturbed for slow evaporation. Rhombic, red-brown crystals were obtained during a time period of one week. Yield: ~ 20%. Anal. Calc. for a dried sample with the expected formula C₈₅H₈₇ClMn₁₃N₅O₄₅P₁₀, Expected: C% 34.51, H% 2.96, N% 2.37, Cl% 1.20. Found: C% 34.74, H% 2.49, N% 2.17, Cl% 0.94. FT-IR (cm⁻¹) $\nu_{\max}$: 3503(w), 3055 (w), 1601(m), 1485(s), 1438(m), 1120(s), 1084(s), 1032 (sh), 1003 (sh), 971(s), 753(s), 721(m), 695(s). UV/Vis (CH₃CN): $\lambda_{\max}$ (ϵ) = 270 nm (162000 L mol⁻¹ cm⁻¹), 446 nm (3400 L mol⁻¹ cm⁻¹).

5.3.12 Synthesis of $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_5\text{H}_5\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$ (12)

$\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.198 g, 1.000 mmol), KMnO_4 (0.039 g, 0.250 mmol) and benzylphosphonic acid (0.102 g, 0.600 mmol) were dissolved under stirring in a mixture of $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ (5/5 mL), at room temperature, and 0.5 mL of pyridine were added. The reaction mixture was stirred for 5h, filtered and left undisturbed for slow evaporation. Rectangular, brown crystals were obtained within four days. Yield: ~ 23%. Anal. Calc. for a dried sample with the expected formula $\text{C}_{100}\text{H}_{116}\text{ClMn}_{13}\text{N}_6\text{O}_{47}\text{P}_{10}$, Expected: C% 37.38, H% 3.64, N% 2.62. Found: C% 36.95, H% 3.13, N% 2.17. FT-IR (cm^{-1}) ν_{max} : 3423(br), 3028(w), 2918(w), 2815(w), 1601(m), 1495(m), 1446(m), 1409(w), 1240(m), 1192(w), 1133(sh), 1116(sh), 1066(sh), 982(s), 830(m), 788(m), 730(m), 693(s). UV/Vis (CH_3CN): λ_{max} (ϵ) = 257 nm ($61000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 443 nm ($4500 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.13 Synthesis of $[\text{Mn}^{\text{III}}_{13}(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_2\text{-OH})_2(\mu_2\text{-CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_{10}(\text{C}_6\text{H}_5\text{-C}_3\text{H}_6\text{-C}_5\text{H}_4\text{N})_6]\text{Cl}\cdot 5\text{H}_2\text{O}$ (13)

$\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.198 g, 1.000 mmol), KMnO_4 (0.039 g, 0.250 mmol) and benzylphosphonic acid (0.102 g, 0.600 mmol) were dissolved under stirring in CH_3OH (20 mL), at room temperature, and 1 mL of 4-(3-phenylpropyl)-pyridine was added. The reaction mixture was stirred for 5h, filtered and left undisturbed for slow evaporation. Rectangular, brown crystals were obtained within one week. Yield: ~ 37%. Anal. Calc. for a dried sample with the expected formula $\text{C}_{154}\text{H}_{176}\text{ClMn}_{13}\text{N}_6\text{O}_{47}\text{P}_{10}$, Expected: C% 47.16, H% 4.52, N% 2.14, Cl% 0.90. Found: C% 47.19, H% 4.16, N% 2.03, Cl% 1.08. FT-IR (cm^{-1}) ν_{max} : 3471(br), 3026(w), 2921(w), 1952(w), 1615(m), 1558(w), 1495(m), 1453(m), 1426(m), 1240(w), 1193(w), 1118(sh), 1067(s), 984(s), 828(m), 789(m), 730(m), 695(s). UV/Vis (CH_3CN): λ_{max} (ϵ) = 256 nm ($41000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 446 nm ($3600 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5.3.14 Synthesis of $\text{K}(\text{H}_2\text{O})_4[\text{Mn}^{\text{III}}_{12}(\mu_3\text{-O})_6(\text{CH}_3\text{OH})_6(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3\text{H})_7(\text{C}_6\text{H}_5\text{CH}_2\text{PO}_3)_8]\text{Cl}_2\cdot 3\text{CH}_3\text{OH}\cdot 4\text{H}_2\text{O}$ (14)

$\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.198 g, 1.000 mmol), KMnO_4 (0.019 g, 0.125 mmol) and benzylphosphonic acid (0.079 g, 0.450 mmol) were dissolved under stirring in CH_3OH (20 mL), at room temperature, and 4,4'-bipyridine (0.015 g, 0.096 mmol) was added. The

reaction mixture was stirred for 5h, filtered and left undisturbed for slow evaporation. Rectangular, brown crystals were obtained within one week. Yield: ~ 38%. Anal. Calc. for a dried sample with the expected formula $C_{105}H_{140}Cl_2KMn_{12}O_{65}P_{15}$, Expected: C% 34.31, H% 3.84. Found: C% 34.29, H% 3.49. FT-IR (cm^{-1}) ν_{max} : 3029(vbr), 1602(w), 1495(m), 1454(m), 1406(w), 1245(w), 951(s), 781(m), 727(m), 675(s). UV/Vis (CH_3CN): λ_{max} (ϵ) = 257 nm ($36000 L mol^{-1} cm^{-1}$), 488 nm ($3200 L mol^{-1} cm^{-1}$).

5.3.15 Synthesis of $K(H_2O)_4[Mn^{III}_{12}(\mu_3-O)_6(CH_3OH)_6(C_6H_5CH_2PO_3H)_7(C_6H_5CH_2PO_3)_8]Br_2 \cdot 2CH_3OH \cdot 2H_2O$ (15)

$MnBr_2 \cdot 4H_2O$ (0.143 g, 0.500 mmol), $KMnO_4$ (0.019 g, 0.125 mmol) and benzylphosphonic acid (0.158 g, 0.918 mmol) were dissolved in CH_3OH (20 mL), at room temperature, and stirred for 5h. The resulting orange - brown solution was filtered and left undisturbed for slow evaporation. Small, brown crystals were obtained during a time period of ten days. Yield: ~ 26%. Anal. Calc. for a dried sample with the expected formula $C_{105}H_{136}Br_2KMn_{12}O_{63}P_{15}$, Expected: C% 33.82, H% 3.68. Found: C% 33.74, H% 3.32. FT-IR (cm^{-1}) ν_{max} : 3417(br), 3028(w), 1602(m), 1495(m), 1453(m), 1407(w), 1256(w), 1071(s), 960(s), 831(m), 786(s), 730(s), 679(s). UV/Vis (CH_3CN): λ_{max} (ϵ) = 258 nm ($52000 L mol^{-1} cm^{-1}$), 489 nm ($4000 L mol^{-1} cm^{-1}$).

5.3.16 Synthesis of $(H_3O)_4[Mn^{III}_2Mn^{II}_4(\mu_4-O)_2(H_2O)_2(CH_3CN)_2\{(C_6H_5)_3CPO_3\}_6]Cl_2 \cdot 2CH_3CN \cdot 4H_2O$ (16)

$MnCl_2 \cdot 4H_2O$ (0.099 g, 0.500 mmol), $KMnO_4$ (0.039 g, 0.250 mmol) and triphenylmethylphosphonic acid (0.324 g, 1.000 mmol) were dissolved under stirring in a mixture of CH_3CN/CH_2Cl_2 (10/10 mL), at room temperature. 1.2 mL of triethylamine was added and the reaction mixture was further stirred for 5h, filtered and left undisturbed for slow evaporation. Rectangular red-brown crystals were obtained within five days. Yield: ~ 16%. Anal. Calc. for a dried sample with the expected formula $C_{116}H_{113}Cl_2Mn_6NO_{28}P_6$, Expected: C% 54.52, H% 4.46, N% 0.55. Found: C% 54.14, H% 3.98, N% 0.25. FT-IR (cm^{-1}) ν_{max} : 3590(w), 3054(w), 1594(m), 1491(m), 1444(m), 1188(w), 1121(s), 1076(s), 1037(s), 1005(s), 959(s), 931(s), 894(w), 851(w), 745(s), 699(s). UV/Vis (CH_3CN): λ_{max} (ϵ) = 263 nm ($87000 L mol^{-1} cm^{-1}$), 487 nm ($900 L mol^{-1} cm^{-1}$).

5.3.17 Synthesis of $(\text{H}_3\text{O})\{\text{Mn}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_2[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ (17)

1,3,5-Tris(4-phosphonophenyl)benzene (P-TPB) (0.081 g, 0.150 mmol) was reacted with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.029 g, 0.150 mmol) in CH_3OH (10 mL). The resultant pale orange solution was stirred at room temperature for 1 hour, and then it was left undisturbed for slow evaporation. During a time period of four days rectangular yellow crystals of **17** were separated from the solution. Yield: ~ 33%. Anal. Calc. for a dried sample with the expected formula $\text{C}_{32}\text{H}_{63}\text{MnO}_{23}\text{P}_3$, Expected: C% 39.88, H% 6.59. Found: C% 40.19, H% 6.94. FT-IR (cm^{-1}) ν_{max} : 3189(br), 2278(w), 1647(w), 1597(m), 1385(m), 1135(s), 1036(s), 908(s), 818(s), 689(s).

5.3.18 Synthesis of $(\text{H}_3\text{O})\{\text{Cu}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{PO}_3\text{H})_3]\} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$ (18)

1,3,5-Tris(4-phosphonophenyl)benzene (P-TPB) (0.081 g, 0.150 mmol) was reacted with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.050 g, 0.300 mmol) in CH_3OH (10 mL). The resultant pale green solution was stirred at room temperature for 1 hour, and then it was left undisturbed for slow evaporation. During a time period of five days pale green crystals were separated from the solution. Yield: ~ 34%. Anal. Calc. for a dried sample with the expected formula $\text{C}_{24}\text{H}_{28}\text{CuO}_{13.5}\text{P}_3$, Expected: C% 41.84, H% 4.10. Found: C% 41.86, H% 3.62. FT-IR (cm^{-1}) ν_{max} : 2943(vbr), 2285(w), 1597(m), 1557(w), 1505(w), 1385(w), 1135(s), 1003(s), 914(s), 817(s), 688(s).

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APPENDIX

Self-Assembly of Hybrid Organic–Inorganic Polyoxomolybdates: Solid-State Structures and Investigation of Formation and Core Rearrangements in Solution

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Received August 17, 2010

We report here a facile synthetic and analytical approach that allows us to identify and characterize functionalized polyoxomolybdate clusters that form upon the partial reduction of Mo^{VI} salts in the presence of organoarsenate ligands. We demonstrated that electrospray ionization mass spectrometry, in combination with X-ray crystallography, provides an extremely powerful tool, allowing us to exploit slight perturbations of the ligand structures for the preparation of a series of unprecedented cluster compounds. Redox-active transition metals that adopt cubane or related structures are of particular interest because of their resemblance to active sites of enzymes. Our investigations underline the stability of the hybrid compounds in solution, an essential requirement for potential applications as catalysts. Supplemental analyses include measurements of the magnetic properties, NMR, IR, UV/vis, and bond-valence-sum analyses. Our results highlight the possibility of exploring real-time growth reactions of polyoxometalates that emerge in solution and transform to produce hybrid organic–inorganic polyoxometalate clusters.

Introduction

The chemistry of polyoxometalates (POMs) is one of the most active and rapidly advancing areas of inorganic chemistry.^{1,2} The interest in the oxo clusters of the early-transition-metal ions

is based on their unique structural characteristics and chemical attributes (including redox and photochemical activity and optical properties, charge distribution, and band structures), which promote applications as catalysts, sensors, photocatalysts, electrochromic materials, energy storage, and conversion devices.^{2,3} Their reactions in aqueous solution and the resulting structures can often be rationalized by aggregations of small molecular species, producing oligomeric complexes, large nanoscale clusters, or infinite oxides.^{4,5} The early-transition-metal ions are able to polarize terminal M–O bonds stabilizing large molecular cage structures and other aggregates. However, these bonds, which are characterized by d– π contributions and reveal significant double-bond character, also impede functionalization. Functionalization approaches to generate hybrid POM structures or advanced inorganic materials remain an ongoing challenge, and new synthetic and analytical approaches are pivotal to the progress of the field.^{1,6} We are interested in the chemistry

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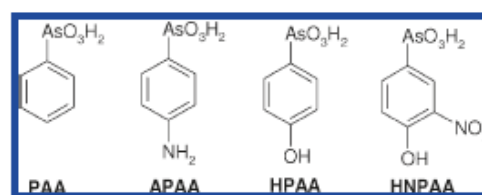
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of hybrid organic–inorganic materials,⁷ and we decided to explore the formation of mixed-valent molybdates in the presence of organoarsonates and -phosphonates. Phosphonate- and arsonate-stabilized oxo clusters that contain redox-active metal centers are of interest for applications in catalysis.^{3c–g} The geometrical characteristics of the functional groups of the organophosphonates and -arsonates might promote the formation of structures that enhance the electrochemical splitting of water and reduce overpotentials when deposited on electrodes.⁸ Several organoarsonate-stabilized polyoxomolybdates of varying nuclearity and containing different core structures have been reported. Examples include $\text{Mo}_4\text{O}_{10}(\text{O}_3\text{AsR})_4^{4-}$, $\{\text{Mo}_6\text{O}_{12}(\text{O}_3\text{AsR})\}^{4+}$, $\{\text{Mo}_6\text{O}_{18}(\text{O}_3\text{AsR})_2\}^{4-}$, and $\{\text{Mo}_{12}\text{O}_{34}(\text{O}_3\text{AsR})_4\}^{4-}$ ($\text{R} = \text{CH}_3$, C_6H_5 , $\text{C}_6\text{H}_4\text{CH}_3$, $\text{C}_6\text{H}_4\text{-4-NH}_2$, $\text{C}_6\text{H}_4\text{-4-OH}$, $\text{C}_6\text{H}_4\text{-4-COOH}$, $\text{C}_6\text{H}_3\text{-4-OH-3-NO}_2$, $\text{C}_6\text{H}_4\text{-4-CN}$, $\text{C}_6\text{H}_3\text{-4-OH-3-NOC}_2\text{H}_4$).^{9a–i}

Despite an ever-increasing interest in POM complexes, it is surprising that their solution behavior, i.e., formation reactions that often prevail through a set of consecutive condensation reactions, is often fairly poorly understood. However, speciation within POM solutions not only is important to devise rational synthetic approaches to desired products but is, moreover, a prerequisite to improve catalytic processes that draw on the active sites or electronic characteristics of POMs. Recent accounts demonstrate that electrospray ionization mass spectrometry (ESI-MS) provides a very powerful analytical tool to characterize the

Scheme 1. Organoarsonic Acids Used in These Studies: Phenylarsonic Acid (PAA), 4-Aminophenylarsonic Acid (APAA), 4-Hydroxyphenylarsonic Acid (HPAA), 4-Hydroxy-3-nitrophenylarsonic Acid (HNPAAs)



formation and reactivity of complex POM clusters in solution.¹⁰

Results and Discussion

We decided to use ESI-MS to investigate the self-assembly process of hybrid polyoxomolybdates that form upon the partial reduction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in the presence of aromatic organoarsonates (Scheme 1). We were interested in exploring how perturbations of the ligand functionality influence the formation of unprecedented species. Although several arsonate-stabilized molybdates had previously been reported,⁹ mass spectrometry allowed us to selectively identify species with unprecedented core structures. Here we report the solution characterization, structures, and properties of four hybrid cluster anions that self-assemble under these reaction conditions: $[\text{Mo}^{\text{IV}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_5)_4]^{4-}$ (**1**), $[\text{Mo}^{\text{IV}}_4\text{O}_8(\text{O}_3\text{AsC}_6\text{H}_4\text{NH}_2)_4]^{4-}$ (**2**), $[\text{Mo}^{\text{VI}}_2\text{Mo}^{\text{V}}_2\text{O}_{11}(\text{O}_3\text{AsC}_6\text{H}_4\text{OH})_5]^{5-}$ (**3**), and $[\text{Mo}^{\text{VI}}_4\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_3\text{NO}_2\text{OH})_4]^{4-}$ (**4**). Utilizing ESI-MS during the screening process of the reaction mixtures, we could identify new species whose structures and composition were later confirmed by standard single-crystal X-ray diffraction studies. A summary of the assignments of the ESI-MS spectra and the experimental conditions is given in the Supporting Information (Table S5). Further supplemental analyses include NMR spectroscopy, elemental analysis, magnetic studies, thermogravimetric analyses, powder X-ray diffraction, and bond-valence-sum analyses.

Phenylarsonic Acid (PAA)– $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ Reaction System. The partial reduction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in the presence of PAA and acetic acid using $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ results in a deep-blue solution. When the initial reaction mixture is examined by ESI-MS, the spectrum reveals isotopic envelopes in the high-molecular-mass region centered at m/z 1315.3 and 1659.2 (Figure 1). Within a time period of 3 weeks, dark-red crystals of $(\text{NH}_4)_2\text{H}_2[1] \cdot 5\text{H}_2\text{O}$ separate from this reaction mixture.

Single-crystal X-ray analysis reveals that **1** contains a tetranuclear molybdenum complex in which the Mo atoms and bridging O donors adopt a typical $[\text{Mo}_4(\mu_3\text{-O})_4]^{12+}$

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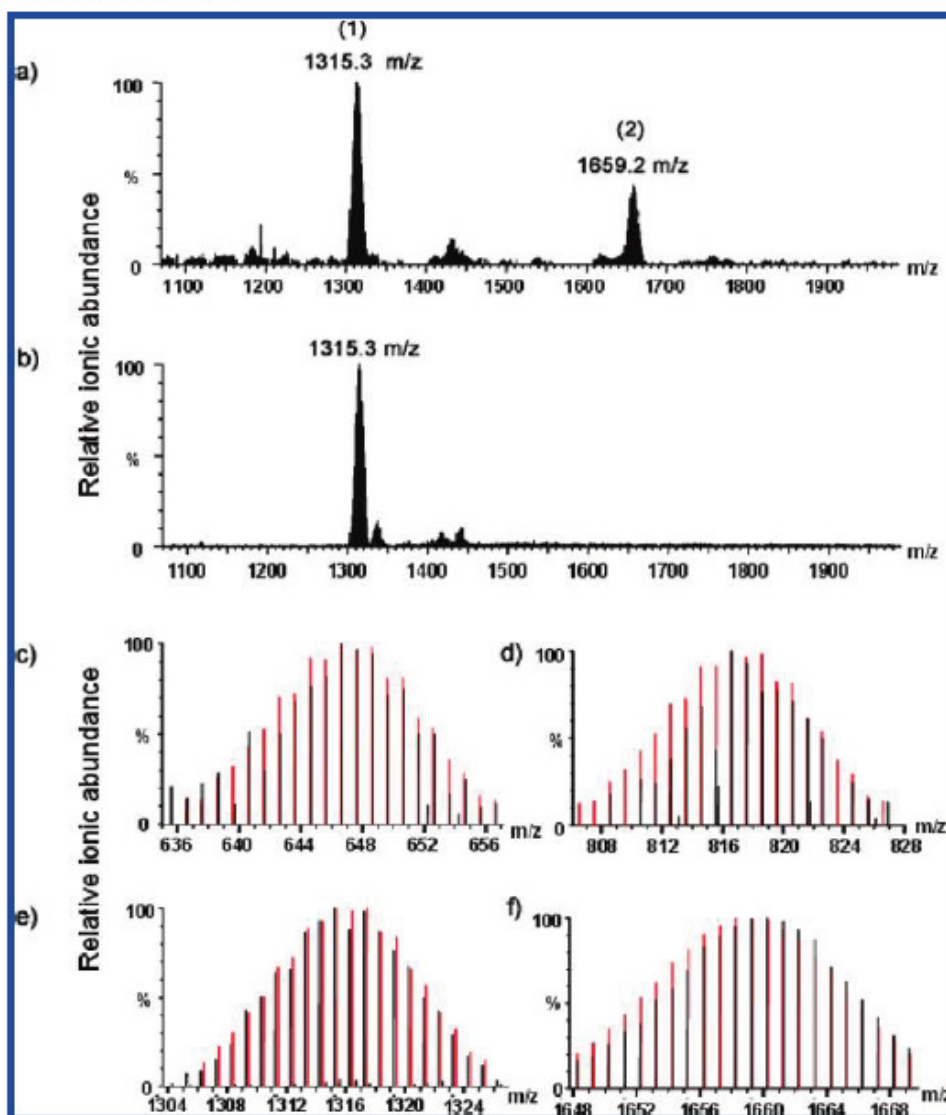


Figure 1. Negative-mode ESI-MS spectra to identify **1**: (a) reaction mixture 24 h after preparation [signal (1) centered at m/z 1315.3 corresponds to $\{H_3[Mo^V_4O_8(O_3AsC_6H_5)_4]\}^-$; signal (2) centered at m/z 1659.2 corresponds to $\{(NH_4)_2H_4[Mo^V_4Mo^{IV}_2O_{12}(OH)_3(O_3AsC_6H_5)_4]\}^-$; (b) crystals of **1** dissolved in DMSO. (c–f) Comparison of experimental isotopic envelopes (black spectra) with simulated patterns (red spectra) for (c) $[Mo^{VI}_4O_{16}H_7]^-$ centered at m/z 646.6, (d) $[H_9[Mo^V_4O_{14}(O_3AsC_6H_5)_3]]^-$ centered at m/z 816.6, (e) $[H_3[Mo^V_4O_8(O_3AsC_6H_5)_4]]^-$ centered at m/z 1315.3; (f) $[(NH_4)_2H_4[Mo^V_4Mo^{IV}_2O_{12}(OH)_3(O_3AsC_6H_5)_4]]^-$ centered at m/z 1659.2 (cone voltage: 30 V).

cubane structure. The structure is shown in Figure 2. In this structure, the four Mo atoms are situated diagonally across from each other, occupying four corners of a cube. Four O^{2-} oxo ligands occupy the remaining four corners of the cube, and each one binds to three Mo atoms. The structure is further stabilized by four fully deprotonated PAA ligands that each bind in a μ -syn,syn bridging mode to two Mo ions, resulting in an overall octanuclear compound (the As atoms are also considered to be core atoms). The slightly distorted octahedral coordination environment of each of the four Mo ions is completed by terminal Mo=O bonds. These are situated in trans positions to the μ_3 -O donors. The bond lengths of these Mo=O bonds range between 1.660(4) and 1.679(4) Å and are, as expected, significantly shorter than the Mo– μ_3 -O distances [2.364(4)–2.424(4) Å].

The core structure $[Mo_4(\mu_3-O)_4]^{12+}$ deviates slightly from the geometry of an ideal cube. The Mo–O–Mo and O–Mo–O angles range between 83.82(3) and 104.04(1)° and between 76.2(4) and 89.7(4)°, respectively, differing from the ideal angle of 90°. Bond-valence-sum analysis

(Supporting Information) confirms that all four Mo atoms in **1** adopt the oxidation state V+. Short Mo(1)–Mo(2) and Mo(3)–Mo(4) contacts of 2.647(1) and 2.642(1) Å, respectively, are in agreement with the assigned V+ oxidation states. The packing arrangement of the clusters **1** in the crystal structure (see the Supporting Information) is stabilized by weak hydrogen bonds between the cluster anions and constitution water molecules and NH_4^+ counterions that are situated in small channels that run in the direction of the crystallographic a axis. Structurally related cubane structures were previously isolated using squaric acid, diphenylphosphinic acid, and dimethylphosphinic acid as ligands. However, it is noteworthy that the cubane arrangement of Mo^V atoms is far less frequently observed than the structurally related rhombic planar arrangement.¹¹

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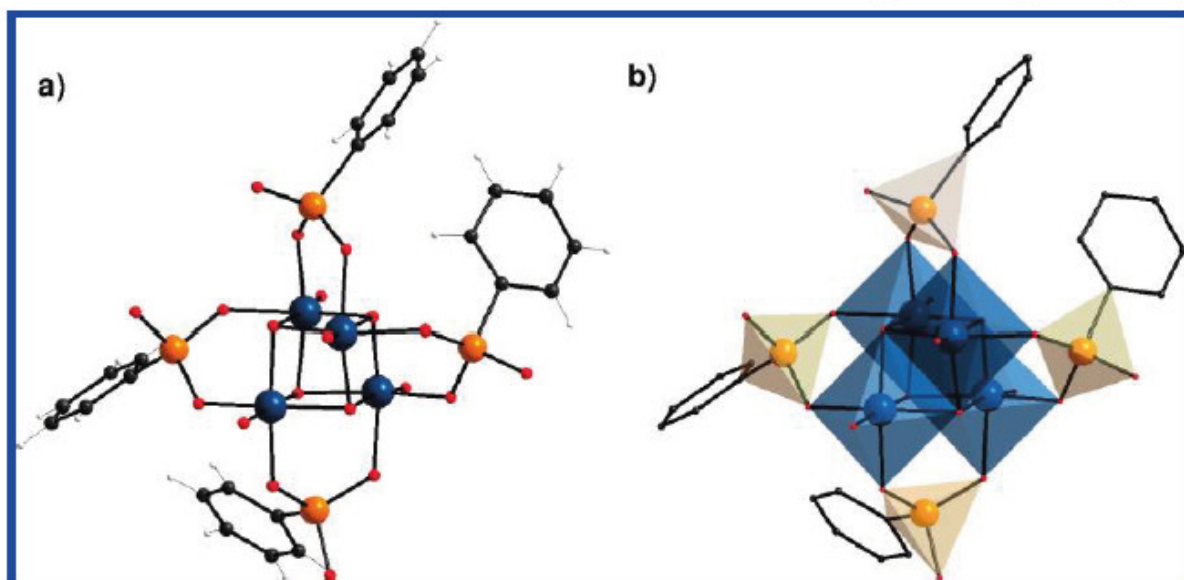


Figure 2. Crystal structure of **1** in $(\text{NH}_4)_2\text{H}_2[\text{1}] \cdot 5\text{H}_2\text{O}$: (a) ball-and-stick representation; (b) polyhedral presentation. Color code: Mo^V, blue; As, orange; O, red; C, gray; H, white. H atoms were omitted for clarity in part b.

The signal centered at m/z 1315.3 in the mass spectrum of the reaction mixture that produced **1** is in agreement with the crystallographically determined formula of the cluster anion in $(\text{NH}_4)_2\text{H}_2[\text{1}] \cdot 5\text{H}_2\text{O}$. The signal can be reproduced by recording a spectrum of pristine crystals of $(\text{NH}_4)_2\text{H}_2[\text{1}] \cdot 5\text{H}_2\text{O}$ dissolved in dimethyl sulfoxide (DMSO), further confirming that the cluster core of $(\text{NH}_4)_2\text{H}_2[\text{1}] \cdot 5\text{H}_2\text{O}$ is stable in this polar solution. Lower-molecular-mass signals in the ESI-MS spectrum centered at m/z 816.6 and 646.6 originate from the cubane cluster and can be assigned to the species $\{\text{H}_9[\text{Mo}^{\text{V}}_4\text{O}_{14}(\text{O}_3\text{AsC}_6\text{H}_5)_3]\}^-$ and $[\text{Mo}^{\text{VI}}_4\text{O}_{16}\text{H}_7]^-$, respectively. The ESI-MS spectrum of the reaction mixture further contains a high-molecular-mass signal centered at m/z 1659.2. We were able to assign this signal to a species with the formula $\{(\text{NH}_4)_2\text{H}_4[\text{Mo}^{\text{V}}_4\text{Mo}^{\text{IV}}_2\text{O}_{12}(\text{OH})_3(\text{O}_3\text{AsC}_6\text{H}_5)_4]\}^-$. A closely related core structure that is stabilized by phosphonates has previously been isolated in a compound $\{\text{Na}[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]\}^{9-}$.¹²

It can be crystallized from comparable reaction mixtures that contain alkali-metal ions, producing a solid-state structure in which two $[\text{Mo}^{\text{V}}_6\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]^{5-}$ fragments are linked through monovalent ions (Figure 3). Within each fragment, six Mo ions form distorted octahedral coordination polyhedra, each sharing two common edges with adjacent polyhedra to form a six-membered ring. Three organic ligands are situated on the periphery of the resulting ring, each bridging two Mo ions in a μ -syn,syn-bridging mode. The tetrahedrally arranged O donors of a fourth organic ligand cap the central cavity of the ring and provide μ -O-bridging donors of three dimeric edge-sharing subunits. The aromatic moieties of the four organic ligands are arranged approximately perpendicular to the mean plane of the six-membered ring. For all of the identified species and decomposition products of **1** that originate from the reaction mixture, we successfully simulated the isotopic envelopes (Figure 1), and good fits between experimental and theoretical data

further confirm our structural and constitutional assignments. The ESI-MS analysis further supports the assignment of the oxidation states and, in addition, suggests the presence of other relatively labile species in the solution. The effect of cone voltage variations on the ESI-MS spectra is shown in Figure S4 in the Supporting Information. We and others observe that higher cone voltages result in defragmentation of the coordination clusters within the spraying chamber.

Cubane complexes containing redox-active transition-metal ions represent an interesting class of compounds. Bioinorganic research approaches try to mimic the structure and reactivity of photosystem II, an enzyme that contains a $\{\text{Mn}_3\text{Ca}\}$ cubane-like core in its active site and that catalyzes the photooxidation of water to oxygen.^{13a,c} Selected cubane oxo clusters show remarkable catalytic activities and redox and magnetic properties;^{13c-e} they can be used as secondary building units producing microporous hybrid materials with large internal surface areas, revealing interesting sorption properties that give rise to applications as exchange/separation materials.^{13f-h}

***p*-Aminophenylarsonic Acid–Mo^{VI}/Mo^V Reaction System.** Encouraged by these results, we decided to alter the ligand functionality and introduced an amino group in the para position to the arsonate functionality. When this ligand is used to control the self-assembly process upon reduction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, we obtain, as in the previous case, a blue solution. The ESI-MS spectrum of this reaction mixture (Figure 4) only contains one isotopic envelope in the high-mass region centered at m/z 1374.4,

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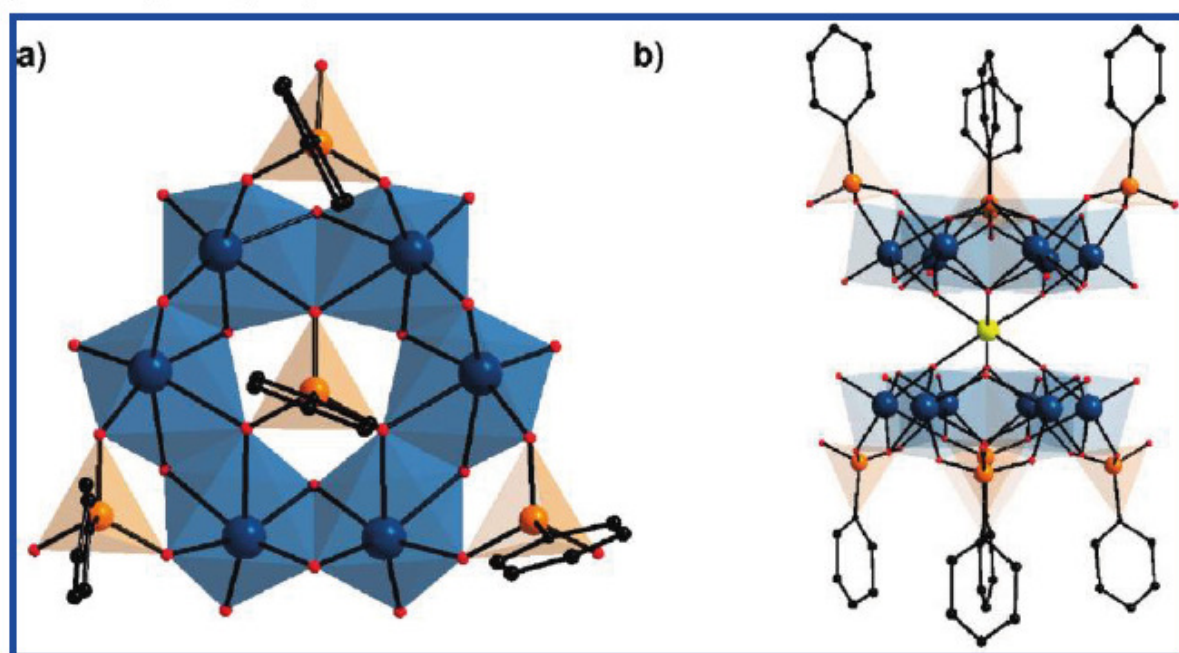


Figure 3. (a) Structure of the cluster anion $[\text{Mo}_6^{\text{V}}\text{O}_{12}(\text{OH})_3(\text{O}_3\text{PC}_6\text{H}_5)_4]^{5-}$. (b) Cluster core isolated as dimeric species in which two cluster anions are linked through an alkali-metal ion.¹² Color code: Mo, blue; P, orange; O, red; C, gray; alkali metal, yellow. H atoms have been omitted for clarity.

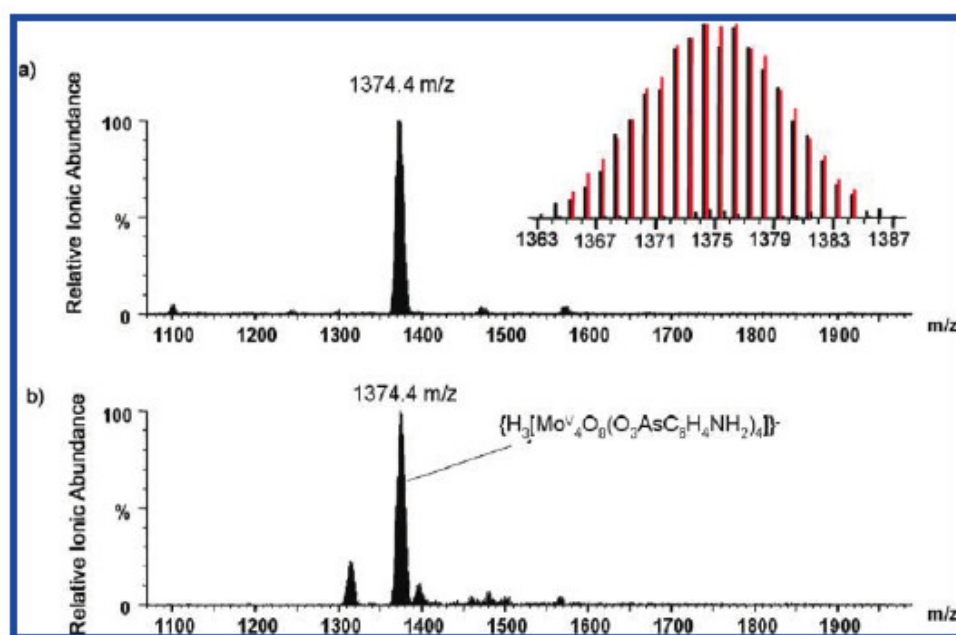


Figure 4. Negative-mode ESI-MS spectra to identify 2: (a) reaction mixture 24 h after preparation [the signal centered at m/z 1374.4 corresponds to $\{\text{H}_3[\text{Mo}_6^{\text{V}}\text{O}_{12}(\text{O}_3\text{AsC}_6\text{H}_5\text{NH}_2)_4]\}^-$]; (b) crystals of 2 dissolved in DMSO. Inset: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for 2 centered at m/z 1374.4 (cone voltage: 30 V).

corresponding to the cubane structure in $(\text{NH}_4)_2\text{H}_2[2] \cdot \text{DMF} \cdot 4\text{H}_2\text{O}$, which crystallizes from this solution as red rod-shaped crystals. ESI-MS and NMR analyses of the isolated compound in DMSO further confirm our assignments [both $(\text{NH}_4)_2\text{H}_2[1] \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{H}_2[2] \cdot \text{DMF} \cdot 4\text{H}_2\text{O}$ are insoluble in H_2O]. ESI-MS cone voltage variations are provided in the Supporting Information.

This cluster core is almost isostructural to 1, having only slightly different structural and geometrical parameters; the bond valence sums and underlying M–O and Mo–Mo distances agree very well with those observed for 1. The amine functionalities of the organic ligands only impose an influence on the packing arrangement of the clusters in the crystal structure, resulting in a gridlike

packing arrangement, with small intercluster cavities (filled with solvent molecules) running the direction of the crystallographic a axis (Supporting Information).

***p*-Hydroxyphenylarsonic Acid (HPAA)– $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ Reaction System.** Surprisingly, when HPAA is used as a stabilizing ligand under the same reaction conditions, we obtain a reaction mixture whose ESI-MS spectrum is complex and is characterized by four major isotopic envelopes centered at m/z 1377.3, 1522.2, 1704.1, and 1740.2 in the higher mass region of the spectrum (Figure 5). The signal at m/z 1377.3 can be assigned to the cubane structure, also observed in the previously examined reaction mixtures, while the high-molecular-mass signal centered at m/z 1740.2 originates from a new pentanuclear

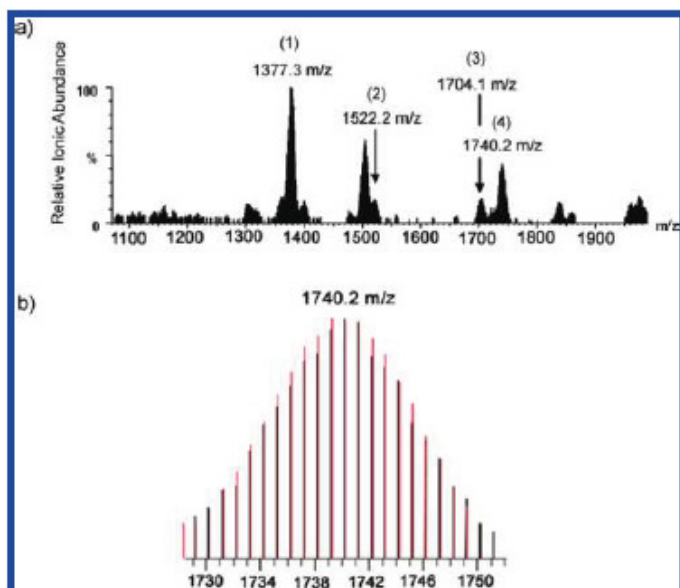


Figure 5. (a) Negative-mode ESI-MS spectra to identify **3** [reaction mixture 24 h after preparation; signal (1) at m/z 1377.3 corresponds to $\{H_3[Mo^V_4O_8(O_3AsC_6H_4OH)_4]\}^-$, signal (2) at m/z 1522.2 to $\{H_2[Mo^{VI}_2Mo^V_3O_{11}(O_3AsC_6H_4OH)_4]\}^-$, signal (3) at m/z 1704.1 to $\{(NH_4)H_3[Mo^V_6O_{12}(OH)_3(O_3AsC_6H_4OH)_4]\}^-$, and signal (4) at m/z 1740.2 to $\{H_4[Mo^V_2Mo^V_3O_{11}(O_3AsC_6H_4OH)_5]\}^-$. (b) Expanded view of the signal centered at m/z 1740.2. Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for **3** (cone voltage: 30 V).

mixed-valent Mo cluster **3**. The signal at m/z 1522.2 can be attributed to a defragmentation product of **3**, in which one organic ligand is abstracted from the cluster anion.

The ESI-MS spectrum of the reaction mixture of **3** displays a fourth signal at m/z 1704.1, which can be assigned to a hexanuclear compound $\{(NH_4)H_3[Mo^V_6O_{12}(OH)_3(O_3AsC_6H_4OH)_4]\}^-$. A similar compound was also observed during analysis of the previously described reaction systems. ESI-MS analysis including cone voltage variations (Supporting Information) clearly confirms that the tetranuclear cubane structure and the pentanuclear complex **3** form in solution in the same reaction mixture; the formation of the latter hexanuclear species might possibly be a result of processes occurring in the spraying chamber.

We succeeded in isolating **3** in $(NH_4)_5[3] \cdot 9H_2O$. The compound crystallizes as dark-blue rectangular blocks, allowing us to verify our constitutional assignment using single-crystal X-ray diffraction. $(NH_4)_5[3] \cdot 9H_2O$ contains a mixed-valent pentanuclear cluster that is stabilized by five HPAA ligands. The structure of the cluster anion is shown in Figure 6. All Mo ions in the structure are distorted octahedrally surrounded by O donors. The coordination polyhedra of Mo(1), Mo(2), Mo(3), and Mo(5) share common edges. The polyhedron of Mo(4) shares common vertices with the polyhedra of Mo(3) and Mo(5) and closes the circular entity. Four organic ligands are situated on the outer side of the ring, and each binds via its deprotonated arsonate functionalities in a μ -syn,syn-bridging mode to two Mo ions. The organic ligands bridge between Mo(2) and Mo(3), Mo(3) and Mo(4), Mo(4) and Mo(5), and Mo(5) and Mo(1), respectively. The fifth ligand is situated above the center of the $\{Mo_5\}$ ring and binds with its three O atoms to all Mo ions [O(26) binds to Mo(4) and O(3) and O(8) bridge between Mo(2) and

Mo(3) and between Mo(5) and Mo(1), respectively]. The aromatic ring systems of the ligands all point in one direction and project perpendicularly to the virtual plane of the $\{Mo_5\}$ ring. The phenolic OH functionalities of the organic ligands remain protonated and are engaged in H bonds within the crystal structure. The Mo–O bond distances of Mo(3) and Mo(5) are significantly shorter than the corresponding distances of the other Mo ions in the structure. Further bond-valence-sum analyses confirm that these two Mo ions have the oxidation state VI+, while Mo(1), Mo(2), and Mo(4) are in oxidation state V+. This assignment is also in agreement with the protonation observed in the mass spectrum. The polyoxomolybdate cluster carries an overall charge of 5−, which is compensated for by NH_4^+ counterions. In the crystal structure, the cluster packs to form a layered lamellar structure with alternating inorganic and organic areas (Supporting Information).

ESI-MS studies on the crystalline material reveal that compound $(NH_4)_5[3] \cdot 9H_2O$ undergoes structural transformations when dissolved in distilled water but is stable in a DMSO environment (Supporting Information). The assignments of the oxidation states of the Mo atoms in **3** are in agreement with the observed magnetic properties of $(NH_4)_5[3] \cdot 9H_2O$. At room temperature, the χT product is $0.37 \text{ cm}^3 \text{ K mol}^{-1}$, in good agreement with the presence of one $S = 1/2$ Mo^V metal ion (expected value: $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ for $g = 2$). The two other Mo^V ions appear to be magnetically silent, as expected for two spin centers that are strongly antiferromagnetically coupled ($|J| \gg 500 \text{ K}$, with the Hamiltonian definition $H = -2JS_1S_2$) to give a diamagnetic dinuclear unit. Such strong antiferromagnetic exchange is common in polyoxomolybdates that feature edge- and face-sharing dinuclear molybdenum octahedra.¹⁴ When the temperature is lowered, the χT product at 1000 Oe remains constant at $0.37 \text{ cm}^3 \text{ K mol}^{-1}$ down to 1.8 K, indicating a Curie-type paramagnetism. From the Curie constant ($0.37 \text{ cm}^3 \text{ K mol}^{-1}$), the g value is estimated to be very close to 2. The assignment of the oxidation states is further substantiated by the observed Mo–Mo distances within **3**. The short interatomic distance of $2.574(1) \text{ \AA}$ between Mo(1) and Mo(2) is indicative for Mo–Mo bonds and in agreement with the V+ oxidation states and the observed diamagnetism. Comparable Mo^V – Mo^{VI} distances are expectedly significantly longer [Mo(1)–Mo(5) $3.359(1) \text{ \AA}$, Mo(2)–Mo(3) $3.353(3) \text{ \AA}$, Mo(3)–Mo(4) $3.680(2) \text{ \AA}$, and Mo(4)–Mo(5) $3.671(5) \text{ \AA}$]. Its mixed-valent nature distinguishes **3** from many other organoarsenate-stabilized polyoxomolybdates, which tend to exist, with few exceptions,^{9a,b} predominantly in their fully oxidized forms.

4-Hydroxy-3-Nitrophenylarsonic Acid (HNPA)– Mo^{VI} / Mo^{VI} Reaction System. We decided to investigate the influence of a disubstituted arsonate ligand on the self-assembly process of hybrid polyoxomolybdates under the same outlined reaction conditions that led to the formation of **1–3**. Using a substituted arsonate ligand with a hydroxyl group in the para position and a nitro group in

(14) (a) Zhang, X.; Xu, J. Q.; Yu, J. H.; Lu, J.; Xu, Y.; Chen, Y.; Wang, T. G.; Yu, X. Y.; Yang, Q. F.; Hou, Q. *J. Solid State Chem.* 2007, 180, 1949–1956. (b) Ma, Y.; Li, Y. G.; Wang, E. B.; Lu, Y.; Wang, X. L.; Xiao, D. R.; Xu, X. X. *Inorg. Chim. Acta* 2007, 360, 421–430.

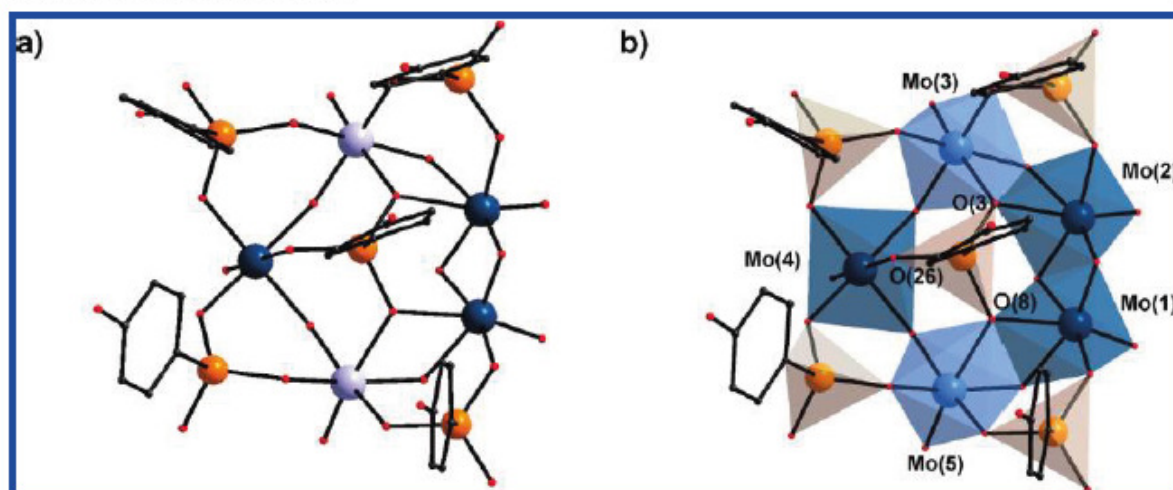


Figure 6. Crystal structure of **3** in $(\text{NH}_4)_3[\text{3}] \cdot 9\text{H}_2\text{O}$: (a) ball-and-stick representation; (b) polyhedral representation of the mixed-valent pentanuclear cluster and ball-and-stick representation of the organic ligand that stabilizes **3**. Color code: Mo^{VI} , cyan; Mo^{V} , blue; As, orange; O, red; C, gray. H atoms were omitted for clarity.

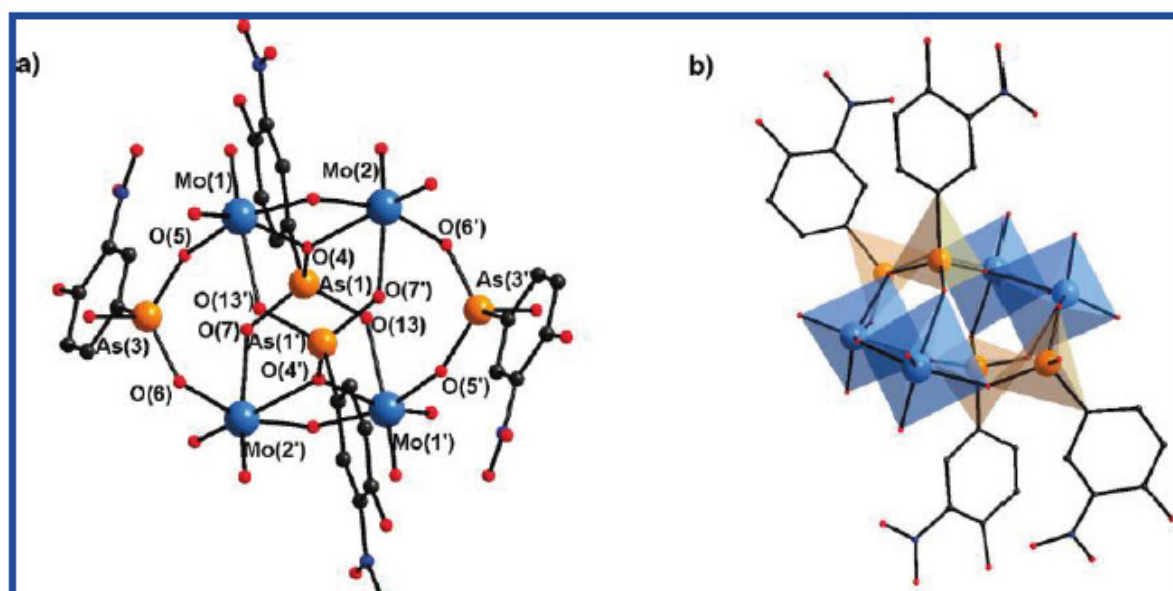


Figure 7. Crystal structure of **4** in $(\text{NH}_4)_4[\text{4}] \cdot 2\text{H}_2\text{O}$: (a) ball-and-stick representation; (b) polyhedral presentation. Color code: Mo^{VI} , cyan; As, orange; O, red; C, gray. H atoms were omitted for clarity.

the meta position, we obtain a dark-green solution, which undergoes a color change to red orange within approximately 10 days. The ESI-MS spectrum of this reaction mixture is complex, showing the presence of multiple species in the higher mass region of the spectrum. We were able to identify unambiguously the composition of one of these species. Its isotopic envelope is centered at m/z 1615.4 and corresponds to the formula of a tetranuclear molybdenum complex with the composition $\{\text{H}_9[\text{Mo}^{\text{V}}_2\text{Mo}^{\text{IV}}_2\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_3\text{NO}_2\text{OH})_4] \cdot \text{H}_2\text{O}\}^-$. Orange crystals of a closely related compound, $(\text{NH}_4)_4[\text{4}] \cdot 2\text{H}_2\text{O}$, were obtained from the reaction mixture within a time period of 3 weeks, and single-crystal X-ray studies were performed. The core structure of **4** is related to those observed in $(\text{Et}_3\text{NH})_4[\text{Mo}_4\text{O}_{10}(\text{C}_6\text{H}_5\text{PO}_3)_4] \cdot 2\text{CH}_3\text{CN}$ and $(\text{Et}_3\text{NH})_4[\text{Mo}_4\text{O}_{10}(\text{C}_6\text{H}_5\text{AsO}_3)_4] \cdot 4\text{H}_2\text{O}$, respectively.^{9f} The anionic cluster $[\text{Mo}^{\text{VI}}_4\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_3\text{NO}_2\text{OH})_4]^{4-}$ (**4**; Figure 7) contains two $\{\text{Mo}_2\text{O}_{10}\}^{8-}$ subunits in which octahedrally coordinated Mo atoms share a common edge [Mo(1)/Mo(2) and Mo(1')/Mo(2')]. The

dimeric units are connected by four deprotonated arsonate ligands. Two of the ligands have their As atoms [As(3) and As(3')] arranged nearly coplanar to the four Mo atoms. Each of the ligands is bridging between two Mo ions in a μ -syn,syn-bridging mode to form a six-membered $\{\text{As}_2\text{Mo}_4\}$ ring. The remaining two arsonate ligands cap both sides of the central cavity of the ring, and each provides one μ -bridging O donor [O(4) and O(4')] of the common edges of the $\{\text{Mo}_2\text{O}_{10}\}^{8-}$ dimers. The other two O atoms of the tetrahedral arsonate functionality of each of the ligands [O(7), O(13) and O(7'), O(13') respectively] link to the adjacent $\{\text{Mo}_2\text{O}_{10}\}^{8-}$ moiety and interconnect the dimeric subunits. The involved O donors bridge in a μ -syn,syn-bridging mode and occupy two apical positions of the octahedrally coordinated Mo atoms within the dimer units. All four Mo atoms show distorted octahedral coordination environments. Each Mo ion in **4** is involved in two short Mo=O bonds [range between 1.692(3) and 1.707(3) Å] and three elongated Mo– μ -O bonds that range between 2.276(3) and 2.427(3) Å.

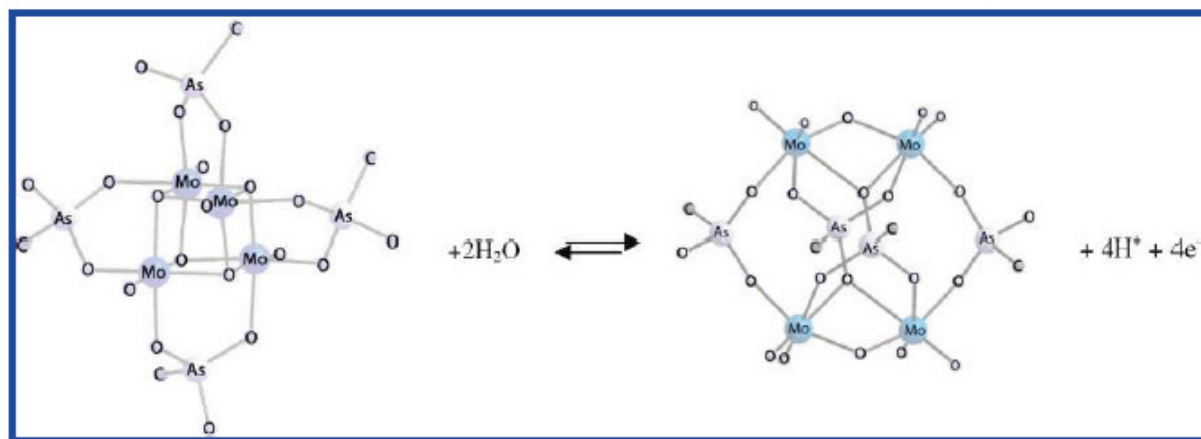


Figure 8. Formal rearrangement of the {Mo₄} core structure in **1** or **2** to give **4**.

Bond-valence-sum analyses confirm that all four Mo atoms in **4** adopt the oxidation state VI+. As expected, the disubstituted arsonate ligand imposes an influence on the self-assembly process under the investigated conditions that produce **1** and **2**. In fact, the composition of the cluster anion **4** is closely related to that of **1** and **2**. However, it seems that the OH and NO₂ functionalities of the organic ligands enforce a rearrangement of the cubane core structure. The rearrangement can formally be explained by an intramolecular condensation reaction under acidic conditions, releasing two water molecules (Figure 8). ESI-MS studies on the crystalline material reveal that **4** is unstable in solution and decomposes into inorganic or polymeric insoluble materials when dissolved in H₂O or DMSO.

The packing arrangement of the [Mo^{VI}₄O₁₀(O₃AsC₆H₃NO₂OH)₄]⁴⁻ clusters in the crystal structure is characterized by small intercluster channels (filled with constitution water molecules and NH₄⁺ counterions) that run in the direction of the crystallographic *a* axis (Supporting Information).

Further Physicochemical Characterization of the Isolated Compounds. Supplemental analyses include thermogravimetric studies, NMR, and bond-valence-sum analyses (see the Supporting Information). The thermal stabilities of all isolated compounds were investigated under a dinitrogen gas atmosphere. All compounds reveal similar decomposition behavior. The first thermogravimetric steps are the result of the loss of assigned constitution solvent molecules of the compounds and occur in a temperature range between 25 and 200 °C. Cluster degradation processes and oxidation of the organic ligands prevail in the temperature range between 200 and 600 °C. ¹H NMR analyses underline the stability of **1** and **2** in DMSO and are in agreement with the ESI-MS and X-ray data. The NMR spectrum of **3** is characterized by very broad signals, which are in agreement with the paramagnetic nature of the compound. Bond-valence-sum analyses confirm the assigned oxidation states of compounds **1–4**.

Conclusion

Our efforts focus on the application of analytical techniques that allow us to monitor and direct complex condensation reactions to produce novel functionalized hybrid materials. We report here a facile synthetic approach to

functionalizing polyoxomolybdate clusters that involve the partial reduction of Mo^{VI} salts in the presence of organoarsenate ligands. We demonstrate how slight perturbations of the ligand structures can be exploited to stabilize unprecedented core structures. Our investigations underline the stability of **1–3** in solution, an essential requirement for potential applications as catalysts. Redox-active transition metals that adopt cubane or related structures are of particular interest to scientists because of their resemblance to active sites of enzymes, and it has recently been suggested that such oxo clusters might hold the key to catalyzing the splitting of water,^{8,13a–13c} a process that might have an impact on future energy requirements providing a conceptional solution to climate issues. We demonstrate that the cubane structures **1** and **2** tolerate polar and oxophilic functional groups in the para position to the arsonate group, a characteristic that might allow the tethering of clusters to surfaces, for instance, electrodes. We have demonstrated that ESI-MS, in combination with X-ray crystallography, provides an extremely powerful tool to identify and characterize new species that form in solution. Our approach allowed us to use simple, common, well-investigated, and commercially available ligands and to screen their involvement in condensation reactions, providing us with a time-effective protocol to selectively isolate and structurally characterize a series of novel species. The effectiveness of mass spectrometry in this field science has only recently been highlighted, and our efforts extend accomplishments to complex hybrid structures. Our results underline the possibility of exploring real-time growth reactions of polyoxometals that emerge in solution, transforming from small or oligonuclear species and aggregating into large nanosized molecular clusters.

Experimental Section

All reagents were purchased from Sigma Aldrich and ABCR and used without further purification.

1: (NH₄)₆Mo₇O₂₄·4H₂O (0.224 g, 0.180 mmol) and CH₃COONH₄ (0.500 g, 6.488 mmol) were dissolved under stirring in H₂O (10 mL) at room temperature, and N₂H₄·H₂SO₄ (0.032 g, 0.244 mmol) was added as a reducing agent. Then phenylarsonic acid (PAA; 0.612 g, 3.030 mmol) was added, and the resulting reaction mixture was stirred for 10 min. Subsequently, the pH was adjusted to pH = 3.9 (20 °C) through the addition of 3.32 mL of an aqueous CH₃COOH solution (50%, v/v). After 3 weeks, red-brown crystals were collected from a dark-blue solution

Table 1. Crystal Data and Structural Refinement Parameters

	(NH ₄) ₂ H ₂ [1]·5H ₂ O	(NH ₄) ₂ H ₂ [2]·DMF·4H ₂ O	(NH ₄) ₅ [3]·9H ₂ O	(NH ₄) ₄ [4]·2H ₂ O
empirical formula	C ₂₄ H ₄₀ As ₄ Mo ₄ N ₂ O ₂₅	C ₂₇ H ₄₉ As ₄ Mo ₄ N ₇ O ₂₅	C ₆₀ H ₁₂₆ As ₁₀ Mo ₁₀ N ₁₀ O ₈₀	C ₂₄ H ₃₆ As ₄ Mo ₄ N ₈ O ₃₆
temperature (K)	118(2)	118(2)	108(2)	108(2)
cryst color/shape	red/triangular plate	red/rod-shaped	blue/rectangular plate	orange/rectangular plate
cryst size/mm ³	0.20 × 0.20 × 0.05	0.20 × 0.15 × 0.10	0.50 × 0.40 × 0.40	0.20 × 0.20 × 0.20
molecular mass/g mol ⁻¹	1440.02	1555.16	3976.27	1696.02
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.009(4)	10.207(4)	19.417(4)	10.7255(19)
<i>b</i> /Å	15.767(5)	13.740(5)	21.040(4)	10.937(3)
<i>c</i> /Å	17.287(5)	19.700(8)	21.562(4)	12.000(3)
α /deg	117.09(2)	87.426(13)	113.09(3)	89.474(13)
β /deg	96.03(2)	82.265(10)	112.90(3)	66.129(10)
γ /deg	98.454(18)	71.005(11)	99.16(3)	63.926(7)
<i>V</i> /Å ³	2356.1(14)	2588.6(17)	6941(2)	1131.6(5)
<i>Z</i>	2	2	2	1
density/Mg m ⁻³	2.001	1.978	1.864	2.465
abs coeff/mm ⁻¹	3.906	3.567	3.334	4.109
<i>F</i> (000)	1356	1494	3732	808
2 θ_{max} /deg	50	50	50	50.04
reflns collected	36 989	39 817	103 006	14 710
indep reflns	8303 [<i>R</i> (int) = 0.1174]	9114 [<i>R</i> (int) = 0.1044]	24429 [<i>R</i> (int) = 0.0648]	3987 [<i>R</i> (int) = 0.0313]
parameters	577	604	1587	343
<i>S</i> on <i>F</i> ²	1.036	1.006	1.059	1.036
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0985, 0.2684	0.0836, 0.1961	0.0704, 0.1844	0.0282, 0.0817
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1171, 0.2869	0.0892, 0.2006	0.0789, 0.1930	0.0303, 0.0831

and washed with cold water. Yield: 57%. Anal. Calcd for As₄C₂₄H₄₀Mo₄N₂O₂₅: C, 20.01; H, 2.79; N, 1.94. Found: C, 19.65; H, 2.15; N, 1.69. FTIR (cm⁻¹): ν_{max} 2981(b), 1641(w), 1439(m), 1092(m), 966(vs), 743(vs). ¹H NMR (400 MHz, DMSO): δ 7.67 (m, 12H, H^{aromatic}), 7.97 (d, *J* = 7.0 Hz, 8H, H^{aromatic}). UV/vis (DMF): λ_{max} (ϵ) = 456.60 nm (1000 L mol⁻¹ cm⁻¹).

2: N₂H₄·H₂SO₄ (0.032 g, 0.244 mmol) was added to a mixture of (NH₄)₆Mo₇O₂₄·4H₂O (0.224 g, 0.180 mmol), CH₃COONH₄ (0.500 g, 6.488 mmol), H₂O (5 mL), and *N*, *N*-dimethylformamide (DMF; 5 mL). The solution was vigorously stirred for 5 min, and *p*-arsanilic acid (0.659 g, 3.030 mmol) was added. The resulting reaction mixture was further stirred for 10 min, and subsequently the pH was adjusted to pH = 4.9 (20 °C) through the addition of an aqueous CH₃COOH solution (50%, v/v). Red-brown crystals were obtained after 5–7 days. Yield: 53%. Anal. Calcd for As₄C₂₇H₄₉Mo₄N₇O₂₅: C, 20.85; H, 3.17; N, 6.30. Found: C, 21.14; H, 2.61; N, 6.23. FTIR (cm⁻¹): ν_{max} 3329(m), 3209(m), 1714(w), 1628(m), 1594(s), 1502(m), 1425(m), 1295(w), 1182(w), 1095(m), 958(s), 768(vs), 692(s). ¹H NMR (400 MHz, DMSO): δ 5.80 (s, 8H, NH₂), 6.73 (d, *J* = 8.5 Hz, 8H, H^{aromatic}), 7.56 (d, *J* = 8.5 Hz, 8H, H^{aromatic}). UV/vis (DMF): λ_{max} (ϵ) = 460.38 nm (1000 L mol⁻¹ cm⁻¹).

3: (NH₄)₆Mo₇O₂₄·4H₂O (0.224 g, 0.180 mmol) and CH₃COONH₄ (0.500 g, 6.488 mmol) were dissolved under stirring in H₂O (10 mL) at room temperature, and N₂H₄·H₂SO₄ (0.032 g, 0.244 mmol) was added as a reducing agent. Then HPAA (0.660 g, 3.030 mmol) was added, and the resulting reaction mixture was stirred for 10 min. Subsequently, the pH was adjusted to pH = 4.0 (20 °C) through the addition of 3.32 mL of an aqueous CH₃COOH solution (50%, v/v). Dark-blue crystals were collected after 1 week and washed with cold water. Yield: 53%. Anal. Calcd for As₅C₃₀H₆₃Mo₅N₅O₄₀: C, 18.12; H, 3.19; N, 3.52. Found: C, 19.03; H, 2.70; N, 3.20. FTIR (cm⁻¹): ν_{max} 2998(vbr), 1582(m), 1500(w), 1425(s), 1253(m), 1171(w), 1092(s), 944(s), 729(s). UV/vis (DMF): λ_{max} (ϵ) = 531.24 nm (2700 L mol⁻¹ cm⁻¹).

4: The same synthetic procedure as that for (NH₄)₂H₂[1]·5H₂O, using HNPA (0.797 g, 3.030 mmol) as the ligand, was used. The pH was adjusted to pH = 3.9 (20 °C) through

the addition of 3.32 mL of an aqueous CH₃COOH solution (50%, v/v), and orange crystals of (NH₄)₄[Mo₄O₁₀-(O₃AsC₆H₃NO₂OH)₄]·2H₂O were obtained within 3 weeks. Yield: 75%. Anal. Calcd for As₄C₂₄H₃₆Mo₄N₈O₃₆: C, 17.00; H, 2.14; N, 6.61. Found: C, 16.52; H, 2.06; N, 5.61. FTIR (cm⁻¹): ν_{max} 3189(br), 1614(m), 1570(w), 1532(w), 1407(m), 1355(w), 1327(m), 1247(w), 1158(m), 1099(m), 940(w), 810(vs), 762(s). ¹H NMR (400 MHz, DMSO): δ 6.47 (d, *J* = 9.0 Hz, 4H, H^{aromatic}), 7.17 (dd, *J* = 9.0 and 2.0 Hz, 4H, H^{aromatic}), 8.05 (d, *J* = 2.0 Hz, 4H, H^{aromatic}).

Crystallographic Data. Single-crystal analyses were performed at 150 K with a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.710 73 Å). A full sphere of data was obtained using the ω scan method. Data were collected, processed, and corrected for Lorentz and polarization effects using *SMART* and *SAINT-NT* software.¹⁵ The structures were solved using direct methods and refined with the *SHELXTL* program package.¹⁶ The crystallographic data for 1–4 are given in Table 1. Crystallographic data, CCDC 767645–767648, can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. The authors thank the Science Foundation Ireland (SFI) for financial support (Grants 06/RFP/CHE173 and 08/IN.1/I2047). Financial support from IRCSET (fellowship for L.Z.), the University of Bordeaux, ANR (NT09_469563, AC-MAGnets project), Région Aquitaine, GIS Advanced Materials in Aquitaine (COMET Project), and MAGMANet (NMP3-CT-2005-515767) is also gratefully acknowledged.

Supporting Information Available: Additional figures of the isolated compounds, bond-valence-sum analyses; experimental conditions for ESI-MS experiments; additional assignments,

(15) (a) *SMART*, version 5.629; Bruker-AXS Inc.: Madison, WI, 1997–2003. (b) *SAINT-Plus*, version 6.22; Bruker-AXS Inc.: Madison, WI, 1997–2003.

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and ESI-MS cone voltage variations, analysis of the magnetic properties of $(\text{NH}_4)_5[3] \cdot 9\text{H}_2\text{O}$, powder X-ray diffraction of $(\text{NH}_4)_2\text{H}_2[1] \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{H}_2[2] \cdot \text{DMF} \cdot 4\text{H}_2\text{O}$, thermogravimetric analyses of isolated compounds, NMR spectroscopy of $(\text{NH}_4)_2\text{H}_2[1] \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{H}_2[2] \cdot \text{DMF} \cdot$

$4\text{H}_2\text{O}$, UV/vis spectroscopy of $(\text{NH}_4)_2\text{H}_2[1] \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{H}_2[2] \cdot \text{DMF} \cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_5[3] \cdot 9\text{H}_2\text{O}$, IR spectra of the compounds, and ORTEP diagrams of the asymmetric units of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Supramolecular Approach by Using Jahn–Teller Sites to Construct a {Mn₁₃}-Based Coordination Polymer and Modify its Magnetic PropertiesLei Zhang,^[a] Rodolphe Clérac,^[b, c] Camelia I. Onet,^[a] Munuswamy Venkatesan,^[d] Pierre Heijboer,^[a] and Wolfgang Schmitt^{*,[a]}

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) have attracted scientific interest due to their unique chemical and physical attributes, which promote applications as catalysts, gas-storage, ion-exchange or drug-delivery materials.^[1] Their properties and the performances in these targeted areas are determined by the composition and structural characteristics of their inorganic nodes and organic linkers, giving rise to unprecedented surface areas and shape/size-selective framework topologies.^[2] Recently developed preparative approaches that involve the incorporation of guest molecules into the framework structures may provide means to alter or enhance the physical attributes of these complex supramolecular materials.^[3] Polynuclear manganese complexes constitute an intriguing class of potential secondary building units (SBUs) for the preparation of multi-functional PCPs as they may reveal superparamagnetic properties and static or dynamic quantum behaviour.^[4,5] However, it still remains a formidable synthetic challenge to incorporate polynuclear Mn complexes into polymeric open frameworks and to the best of our knowledge PCPs consisting of larger {Mn_n} oxo-clusters ($n > 8$) have not yet been reported.^[6]

Rational methodologies for the preparation of complex metallo-supramolecular systems rely on the identification of stable inorganic SBUs, which contain distinct kinetically labile coordination sites that point into defined directions of space and that allow functionalization by organic ligands to direct the assembly into the desired structure topologies.^[7,8] Based on previous reports, it appears feasible that tetragonally elongated Jahn–Teller sites provide such kinetically active positions;^[9] in particular distorted d⁴ Mn^{III} environments are characterised by high kinetic lability and high

water-exchange rates ($> 10^7$ s^{−1} at 298 K), clearly highlighting the potential of such sites for selective functionalization.^[10] Here we report an approach (Scheme 1) that demonstrates how active Jahn–Teller sites of a tridecanuclear Mn^{III} coordination complex, [(Mn^{II}_{0.5}Mn^{III}_{0.5})Mn^{III}₁₂(μ₄-O)₆(μ-OH)₂(μ-CH₃O)₄(CH₃OH)₂(*tert*-butyl-PO₃)₁₀(4-picoline)₄]^{0.5+} (**1**), can be exploited for the selective linkage of the entities to give a coordination polymer, [(Mn^{II}_{0.5}Mn^{III}_{0.5})Mn^{III}₁₂(μ₄-O)₆(μ-OH)₂(μ-CH₃O)₄(CH₃OH)₂(*tert*-butyl-PO₃)₁₀(4,4-TDP)₂]^{0.5+} (**2**), for which the packing structure is characterised by large voids. Furthermore, we demonstrate that the framework structure, which is internally decorated by additional Jahn–Teller sites, allows the post-synthetic modification by which the solution adsorption of tetracyanoquinodimethane (TCNQ) guests significantly influences the magnetic properties of this molecule-based system.

The com-proportionation reaction between MnCl₂·4H₂O and KMnO₄, in the presence of *tert*-butyl-PO₃H₂ and 4-picoline in methanol produces red crystals of [(Mn^{II}_{0.5}Mn^{III}_{0.5})Mn^{III}₁₂(μ₄-O)₆(μ-OH)₂(μ-CH₃O)₄(CH₃OH)₂(*tert*-butyl-PO₃)₁₀(4-picoline)₄]_{Cl_{0.5}}·1.5H₂O ([**1**]_{Cl_{0.5}}·1.5H₂O) in good yield (see the Supporting Information). Single-crystal X-ray diffraction analysis reveals that the {Mn₁₃} core consists of a typical hexagonal “brucite”-type {Mn₇} subunit in which a central Mn ion is located on an inversion centre and connected to six adjacent Mn^{III} ions through six μ₄-O^{2−} ligands (Figure 1). Related mixed-valent oxo-cluster topologies that contain the aforementioned brucite core have previously been reported.^[11] In **1**, there are three Mn^{III} ions located above and three symmetry-related Mn^{III} ions below the hexagonal plane, each connected to it through the latter oxo-ligands and deprotonated phosphonate ligands. The three Mn ions consist of a single Mn centre and a dinuclear {Mn-(OH)-Mn} unit, which are connected by O-donor atoms of two phosphonate ligands. The single Mn^{III} centres are further linked to the {Mn₇} unit through two μ-CH₃O[−] ligands. Bond valence sum (BVS) calculations of the outer 12 Mn centres all give values slightly higher than +3, confirming the +III oxidation states of these Mn ions. However, the central Mn atom has a BVS value of 2.594 which is distinctly lower than the others and clearly suggesting partial occupancy of the central position by Mn^{II} and Mn^{III} ions at 50:50% ratio.

The Jahn–Teller distorted coordination environments of the outer Mn^{III} centres provide chemical functionality to **1**.

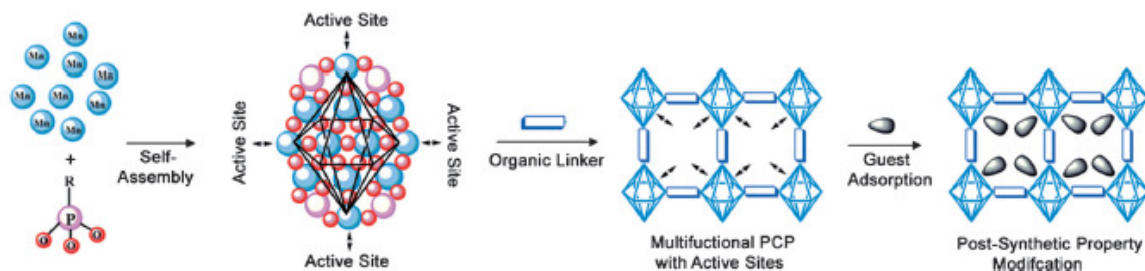
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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201202297>.



Scheme 1. Supramolecular approach for the preparation of Mn-cluster-based PCPs and their post-synthetic modification by active Jahn-Teller sites.

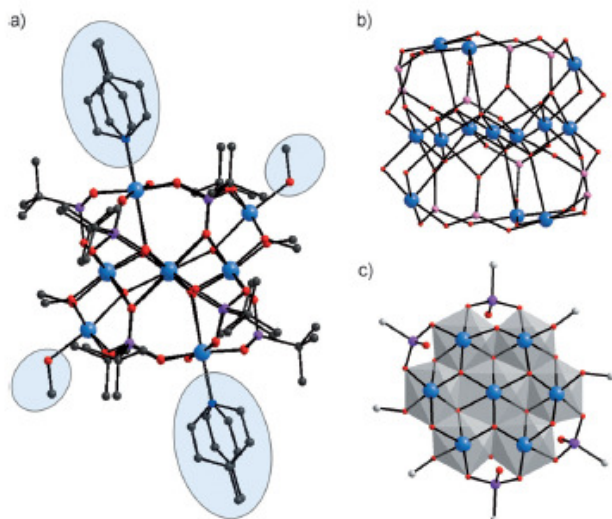


Figure 1. a) Crystal structure of **1**, highlighting the Jahn-Teller sites. b) The core structure of **1**. c) The hexagonal brucite-type $\{Mn_7\}$ subunit in **1**: colour code; Mn light blue, O red, P pink, N blue, C black.

analysis (see the Supporting Information) and their magnetic properties (Figure 3).

In the solid state the resulting 1D polymer chains in which the molecular entities are doubly bridged by 4,4'-trimethylenedipyridine linkers align parallel to the crystallographic *a* axis and pack so that the $\{Mn_{13}\}$ units are arranged into sheets that extend parallel to the *bc* plane. This packing motif in which the 4,4'-trimethylenedipyridine moieties essentially act as pillars between the sheets, gives rise to the formation of two types of channels that both extend in the direction of the crystallographic *b* axis (Figure 2b). The smaller channels that arise from intramolecular spaces between the 4,4'-trimethylenedipyridine ligands within the 1D chains only provide limited voids to accommodate constitutional MeOH molecules. Significantly larger channels with pore openings of about (10×12) Å that arise from the packing of the 1D polymers, are filled by methanol solvent molecules and chloride counterions. The walls of these channels comprise of 4,4'-trimethylenedipyridine ligand moieties and *tert*-butyl groups of the phosphonate ligands, endowing the

A MeOH ligand completes the tetragonally distorted octahedral coordination environment of the isolated Mn centre whereas two terminal 4-picoline ligands occupy apical, elongated positions to stabilise the dinuclear $\{Mn(OH)Mn\}$ moiety. The chemical lability of these latter coordination sites can be demonstrated by the use of bidentate 4,4'-trimethylenedipyridine (4,4'-TDP) ligands, which allow the substitution of the four 4-picoline ligands to produce the coordination polymer $[2]Cl_{0.5} \cdot 8CH_3OH$. The X-ray analysis confirms that the composition and geometrical parameters of the $\{Mn_{13}\}$ unit in **2** is virtually identical to that in **1** (Figure 2). This relationship is further reflected by the ESI-MS

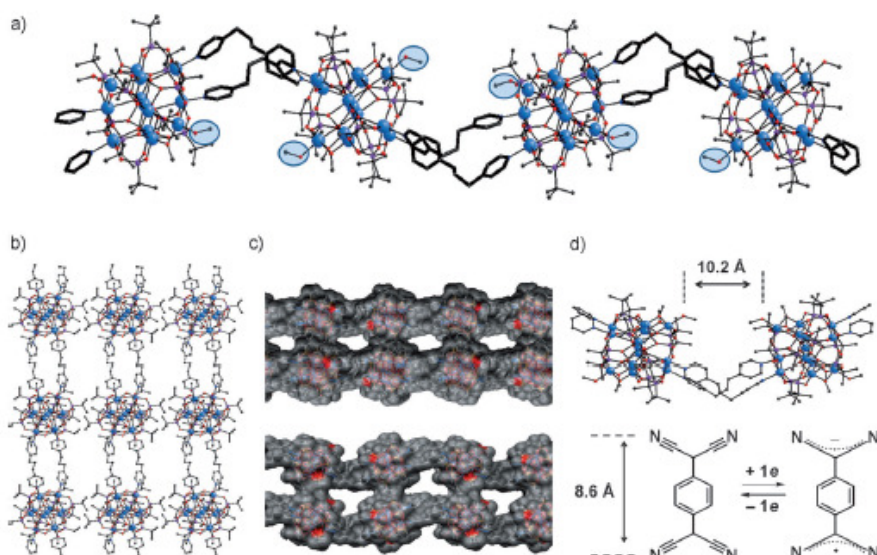


Figure 2. a) Crystal structure of the 1D polymer **2**, highlighting the 4,4'-TDP bridges that occupy the Jahn-Teller sites. b) Packing structure of **2** with a view in the direction of the crystallographic *b* axis. c) Space filling model of the pores and void spaces in **2** with views from two different directions. d) Comparison of the dimension of TCNQ molecules with distances between two methanol ligands of two adjacent $\{Mn_{13}\}$ entities: colour code; Mn light blue, O red, P pink, N blue, C black.

inner surface of the cavities with a predominantly hydrophobic character. The terminal coordinating MeOH ligands situated on Jahn–Teller axes point inside these larger cavities decorating the walls with potential labile or active ligand sites. The calculated total potential solvent accessible volume for **2**, upon removal of guest solvent molecules, is about 38 % of the cell volume (5938.3 Å³ of the 15758.0 Å³ unit cell volume).^[12]

Crystals of compound **2** [2]Cl_{0.5}·8CH₃OH readily desolvate in air and lose their crystallinity, however, they maintain their integrity for several months when immersed in common organic solvents, for example, in acetonitrile. This stability and the structural characteristics of this open-framework material, which contains large hydrophobic channels with active ligand sites, prompted us to investigate its suitability for the solution adsorption of TCNQ. The ideal size (ca. (4.2 × 8.6) Å) and hydrophobic nature make TCNQ an ideal target molecule for these absorption studies. In addition, TCNQ has the ability to form radical anions that allow tuning of magnetic and electronic charge-transfer attributes of the {Mn₁₃} assembly. It has previously been demonstrated that TCNQ^{•−} ions can provide an efficient pathway for magnetic superexchange, promoting ferromagnetic interactions when bridging two spin centres.^[13] In addition, TCNQ-based coordination compounds or charge-transfer salts with high charge mobility and delocalised radical charges may produce materials with high metallic conductivity.^[14]

A TCNQ acetonitrile solution exhibits a strong absorption band at around 400 nm, which can be assigned to the characteristic ¹A_g → ¹B_{3u} transition.^[15] Weaker absorbances at 700–900 nm may arise from small quantities of the mono-anion TCNQ^{•−} in the solution. To avoid structural degradation, crystals of **2** [2]Cl_{0.5}·8CH₃OH were stored in acetonitrile and directly transferred into a TCNQ acetonitrile solution. The UV/Vis spectrum recorded after one day clearly shows that the absorbance of the 400 nm band decreases over time (Figure 3a). Concurrently, the absorbances at 700–900 nm disappear, indicating that there is almost no TCNQ^{•−} present in the solution anymore. Spectra recorded at later dates underline this trend and show a continuous decrease of the intensity of the 400 nm band, clearly indicating the adsorption of TCNQ by **2** [2]Cl_{0.5}·8CH₃OH. After about two weeks, the absorbance decrease of the 400 nm signal halts at a value that is almost negligible. The observed TCNQ uptake is accompanied by a decolourisation of the solution by which the characteristic red-coloured TCNQ solution turns colourless (Figure S1 in the Supporting Information). During the adsorption process, the brown crystals of **2** [2]Cl_{0.5}·8CH₃OH turn black; they maintain their characteristic shape and morphology, but single-crystal X-ray diffraction experiments did not allow the determination of the molecular structure of the functionalised material. Elemental analysis of crystals that were immersed in a saturated MeCN/TCNQ solution for one month, washed with absolute MeCN and dried under vacuum at 100 °C, reproducibly confirm a constitutional composition of [Mn^{III}₁₃(μ₄-O)₆(μ-OH)₂(μ-CH₃O)₄-

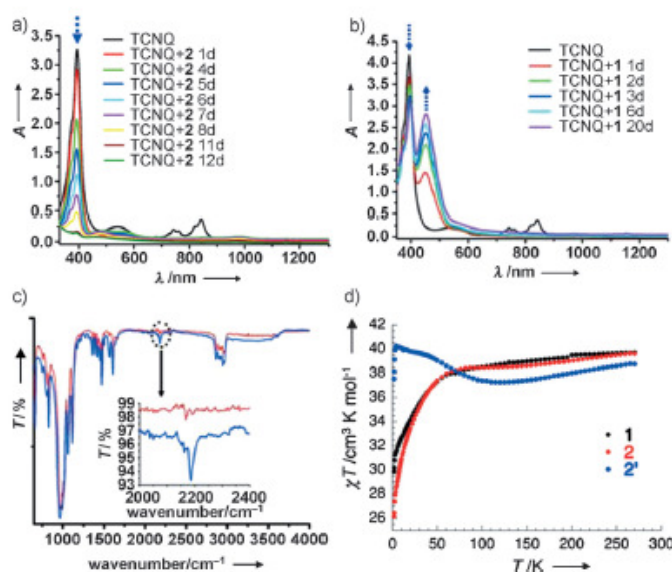
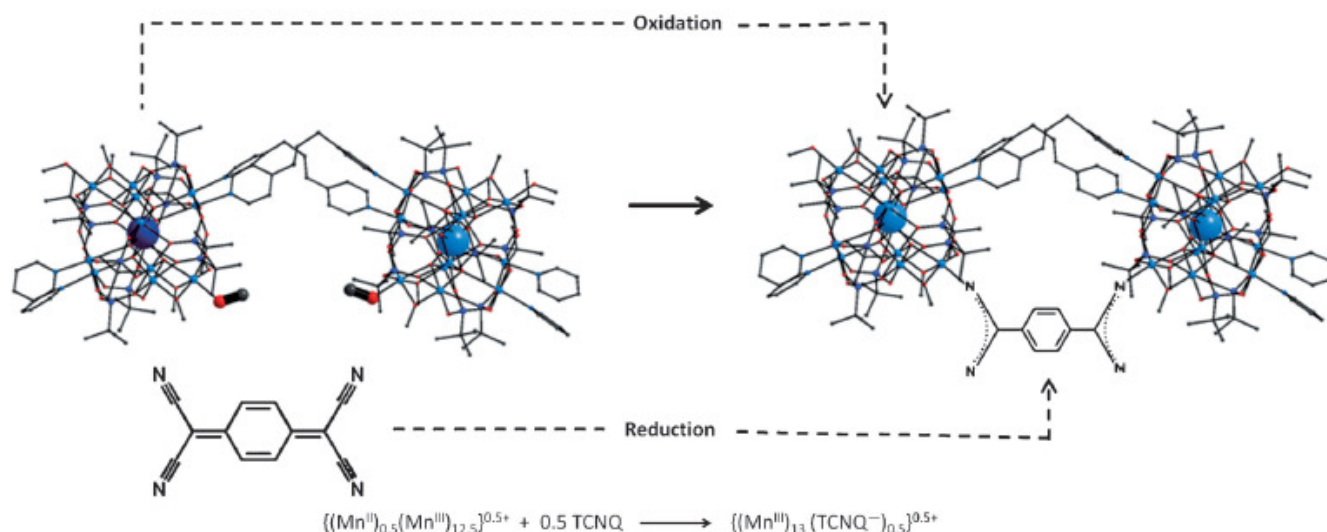


Figure 3. a) UV spectral changes during the adsorption of TCNQ by **2**. The characteristic ¹A_g → ¹B_{3u} absorbance at 400 nm and the band at 700–900 nm decrease over time until there is almost no TCNQ present in the solution. b) UV spectral changes of TCNQ acetonitrile solution in the presence of **1**. The moderate decrease of the ¹A_g → ¹B_{3u} absorbance at 400 nm is accompanied by the emergence of a new band at around 450 nm, corresponding to the formation of TCNQ anions present in solution. c) The comparison of the IR spectra of **2** [2]Cl_{0.5}·8CH₃OH (red) and **2'** [(TCNQ)_{0.5}Cl_{0.5}] (blue) confirms the incorporation of TCNQ^{•−} species. d) Temperature dependence of the χT product for **1**, **2** and **2'**, highlighting the change of the magnetic properties upon incorporation of TCNQ.

(CH₃OH)(*tert*-butyl-PO₃)₁₀(4,4-TDP)₂[(TCNQ)_{0.5}Cl_{0.5}]₂ [(**2'**)(TCNQ)_{0.5}Cl_{0.5}]. ESI-MS spectra of **2'** [(TCNQ)_{0.5}Cl_{0.5}] dissolved in methanol reveal a signal at *m/z* = 240 and clearly confirming the presence of TCNQ in the functionalised material. The ESI-MS study undoubtedly confirms that the functionalised material contains the {Mn₁₃} building block parent to the pristine coordination polymer **2**. IR spectra of **2** [2]Cl_{0.5}·8CH₃OH and **2'** [(TCNQ)_{0.5}Cl_{0.5}] are almost identical (Figure 3c). However, the spectrum of **2'** [(TCNQ)_{0.5}Cl_{0.5}] has an additional band at around 2186 cm^{−1}. In agreement with other reports, this signal is characteristic for TCNQ^{•−}, differing significantly from the bands for the neutral TCNQ (ca. 2222 cm^{−1}) or the dianionic TCNQ^{2−} (<ca. 2160 cm^{−1}) species.^[16] The constitutional assignment and the adsorption of 0.5 equivalents of TCNQ is in agreement with the redox process shown in Scheme 2, in which the Mn^{II} ions at the centre of the {Mn₁₃} entities are oxidised to Mn^{III} by TCNQ molecules to form the parent mono-anions. As a control experiment, UV/Vis studies with a TCNQ acetonitrile solution were also carried out in the presence of **1** (Figure 3b). In contrast to the previous findings, here the ¹A_g → ¹B_{3u} absorbance at 400 nm decreases only moderately, whereas a new band at around 450 nm emerges. The latter signal can be attributed to free TCNQ anions, the formation of which further substantiates the proposed redox process, involving the {Mn^{II}_{0.5}Mn^{III}_{0.5}Mn^{III}₁₂} entities.



Scheme 2. Proposed redox process occurring upon adsorption of TCNQ by **2**: colour code; Mn^{II} blue, Mn^{III} light blue.

Based on the dimensions of the channels in **2** and by considering the inter-complex distances, the formation of a 3D network structure upon TCNQ adsorption can be ruled out. Our structural analysis of **2** moreover suggests that TCNQ[−] is most likely to replace or interact with the kinetically activated MeOH ligands. The intra-chain distance between two adjacent MeOH ligands of about 10 Å corresponds well with the axial N⋯N distance of TCNQ (ca. 8.6 Å) and results in a proposed binding mode by which the TCNQ[−] ligand strengthens the connectivity between the {Mn₁₃} moieties of the 1D chain structure (Scheme 2).

This proposed bridging binding mode of TCNQ[−], by which each TCNQ[−] molecule links two {Mn₁₃} complexes, is indeed supported by the magnetic properties of this functionalised material. The studies of the magnetic properties (Figure 3d and S16 in the Supporting Information) confirm a pronounced change of the temperature dependence of the χT product upon TCNQ adsorption. The room temperature χT products of **[1]**Cl_{0.5}·1.5H₂O and **[2]**Cl_{0.5}·8CH₃OH are 39.8 and 39.7 cm³K mol^{−1}, respectively, and in agreement with the presence of 12.5 *S* = 2 Mn^{III} and 0.5 *S* = 5/2 Mn^{II} ions (expected value 39.7 cm³K mol^{−1} with *g* = 2). When the temperature is lowered, the χT products decrease continuously, indicating the presence of intra-complex antiferromagnetic interactions between the Mn spins, most likely stabilising an *S*_T ≠ 0 moderated spin ground state (*S*_T ≤ 7). The isolated {Mn₁₃} complexes in **1** and the 1D polymer **2** have almost identical magnetic properties. Minor differences most likely arise from the bridging 4,4'-trimethylenedipyridine ligands, which promote slightly enhanced magnetic-exchange interactions between the {Mn₁₃} cores in comparison with the weaker dipolar interactions in **1**. In contrast, the functionalised **[2']**(TCNQ)_{0.5}Cl_{0.5} material displays a significantly different magnetic behaviour. The room temperature χT product of 38.9 cm³K mol^{−1} is in agreement with the presence of 13 *S* = 2 Mn^{III} ions and 0.5 *S* = 1/2 TCNQ[−] radical anions (expected value 39.2 cm³K mol^{−1} with *g* = 2). When the tem-

perature is lowered, the χT product decreases to a minimum value of 37.2 cm³K mol^{−1} at around 120 K and then increases up to 40.2 cm³K mol^{−1} around 5 K. This thermal behaviour is typical of a ferrimagnetic arrangement of the spin carriers. In the present system, these magnetic data suggest a relatively strong antiferromagnetic exchange between the *S* = 1/2 TCNQ[−] radical anions and the neighbouring paramagnetic 0 < *S*_T ≤ 7 {Mn₁₃} moieties that would lead to a ferrimagnetic organisation of the magnetic species along the [TCNQ[−]{Mn₁₃}]_{*n*} chains. Below 5 K, the χT product decreases down to 37.5 cm³K mol^{−1} at 1.8 K as a signature of the magnetic anisotropy of the Mn^{III} sites and/or inter-chain antiferromagnetic interactions.

In conclusion, we report the synthesis and characterisation of a {Mn₁₃} coordination cluster and demonstrate how kinetically labile coordination sites can be exploited to rationally link this SBU into a coordination polymer that is characterised by an open-framework structure, containing large voids and channels. We apply a post-synthetic approach to modify the magnetic properties of the material, by which the incorporation of TCNQ[−] radical anions into the framework structure promotes a ferrimagnetic arrangement of the {Mn₁₃} spin carriers and radical species. Our studies strongly suggest that this supramolecular approach, which takes advantage of kinetically labile Jahn–Teller sites, is applicable to other Mn coordination complexes to create multi-functional porous materials.

Acknowledgements

The authors thank the Science Foundation Ireland (SFI; 06/RFP/CHE173 and 08/IN.1/2047), IRCSET (fellowship for L.Z.), the University of Bordeaux, the ANR (NT09 469563, AC-MAGnets project), the Région Aquitaine, the GIS Advanced Materials in Aquitaine (COMET Project), and the CNRS for financial support. We thank Dr. Martin Feeney for help with the ESI MS analyses.

Keywords: coordination polymers • Jahn–Teller sites • magnetic properties • manganese • tetracyanoquinodimethane

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Received: June 28, 2012

Published online: September 20, 2012

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