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Abstract

The main purpose of the current study was to expand, and fully explore, the library of known coordination compounds that form from the aqueous *hpdt*a reaction system. The study examines the role *hpdt*a coordination compounds play in the fixation of aerial carbon dioxide and their potential applications as catalysts in the reduction of carbon dioxide. Also considered is the potential application of *hpdt*a based supramolecular assemblies as materials for gas storage and separation. The study uses ^{27}Al , ^{13}C and ^1H nuclear magnetic resonance (NMR) combined with electrospray ionisation mass spectrometry (ESI-MS $^-$) and Ultraviolet-visible (UV-Vis) spectroscopic analyses in order to gain insights into the solution behaviours of the Fe^{III} and Al^{III} *hpdt*a based reaction system; Engages Gas-chromatography-mass spectrometry (GC-MS) headspace analyses coupled with ESI-MS $^-$ in order to investigate the reversible fixation of atmospheric carbon dioxide using tetranuclear Fe^{III} *hpdt*a compounds; and employs cyclic voltammetry in combination with fluorescence spectrophotometry to establish the compounds' redox activities and electron scavenging characteristics. The research also applies the *Sieverts Method* to determine the gas storage capabilities and BET surface areas of novel $\{\text{Al}_{15}\}$ *hpdt*a supramolecular assemblies. The first chapter of this thesis outlines the specific aims of the research and introduces the reader to supramolecular chemistry and the applications of porous materials such as zeolites and metal-organic frameworks (MOF's) for gas storage and separation. Also considered is the use of transition metal complexes in the reduction of CO_2 .

Chapter two, details the speciation studies of the Fe^{III} and Al^{III} compounds **1-3** and **5-7**. ^{27}Al , ^{13}C and ^1H NMR and UV-Vis spectroscopy in combination with ESI-MS $^-$ were employed to develop speciation protocols for *hpdt*a-based compounds in solution. The protocols were used to confirm the core tetranuclear species stability in solution and the structural integrity of compounds **3** and **5-7** in appropriate pH environments. Chapter three reports the synthesis and structural characterisation of five novel *hpdt*a coordination compounds. Specifically, the dinuclear Fe^{III} compound $(\text{NH}_3\text{C}_3\text{H}_6\text{NH}_3)_{0.5}\text{K}[\text{Fe}_2(\text{hpdt})_2(\text{H}_2\text{hpdt})]\cdot 4\text{H}_2\text{O}\cdot \text{NH}_2\text{C}_3\text{H}_6\text{NH}_2$ (**8**), compound **9** $\text{Na}_7\{[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{CO}_3)(\text{H}_2\text{O})_2]\{\text{Fe}_6(\mu\text{-O})(\mu\text{-OH})_5(\text{hpdt})_3\}}\cdot 4\text{H}_2\text{O}$, and the trinuclear compound $\text{Na}[\text{Fe}_3(\text{H}_2\text{O})_2(\mu\text{-O})(\text{C}_9\text{H}_5\text{N}_2\text{O}_7)_2]\cdot 6\text{H}_2\text{O}$ (**10**). The mononuclear and tetranuclear compounds $\text{enH}_2[\text{Ni}(\text{H}_1\text{hpdt})]\cdot 2\text{H}_2\text{O}$ (**11**) and $\text{Na}_8[\text{V}_4(\mu\text{-O})_2(\text{hpdt})_2(\text{O})_4]\cdot 3\text{H}_2\text{O}$ (**12**) formed upon the addition of Ni^{II} and V^{III} metal ions to aqueous *hpdt*a ligand solutions.

In chapter four, the *hpdt*a system's affinity towards carboxylate bearing ligands is examined through the isolation of six novel *hpdt*a compounds. Namely, $\text{Na}_3\{[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2]\{(\text{OOC}\text{C}_6\text{H}_5)\}_2\}\cdot 12\text{H}_2\text{O}\cdot \text{DMF}$ (**13**), $\text{Na}_8\{[\text{Fe}_4(\mu\text{-O})_2(\text{hpdt})_2]\{(\text{OOC}\text{C}_6\text{H}_4\text{COO})\}_2\}\cdot 43\text{H}_2\text{O}$ (**14**), $\text{Na}_8\{[\text{Fe}_4(\mu\text{-O})_2(\text{hpdt})_2]\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})\}_2\}\cdot 35\text{H}_2\text{O}$ (**15**), $\text{Na}_{10}\{[\text{Fe}_4(\mu\text{-O})_2(\text{hpdt})_2]\{(\text{OOC}\text{C}_8\text{H}_8\text{COO})\}_2\}\cdot 25\text{H}_2\text{O}$ (**16**), $\text{Na}_8\{[\text{Al}_4(\mu\text{-O})_2(\text{hpdt})_2]\{(\text{OOC}\text{C}_8\text{H}_8\text{COO})\}_2\}\cdot 39\text{H}_2\text{O}$ (**17**) and $\text{Na}_8\{[\text{Mn}_4(\mu\text{-O})_2(\text{hpdt})_2]\{(\text{OOC}\text{C}_8\text{H}_8\text{COO})\}_2\}\cdot 25\text{H}_2\text{O}$ (**18**). Chapter five establishes the role of tetranuclear Fe^{III} compounds in the, reversible, fixation of aerial carbon dioxide; and confirms the compounds electrochemical and photophysical characteristics in order to evaluate their potential applications as catalysts in the reduction of CO_2 .

Chapter six examines the counter-ion mediated formation of a series of novel $\{\text{Al}_{15}\}$ complexes; $(\text{H}_3\text{O})_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4]\cdot 23\text{H}_2\text{O}$ (**26**), $\text{Rb}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4]\cdot 43\text{H}_2\text{O}$ (**27**), $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4]\cdot 36\text{H}_2\text{O}$

Towards the Fixation, Storage and Activation of Carbon dioxide using Iminodiacetic Acid-based Coordination Compounds

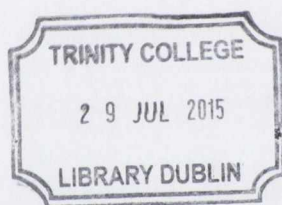
Annemarie O Toole



School of Chemistry
University of Dublin.

May 2015

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



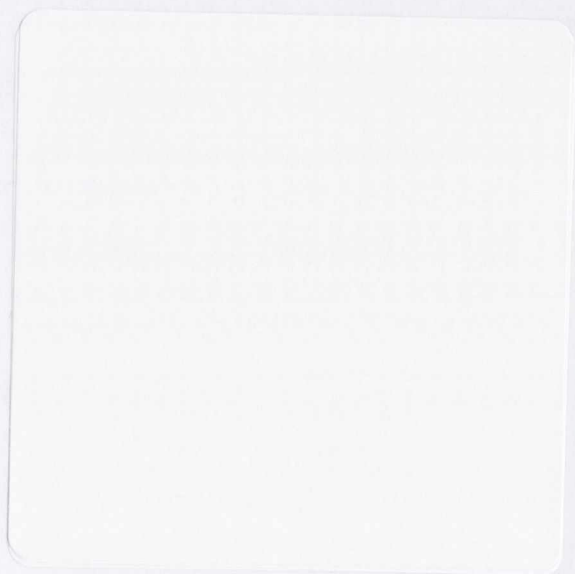
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Summary

The main purpose of the current study was to expand, and fully explore, the library of known coordination compounds that form from the aqueous *hpdta* reaction system. The study examines the role *hpdta* coordination compounds play in the fixation of aerial carbon dioxide and their potential applications as catalysts in the reduction of carbon dioxide. Also considered is the potential application of *hpdta* based supramolecular assemblies as materials for gas storage and separation. The study uses ^{27}Al , ^{13}C and ^1H nuclear magnetic resonance (NMR) combined with electrospray ionisation mass spectrometry (ESI-MS $^-$) and Ultraviolet-visible (UV-Vis) spectroscopic analyses in order to gain insights into the solution behaviours of the Fe^{III} and Al^{III} *hpdta* based reaction system; Engages Gas-chromatography-mass spectrometry (GC-MS) headspace analyses coupled with ESI-MS $^-$ in order to investigate the reversible fixation of atmospheric carbon dioxide using tetranuclear Fe^{III} *hpdta* compounds; and employs cyclic voltammetry in combination with fluorescence spectrophotometry to establish the compounds' redox activities and electron scavenging characteristics. The research also applies the *Sieverts Method* to determine the gas storage capabilities and BET surface areas of novel $\{\text{Al}_{15}\}$ *hpdta* supramolecular assemblies. The first chapter of this thesis outlines the specific aims of the research and introduces the reader to supramolecular chemistry and the applications of porous materials such as zeolites and metal-organic frameworks (MOFs) for gas storage and separation. Also considered is the use of transition metal complexes in the reduction of CO_2 .

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In chapter four, the *hpdta* system's affinity towards carboxylate bearing ligands is examined through the isolation of six novel *hpdta* compounds. Namely, $\text{Na}_3[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2\}\{(\text{OOC}\text{C}_6\text{H}_5)\}_2]\cdot 12\text{H}_2\text{O}\cdot\text{DMF}$ (13), $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2\{(\text{OOC}\text{C}_6\text{H}_4\text{COO})\}_2]\cdot 43\text{H}_2\text{O}$ (14), $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2\{(\text{OOC}\text{C}_6\text{H}_4\text{COO})\}_2]\cdot 35\text{H}_2\text{O}$ (15), $\text{Na}_{10}[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})_2]\cdot 35\text{H}_2\text{O}$ (16), $\text{Na}_8[\{\text{Al}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\text{Cl}_2\cdot 25\text{H}_2\text{O}$ (17), and $\text{Na}_8[\{\text{Mn}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\cdot 39\text{H}_2\text{O}$ (18). Chapter five establishes the role of tetranuclear Fe^{III} compounds in the, reversible, fixation of aerial carbon dioxide; and confirms the compounds electrochemical and photophysical characteristics in order to evaluate their potential applications as catalysts in the reduction of CO_2 .

Chapter six examines the counter-ion mediated formation of a series of novel $\{\text{Al}_{15}\}$ complexes; $(\text{H}_3\text{O})_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 23\text{H}_2\text{O}$ (**26**), $\text{Rb}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 43\text{H}_2\text{O}$ (**27**), $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 36\text{H}_2\text{O}$ (**28**), $\text{K}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 22\text{H}_2\text{O}$ (**29**) and $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 41\text{H}_2\text{O}$ (**30**). The *Sieverts Method* is employed to confirm the porosities of compounds **24**, **27-29** and establish their N_2 BET surface areas that range from 538 m^2/g to 651 m^2/g . Their CO_2 and H_2 adsorption isotherms revealed CO_2 uptakes ranging from ca. 132 to 207 mg/g and H_2 storage capacities of between ca. 7 and 11 mg/g. Together these results provide important insights into their potential applications as gas storage materials. Chapter seven provides concluding remarks and chapter eight discusses the experimental details of the synthesis and characterisations of the compounds described in this study.

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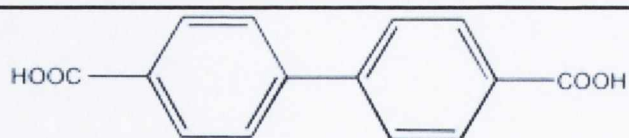
List of Compounds

- 1a**= $\text{NH}_4[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4] \cdot 12.5\text{H}_2\text{O}$ ^{1 2}
1b= $(\text{enH})[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4] \cdot n\text{H}_2\text{O}$
2a= $(\text{pipH}_2)_{1.5}[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})_3(\text{hpdta})_2] \cdot 6\text{H}_2\text{O}$ ³
2b= $(\text{enH}_2)_{1.5}[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})_3(\text{hpdta})_2] \cdot n\text{H}_2\text{O}$
3= $(\text{enH})[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2] \cdot 6.5\text{H}_2\text{O}$ ²
4= $\text{Na}_2[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{CO}_3)_2] \cdot \text{ca. } 20\text{H}_2\text{O}$ ²
5= $(\text{enH})[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4] \cdot n\text{H}_2\text{O}$
6= $(\text{enH}_2)[\text{Al}_4(\mu\text{-OH})_4(\text{hpdta})_2] \cdot 7.5 \text{H}_2\text{O}$ ³
7= $(\text{enH})[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2] \cdot n\text{H}_2\text{O}$
8= $(\text{NH}_3\text{C}_3\text{H}_6\text{NH}_3)_{0.5}\text{K}[\text{Fe}_2(\text{hpdta})(\text{H}_2\text{hpdta})] \cdot 4\text{H}_2\text{O} \cdot \text{NH}_2\text{C}_3\text{H}_6\text{NH}_2$
9= $\text{Na}_7[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{CO}_3)(\text{H}_2\text{O})_2\}\{\text{Fe}_6(\mu\text{-O})(\mu\text{-OH})_5(\text{hpdta})_3\}] \cdot 4\text{H}_2\text{O}$
10= $\text{Na}[\text{Fe}_3(\text{H}_2\text{O})_2(\mu\text{-O})(\text{C}_9\text{H}_5\text{N}_2\text{O}_7)_2] \cdot 6\text{H}_2\text{O}$
11= $\text{EnH}_2[\text{Ni}(\text{H}_1\text{hpdta})] \cdot 2\text{H}_2\text{O}$
12= $\text{Na}_8[\text{V}_4(\mu\text{-O})_2(\text{hpdta})_2(\text{O})_4] \cdot 3\text{H}_2\text{O}$
13= $\text{Na}_3[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2\}\{(\text{OOC}\text{C}_6\text{H}_5)_2\}] \cdot 12\text{H}_2\text{O} \cdot \text{DMF}$
14= $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2\{(\text{OOC}\text{C}_6\text{H}_4\text{COO})_2\}] \cdot 43\text{H}_2\text{O}$
15= $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2\text{hpdta})_2\}_2\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})_2\}] \cdot 35\text{H}_2\text{O}$
15a= $\text{Na}_5 \cdot \text{H}_3\text{O}[\{\text{Fe}_4(\mu\text{-O})_2\text{hpdta})_2\}_2\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})_2\}] \cdot 15\text{H}_2\text{O} \cdot \text{DMA} \cdot \text{ligand}$
16= $\text{Na}_{10}[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\text{Cl}_2 \cdot 25\text{H}_2\text{O}$
17= $\text{Na}_8[\{\text{Al}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2] \cdot 39\text{H}_2\text{O}$
18= $\text{Na}_8[\{\text{Mn}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2] \cdot 25\text{H}_2\text{O}$
19= $\{\text{Na}\}_5[\text{Fe}^{\text{III}}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{CO}_3)_2] \cdot 15\text{H}_2\text{O}$
20= $(\text{NH}_2\text{C}_4\text{H}_8\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_4\text{H}_8\text{NH}_3)_2] \cdot 10\text{H}_2\text{O}$
21= $(\text{NH}_2\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHNNH}_3)_2] \cdot 9\text{H}_2\text{O}$
22= $(\text{NH}_2\text{C}_6\text{H}_{12}\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_6\text{H}_{12}\text{NH}_3)_2] \cdot 9\text{H}_2\text{O}$
23= $(\text{NHC}_2\text{H}_4\text{NC}_4\text{H}_8\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NC}_4\text{H}_8\text{NH}_2)_2] \cdot 8\text{H}_2\text{O}$
24= $(\text{pipH}_2)(\text{H}_3\text{O})[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot \text{pipz} \cdot 41\text{H}_2\text{O}$ ⁴
25= $(\text{EnH}_2)(\text{H}_3\text{O})[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot n\text{H}_2\text{O}$ ⁴
26= $(\text{H}_3\text{O})_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 23\text{H}_2\text{O}$
27= $\text{Rb}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 43\text{H}_2\text{O}$
28= $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 36\text{H}_2\text{O}$
29= $\text{K}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 22\text{H}_2\text{O}$
30= $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 41\text{H}_2\text{O}$

Ligand Structures

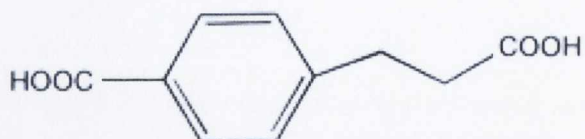
Ligand Code	Chemical Structure
L1	H5HPDTA (3-diamino 2-hydroxy propane-N,N,N',N'-tetra acetate)
L2	Hemin
L3	Benzoic Acid
L4	Terephthalic acid

L5



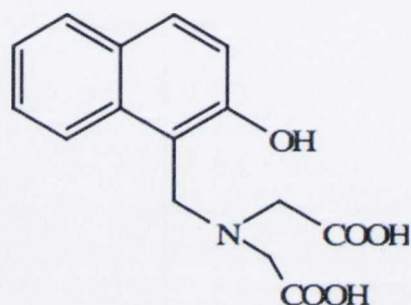
4,4'-biphenyl-dicarboxylic acid

L6

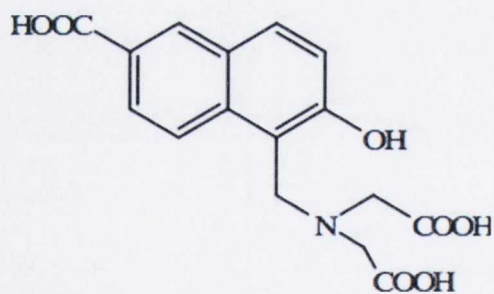


3-(4-Carboxy-phenyl)propionic acid

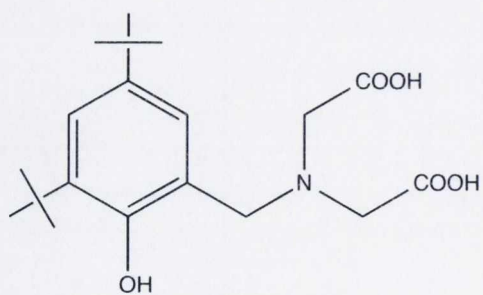
H₃hnida



H₄chnida



tBu₂hda



Abbreviations

^{13}C	Carbon - 13
1D	One dimensional
^1H	Proton
^{27}Al	Aluminium - 27
2D	Two dimensional
3D	Three dimensional
aep	1-(2-aminoethyl) piperazine
aq	Aqueous
ATM	Atmospheric pressure
AU	Arbitrary units
BET	Brunauer-Emmett-Teller
BNAH	1-benzyl-1,4-dihydronicotinamide
BPY	Bipyridine
CCS	Carbon capture systems
CHN	Carbon, hydrogen, nitrogen elemental analysis
CPS	Counts per second
CV	Cyclic Voltammetry
Cyclam	Tetraazacyclotetradecane
DAB	Diaminobutane
Dah	Diaminoheptane
DAO	Diaminooctane
DCM	Dichloromethane
DMA	N,N'-dimethylacetamide
DMB	Diisocyano-p-menthane
DMF	N,N'-dimethylformamide
EDX	Energy-dispersive X-ray
en	Ethylenediamine
EPA	Environmental protection agency
ESI-MS	Electrospray ionisation- mass spectrometry
FT-IR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometry

H ₃ hnida	[Carboxymethyl-(2-hydroxy-naphthalen-1-ylmethyl)-amino]-acetic acid
H ₄ chnida	5-[(Bis-carboxymethyl-amino)-methyl]-6-hydroxy-naphtalene-2-carboxylic acid
H ₅ hpdta	Hydroxypropane-1,3-diamine- <i>N,N,N',N'</i> -tetraacetic acid
hda	(hydroxybenzyl)iminodiacetic acid
hmd	Hexamethylenediamine
HPLC	High-performance liquid chromatography
HSQC	heteronuclear single quantum coherence
hyd	Hydrazine
Hz	Hertz
IPCC	Intergovernmental panel on climate change
IUPAC	International Union of Pure and Applied Chemistry
m/z	Mass to charge ratio
MEA	Monoethanolamine
mM	Millimolar
mm	Millimetre
MOF	Metal organic framework
MV ²⁺	Methyl viologen
NIR	Near infrared
NMR	Nuclear magnetic resonance
P	Pressure
P-XRD	Powder X-ray diffraction
P ₀	Saturation pressure
pn	Propylenediamine
ppm	Parts per million
ppmV	Parts per million volume
φ	Quantum yield
rel	Relative
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
TEA	Triethylamine

TEOA	Triethanolamine
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-visible
WATERGATE	WATER suppression by GrAdient Tailored Excitation
wt%	Weight percentage
Δ	Chemical shift
E	Extinction coefficient
Λ	Wavelength
$\lambda_{\max}$	Maximum wavelength
μM	Micromolar
ν_{as}	Asymmetric stretch
ν_{sym}	Symmetric stretch

Chapter 1 Introduction:

The aim of this introduction is to provide insight into the realm of hybrid inorganic-organic materials. The concepts of crystal engineering and supramolecular chemistry will be outlined. The classification of such materials in addition to the unique applications of metal organic frameworks (MOFs) will be discussed. There will be a particular emphasis on MOFs' adventitious applications as gas storage materials over traditional sorbents such as activated carbon or zeolites. The introduction further serves to highlight the carbon dioxide problem and provide an insight into the current research undertaken to photochemically reduce CO₂. Also considered is the use of transition metal compounds as catalysts in the photochemical reduction of CO₂ and the various catalytic routes that can be used in the CO₂ photo-reduction process. The aminocarboxyl ligand *H₅hpdt*a is introduced with particular emphasis on the use of tetranuclear carbamate and carbonate compounds (which contain *hpdt*a) as catalysts in the photoreduction of CO₂.

1.1 Supramolecular chemistry and crystal engineering

It is the ultimate aim of crystal engineers to create novel materials with pre-determined structures and properties. Schmidt first proposed the concept of crystal engineering in 1971. He recognised that crystal lattices were stabilised by intermolecular forces and believed that an in-depth understanding of these forces could lead to the "control of molecular packing" and the ability to predetermine crystal structures with specific chemical properties.⁵ The term was later defined by Desiraju and co-workers to include "the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties".⁶⁻⁸ In recent times extensive time and effort has been placed into the engineering of inorganic supramolecular materials by means of a 'building block approach'.⁹ The approach visualizes crystal structures as networks where molecules, metals and ions are nodes and the intermolecular interactions or coordination bonds act as connections between the nodal points. The metal ion and ligand selections direct the geometry and structure of the supramolecular compounds.

Supramolecular chemistry is often considered as 'the chemistry beyond a single molecule'.¹⁰ Crystal engineering is discriminately focused on compounds that assemble through strong covalent bonds. Supramolecular chemistry includes molecules that self-

assemble into predetermined structures through weaker, reversible, non-covalent interactions such as van der Waal forces, hydrogen bonding and π - π interactions.

The most inherent example of supramolecular chemistry, and the requirement of complementarity for all non covalent bonds in molecules, is elegantly demonstrated by the building blocks of life, deoxyribonucleic acid (DNA). DNA is composed of two strands of simple units called nucleotides. Each strand consists of a phosphorylated backbone linked to a series of four purine and pyrimidine bases that arrange in a double helix. Complementary base pairings form distinct bonds between bases units on opposing strands of DNA. The base adenine (A) exclusively forms hydrogen bonds with thymine (T), whilst guanine (G) pairs with cytosine as seen in Figure 1.1. The reversibility of hydrogen bonding facilitates the 'unzipping', and subsequent reformation, of the DNA double helix under specific environmental conditions, in the life forming process known as DNA replication.¹¹

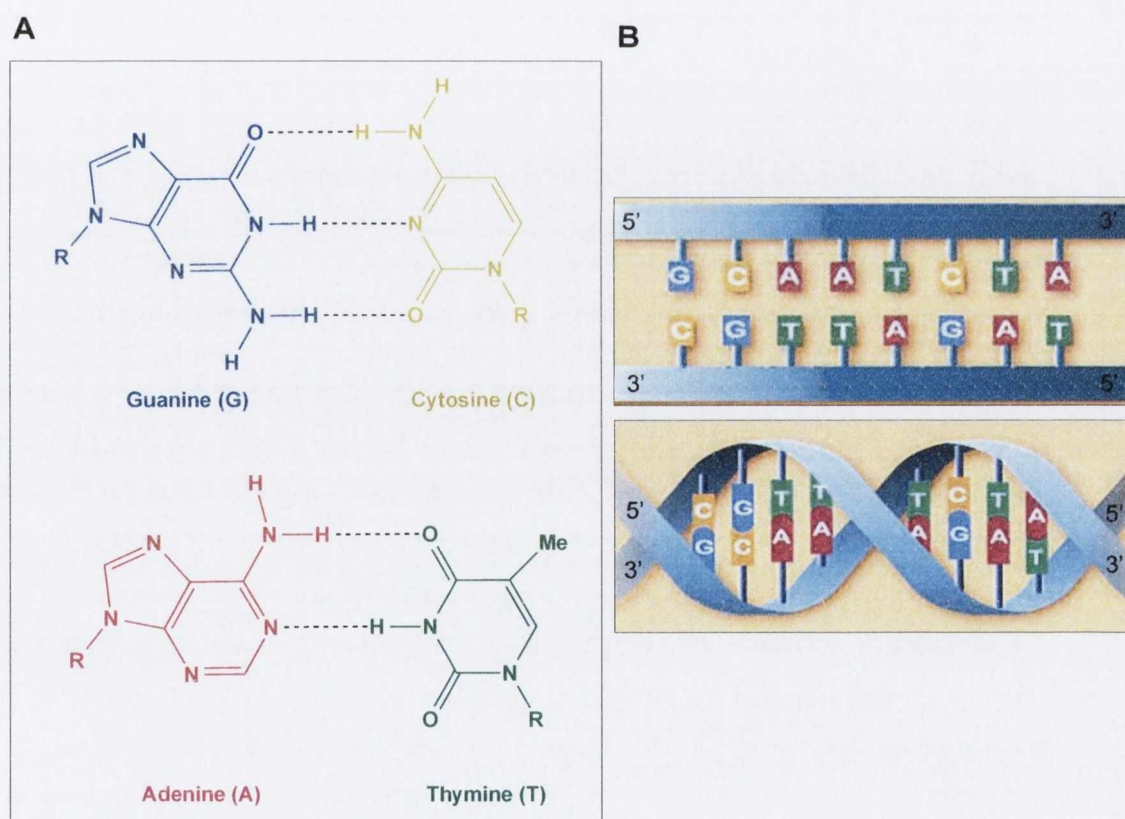


Figure 1.1: A) Complimentary pairing between purine and pyrimidine bases, hydrogen bonding represented by dashed line. B) Simplified diagram of the antiparallel strands of DNA and the hydrogen bonded double helix. G guanine, C cytosine, A adenine, T thymine.¹¹

The realm of supramolecular chemistry can be divided into zeolitic materials and hybrid inorganic-organic materials such as discrete coordination molecules, one dimensional

coordination polymers or two and three dimensional coordination networks commonly termed metal organic frameworks (MOFs), Figure 1.2.

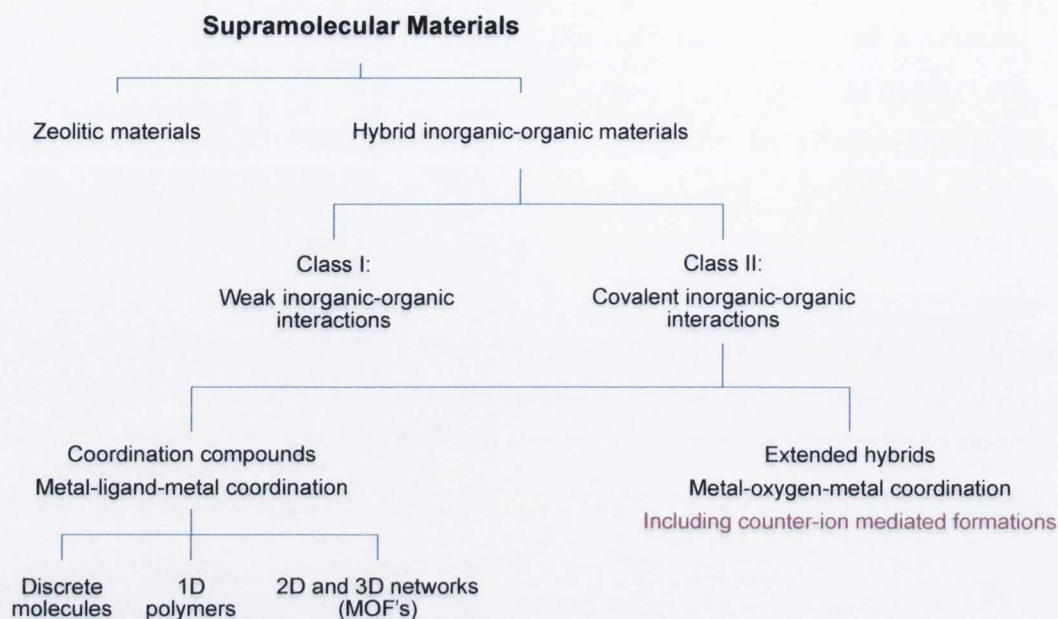


Figure 1.2: Classification of supramolecular materials.

1.2 Aluminium clusters, zeolitic materials and aluminogallophosphates

Aluminium-based materials have received extensive attention in the past decades. This is predominantly owing to the versatility of the lightweight aluminium ions that can adopt both octahedral and tetrahedral coordination geometries and exhibit prolific hydrolytic activity in aqueous solution. These characteristics lead to the formation of a diverse array of oxo- and hydroxo- bridged purely inorganic and hybrid inorganic-organic materials.^{1, 12} Examples of polynuclear oxo/hydroxo-bridged aluminium complexes in the literature range from the smallest oligomer, $\{[\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{18}](\text{SO}_4)_5 \cdot 16\text{H}_2\text{O}\}$, the cationic $\{\text{Al}_{13}\}$ complex $\{\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}\}^{7+}$, to the largest $\{\text{Al}_{30}\}$ cluster composed of two $\{\text{Al}_{13}\}$ units separated by an $\{\text{AlO}_6\}_4$ bridge.^{1, 12-14} The latter two examples are remarkable as twelve $\{\text{AlO}_6\}$ units surround the tetrahedral $\{\text{AlO}_4\}$ centres in an octahedral arrangement to form $\{\text{Al}_{13}\}$ clusters, as seen in Figure 1.3. Thus they provide examples of lightweight aluminium complexes containing the, inherently stable, Keggin structure Figure 1.3B. Complexes that contain the Keggin structure play an important role in polymerisation, hydration and oxidation reactions due to their intrinsic catalytic properties.^{1, 8, 12, 15} A further example of an important supramolecular Al-based material is provided by the

$\{\text{Al}_{15}\}$ complex, $[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4]$. It contains a central core that is comparable to the minerals barite and gibbsite except in this case the central hole is unoccupied, as seen in Figure 1.4.⁴

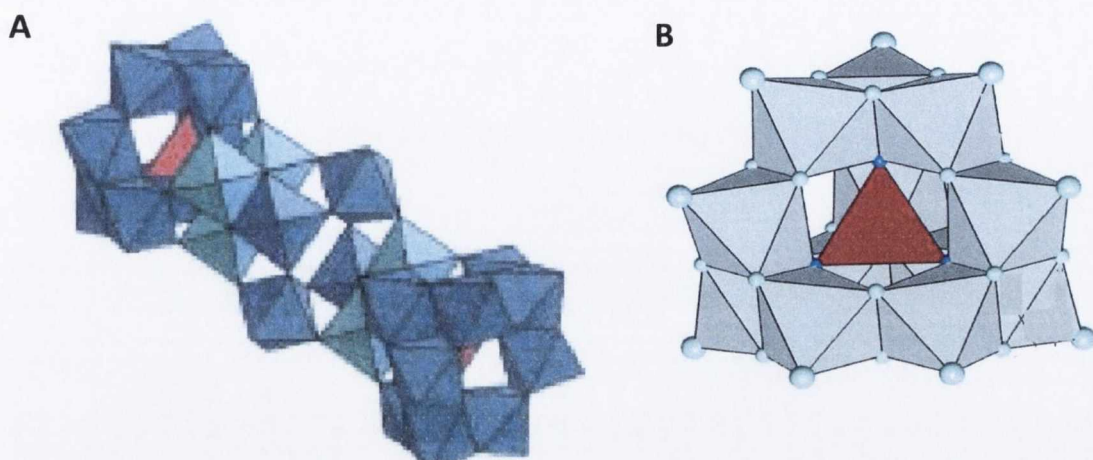


Figure 1.3: A) Polyhedral representation of the $\{\text{Al}_{30}\}$ cluster containing two $\{\text{Al}_{13}\}$ 'Keggin units' bridged by four $\{\text{AlO}_6\}$ units, Al centres dark blue. B) a polyhedral representation of the Keggin structure in $\{\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}\}^{7+}$, demonstrating a tetrahedrally coordinated AlO_4 centre, highlighted in red, surrounded by twelve octahedrally coordinated, AlO_6 sub-units, highlighted in grey.^{1, 4, 12-14}

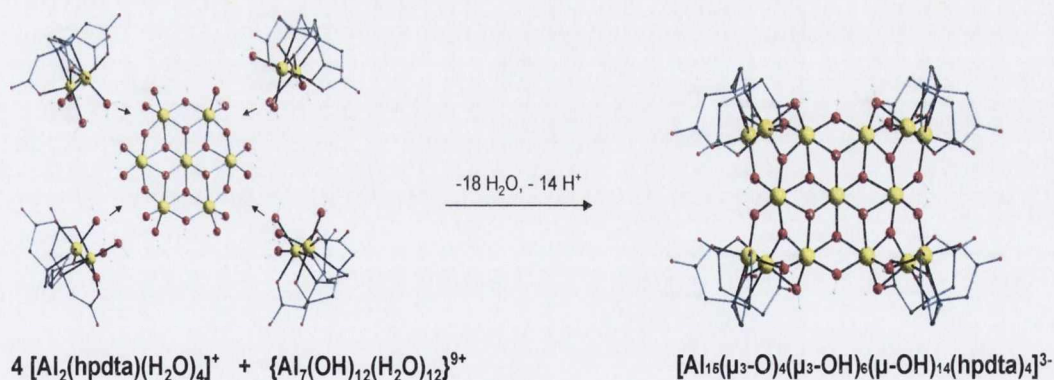


Figure 1.4: The encapsulation of a central $\{\text{Al}_7(\text{OH})_{12}\}^{9+}$ fragment by dinuclear $\{\text{Al}_2 \text{hpdt}\}^+$ units via a series of hydrolytic condensation reactions to form $\{\text{Al}_{15}\}$ supramolecular assemblies.³

Zeolites are one of the earliest examples of microporous materials. They are composed of hydrated alkaline or alkaline earth aluminosilicates and contain frameworks of AlO_4 or SiO_4 tetrahedra that condense to generate interconnected cages or tunnels. The removal of water molecules from the pores and cavities of these anionic clusters gives rise to

their applications as porous materials in a broad range of specialties including agents in water treatment and gas separation processes, as controlled-release nitrogen and phosphorous fertilizers and catalysis.¹⁶ A classic example of a, commercially viable, porous zeolite is provided by the aluminosilicate zeolite A, $\{\text{Na}_{12}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48})\cdot 27\text{H}_2\text{O}\}$. Its 3-D primitive cubic structure is constructed of truncated α - and β - cages as demonstrated in Figure 1.5.¹⁷⁻¹⁹

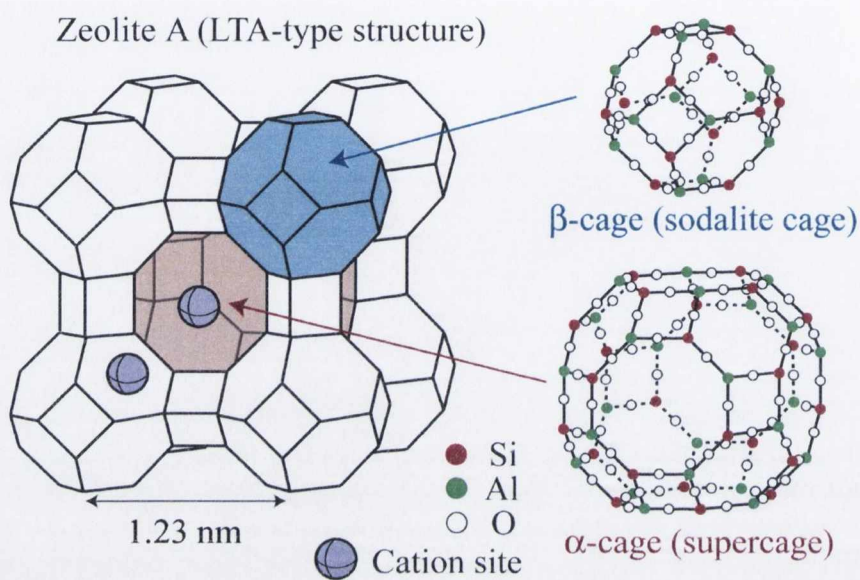


Figure 1.5: Structure of zeolite A comprising α - and β - cages. Each corner and intersection of the cage is occupied by either Si or Al ions. An oxygen atom is located at the edge centre. Al green, Si red, O white.²⁰

Aluminogallophosphates are structurally related to zeolites and form mixed tetrahedral-octahedral (or bipyramidal) frameworks of general formula $\text{Al}(\text{Ga})\text{PO}_4$. The presence of Al and Ga ions permits for a greater variation in connectivity within the framework and offers a step towards the ability to control the pore-size of these zeolitic type materials. Their structures can be described in terms of oligomeric units consisting of n -polyhedra that are three dimensionally connected and allow for the formation of larger pores, as demonstrated in Figure 1.6.²¹ Aluminium complexes such as those described above can be incorporated into the aluminogallophosphates' framework as secondary building units to form novel porous materials.²²⁻²⁴

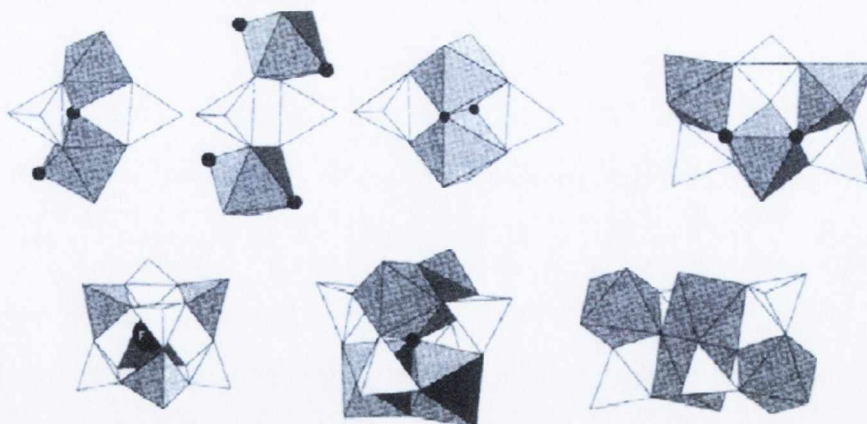


Figure 1.6: Seven aluminogallophosphates SBUs.²¹

1.3 Hybrid inorganic-organic materials

Hybrid inorganic-organic materials are an important class of supramolecular materials. Their inorganic and organic counter-parts provide a creative alternative for the design of novel materials with unprecedented porosities. The materials can be classified according to the interactions between inorganic and organic assemblies, i.e. either robust covalent bonds (Type II materials Figure 1.2) or weak intermolecular interactions (Type I materials Figure 1.2). The former are of particular importance and have been extensively reported for their potential applications as optical, gas storage and catalytic materials.²⁵

Hybrid inorganic-organic materials are typically isolated using a bottom up approach whereby metal complexes self-assemble in the presence of multifunctional organic ligands. An alternative synthetic method involves a series of pH controlled condensation reactions in which hydrated metal sub-units form via M-O-M linkages.²⁶ Further classifications can be considered in terms of the crystallization methods succeeded in their synthesis for example hydro- / solvo- thermal or slow diffusion crystallization processes. The reactions are often performed at elevated temperatures that reduce the solvents dielectric constant thus increasing the solubility of the inorganic and organic components. This provides ample opportunity for the formation of novel hybrid inorganic-organic materials through condensation reactions. The reactions can be further influenced through variation of the ligand to metal ratios, the pH of the system and the solvent mixtures of the reactions.²⁷ A successful example is provided by Forster and co-workers who successfully demonstrated that varying the temperature of a reaction system from between 60 °C and 250 °C results in the formation of five distinct cobalt structures, $\text{Co}(\text{H}_2\text{O})_4(\text{C}_4\text{H}_4\text{O}_4)_2$, $\text{Co}(\text{H}_2\text{O})_2(\text{C}_4\text{H}_4\text{O}_4)_2$, $\text{Co}_4(\text{H}_2\text{O})_2(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$,

$\text{Co}_6(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_4)_5 \cdot 2\text{H}_2\text{O}$ and $\text{Co}_5(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_4)_4$.²⁸⁻²⁹ Stock and co-workers also demonstrated that the selection of metal salt influences the crystal structure formation in the $\text{Co}^{2+}/(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{-NCH}_2\text{C}_6\text{H}_4\text{COOH (H}_5\text{L)}/\text{NaOH}$ reaction system.³⁰

The first example of a hybrid material was provided by Hofmann as early as the nineteenth century with a cyano-bridged Ni complex arranged in a cubic network with channels that were occupied by coordinating benzene molecules.³¹⁻³³ Since then hybrid inorganic-organic materials have been characterized according to their organic ligand directionalities and metal ion connectivity's. For example $[\text{Mn}(\text{H}_2\text{O})(1,3\text{-CHDC})(1,10\text{-phen})]_2$, Figure 1.7a, is considered to be a discrete molecule with zero dimensionality with respect to the inorganic and organic assemblies. Yaghi's secondary building unit MOF-5 $[\text{Zn}_4\text{O}(\text{1,4-BDC})_3]$ displays a Metal-Ligand-Metal (M-L-M) connectivity of 3 and an inorganic connectivity of 0, Figure 1.7b. $[\text{Cd}(\text{H}_2\text{O})_2(1,3\text{-BDC})]$, Figure 1.7c, provides an example of one dimensional (1D) hybrid inorganic-organic ion connectivity. Whilst $[\text{Cd}(1,2\text{-CHDC})]$ is considered to display two-dimensional (2D) ion connectivity's and zero organic ligand dimensionality, Figure 1.7d. Finally, the heptanuclear Ni complex $[\text{Ni}_7(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_4)_6(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ is a three dimensional (3D) structure characterized by 3D Ni directionality and zero dimension ligand connectivity, Figure 1.7e. A similar formation is demonstrated by the mononuclear cadmium structure $[\text{Cd}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ as observed in Figure 1.7f.

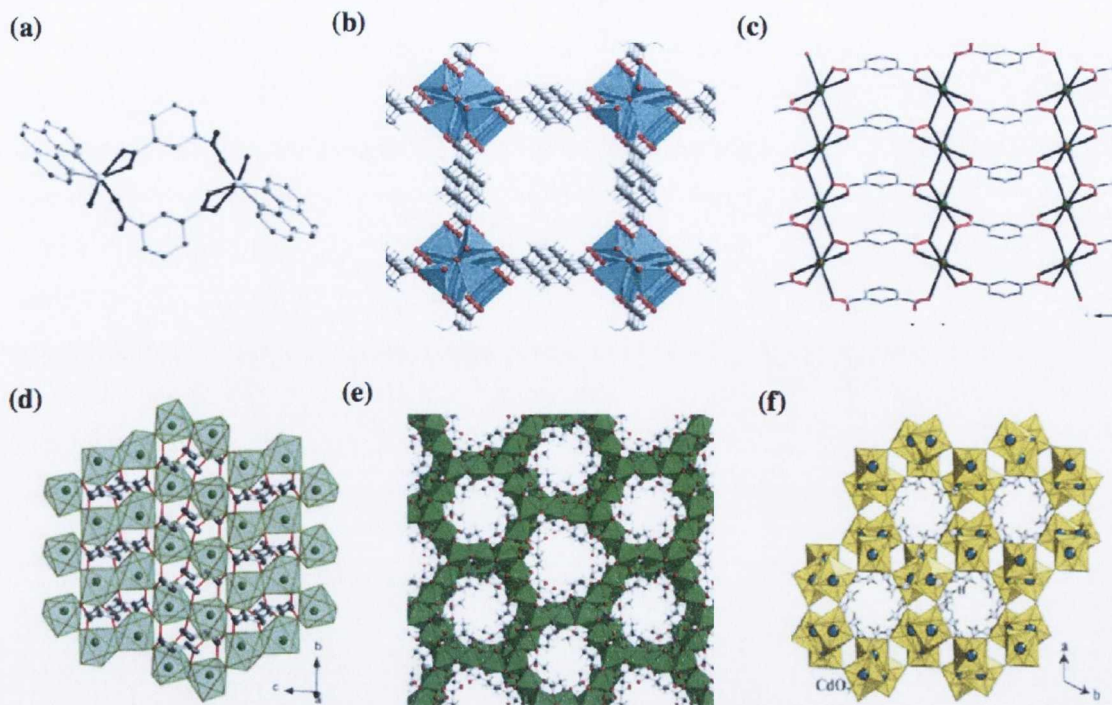


Figure 1.7: Demonstrates structures of hybrid inorganic-organic materials that are classified according to their metal ion and ligand dimensionalities. I^mO^n signifies the overall dimensionality, n = dimensionality of inorganic component and m = dimensionality of bridging ligand. (a) Mn-1,3-cyclohexanedicarboxylate, $[Mn(H_2O)(1,3-CHDC)(1,10-phen)]_2$, I^0O^0 .³⁴ (b) Zn-1,4-benzenedicarboxylate, $[Zn_4O(1,4-BDC)_3]$, I^0O^3 .³⁵ (c) Cd-1,3-benzenedicarboxylate, $[Cd(H_2O)_2(1,3-BDC)]$, I^1O^1 .³⁶ (d) Cd-1,3-cyclohexanedicarboxylate, $[Cd(1,2-CHDC)]$, I^2O^0 .³⁴ (e) Ni-succinate, $[Ni_7(OH)_2(C_4H_4O_4)_6(H_2O)_2] \cdot 2H_2O$, I^3O^0 .³⁷ (f) Cd-malonate, $[Cd(C_3H_2O_4)(H_2O)] \cdot H_2O$, I^3O^0 .^{20,38}

1.4 Metal-organic frameworks and extended hybrids

Isorecticular synthesis and the advancement of crystal engineering

The development of a reticular synthetic approach to crystal engineering has reinvigorated the research into supramolecular chemistry. The concept is described as “assembling judiciously designed rigid molecular building blocks into predetermined ordered structures (networks), which are held together by strong bonding” at the turn of the century.³⁹ The strong coordination creates rigid molecular building blocks or secondary building units (SBUs).⁴⁰ The strength of the isorecticular synthetic approach was realized through the isolation of SBUs based on the octahedral $\{Zn_4O(CO_2)_6\}$ sub-unit, seen in Figure 1.8A. The sub-unit, containing four metal ions that link to a central oxygen atom and are capped by six carboxylate groups, has been extensively employed as a secondary building unit for the preparation of metal organic frameworks. The key to the success of isorecticular synthesis is the retention of a primitive cubic topology that

facilitates the isolation of pre-determined coordination networks with controllable porosity.⁴¹ The 3D networks form through coordination of the subunits by carboxylated or amido functionalised organic ligands. The networks, with primitive cubic topology, are known as metal organic frameworks (MOFs) whose void volumes are controllable through expansion. Expansion is achieved through systematic alteration of the distance and rigidity between the carboxylate moieties of organic ligands. This is exemplified by the isorecticular design and construction of MOF-5 and related frameworks based on the MOF-5 skeleton, Figure 1.8. The successive substitution of organic linkers, ranging from terephthalic acid to triphenyldicarboxylic acid, demonstrates an ability to vary pore function and size thus increasing the accessible void volume from 56 % to 91% without compromising the topology.^{39,42-44}

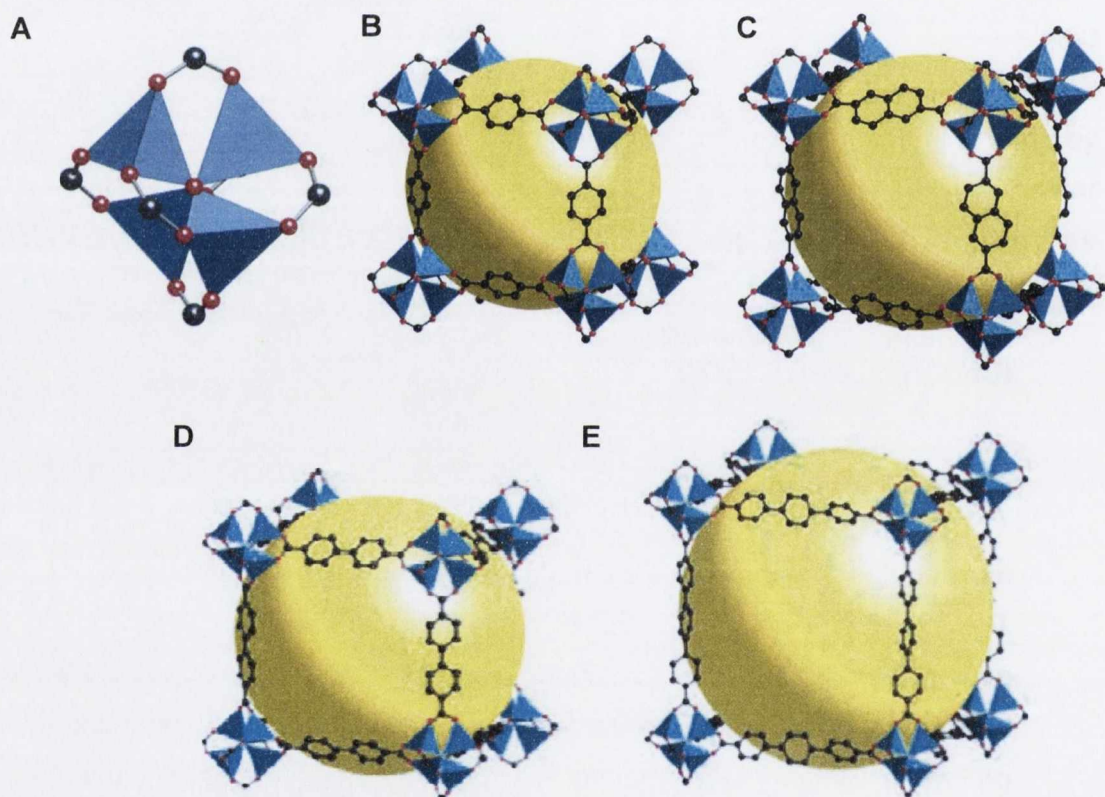


Figure 1.8: A) $\{Zn_4O(CO_2)_6\}$ secondary building unit (SBU). B) MOF-5, SBU linked by benzene dicarboxylate ligands. C) IRMOF-8, stabilised by naphthalene dicarboxylates. D) IRMOF-10 coordinated by biphenyldicarboxylic ligands. E) IRMOF-14 linked by triphenyldicarboxylic acid.^{39,42} The yellow spheres represent the available void volume. C Black, O Red, Zn Blue.

The versatility and synthetic capabilities of the isorecticular approach is exemplified by Yaghi and co-workers isolation of the ultrahigh porous metal organic framework, MOF-210, with formula of $\text{Zn}_4\text{O}(\text{BTE})_4/3(\text{BPDC})$. The MOF contains $\{\text{Zn}_4\text{O}(\text{CO}_2)_6\}$ sub-units that are coordinated by BTE and BPDC organic linkers, as demonstrated in Figure 1.9. It has a pore volume of $3.60 \text{ cm}^3/\text{g}$ and a BET surface area of $6240 \text{ m}^2/\text{g}$, hydrogen (H_2), carbon dioxide (CO_2) and methane (CH_4) gas uptakes values of 176 mg/g at 77K , 264 mg/g and 2400 mg/g at 298 K , respectively.⁴⁵

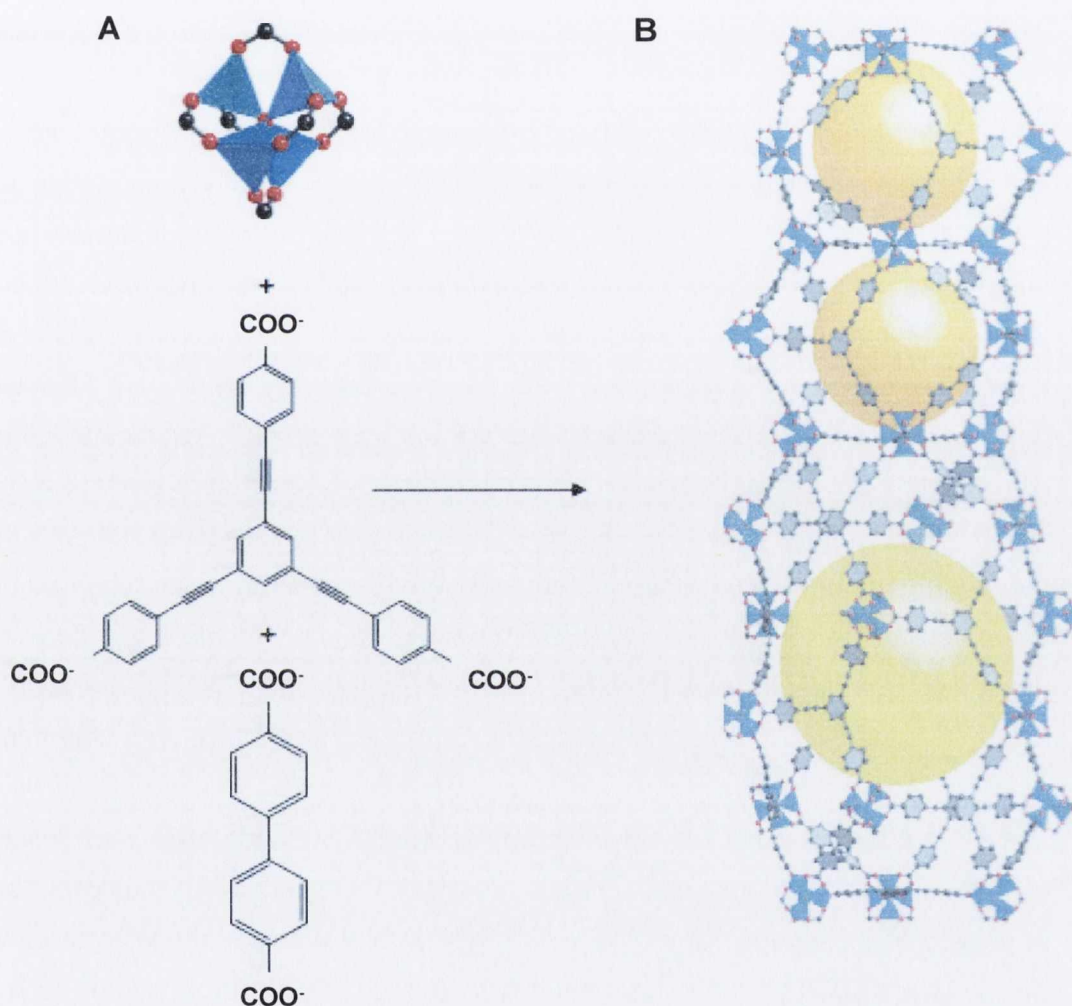


Figure 1.9: A) The secondary building unit and organic ligands involved in the formation of MOF-210. B) Crystal structure of MOF-210. Void volume represented by orange and yellow spheres. C dark grey, O red. $\{\text{ZnO}_4\}$ sub-units represented as blue polyhedra.⁴⁵

1.5 Gas Storage in porous materials

With the rapid onset of global warming MOFs and supramolecular assemblies are increasingly perused for their potential hydrogen and carbon dioxide storage capacities.⁴⁶⁻⁴⁸ They have a distinct advantage over traditional inorganic and organic porous materials, such as zeolites, charcoal or carbon nanotubes, as they are robust, highly crystalline and characteristically form uniform structures with minimal defects. Their synthesis can also be controlled and adapted to form unprecedented porous materials.^{41, 49 47-48}

Surface area determination and gas storage capabilities of porous materials

The gas storage capabilities and BET surface areas of porous materials can be evaluated by either gravimetric or volumetric methods. Gravimetric approaches use high precision microbalances to monitor the change in mass of porous materials upon gas adsorption. Volumetric measurement, or the *Sieverts Method*, is concerned with changes in pressure that occurs in a sealed chamber when gaseous molecules are adsorbed onto the surface of crystalline porous material.⁵⁰ There are drawbacks and advantages to each technique. The main disadvantage to gravimetric method is that the measurements are affected by the adsorption of water molecules that are often present in the gas stream. In volumetric measurements the gas adsorption is calculated indirectly thus the measurements often contain accumulative errors. Such errors are caused by discrete variances in the temperature, pressure or mass of the sample and often result in erroneous reports of surface areas.⁵⁰ However, given the ease of operation of the volumetric approach it is the widely accepted approach for surface area determinations.

The surface area is routinely calculated by applying the Brunauer-Emmet-Teller (BET) to N₂ adsorption isotherms, measured at 77 K. BET theory is adventitious over Langmuir approach as it accounts for multilayer adsorption and provides more accurate values. The classical "BET" linear range extends over relative pressures of 0.05 to 0.3. The appropriate range for materials with cross sectional diameters less than 20 Å, i.e. microporous materials, is typically at relative pressures less than 0.1. It is necessary to identify the appropriate pressure regions in order to obtain meaningful BET surface areas for microporous materials. The criteria for successfully applying the BET theory to microporous materials are as follows:⁵¹⁻⁵²

- 1 "The pressure range selected should have values of $V(P_0 - P)$ increasing with P/P_0 ."
- 2 "The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero."

The most accurate evaluation of gas adsorption is the total volume of gas stored in the pores and adsorbed onto the surface of the porous material, i.e. the absolute adsorption value. However, the difficulties that arise when attempting to experimentally quantify the precise volume of gas stored within the pores and cavities necessitate its substitution with an estimated theoretical value. This is the main reason why the gas storage capabilities of MOFs and related porous materials are often expressed as the total amount of gas adsorbed onto their surface, i.e. as excess adsorption.⁵³

Gas Storage In MOFs

Kitagawa and co-workers pioneered the applications of MOFs as gas storage materials. They provided the first instances of N_2 , CH_4 and O_2 gas storage in MOFs using Co^{II} , Ni^{II} and Zn^{II} analogues of $M_2(4,4'-bipyridine)_3(NO_3)(H_2O)$.⁵⁴ Yaghi and co-workers later successfully demonstrated a 4.5 wt% hydrogen uptake, at 77 K, for MOF-5.⁴² This revolutionized the concept of gas storage and spurred an interest into the exploration and development of MOFs with distinct hydrogen storage capacities.

Since then, the highly porous MOF-177 with BET surface area of $4750 \text{ m}^2 \text{ g}^{-1}$ increased the H_2 storage benchmark to 7.7 wt% at 77 K for excess hydrogen adsorption.⁵³ In general, the hydrogen storage capacities at 77 K are directly related to their N_2 BET surface areas, as illustrated in Figure 1.10.⁵⁵ However, recent theoretical and experimental studies reveal that hydrogen adsorption decreases with the increasing thermal vibrations that accompany increasing experimental temperatures. Therefore H_2 adsorption values measured at ambient temperatures (298 K) are significantly less than those reported at 77 K.⁵⁶ Computer simulations of the H_2 adsorption characteristics of ten IRMOFs at 77 K, performed by Snurr and co-workers, revealed that H_2 adsorption is influenced by the heat of hydrogen adsorption at low temperatures, the MOF surface areas at pressure up to 30 bar and proportional to the MOFs accessible void volume at high pressures of 120 Barr.⁵⁷ Subsequent studies confirmed that these correlations do not hold true at ambient temperatures of 298 K. At low H_2 loading the absolute H_2 adsorption was found to correlate with free volume whilst under similar conditions excess H_2 adsorption is responsive to hydrogen heat of adsorption. It was found that at high

pressures hydrogen adsorption was dependent on surface areas rather than accessible void volume.⁵⁸ This is particularly important considering the American department of the environments (DOE) targets for gravimetric hydrogen storage of 5.5 wt% in the temperature range from ca. 314 K to 353 K at pressures up to 100 atm by the year 2015.⁵⁹ It has been suggested that ambient hydrogen storage capacities of 9 wt% can be achieved from MOFs that provide an isosteric heat of hydrogen absorption of 15 kJ/mol, a free volume of ca. 2.5% and void volume fractions of at least 85%.⁵⁸ Thus the research in this arena has been directed towards the development of porous materials with isosteric heat capacities greater than the current energies of 5-9 kJ/mol, increased surface areas in combination with smaller pore sizes. A promising example is provided by MOF-210 displaying a N₂ BET surface area of 6240 m² g⁻¹ and H₂ storage capacities of 8.6 wt% at 77 K.⁵⁸ MOFs that contain smaller pores, such as the copper framework HKUST-1, and those displaying interpenetrated frameworks* have been shown to increase interactions between the gas molecules and MOFs thus improving their hydrogen adsorption capacities.⁶¹⁻⁶⁶

* Interpenetration or catenation refers to a form of entanglement that occurs when the pores of a MOF are sufficiently large to accommodate the metal carboxylate cluster of a second network resulting in intertwined co-extension with maximum displacement.⁶⁰

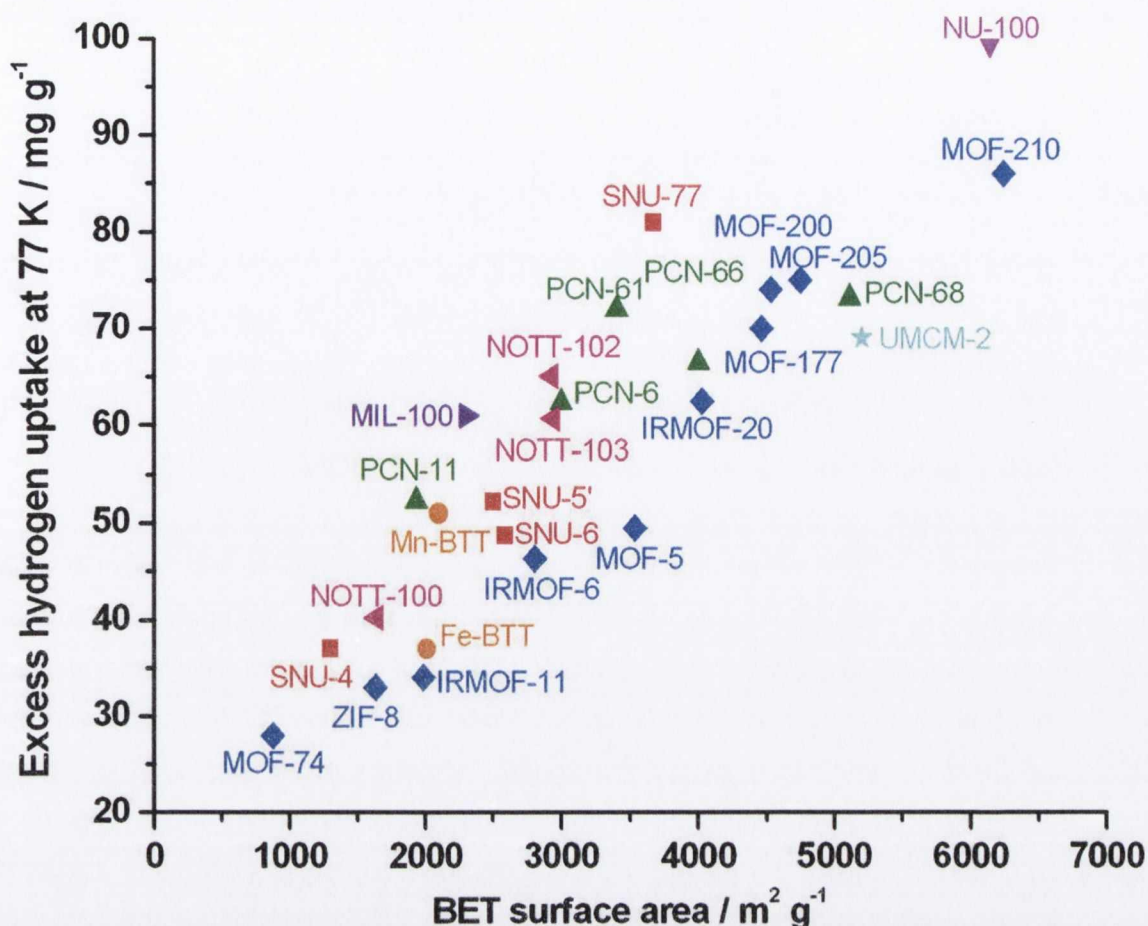


Figure 1.10: Displays the correlation between BET N₂ surface areas and excess high pressure H₂ storage capacities at 77 °K and 56 bar for a series of MOFs with surface areas greater than 900 m² g⁻¹.^{55, 67}

Carbon Dioxide – General aspects

Carbon dioxide is a well-known greenhouse gas and the role of increasing atmospheric CO₂ concentrations on the global warming process has been well established. Historically the photosynthetic process regulated the balance between the production and removal of atmospheric CO₂. However, widespread combustion of fossil fuels has disturbed this natural equilibrium and has led to the emission of over 6 billion tonnes of CO₂ per annum. Industrial activity has raised the levels of atmospheric CO₂ from ~280 ppmV in preindustrial times to ca. 388 ppmV at present.⁶⁸ In the 2007 report from the Intergovernmental Panel on Climate Change (IPCC) it was predicted that if actions are not taken to curtail and remediate the carbon dioxide problem that atmospheric concentrations will reach 450 ppmV by the year 2050.⁶⁹⁻⁷⁰ These predictions, coupled with the rapid depletion of fossil fuels and the increasing cost of non-renewable energy, have motivated scientists to develop systems, such as artificial photochemical systems, which could economically fix carbon dioxide and transform it into useful fuels and chemicals.^{55, 71-84}

CO₂ Storage in MOFs

In the absence of commercially viable techniques that can convert CO₂ to fuel and useful chemicals, such as those discussed in the following sections, there exists an immediate need to develop efficient, highly stable, CO₂ sequester technologies to control the emissions of CO₂ from energy intensive industrial processes. The viability of these systems depends on their ability to negate the energy intensive, and costly, carbon dioxide capture step associated with current carbon capture systems (CCS) whilst displaying elevated CO₂ selectivities and intermediate CO₂ affinities.⁸⁵⁻⁸⁷

The controlled and adaptable synthetic protocol that leads to the isolation of MOFs provides opportunity to create next-generation materials that are specifically engineered for applications in carbon capture technologies. MOFs are a promising alternative to the aqueous alkanolamine solutions such as monoethanolamine (MEA) and, less frequently, porous solids, such as zeolites and activated carbons that are employed in current CO₂ capturing processes. Their potential applications extend from membranes or mixed matrix membranes in pre-combustion carbon dioxide capture systems to adsorbates in pressure-swing adsorption based separations.⁸⁸⁻⁹⁰ They have the potential to revolutionise the CO₂ capturing approach with the added benefit of their retrospective incorporation into current carbon capture membranes. Furthermore, there exists the potential to form, novel, and continuous films of metal organic frameworks. Yaghi and co-workers consider the later to be particularly important for the development of MOF based CCS's and have successfully used microwave-assisted reactions to form layers of MOF-5 deposited on porous alumina substrates.⁹¹⁻⁹²

The CO₂ adsorption properties of Mg-MOF-74, {Mg₂(dobdc)}, have been well established. The framework is characterised by honeycomb-type topologies with hexagonal 1D channels, Figure 1.11.⁹³⁻⁹⁴ It provides a benchmark value of ca. 180 ml/g CO₂ at 298 °K and 1 ATM for CO₂ adsorption onto MOF.⁹⁵⁻⁹⁸ Systematic CO₂ adsorption studies of the Mn, Fe, Co, Ni and Zn analogues of Mg-MOF-74 reveal an increase in the, reversible, CO₂ adsorption from ca. 100 ml/g to ca. 180 ml/g upon substituting the Zn metal ions of the original MOF-74 with Mg metal ions.⁹³ It is believed that the enhanced CO₂ uptake is a result of the increased ionic nature of the Mg-O bond, as compared to the bonds between oxygen atoms and the Mn, Fe, Co, Ni or Zn metal ions.⁹³ These observations are of particular significance as they recognise the potential to fine tune MOFs for CCS applications through metal ion substitution.

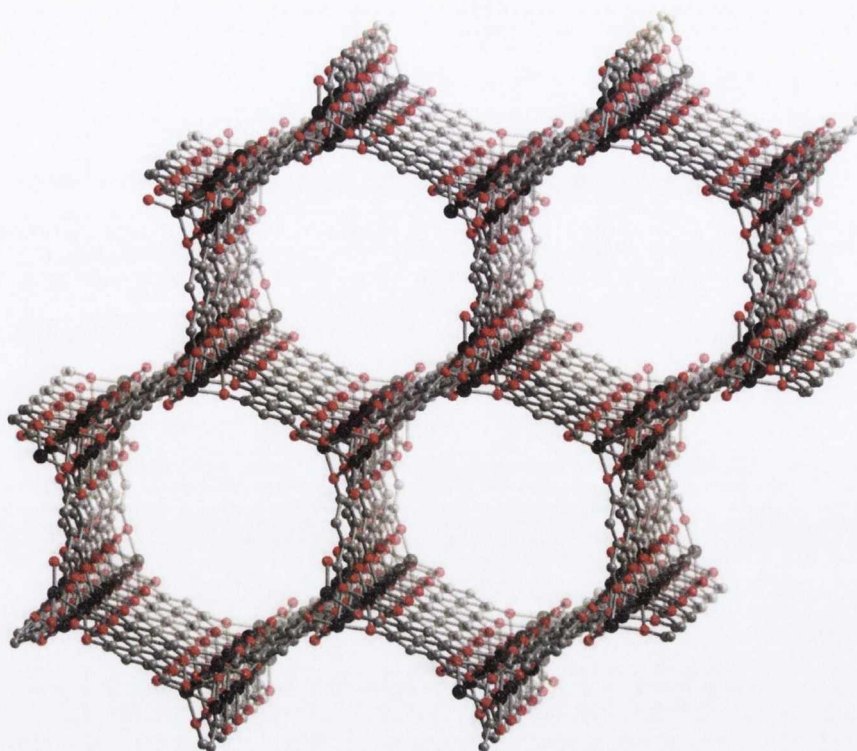
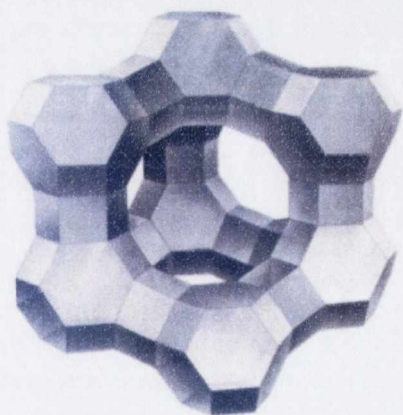


Figure 1.11: A portion of the crystal structure of M-MOF-74, $M_2(\text{dobdc})$. $M = \text{Mg, Fe, Co, Ni or Zn}$. M black, C grey, O red. Hydrogen atoms are omitted for clarity.

A



B

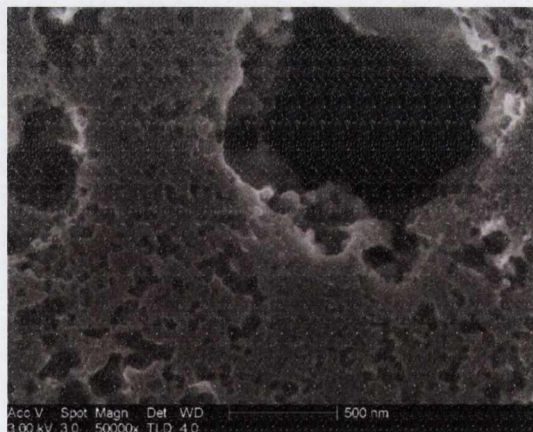


Figure 1.12: A) The typical zeolite type X structure adapted by zeolite 13X.¹⁰¹ B) Scanning electron microscope (SEM) image of the micro pores contained in activated carbon materials such as Norbit RB2 and MAXSORB (50,000 magnification).¹⁰²

An additional advantage to MOFs is their high internal surface areas that provide increased opportunity for CO_2 adsorption. A pertinent example is provided by MOF-177 which adsorbs 320 ml/cm^3 of CO_2 at room temperature and 30 bars of pressure.⁹⁹ This

is higher CO₂ adsorption values reported for traditional porous materials such as zeolite 13X, Norbit RB2 and MAXSORB, Figure 1.12.¹⁰⁰

Zaworotko and co-workers provide the most recent example of engineered MOFs for specific CCS applications. Their novel crystal engineering strategy offers specific control over “pore functionality and size in a series of metal organic membranes with coordinately saturated metal centres and periodically arrayed hexafluorosilicate (SiF₆²⁻) anions”.⁹⁸ SIFSIX-2-Cu, SIFSIX-2-Cu-I and SIFSIX-3-Zn as seen in Figure 1.13, have unprecedented selectivity for CO₂ (over H₂ in a CO₂/H₂:30/70 V/V gas mixture) and an elevated adsorption rate at ambient temperatures and low pressures (less than 0.15 bar).⁹⁸ SIFSIX-1-Cu-i was found to adsorb ca. 120 ml/g CO₂ under ambient conditions and low pressures of CO₂ providing the highest reported CO₂ storage capacities, under the examined experimental conditions, to date.⁹⁸

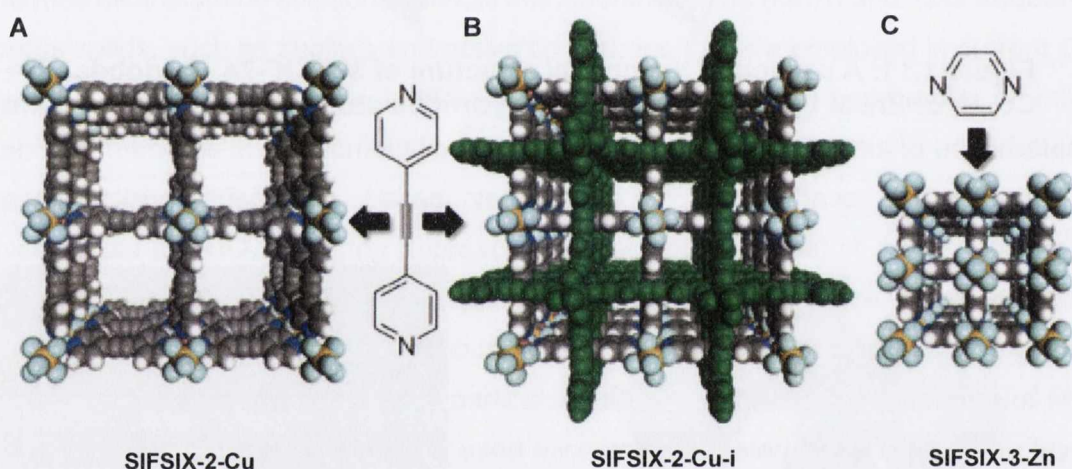


Figure 1.13: Presents frameworks of three SIFSIX-1-Cu variants reported by Zaworotko and co-workers. A) SIFSIX-2-Cu. B) SIFSIX-2-Cu-I containing 4,4'-dipyridylacetylene organic linkers (interpenetrated net presented in green). C) A pyrazine coordinated SIFSIX-3-Zn. Solvent guest molecules have been omitted for clarity. C grey, N blue, Si yellow, F light blue, H white.⁹⁸

A comparison between the CO₂ adsorption capacities of a selection of porous materials, at 298 °K and maximum pressures of 42 bar, is presented in Figure 1.14.

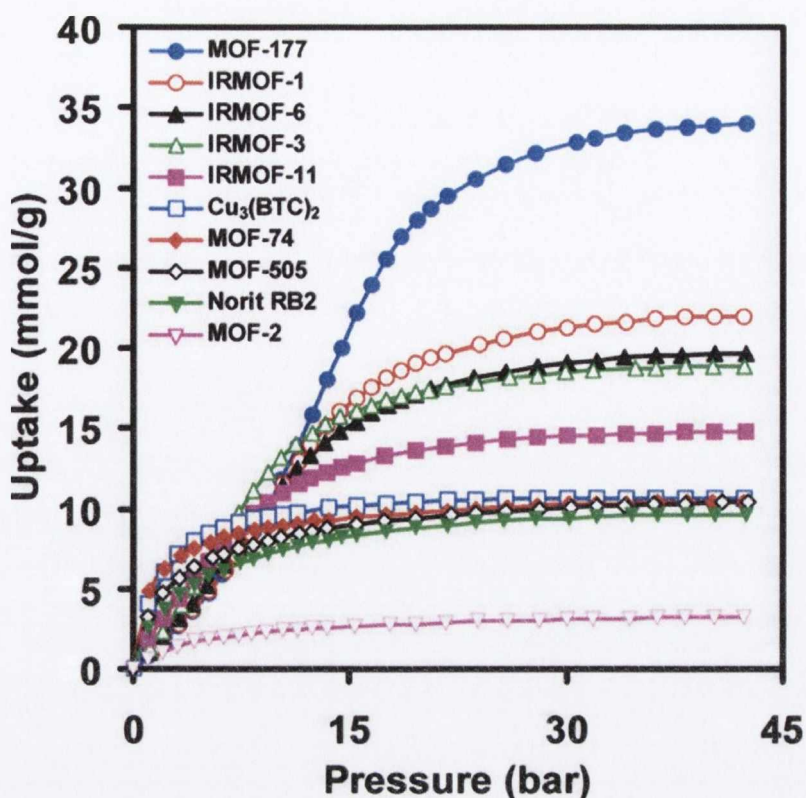


Figure 1.14: Comparison of gravimetric CO₂ capacities for several MOFs and a reference activated carbon sample (Norbit RB2). Investigated at ambient temperature and pressures up to 42 bar.⁹⁹

1.6 Reduction of CO₂

Over the last three decades, scientists have dedicated an extensive amount of time and resources towards developing environmentally sustainable systems that can efficiently reduce CO₂. However, following several years of intensive research, artificial photochemical systems continually suffer from low yields, decreased stability, and poor catalytic activities.^{81,103} The reduction of CO₂ has been achieved by chemical, electrochemical, enzymatic and photochemical approaches. One of the pertinent issues which scientists face in the development of efficient CO₂ reduction systems is the inertness and stability of the, linear, CO₂ molecule. Consequently, the one electron reduction of CO₂ to CO₂⁻ is a thermodynamically unfavourable process that requires the use of catalysts coupled with high potentials of -1.9V vs. NHE. In contrast, its conversion into fuels and useful chemicals, such as CO or HCOOH, through a proton assisted multi-electron reduction occurs at potentials that are more positive. For example, the reduction of CO₂ to formic acid, CO and methanol require potentials of -0.61V, -0.53V and -0.38V, respectively.⁷⁷

1.6.1 Transition metal complexes as catalysts in the photoreduction of CO₂

Transition metal compounds are considered to be ideal candidates for the promotion of the proton assisted photoreduction of CO₂ and have been described by Morris as being at 'the forefront of potential catalyst research'.¹⁰⁴ Fujita describes a compound that consists of a central transition metal atom(s) or ion(s) surrounded by a group of between two and six smaller atoms, ions or molecules, as a transition metal compound. These compounds have many promising characteristics including their ability to absorb a significant portion of the solar spectrum that, as demonstrated by Fujita, can be controlled through appropriate selection of the transition metal component and modification of the coordinating ligands. In addition to this, their long lived excited states can be combined with their ability to promote multi-electron transfer and their stability across a range of oxidation states to activate and reduce CO₂.¹⁰⁵

1.6.2 Photochemical reduction of CO₂

The work described herein focuses on the proton assisted photochemical reduction of CO₂. For the purpose of this report the photoreduction of CO₂ is grouped into two general catalytic systems. Type 1 systems incorporate a photosensitiser and catalysts that work in concert while type 2 systems involve one molecule that acts as both, the light absorber and the catalyst.

1.6.3 Type 1: Photoreductive systems which contain a photosensitiser and a transition metal catalyst working in concert

Type 1 catalysis can be 'considered as a photosensitised CO₂ reduction process'.¹⁰⁴ The process (as seen in Figure 1.15) involves a photosensitiser (P), typically [Ru(bpy)₃]²⁺, absorbing light to generate an excited state (*P). The excited state is quenched through interactions with a sacrificial donor (D), such as triethylamine (TEA), resulting in a reduced complex (P⁻) and an oxidised sacrificial donor (D⁺). This reduced complex transfers electrons to a metal catalyst, or electron mediator, M(II)L, and subsequent reduction of CO₂ to CO and HCOOH occurs through the reduced catalytic species, M(I)L.

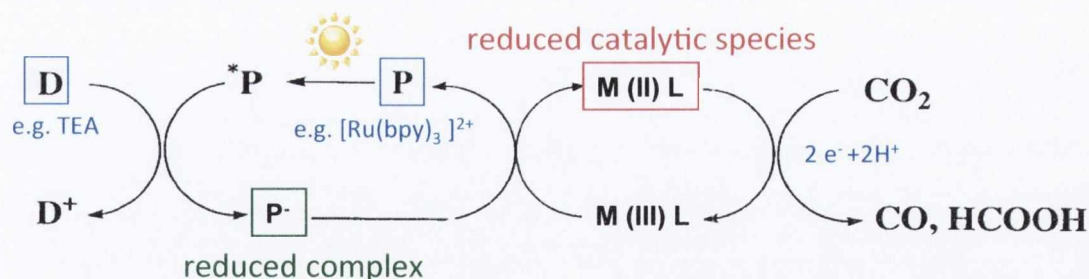


Figure 1.15: The general photochemical process involved in the photosensitised reduction of CO₂ to CO and HCOOH. P = photosensitiser, *P = excited photosensitiser, P[•] = reduced photosensitizer. D = sacrificial donor. M(II)L = metal catalyst, M(I)L = reduced catalytic species.

Systems that contain [Ru(bpy)₃]²⁺ and a transition metal catalyst have been extensively explored.¹⁰⁶⁻¹¹⁰ Examples of the transition metals compounds which have been utilized include [Ru(bpy)₂(CO)H]⁺ and [Ru(bpy)₂(CO)(Cl)₂]⁺ complexes which have been proven to successfully reduce CO₂ to HCOO⁻ with turnover numbers[†] of HCOO⁻ (TN_{HCOO⁻}) of 161 and 163, respectively.¹¹¹ Further examples of transition metal catalysts include Co²⁺/bpy, [Co(HMD)]²⁺ and [Ni(cyclam)]²⁺. These complexes have been reported to reduce CO₂ to CO and HCOOH with mediocre TN_{co} of 9.^{70, 112-114}

In attempts to improve the efficiency of the photosensitised reduction of CO₂ several transition metal compounds have been used in place of [Ru(bpy)₃]²⁺. An example of a promising system is provided by Gholamkhass. He and his co-workers used the transition metal complex [Ru(dmb)₃]²⁺ as a photosensitiser in conjunction with a [ReCl(dmb)(CO)₃] catalyst to reduce CO₂ to CO with a moderate, TN_{co} of ca. 100.¹¹⁵ Further examples have been provided by Ogata *et al* who successfully modified Tinnemans' system, which contained [Ru(bpy)₃]²⁺ and [Co^{III}(cyclam)]²⁺ (Figure 1.16C). They showed that the utilization of phenazine (seen in Figure 2a) as a photosensitiser enhanced the selectivity towards CO₂ reduction and they observed quantum yields[‡], ϕ_{co} , of 0.07. These quantum ϕ_{co} yields are significantly higher than those reported by Tinnemans (ϕ_{co} = 0.005).^{70, 76} As a follow on from Ogata's work, Matsuoka *et al* demonstrated that the quantum yields of CO and COO⁻ can be increased when the

[†] Turnover number (TN) refers to 'the number of reductions that occur per catalyst over the catalyst's lifetime'.¹⁰⁴

[‡] Quantum yield is a 'measure of the molar fraction of incident photons that result in CO₂ reduction products'.¹⁰⁴

conjugated *p*-terphenyl molecule (Figure 1.16B) is used as a photosensitiser in place of phenazine.⁸³

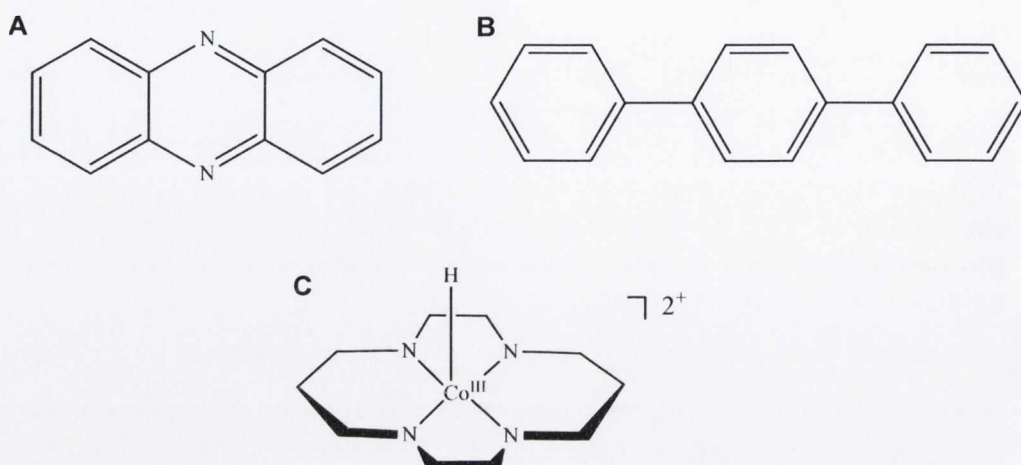


Figure 1.16: Examples of photosensitisers A) phenazine and B) *p*-terphenyl, and a catalyst C) Co^{III} macrocycle that have been used in the photochemical reduction of CO₂.^{70 84 83}

1.6.4 Type 2: Photoreductive systems containing a compound which absorbs light and acts as a catalyst

Type 2 catalysis involves one compound (known as the photocatalyst), which absorbs light and acts as a catalyst in the reduction of CO₂. The photocatalyst is reduced by excited state quenching as described for the photosensitised catalysis in type 1 systems. Type 2 catalysis is a rapidly emerging area of research which generally focuses on 'the MLCT excited states of [Re(bpy)(CO)₃] type compounds and the π - π^* excited states of metallo-macrocycles'.¹⁰⁴

Doherty *et al.* have undertaken extensive research into type 2 catalysis using a series of Re compounds. As part of their research they synthesised three novel fluorinated *fac*-Re^ICl(4,4'-R₂-2,2'-bpy)(CO)₃ compounds (4 and 5 in Figure 1.17) that displayed photocatalytic activity. Subsequent studies performed by Doherty confirmed that these compounds facilitate the reduction of CO₂ to CO in CO₂-saturated dimethylformamide (DMF) and supercritical CO₂ (scCO₂) systems containing triethanolamine (TEOA) or triethylamine (TEA), to give ϕ_{CO} of 0.14.¹¹⁶ Takeda *et al* developed a similar system, using a mixture of [fac-(4,4-(MeO)₂-bpy)(CO)₃Re{P(OEt)₃}][PF₆]:[fac-(bpy)(CO)₃Re(CH₃CN)][PF₆] in a 25:1 ratio. The mixture proved to have a higher

efficiency and an optimised ϕ_{CO} of 0.59.¹¹⁷ This research has subsequently been recognised, by Morris *et al* and Doherty *et al* in their respective reviews on CO₂ reduction, to provide benchmark values for ϕ_{CO} .^{104, 118}

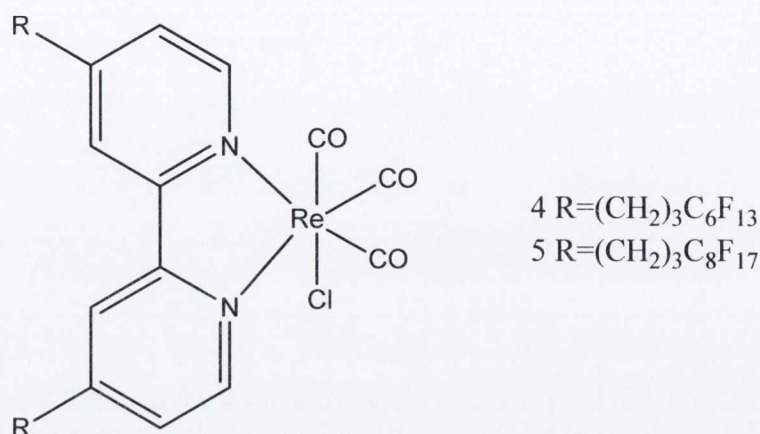


Figure 1.17: The structures of the fluorinated *fac*-Re^ICl(4,4'-R₂-2,2'-bpy)(CO)₃ compounds which were synthesised by Doherty *et al* in their research into the applications of Re compounds which can absorb light and act as catalysts in the photoreduction of CO₂.¹¹⁶

Recently it was proposed that a series of dinuclear heterometallic {Ru^{II}/Re^I}₃ compounds, which are linked through an electronically inert bridge, display an enhanced photocatalytic activity.¹¹⁹ As a follow on from this work, Bian *et al* synthesised two trinuclear Ru₂Re and RuRe₂ compounds (Figure 1.18) that were bridged via an electronically inert tripodal ligand. They reported enhanced TN_{CO} of 190 based on the Ru^{II} moiety in the {RuRe₂} complex and TN_{CO} of 110 based on the Re^I moiety in the {Ru₂Re} complex. It was concluded that the presence of a series of catalytic or photosensitizing units within a hetero-metallic compound dramatically enhances its photo-reductive activity.¹²⁰

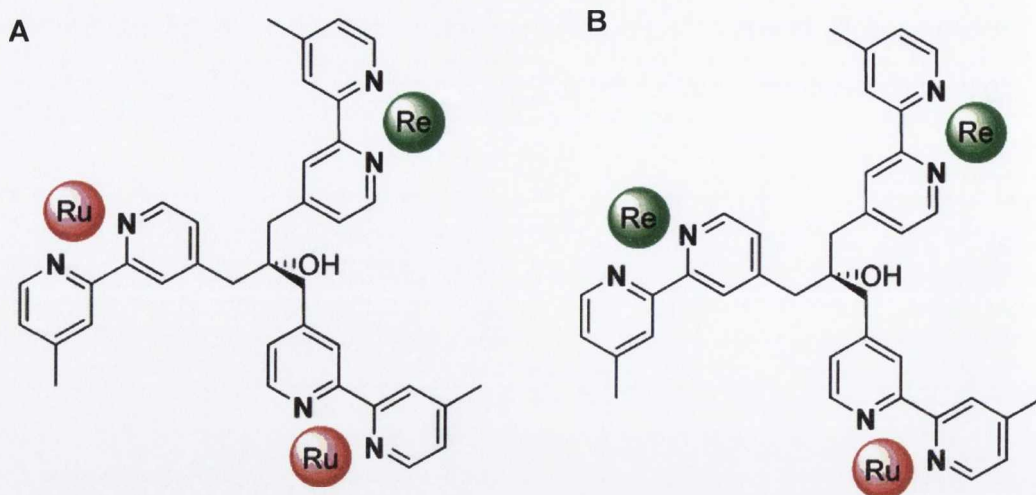


Figure 1.18: The structures of heterometallic compounds A) {Ru₂Re} and B) {RuRe₃} synthesised by Bian *et al* for use in the photoreduction of CO₂.¹²⁰

1.7 The polyaminocarboxylic acid ligand *H₅hpdta*

The heptadentate hydroxypropyl-diaminotetracetic acid ligand, *H₅hpdta* (Figure 1.19) contains two iminodiacetic acid functionalities linked via a 2-hydroxypropane moiety. It can be classified as a polyaminocarboxyl (PAC) ligand and it is frequently used to stabilise transition metal complexes. PAC ligands have attracted significant attention due to their ease of formation, remarkable versatility and their intrinsic stability. Upon deprotonation, they become highly soluble in aqueous systems and are known to form stable complexes with an extensive array of metals.^{4, 121-122}

The versatility of this ligand is exemplified through the diverse array of its, extended hybrid, coordination compounds that have been reported in the literature. For example Schmitt *et al.* have reported an Al^{III} compound (H₃O)[Al₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₃H₆NH₃)₂].13H₂O.2DMA, a Ga^{III} compound (pipH)[Ga₄(μ-O)(μ-OH)(hpdta)₂(O₂CNC₄H₈NH₃)].14H₂O and a Fe^{III} compound (NH₄)₄[Fe₆(μ-O)(μ-OH)₅(hpdta)₃].20.5H₂O.¹²³⁻¹²⁴ Whilst Mukkamala *et al.* have successfully synthesised the Cr^{III} complexes [Cr₄(μ-OH)₄(hpdta)₂]²⁻ and [Cr₆(μ-OH)₈(hpdta)₂(en)₂].¹²⁵ Further examples of compounds which have been stabilized by *hpdta* include Wullen's Bi^{III} compound [Bi₁₂(H₂hpdta)₄(Hhpdta)₆(H₂O)₁₂].80H₂O and Gorun's Mn^{III}-Mn^{II} complex [Mn₄(μ-O)(μ-OH)(hpdta)₂(O₂CCH₃)]⁴⁻.^{122, 126}

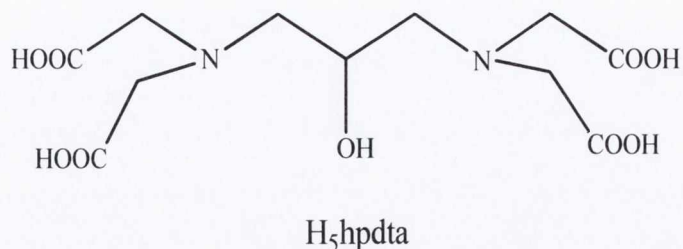


Figure 1.19: The structure of the heptadentate 1,3-Diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid ligand.

1.8 Fixation and activation of atmospheric CO₂ through hydrolytically active [M₄(μ-O)(μ-OH)(hpdta)₂(H₂O)₄]⁻ complexes (M= Fe^{III}, Al^{III} and Ga^{III})

Studies by Schmitt *et al.*, into hydrolytic reactions involving Lewis acid centres, successfully demonstrated that the *H₅hpdta* ligand stabilises tetranuclear complexes [M₄(μ-O)(μ-OH)(hpdta)₂(H₂O)₄]⁻ (M= Fe^{III}, Al^{III} and Ga^{III}). Further investigations revealed that the Fe^{III}, Al^{III} and Ga^{III} complexes containing four terminating aqua ligands can, under alkaline conditions, effectively be utilised to fix atmospheric CO₂ to form carbonate complexes. These complexes divulge further hydrolytic activity and enhance the reaction between CO₂ and amines to give primary and secondary carbamates (Figure 6) that bind to the metal centres in high yields over a relatively short timescale.^{3, 123, 127}

The synthetic approach employed by Schmitt is of particular scientific interest as it can be adapted to produce a series of transition metal carbamate and carbonate complexes that, in addition to their ability to absorb atmospheric CO₂, could act as catalysts in the photoreduction of CO₂. This concept is reinforced by Frohlich and Berger's recent publication in which they claim that secondary carbamates containing electron-withdrawing groups, such as sulfonic acid moieties, can be chemically reduced to give methanol.¹²⁸

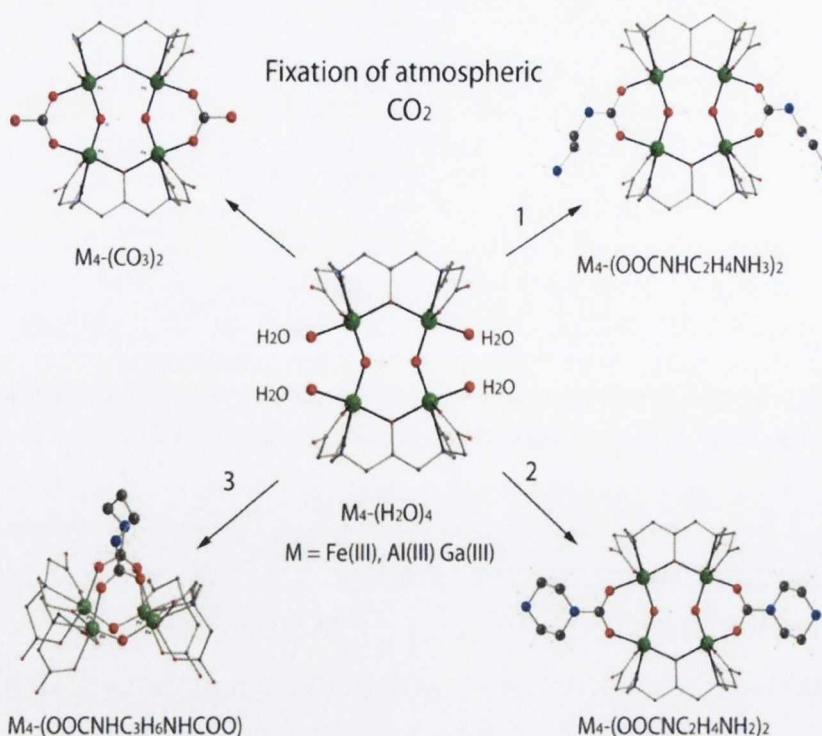


Figure 1.20: Fixation of atmospheric CO₂ through the hydrolytically active tetranuclear [M₄(μ-O)(μ-OH)(hpdta)₂(H₂O)₄]⁻ complexes (M = Fe^{III}, Al^{III} and Ga^{III}). The carbamate complexes form almost quantitatively within 16-36 hours (1: ethylenediamine, 2: piperazine, 3: propylenediamine, pH between 7.0 and 8.5).³

1.9 Research Aims and Objectives

The objective of this research was to increase the library of known hybrid, organic-inorganic coordination compounds that form from the aqueous hydroxypropane-1,3-diamine-N,N,N',N'-tetraacetic acid (*hpdta*) system. We were also interested in developing a protocol to gain an understanding of the solution behaviour of these compounds in distinct pH environments. These investigations were primarily directed towards aqueous solutions containing the rectangular planar and tetrahedral complexes [M^{III}₄(μ-O)(μ-OH)(hpdta)₂(H₂O)₄]⁻, and [M^{III}₄(μ-O)(μ-OH)₃(hpdta)₂]³⁻ or carbon dioxide trapping form, [M^{III}₄(μ-O)(μ-OH)(hpdta)₂(O₂CX)₂]⁻ (M= Al(III) and Fe(III), X = carbamate or carbonate moiety). Additional interests included exploring the applications of infrared spectroscopy as a screening tool to unambiguously distinguish between non-crystalline or microcrystalline samples that precipitated from the investigated systems. Followed by an exploration of the Ni^{II} and V^{III} ions behaviours within the *hpdta* system. Subsequent objectives included an exploration of the Fe^{III} *hpdta* coordination compounds affinity towards carboxylate bearing ligands and aerial carbon dioxide. Followed by an

evaluation of the resultant compounds potential applications as catalysts in the reduction of carbon dioxide. A final objective of this research focused on the counter ion mediated formations of novel $\{Al_{15}\}$ *hpdta* based coordination assemblies and an evaluation of their surface areas and gas storage capabilities.

Specific aims of the research project:

In order to achieve these objectives we set out to:

- Identify an analytical technique that can unambiguously distinguish between samples of closely related compounds $NH_4[Fe_4(\mu-O)(\mu-OH)(hpdta)_2(H_2O)_4] \cdot 12.5H_2O$ (**1a**), $(enH)[Fe_4(\mu-O)(\mu-OH)(hpdta)_2(H_2O)_4] \cdot nH_2O$ (**1b**), $(pipH_2)_{1.5}[Fe_4(\mu-O)(\mu-OH)_3(hpdta)_2] \cdot 6H_2O$ (**2a**), $(enH_2)_{1.5}[Fe_4(\mu-O)(\mu-OH)_3(hpdta)_2] \cdot nH_2O$ (**2b**), $(enH)[Fe_4(\mu-O)(\mu-OH)(hpdta)_2(O_2CNHC_2H_4NH_3)_2] \cdot 6.5H_2O$ (**3**) and $Na_2[Fe_4(\mu-O)(\mu-OH)(hpdta)_2(CO_3)_2] \cdot ca.20H_2O$ (**4**) that were not suitable for single crystal X-ray diffraction experiments.
- Study the behaviour of the aqueous Al^{III} and $Fe^{III}/hpdta$ solutions using ^{27}Al , ^{13}C and 1H NMR in combination with ESI-MS and UV-Vis spectroscopy.
- Explore the reactivity of the active sites, in $[M_4(\mu-O)(\mu-OH)(hpdta)_2(H_2O)_4]^-$, towards CO_2 , using a range of dicarboxylate ligands and transition metal ions.
- Investigate the reaction between a series of diamines with atmospheric CO_2 in the presence of the tetranuclear $[Fe_4(\mu-O)(\mu-OH)(hpdta)_2(H_2O)_4]^-$ complexes.
- Examine the effect that treatment with CO_2 has on the solution behaviour of Fe^{III} *hpdta* complexes using UV-VIS spectroscopy.
- Investigate the CO_2 capture and release characteristics of the carbonate and carbamate compounds using gas-chromatography-mass spectrometry headspace analyses combined with ESI-MS analysis.
- Study the interactions between $[Ru(bpy)_3]^{2+}$ and the carbonate and carbamate compounds.
- Consider the potential applications of carbonate containing compounds as catalysts in the photochemical reduction of CO_2 .
- Investigate the counter-ion mediated formation of a series of $\{Al_{15}\}$ complexes and evaluate their N_2 BET surface areas and gas storage characteristics.

Chapter 2 Speciation studies of the *hpdta* reaction system

2.1 Introduction

Throughout the scientific community it is believed that a water based system, which utilises earth-abundant transition metal ions and has the potential to store multiple electrons, is an ideal candidate to act as a catalyst in the multi-electron reduction of carbon dioxide. The aqueous based *hpdta* system has the potential to meet these requirements. With this in mind we were interested in exploring the solution behaviour of transition metal compounds that are stabilised by the *hpdta* ligand with a view to their potential applications as catalysts in the reduction of CO₂. We were also interested in assessing the use of Fourier transform infrared (FT-IR) spectroscopy as a tool to unambiguously distinguish between the microcrystalline powders that are generated from these systems. Thus the identification of the compound type could be achieved in the absence of large single crystals suitable for single-crystal X-ray diffraction analysis.

We were further interested in developing a protocol that could be readily utilised to probe the solution behaviour of these compounds. Given previous success in the group employing electrospray ionisation mass spectrometry (ESI-MS⁻) techniques to monitor the formation of polyoxometalates from reaction mixtures, we thought it would be interesting to utilise this powerful technique to explore the stability of the explored compounds in solution and to monitor their pH dependent behaviour.¹²⁹ Considering the Fe^{III} *hpdta* based coordination compounds are paramagnetic, it is difficult to employ NMR spectroscopy to study their solution behaviours and therefore we decided to carry out NMR investigations using the structurally related Al/*hpdta* system. Utilising this analogous system would allow us to employ ²⁷Al, ¹³C, and ¹H NMR techniques to explore the solution behaviour. Our investigations would primarily focus on aqueous solutions containing the rectangular planar and tetrahedral complexes [M^{III}₄(μ-O)(μ-OH)(*hpdta*)₂(H₂O)₄]⁻, and [M^{III}₄(μ-O)(μ-OH)₃(*hpdta*)₂]³⁻ or carbon dioxide trapping form, [M^{III}₄(μ-O)(μ-OH)(*hpdta*)₂(O₂CX)₂]⁻ (M= Al(III) and Fe(III), X = carbamate or carbonate moiety).

2.2 Identification of the characteristic stretches in the infrared spectra for Fe^{III}/*hpdta* compounds that form through the adjustment of aqueous reaction systems

In these studies we identified the unique infrared vibrations for three previously reported Fe^{III} structures, NH₄[Fe₄(μ-O)(μ-OH)(hpdta)₂(H₂O)₄]·12.5H₂O (**1a**), (pipH₂)_{1.5}[Fe₄(μ-O)(μ-OH)₃(hpdta)₂]·6H₂O (**2a**), and (enH)[Fe₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₂H₄NH₃)₂]·6.5H₂O (**3**). These three compounds crystallize from aqueous Fe^{III}/*hpdta* reaction systems at pH 4.5, 7.0 and 8.5 respectively when ammonia, piperazine or ethylenediamine are used as hydrolysing agents.^{123, 130} The compounds were prepared according to the literature methods and were obtained in high yields.¹²³ We also identified the characteristic infrared vibrations for the previously reported carbonate compound Na₂[Fe₄(μ-O)(μ-OH)(hpdta)₂(CO₃)₂]ca·20H₂O (**4**), which crystallises from the aqueous Fe^{III}/*hpdta* reaction systems at pH 7.0, upon addition of sodium hydrogen carbonate to the system.²

The infrared spectra for these compounds can be seen in Figure 2.1. The broad signals above 3000 cm⁻¹ observed in each of the spectra were assigned to the O-H functionalities engaged in H-bonds. The signals observed between ca. 1360 cm⁻¹ and ca. 1380 cm⁻¹ in the spectra for compounds **1a-4**, can be attributed to the amine C-N stretches from the *hpdta* ligands. The asymmetric and symmetric stretches that originate from the deprotonated and coordinating COO⁻ functionalities of the *hpdta* ligands were identified at ca. 1605 cm⁻¹ and ca. 1435 cm⁻¹ in the infrared spectra for the carbonate compound Na₂[Fe₄(μ-O)(μ-OH)(hpdta)₂(CO₃)₂]ca·20H₂O. These stretches were observed at slightly different energies for each compound containing the aminocarboxylic acid ligand. The infrared spectrum for the carbonate compound, **4**, exhibits a characteristic stretch at ca. 1480 cm⁻¹ resulting from the CO₃²⁻ ligands.^{1 131 132} The spectrum for (enH)[Fe₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₂H₄NH₃)₂]·6.5H₂O displays a characteristic stretch at ca. 1560 cm⁻¹ that results from the NH⁺ deformation on the triply protonated nitrogen carbamate zwitterion and a characteristic stretch at ca. 1500 cm⁻¹ which can be attributed to the N-H bending vibration of the carbamic acid. These two stretches together with the asymmetric stretch of the deprotonated and coordinating carboxylate moieties of the *hpdta* ligands at ca. 1600 cm⁻¹, form a distinctive 'triplet' like pattern.¹³³ This pattern was also subsequently located within the infrared spectrum of the previously reported Al^{III} compound (H₃O)[Al₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₃H₆NH₃)₂]·13H₂O·2DMA.^{134 3, 135 135} The FT-IR assignments are based on extensive studies by Nakamoto et al and by Johnson et al into the FT-IR vibration spectra of Fe^{III} polycarboxylate coordination compounds.¹³⁶⁻¹³⁸ The assignments are further supported by comparable FT-IR

stretches in La Spina and Mc Keown *et al.*'s' reported compounds $K_2[Cu^{II}(hnida)]_2 \cdot 2H_2O$, $K_4[Cu^{II}(Chnida)]_2 \cdot 4H_2O \cdot 4MeOH$ and $[Fe(tBu_2hda)(H_2O)_2] \cdot 3H_2O$, respectively.¹³⁹⁻¹⁴⁰

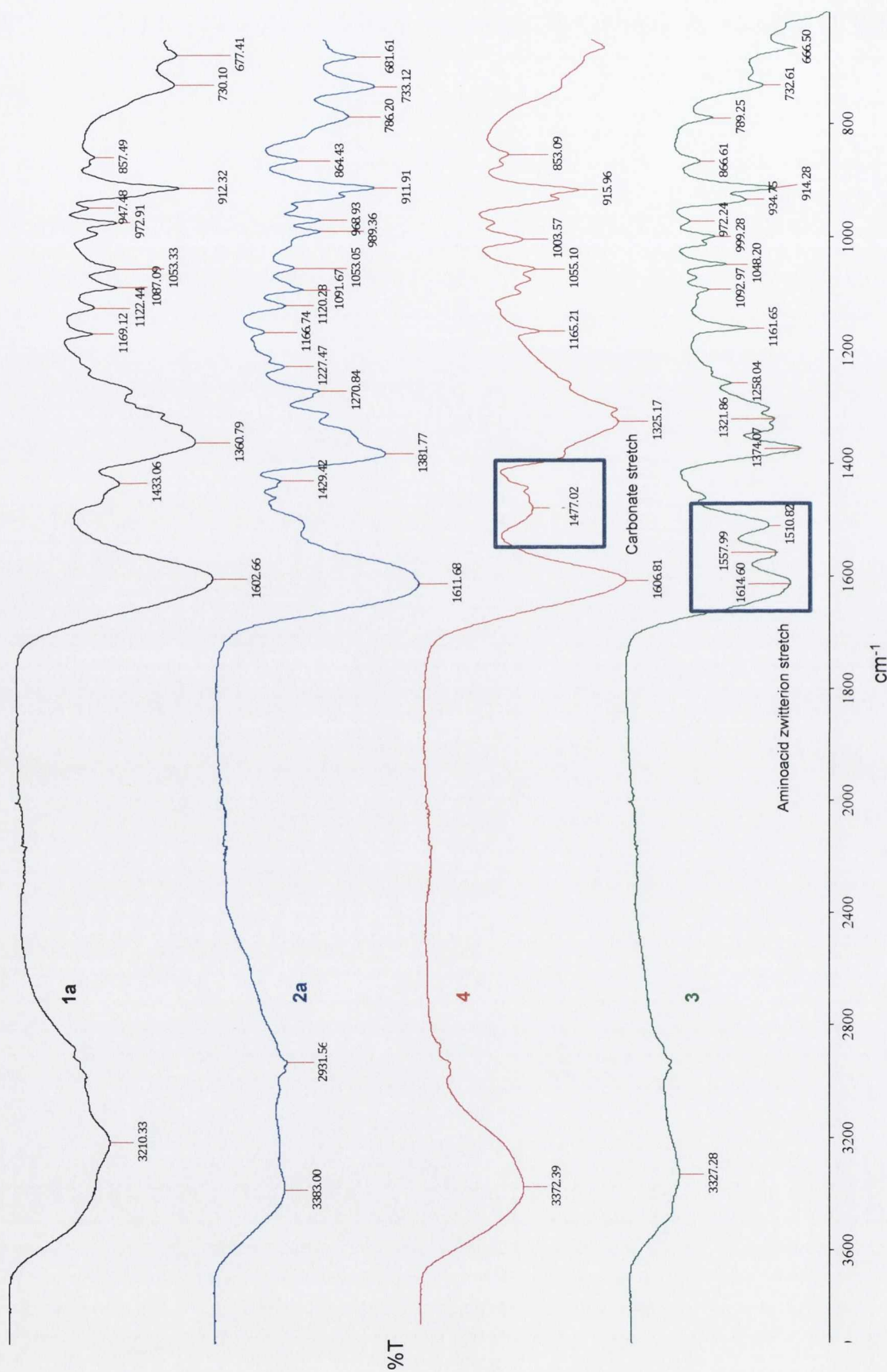


Figure 2.1: FT-IR Spectra displaying the characteristic vibrational bands, blue boxes, for compounds 1a, 2a, 3 and 4. Recorded using a diffuse reflectance sampling accessory.

Table 2.1: The characteristic FT-IR absorptions, and corresponding assignments, for compounds 1a, 2a, 3 and 4. ^{136-138, 137, 138} *res. = respectively.*

Wavenumber (cm ⁻¹)	Compound(s)	Assignment(s)
3310, 3380, 3330 and 3370	1a, 2a, 3 and 4, res.	O-H ν_s and ν_{as} stretches
1600, 1610, 1615 and 1605	1a, 2a, 3 and 4, res.	ν_{as} COO ⁻
ca. 1430 and ca. 1375	1, 2, 4 and 3	ν_s COO ⁻
1560	3	Zwitterionic stretch (NH ₃ ⁺ deformation 1° amine)
1510	3	N-H bend
1480	4	CO ₃ ²⁻ ν_{as} stretch ¹⁴¹⁻¹⁴²
ca. 1360, ca. 1380, ca. 1380 ca. 1375	1a, 2a, 3 and 4, res.	C-N stretches
910, 910, 915, 915	1a, 2a, 3 and 4, res.	Out of plane -OH stretch

2.3 Monitoring the induced transformation in the Fe^{III} and Al^{III} *hpdta* reaction systems

2.3.1 ¹³C NMR, ¹H NMR and ²⁷Al NMR

In these studies nuclear magnetic resonance (NMR) was employed to investigate the stability of the *hpdta* compounds in solution. As mentioned above, the Fe^{III} *hpdta* compounds **1-4** are paramagnetic. This led us to investigate the NMR behaviour of the structurally related, diamagnetic, Al^{III} *hpdta* compounds (enH)[Al₄(μ -O)(μ -OH)(*hpdta*)₂(H₂O)₄].nH₂O (**5**), (enH₂)[Al₄(μ -OH)₄(*hpdta*)₂].7.5 H₂O (**6**) and (enH₂)[Al₄(μ -O)(μ -OH)(*hpdta*)₂(O₂CNHC₂H₄NH₃)₂].nH₂O (**7**). We were interested in exploring the reaction mixtures that led to the crystallisation of compounds **5-7** in order to investigate the formation processes of these species in solution. The stability of the crystallised compounds in deuterated water (D₂O) was also investigated. This approach prompted us to utilise ²⁷Al, ¹³C and ¹H NMR experiments to examine the formation and stability of the Al^{III} species over a range of values. Ethylenediamine was used to adjust the pH of the solution to 4.5, 7.0 and 8.5. The samples for these studies consisted of an aqueous 0.05 M stock solution of both AlCl₃·6H₂O and *hpdta* (2:1) or pristine crystals of compounds **5-7** dissolved in D₂O.

²⁷Al NMR

²⁷Al-NMR is a valuable technique as it can be used to quantify Al species in solution. The signals in ²⁷Al-NMR spectra are relatively nondescript exhibiting broad and overlapping signals. This is particularly evident for spectra of **5**, **6** and **7**. The ²⁷Al nucleus possesses

a nuclear quadrupole moment which arises from a spin quantum number that is greater than 1/2.¹⁴³ As observed in Figure 2.2, the signals for these compounds are indeed very broad and overlapping with an intensely broad signal resonating at ca. 68.0 ppm. This signal arises from the aluminium present in the glass material surrounding the NMR probe.¹⁴⁴ The spectra recorded for **5**, **6** and **7** provide us with an insight into the number of aluminium species that are present in solution and the behaviour of these species in solutions of three distinct pH environments.

The spectra of the reaction mixtures reveal four characteristic signals at 5.5 ppm, 8.0 ppm, 25.0 ppm and 34.7 ppm. The up field signal at 5.5 ppm is unique to the spectrum of the reaction mixture at pH 4.5. Similar resonances have been reported in the literature and are considered to be a result of octahedrally coordinated inorganic species, such as $\{(H_2O)_4Al(OH)_2Al(H_2O)_4\}^{4+}$, $Al(H_2O)_4(OH)^{2+}$ or $\{Al(H_2O)_4(OH)_2\}^+$, present in acidic solutions that contain water and aluminium salts.^{145-146,146} Its presence in the NMR spectra of the reaction mixture post crystallisation of **5** further confirms that it is not conclusively indicative of the crystallised compound **5**. Its absence from the spectra of non-acidic solutions further substantiates our assignment. Although the broad signal at 34.7 ppm was un-assignable, as it overlaps with the signal at 25.0 ppm, its absence from the NMR spectra of the sample post crystallisation of **5** and from the NMR spectra of less acidic solutions, strongly suggests that this signal arises from its presence in solution.

The signal at 25.0 ppm is present in the spectra of the reaction mixtures and in the spectra of all three compounds when dissolved. In the literature a signal at this resonance has been reported to indicate the presence of an aluminium species octahedrally coordinated to five O- atoms and one N- donor atom in solution.¹⁴⁶ This is similar to the coordination environments of the central Al^{III} ions in **5**, **6** and **7**. Thus the signal provides evidence for the existence of the three complexes in solution. It is further noteworthy that the signal disappears from the spectra of the three reaction mixtures upon crystallisation of the respective compounds. Thus the signal also provides an opportunity to monitor the tetranuclear species *in situ*.

The signal at 8.0 ppm emerges from the spectra of the reaction mixture at pH 8.5 upon exposure to the atmosphere. Its appearance indicates the formation of a second Al species in solution. The signal is not present when the sample is prepared under nitrogen. It is also noteworthy that the signal is more intense under conditions that lead to the formation of **7** as compared to its dissolution in D₂O (inset Figure 2.2).

The relationship between the signal at 8.0 ppm and the carbon dioxide fixation was investigated through the addition of stoichiometric quantities of a solid carbamic acid, $\text{H}_3\text{NC}_2\text{H}_4\text{NHCOO}$, to the reaction mixture of **7** at pH 8.5.¹⁴⁷ Interestingly, a characteristic change in signal intensities is observed in the recorded ^{27}Al NMR spectra, Figure 2.3. Whereby the intensity of the signal at 8.0 ppm increases in comparison to the signal at 25.0 ppm. FT-IR characterisation of the precipitate that forms from this solution confirmed its identity as compound **7**. These findings reflect that the formation of compound **7** in solution is dependent on the presence of auxiliary carboxylic ligands (derived from the fixation of CO_2). Furthermore, the similarities in the spectra of reaction mixtures recorded at pH 8.5 and pH 7.0 indicate the existence of similar Al species in solution until a carboxylated ligand is added, or CO_2 fixation occurs. CO_2 fixation was only observed in the reaction mixtures at pH 8.5. This is consistent with the suggested pathway for carbon dioxide fixation using alkaline solutions that contain either tetranuclear iron or aluminium compounds, as described in the literature.²

The assignment of signals at *ca.* 8 ppm and *ca.* 25 ppm is further confirmed by their absence in the spectra of the reaction mixture post crystallisation of compounds **5**, **6** and **7**, respectively. Upon dissolution in D_2O each compound displays the single characteristic signal at *ca.* 25 ppm. This confirms that the coordination environment of the central aluminium ions remain intact upon dissolution at each pH value. However, the signal at *ca.* 35 ppm is absent from the spectrum of **5** while the signal at *ca.* 8 ppm is more defined in the spectra of **7** dissolved in D_2O but still remains a minor signal compared to the one at 25 ppm. Both of these observations could be indicative of a process in which the compounds **5** and **7** interconvert to the tetrahedral form (compound **6**) when dissolved in D_2O .

The presence of the signal at 25.0 ppm in each spectrum coupled with the absence of a sharp low field peak at *ca.* 90 ppm, attributed to the tetrahedrally coordinated $\{\text{Al}(\text{OH})_4\}^-$ species which occur under basic conditions, indicates that the compounds are stable in solution at pH ranges 4.5, 7.0 and 8.5 that match their respective formation condition. The studies indicate that tetrahedral and rectangular square complexes transform into each other upon pH variations.⁵¹

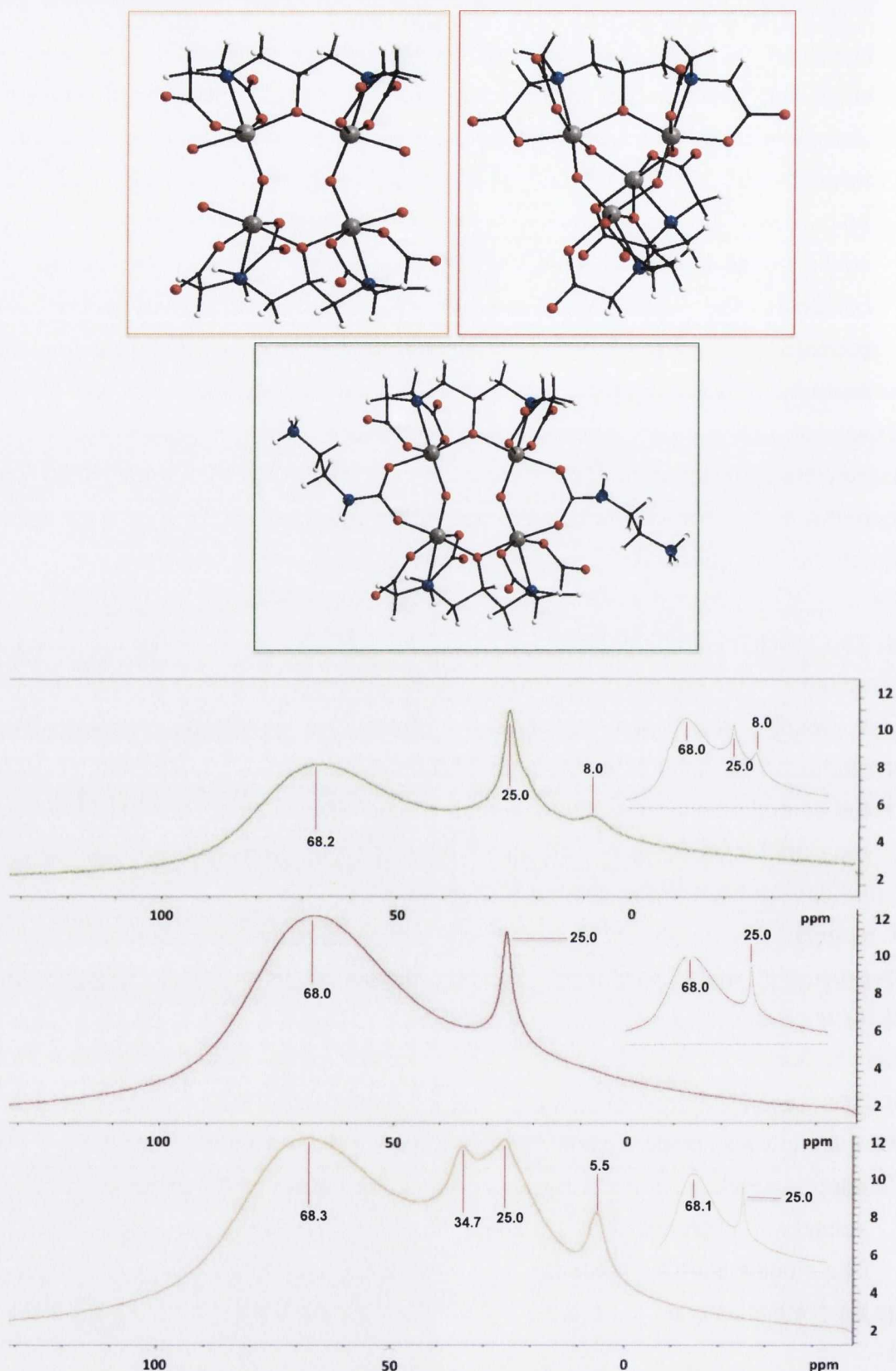


Figure 2.2: ^{27}Al NMR (400 MHz, water with a D_2O lock) spectra for the reaction mixtures that led to the crystallisation of compounds 5 (pH 4.5 orange spectrum), 6 (pH 7.0 red spectrum) and 7 (pH 8.5 green spectrum). Inset: spectra of pristine respective compounds dissolved in D_2O . The structures of tetranuclear complexes in 5, 6 and 7 are displayed in orange, red and green frames, respectively. Colour Code: Al yellow, C black, H white, N blue, O red.

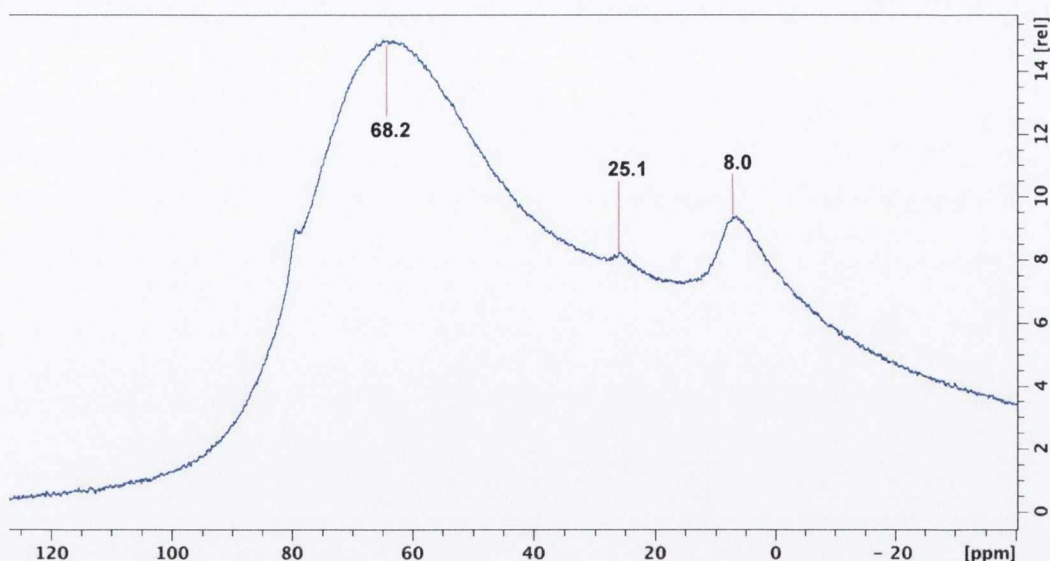


Figure 2.3: ^{27}Al NMR (400 MHz, water with a D_2O lock) spectrum for the reaction mixture, pH 8.5, upon addition of the solid carbamic acid, $\text{H}_3\text{NC}_2\text{H}_4\text{NHCOO}$.¹⁴⁷

Table 2.2: ^{27}Al NMR (400 MHz, water with a D_2O lock) signal assignments for compounds 5-7.^{145-146 146}

Signal (ppm)	Compound	Aluminium species
5.5 34.7	Observed in reaction mixtures that led to the crystallisation of 5, 6 & 7	Octahedrally coordinated inorganic species
25.0		-
8.0		Species that is octahedrally coordinated to 5 Oxygen & 1 Nitrogen atoms. Carbamate species.
	7	

^{13}C NMR

The stability of the tetranuclear aluminium complexes **5**, **6** and **7** in solution was also confirmed using ^{13}C NMR spectroscopy. The studies allowed us to investigate the solution behaviour of compounds **5-7** at three distinctly different pH conditions and to further confirm the presence of the carbamate complex of **7** in solution at pH 8.5.

The ^{13}C NMR spectrum of the *hpdta* ligand was recorded as a reference point for the interpretation of the NMR spectra of **5**, **6** and **7**. The sample was prepared from a 25 mM stock solution of *hpdta* dissolved in a $\text{H}_2\text{O}:\text{D}_2\text{O}$ mixture (1:1) by drop wise addition of ethylenediamine (*en*) to reach a final pH of 9.8. The spectrum of the uncoordinated ligand contained characteristic signals at *ca.* 56.2 ppm, *ca.* 58.8 ppm, *ca.* 67.9 ppm and *ca.* 173.3 ppm. Literature values for carbon shifts and a series of ^1H - ^{13}C heteronuclear

single quantum coherence spectroscopic (HSQC) NMR experiments allowed for the assignment of these signals as C3, C2, C1 and C4, respectively.¹⁴⁸⁻¹⁴⁹ The signal that resonates at *ca.* 173.3 ppm is not observed in the HSQC spectrum confirming its assignment as C4. The ethylenediamine (en) signal is observed in agreement with the literature at *ca.* 39.7 ppm.¹⁵¹

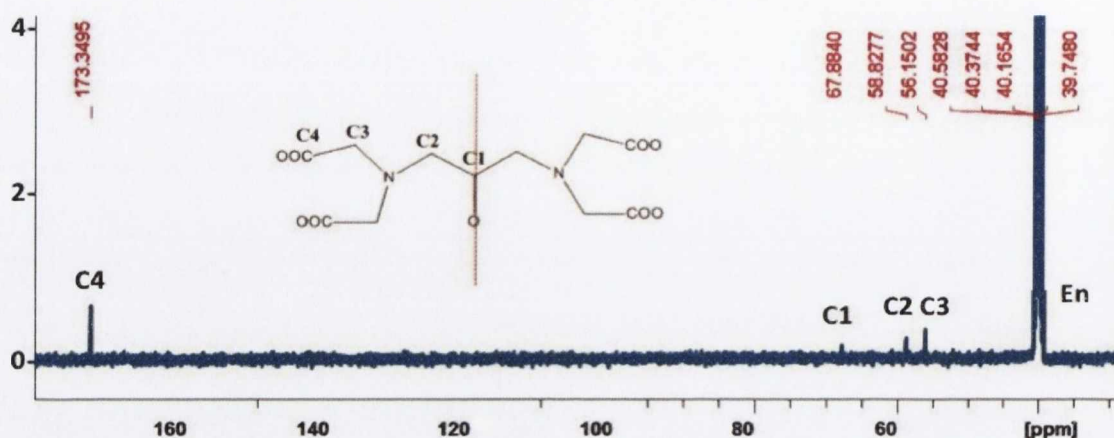


Figure 2.4: ¹³C NMR (400 MHz, H₂O with a D₂O lock) spectrum for *hpdta* ligand dissolved in water by drop wise addition of En, pH 9.8, with assignments.

Table 2.3: ¹³C NMR signals (400 MHz, Water with a D₂O lock) and assignments for *hpdta* ligand dissolved in water by drop wise addition of en, pH 9.8.

Signal (ppm)	Assignment
39.7	En
56.2	C3
58.8	C2
67.9	C1
173.3	C4

With the aid of the *hpdta* reference spectrum coupled with literature reference values the four fundamental signals that characterise the *hpdta* ligand coordinated to the Al^{III} metal ions in solution were identified in the ¹³C NMR spectra of the examined compounds, **5**, **6** and **7**.¹⁴⁸⁻¹⁴⁹ They were observed in the spectra recorded for the reaction mixtures at the three distinct pH values and were also observed in the spectra that were recorded when pristine crystalline samples of **5**, **6** and **7** were dissolved in D₂O/H₂O. Three additional signals were observed in the spectra recorded of **7** and characterise its presence in solution. It was not possible to distinguish between solutions containing the complexes of **5** and **7** under the examined experimental conditions.

The fundamental signals resonate at 60.0 ppm, 62.9 ppm, 69.0 ppm and 175.5 ppm. The signals downfield shifts with respect to the *hpdta* reference spectrum are induced by the octahedral coordination of O- and N- donor atoms to an Al^{III} centre. Their coordination to the Al^{III} ions shields the closely located carbon atoms. The carbon atoms therefore require more energy to achieve resonance and thus their signals are shifted downfield, e.g. the carbon atom at the C4 position, shifts in resonance from 173.3 ppm to 175.5 ppm upon coordination (compare Figure 2.4 vs. Figure 2.5). The closely related spectra and observed shifts provide a strong indication that the core units in **5**, **6** and **7** are present and remain intact in solution.¹⁵² Similar to the assignments for *hpdta*, observed in Table 2.4, the signal at *ca.* 60 ppm was found to arise from the carbon atom, C3. The peak at 62.9 ppm can be attributed to the methylene carbon atom, C2. The peak at 68.98 ppm can be recognized as the carbon atom at the C1 position. The peak at 175.5 ppm can be credited to the C=O resonance arising from the coordinated carboxylate functionality. There are additional signals resonating at *ca.* 175 ppm, *ca.* 62 ppm and *ca.* 60 ppm. These are likely to arise from minor differences between the eight C=O carbons at the 'C4' position, the methylene carbon atom at the C2 position and the carbon atoms at the C3 position respectively. The differences arise from the dynamic nature of this type of polycarboxylate complexes in solution as it is often observed throughout the literature.^{152,153} The peaks at *ca.* 60 and *ca.* 65 ppm in the spectrum of **7** can be attributed to C7 and C6, respectively. The appearance of an additional signal at these resonances indicates inequalities between the CH₂ carbon atoms on the two carbamate moieties. As previously mentioned this is characteristic of the dynamic nature of these complexes in solution. The signal at *ca.* 164 ppm can be attributed to the C-N bonded carbon atom, C5, of the carbamate side chain. The signals suggest the adsorption of aerial carbon dioxide by the reaction mixture at pH 8.5 and further confirms the solution formation of **7** under alkaline conditions. The signals are also observable in the spectrum when solid carbamic acid, H₃NC₂H₄NHCOO⁻, was prepared according to literature methods and added to the reaction mixture in stoichiometric quantities.¹⁴⁷ The spectrum contained other minor signals, which, were similarly found in spectra of the reaction mixtures at pH 4.5 and 8.5; these signals could not be assigned.

The ¹³C NMR spectra of **5** and **6** dissolved in D₂O, insets Figure 2.5, were similar to the NMR spectra for the reaction mixture at pH 7.0, observed in Figure 2.5, the signal arising from ethylenediamine at *ca.* 39 ppm is absent from the spectra. The spectrum of **7** dissolved in D₂O contains the seven characteristic signals. However, the three signals that characterise the presence of the carbamate compound in solution appear as minor signals, which suggest its stability in solution at pH= 8.5 and may be in equilibrium with

the tetrahedral complex under neutral conditions. Similar behaviours were observed in the ^{27}Al NMR spectra of the solutions. The characterising peaks for **5-7** disappear from the NMR spectra upon crystallisation. Whereas the signal at *ca.* 39.0 ppm and the unassignable minor signals remain in the spectra of the reaction mixtures post crystallisation.

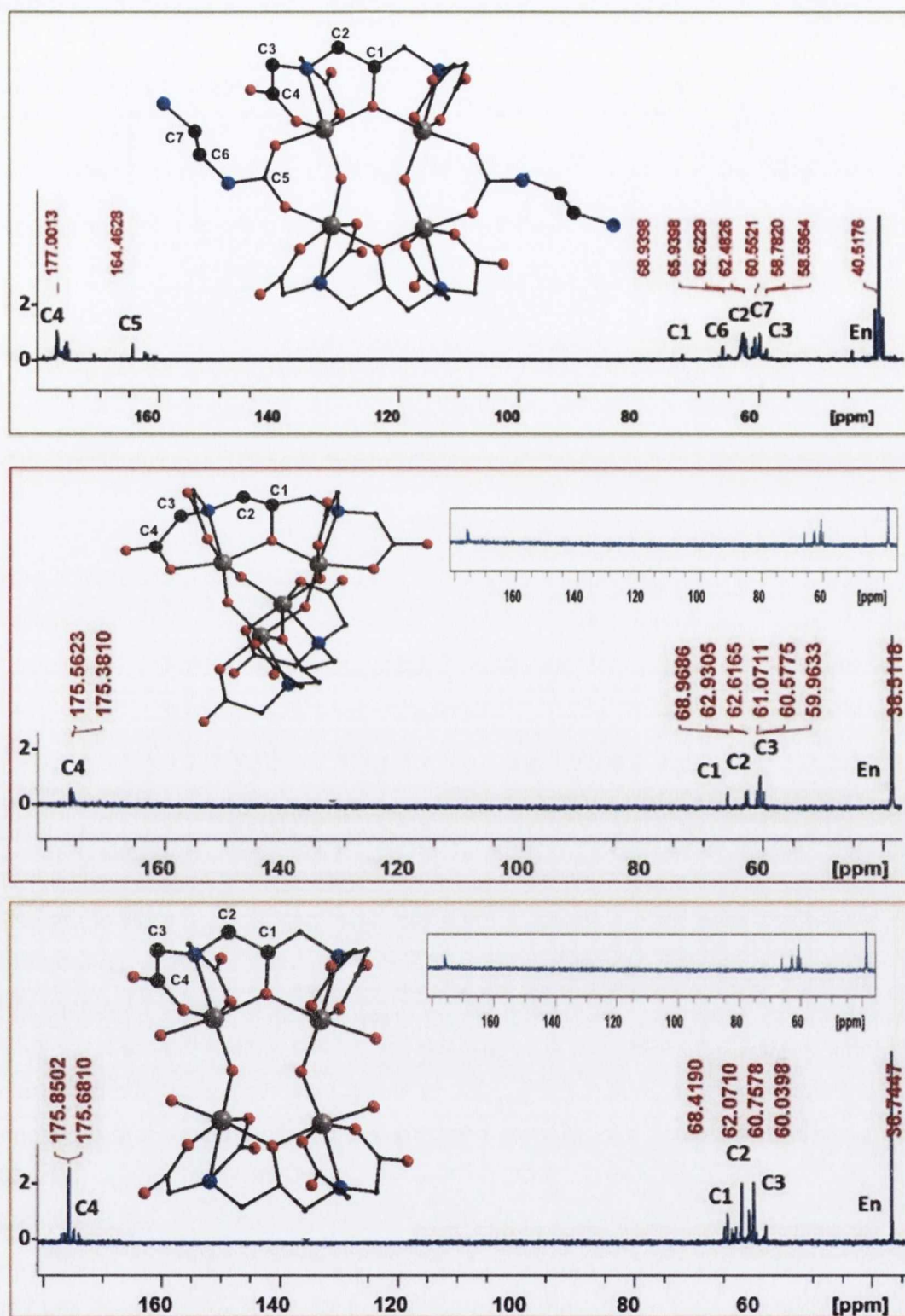


Figure 2.5: ^{13}C NMR (400 MHz, water with a D_2O lock) spectra of the reaction mixtures, with assignments, that led to the crystallisation of compounds 5 (pH 4.5 orange), 6 (pH 7.0 red frame) and 7 (pH 8.5 green frame). Inset: spectra of pristine samples of compounds dissolved in D_2O .

Table 2.4:¹³C NMR (400 MHz, water with a D₂O lock) signals with assignments for compounds 5-7.¹⁴⁵⁻¹⁴⁶

Signal (ppm)	Compound	Assignment
39.0	5, 6 & 7	En
60.0	5, 6 & 7	C3
62.9	5, 6 & 7	C2
68.9	5, 6 & 7	C1
175.5	5, 6 & 7	C4
59.0	7	C7
65.0	7	C6
164.0	7	C5

¹H NMR

Proton NMR is a very useful technique that provides insight into the types of hydrogen atoms in a compound, their electronic environments, their relative numbers and the hydrogen atom environments of their neighbours. However, the technique was not expected to distinguish between the fundamental structures of **5**, **6** and **7** in solution as the protons at the H5 position on the auxiliary water ligands in **5** and the H6-H9 positions in **7**, Figure 2.8, are not observable as they exchange with the deuterium from the D₂O lock. The protons on the bridging ligand, located at the H4 position in Figure 2.8, also exchange with the deuterium lock.¹⁴⁹ Furthermore the ammonium moieties in **7** and the ethylenediamine hydrolysing agent are heavily influenced by the pH of the samples. At pH 4.5 the nitrogen atoms can protonate which influences the resonance of adjacent methylene protons.^{130, 154-155} Increasing the pH causes the electron density at the non-labile methylene protons to increase and an up field shift in their resonance.¹⁵⁴⁻¹⁵⁶ The pH shifts obscure important signals at distinct pH values and effect the coupling constants and signal integrations. This is evident in the spectra of the reaction mixture for all three compounds (Figure 2.8). It is also noteworthy that the reaction mixtures in these studies contain water. The presence of water in samples is particularly problematic in ¹H NMR as it renders the spectra difficult to interpret due to the broad water signal resonating at ca. 3.4 ppm. In these studies the elimination of signals arising from water, was facilitated, with the exception of the *hpdta* spectrum, by executing the experiments with the additional WATER suppression by GrAdient Tailored Excitation (WATERGATE)[§] command. For the reasons described above the following studies cannot be used to

[§] WATERGATE is a method to suppress the intense solvent resonance when ¹H spectra are recorded in H₂O solutions. It is based on a single symmetrical spin-echo that combines selective 180° pulse and two symmetrical PFGs.¹⁵⁷

unambiguously identify the species in solution. Rather, they provide complementarity to the previous ^{27}Al and ^{13}C NMR experiments that unambiguously identify the core tetranuclear structures in solution.

The ^1H NMR of *hpdta* was recorded as a reference point for the interpretation of the spectra for **5**, **6** and **7**. The sample was prepared from a 0.025 M stock solution of *hpdta* dissolved in $\text{H}_2\text{O}:\text{D}_2\text{O}$ mixture by drop wise addition of en. Deuterated water was added to the solutions in order to obtain a D_2O lock. Characteristic signals at 3.65 ppm, 2.73 ppm and 2.55 ppm were observed in the spectra of *hpdta*, Figure 2.6. The assignments for these signals were based on the calculated coupling constants, the known literature values for ^1H shifts in combination with ^1H - ^{13}C HSQC experiments. The signal at 3.65 ppm appeared as a multiplet that was overlapped by the intense water signal at 3.40 ppm. The signal was expected to be split into a quintet as H1 has a total of four neighbouring protons (H2a and b and their symmetrical equivalents). The signal was assigned to H1 as the HSQC spectrum, Figure 2.7, clearly showed it's coupling with C1.

The signal at 2.73 ppm appeared as a doublet of doublets with an integration of two protons. The doublet at 2.55 ppm also integrated to two protons and the HSQC spectrum revealed that the two signals were coupled to C2. This inferred that the two protons on the C2 carbon were in two chemically distinct environments. It was evident from the doublet of doublets, that the signal at 2.73 ppm had two chemically in-equivalent neighbouring protons. If the two neighbouring protons effected the splitting pattern equally then the signal would have been observed as a triplet. Whereas the second proton on C3, resonating at 2.55, was observed as a doublet identifying it as H2b. The coupling constants for the doublet of doublets at 2.73 ppm were 8.0 Hz and 4.28 Hz. These values are indicative of geminal coupling across one carbon atom and vicinal coupling across two carbon atoms respectively. The H2a proton has two neighbouring protons, H2b and H1, respectively. H2b is located one carbon away while the H1 is located two carbons away. The coupling constant for the signal at 2.55 ppm is 7.9 ppm which is indicative of geminal coupling. The coupling constant for the geminal coupling for H2a and H2b further confirm that the two protons are coupled to each other.¹⁴⁹ The intense water signal resonated at 3.41 ppm.¹⁵¹ The signals at 2.68 ppm and 2.50 ppm were attributed to ethylenediamine.¹⁵¹

The signal for the protons at the H3 positions was not observed in the spectrum. However, the ^1H - ^{13}C HSQC spectrum revealed that the carbon at the C3 position was coupled to one type of proton that was masked by the water signal.

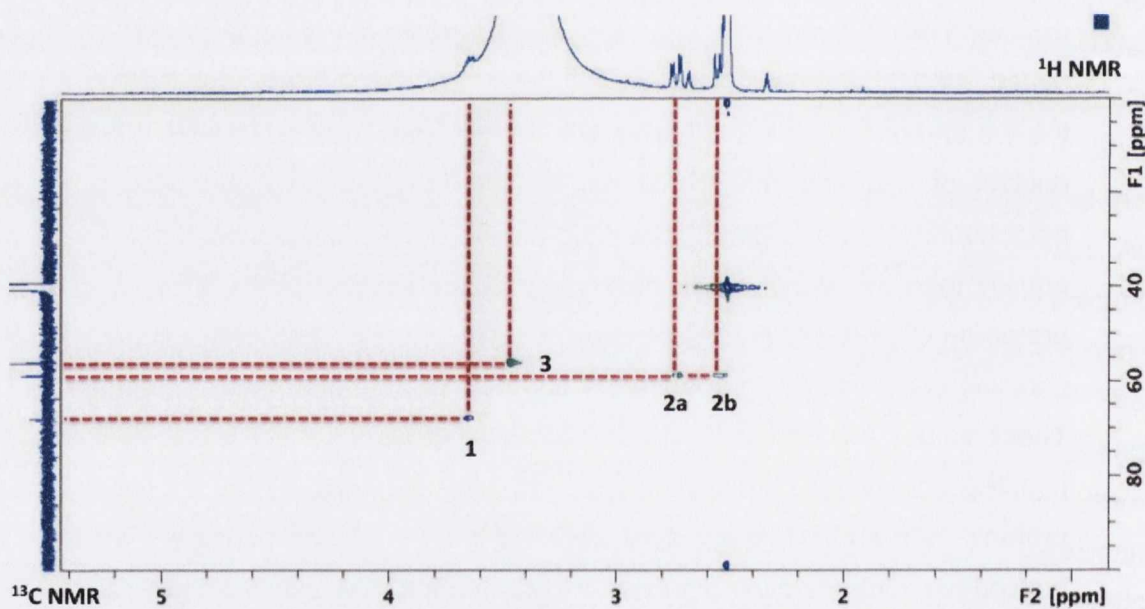
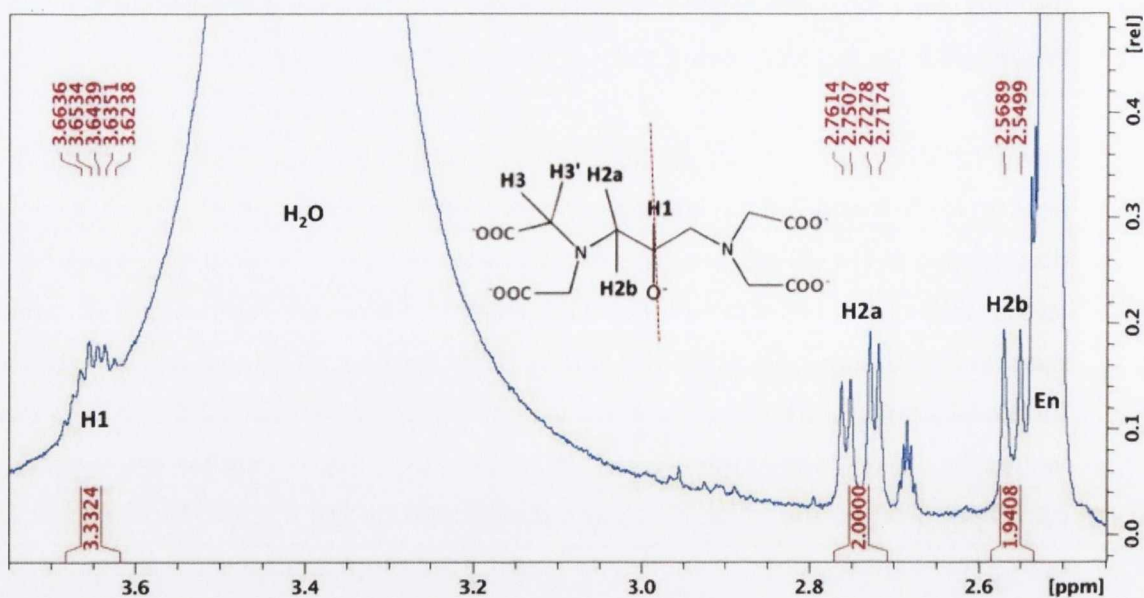
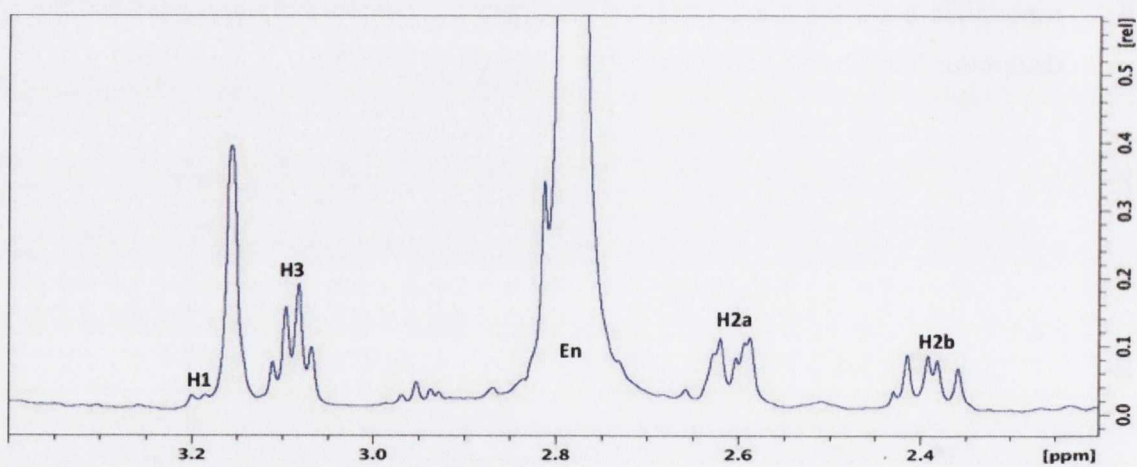
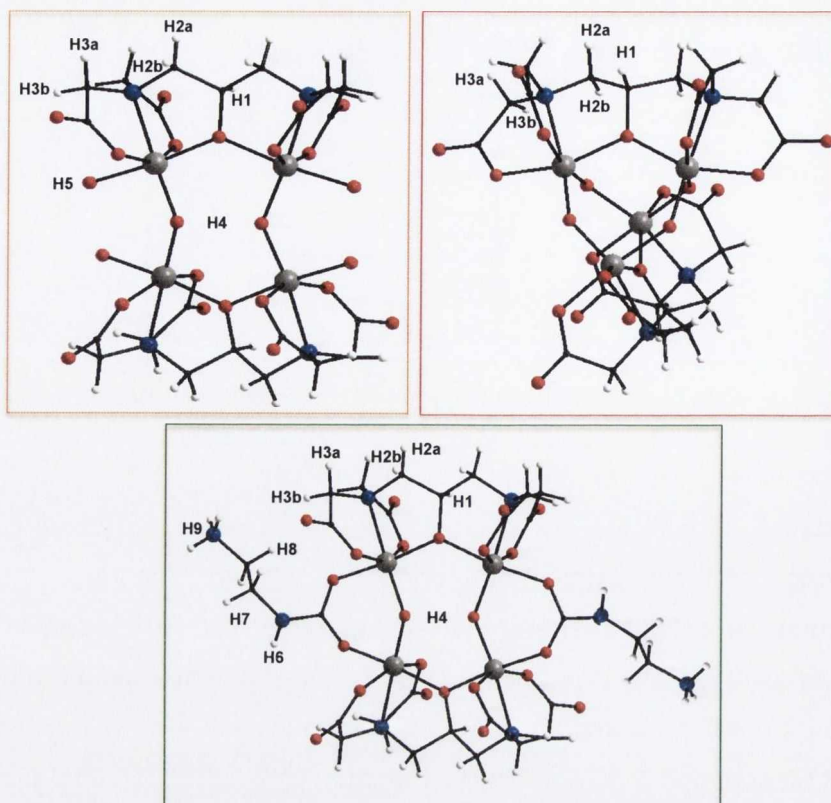


Table 2.5: ^1H NMR signals (400 MHz, Water with a D_2O lock) and assignments for *hpdt*a ligand dissolved in water my drop wise addition of en, pH 9.8. * *not observed in ^1H NMR. Located using ^1H - ^{13}C HSQC spectrum.*

Signal [ppm]	Coupling constant [Hz]	Assignment
2.55 (2H, d)	7.9	H2b
2.735 (2H, dd)	8.0, 4.28	H2a
3.56*	-	H3
3.65 (m)	-	H1

It was possible to identify signals in the ^1H NMR spectra for **5**, **6** and **7**, respectively that were consistent with the characteristic signals observed in the *hpdt*a spectrum. The occurrence of these signals throughout the spectra confirmed the stability of the compounds in solution. The signals assigned to the H3a, H2b, H2a, H3b and H1 positions were observed in spectrum of **5** (pH 4.5). They resonate at 2.49 ppm, 2.72 ppm, 3.02 ppm, 3.53 ppm and 3.59 ppm, respectively. The signals observable at 2.74 ppm, 3.52 ppm and 3.59 ppm in the spectrum of **6** (pH 7.0), were assigned to H2b, H3 and H1. The spectrum of **7** were critically overlapped however, the signals are clearly observed when **7** is dissolved in aqueous en solution at pH 9.8. The shifts in signal resonance are attributable to the distinct pH environments of each sample. The signals disappear from the spectra upon crystallisation of **5**, **6** and **7**, respectively.



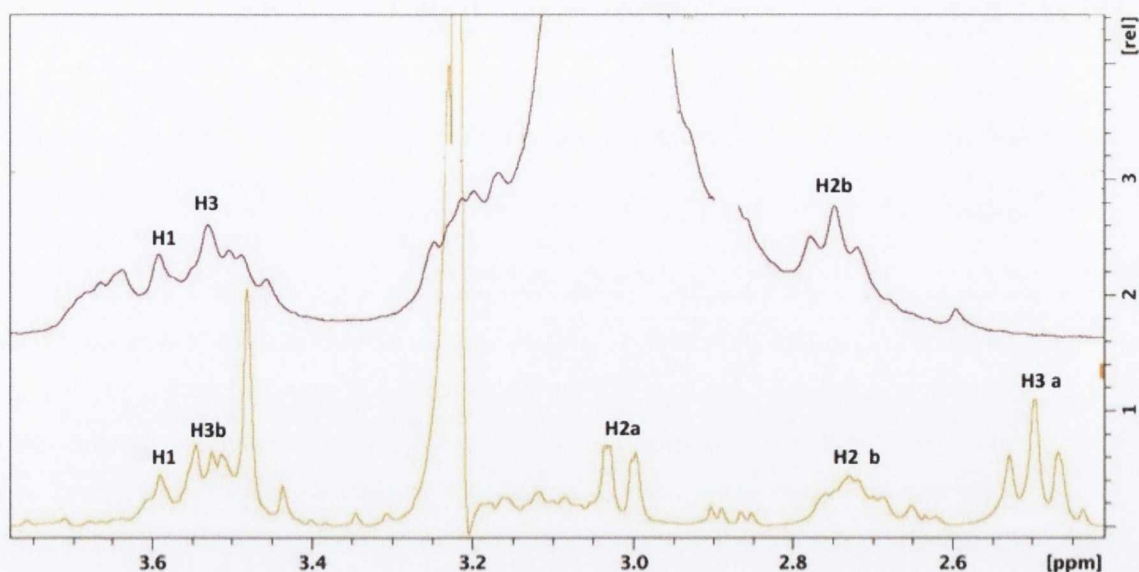


Figure 2.8: ^1H NMR (400 MHz, water with a D_2O lock, recorded using WATERGATE command) spectra for the reaction mixtures that lead to the formation of 5 and 6 at pH 4.5 and 7.0 (orange and red spectra). Blue spectrum is pristine crystals of 7 dissolved in a 0.025 mM ethylenediamine solution (pH 9.8) The structural assignments for tetranuclear complexes in 5, 6 and 7 are displayed in orange, red and green frames, respectively. Colour Code: Al yellow, C black, H white, N blue, O red.

Table 2.6: ^1H NMR (400 MHz, water with a D_2O lock, recorded using WATERGATE command) signals and their assignments for compounds 5-7.

Compound (pH)	Shift (ppm)	Assignment
5 (pH 4.5)	2.49	H3a
	2.72	H2b
	3.02	H2a
	3.53	H3b
	3.59	H1
6 (pH 7.0)	2.74	H2b
	3.52	H3
	3.59	H1
7 dissolved in aqueous en solution (pH 9.8)	2.39	H2b
	2.61	H2a
	3.09	H3
	3.18	H1

2.3.2 Electrospray ionisation mass spectrometry (ESI-MS)

As discussed in section 2.3.1, we utilised ^1H , ^{13}C and ^{27}Al NMR to investigate the solution behaviour of the diamagnetic coordination complexes that form in the aqueous Al^{III} *hpdta* system at pH values of ca. 4.5, 7.0 and 8.5. The results from these studies suggested that the compounds were stable in solution when dissolved at appropriate pH values and indicated that it is possible to observe the formation three distinct compounds that form at different pH values. Although this was very useful information, it was not possible to perform similar studies for the structurally related Fe^{III} *hpdta* system as, owing to its paramagnetic nature, the signals were too broad to provide detailed structural information. However, aqueous Al^{III} and iron Fe^{III} polycarboxylic acid ligand systems, such as systems that are stabilised by the *hpdta* ligand and the structurally related *heidi* ligand, have been reported in the literature for their similarities in reactivity and complexity.^{1-2, 2-3 145} With this in mind and following on from the success of previous electrospray ionisation mass spectrometry (ESI-MS) studies carried out in the group we decided to utilise this technique to investigate the solution behaviour of the Al^{III} *hpdta* and Fe^{III} *hpdta* systems. The results were interpreted in view of the NMR solution studies of the Al^{III} *hpdta* system.¹⁻³

We began by analysing the aluminium system first. In these studies we utilised the 5 mM Al^{III} stock solutions as described above in section 2.3.1, and we recorded the ESI-MS spectra of freshly prepared samples at Al^{III} :*hpdta* molar ratio of 2:1 at pH 4.5, 7.0 and 8.5. We also recorded the spectrum of a sample at pH 8.5 that was exposed to the atmosphere for twelve hours.

These experiments unambiguously confirm that it is possible to differentiate between the three different reaction mixtures at pH 4.5, 7.0 and 8.5. ESI-MS experiments revealed that the carbamate compound forms upon exposure of the reaction mixture at pH 8.5 to the atmosphere for twelve hours.

It is reported in the literature that upon ESI-MS analyses, fragmentation occurs which can lead to the loss of ionisable moieties from compounds such as **5-7**.¹⁵² Compound **5** follows this behaviour as exemplified by the signal at $m/z = 834.1$ in the spectrum of the reaction mixture at pH 4.5, Figure 2.9A. The signal was assigned to **5** with the ion-induced loss of an oxygen atom that may arise from a carboxylate moiety of a *hpdta* ligand, $\{\text{H}_2[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})(\text{hpdta-O})(\text{H}_2\text{O})_4]\}^-$. The observed signal confirms the presence of the coordination compound with square planar topology and terminal

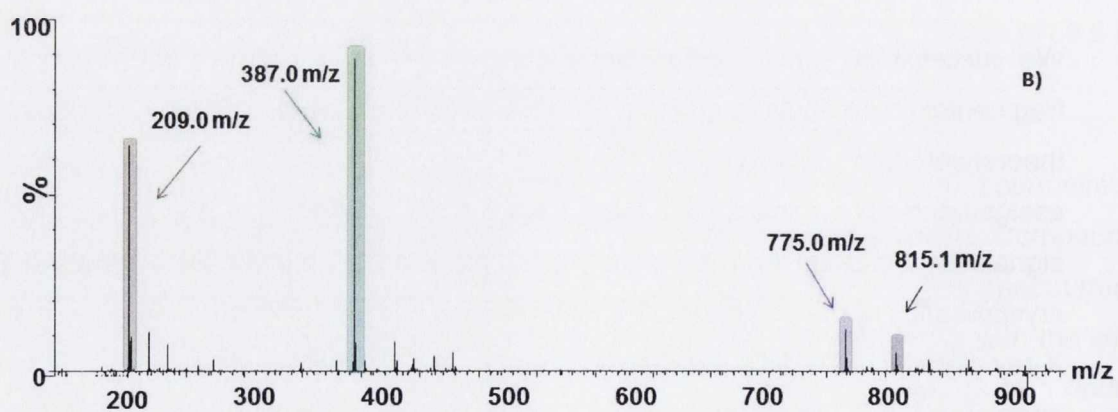
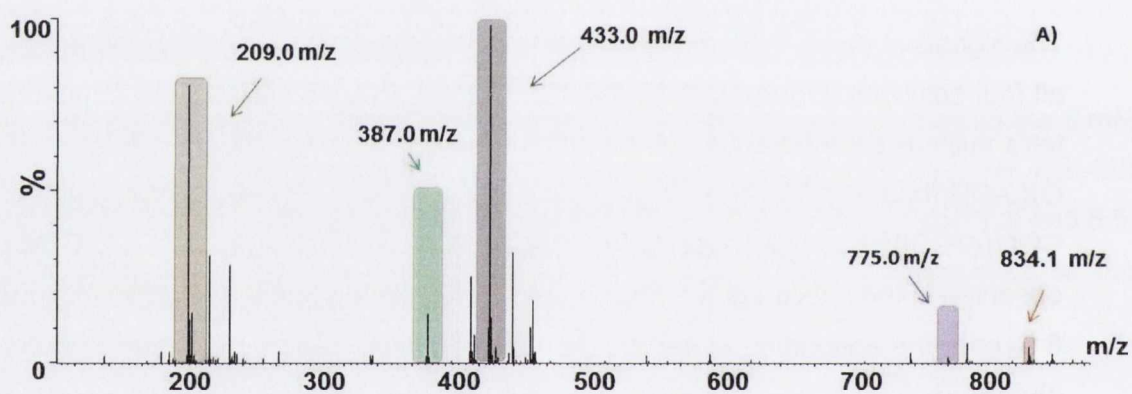
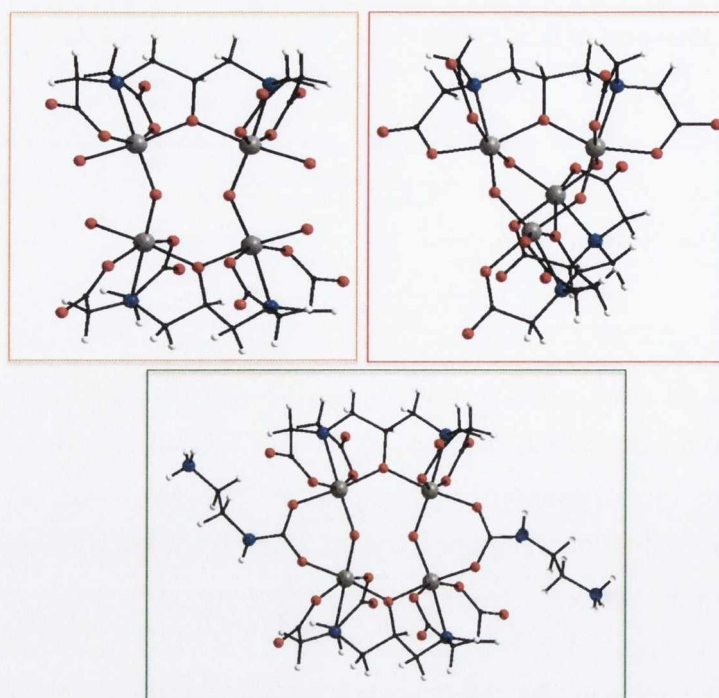
coordination water molecules in solution. This peak disappears from the reaction mixture upon crystallisation of **5**.

The presence of compound **6** with tetrahedral topology in solution is characterised by the signal at $m/z = 815.0$ in the ESI-MS⁻ spectrum of the reaction mixture at pH 7.0, Figure 2.9B. The signal can be successfully assigned to $\{H_3[Al_4(\mu-OH)_4(hpdta)(hpdta-O)] \cdot H_2O\}^-$.

The signal at $m/z = 983.1$ has been assigned to negatively charged $[Al_4(\mu-O)(\mu-OH)(hpdta)_2(O_2CNHC_2H_4NH_3)_2]^-$ complex **7** in solution at pH 8.5 post exposure to the atmosphere for 12 hours. The signal at $m/z = 879.0$ was attributed to the parent compound **7** with the ion induced loss of a carbamate side chain. The notable absence of these peaks in the ESI-MS⁻ of the fresh reaction mixture at pH 8.5 and their subsequent appearance in the ESI-MS⁻ of the solution post exposure to the atmosphere for twelve hours (see Figure 2.9C and D), demonstrates the absorption of CO₂ upon exposure to the atmosphere.

The signals at $m/z = 775$, $m/z = 387.0$ and $m/z = 209.0$ were observed in the spectra of all four solutions, Figure 2.9A-D, and indicate the presence of the core structure in the tetra nuclear compounds for all solutions. They were successfully assigned to $[Al_4(\mu-O)(\mu-OH)(hpdta)_2]^-$, $[Al_4(\mu-O)(\mu-O)(hpdta)_2]^{2-}$ and $\{H_6[Al_2(\mu-O)(\mu-OH)(hpdta-2O-COO) \cdot 4H_2O]\}^{2-}$ species respectively. An additional signal at $m/z = 433.0$ was also observed in the spectra of the reaction mixture at pH 4.5 and the reaction mixture at pH 8.5, prior the adsorption of carbon dioxide. This peak can be attributed to a dinuclear aluminium $\{H_3[Al_2(\mu-O)(\mu-OH)(hpdta-COO) \cdot 3H_2O]\}^-$ fragment. The latter signals are a result of parent molecule ionisation induced decomposition.

We successfully simulated the isotopic envelopes for all of the parent species and fragmentation products listed in Table 2.7. The correlation between the experimental and theoretical data, illustrated in Figure 2.10 and Figure 2.11, further confirms our assignments. The assignments were further substantiated when the above-mentioned signals disappeared from the ESI-MS⁻ of the reaction mixture upon precipitation or crystallisation of the compound from the reaction mixture. Infrared analyses and powder X-ray diffraction (P-XRD) patterns recorded for the precipitates confirmed the identity of compounds **5-7**. The results were consistent with our observations from the NMR analyses.



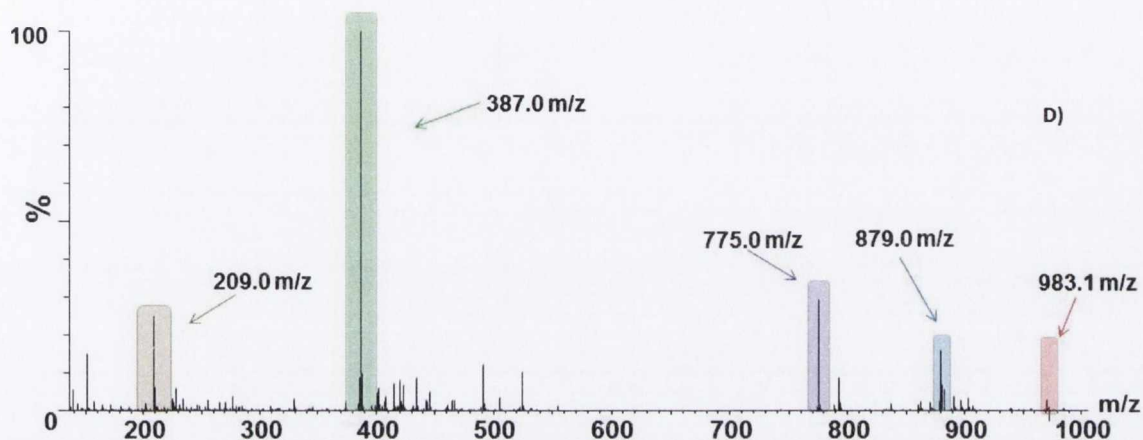
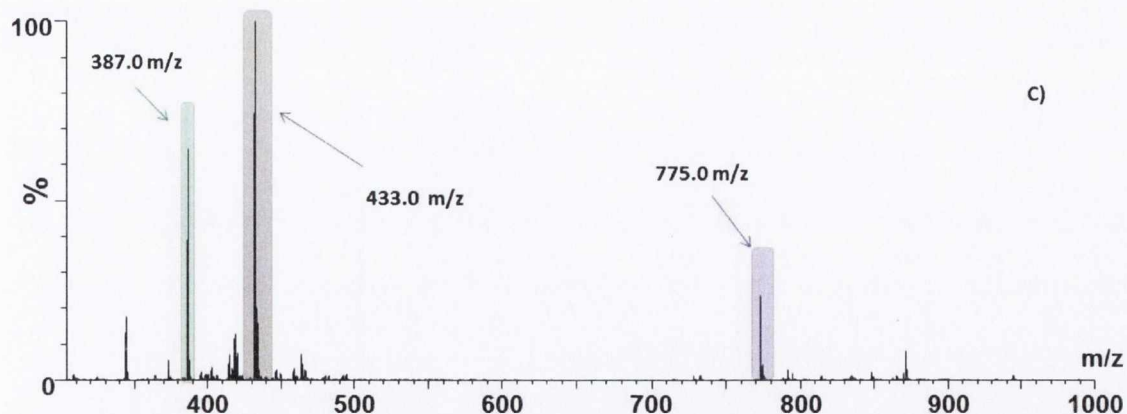


Figure 2.9: Negative-mode ESI-MS spectra for a freshly prepared reaction mixtures that led to the formations of A) Compound 5 (pH 4.5), B) compound 6 (pH 7.0), C) compound 7 (pH 8.5) and D) the reaction mixture at pH 8.5 twelve hours post exposure to the atmosphere (cone voltage: 30 V). The structures of tetranuclear complexes in 5, 6 and 7 are displayed in orange, red and green frames, respectively. Colour Code: Al yellow, C black, H white, N blue, O red.

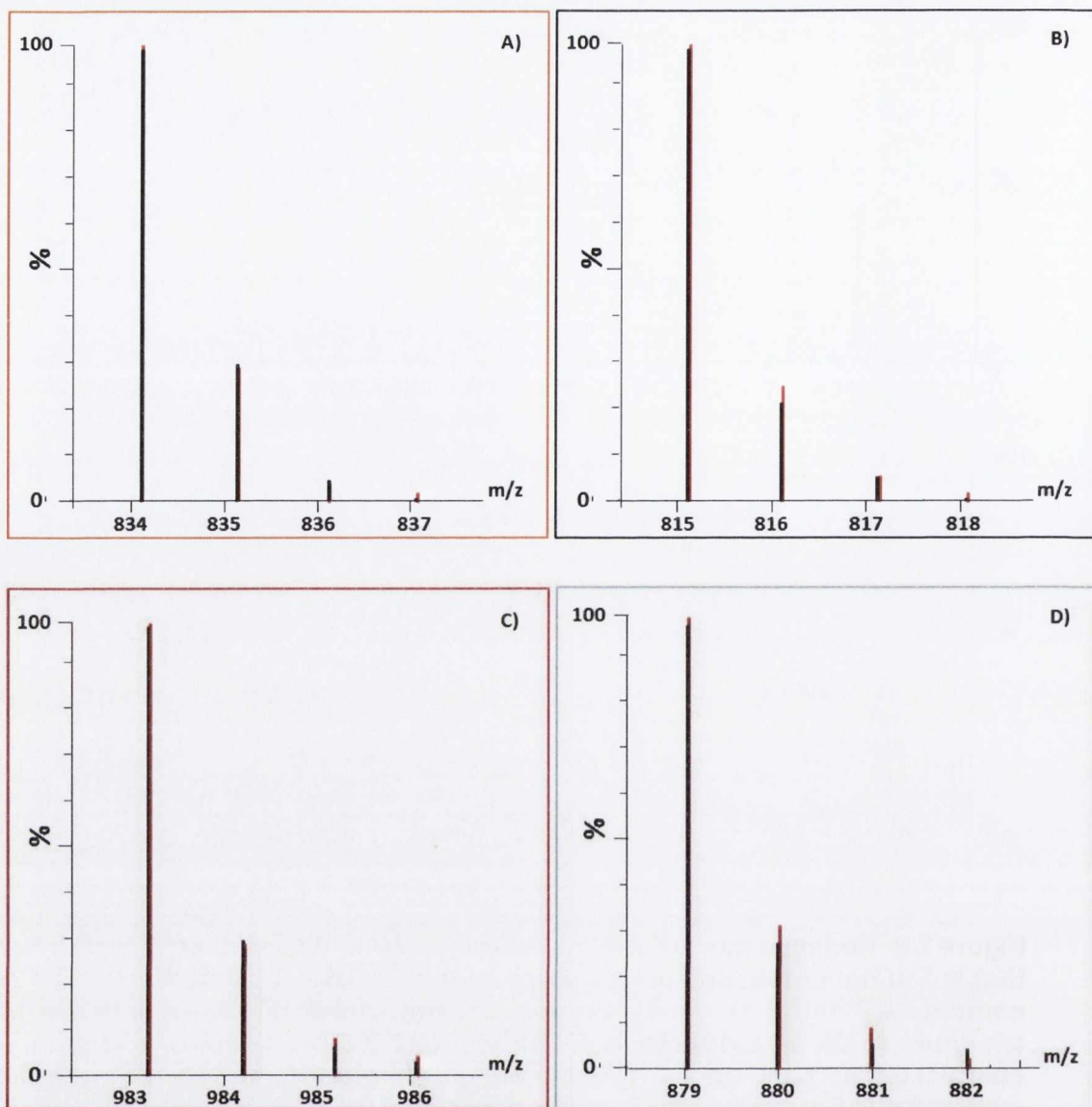


Figure 2.10: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for A) $\{H_2[Al_4(\mu-O)(\mu-OH)(hpdt a)(hpdt a-O)(H_2O)_4]\}^-$, centered at $m/z = 834.1$, B) $\{H_3[Al_4(\mu-OH)_4(hpdt a)(hpdt a-O)] \cdot H_2O\}^-$, centered at $m/z = 815.1$, C) $[Al_4(\mu-O)(\mu-OH)(hpdt a)_2(O_2CNHC_2H_4NH_3)_2]^-$, centered at $m/z = 983.1$ and D) $[Al_4(\mu-O)(\mu-OH)(hpdt a)_2(O_2CNHC_2H_4NH_3)]^-$, centered at $m/z = 879.0$ (cone voltage: 30 V).

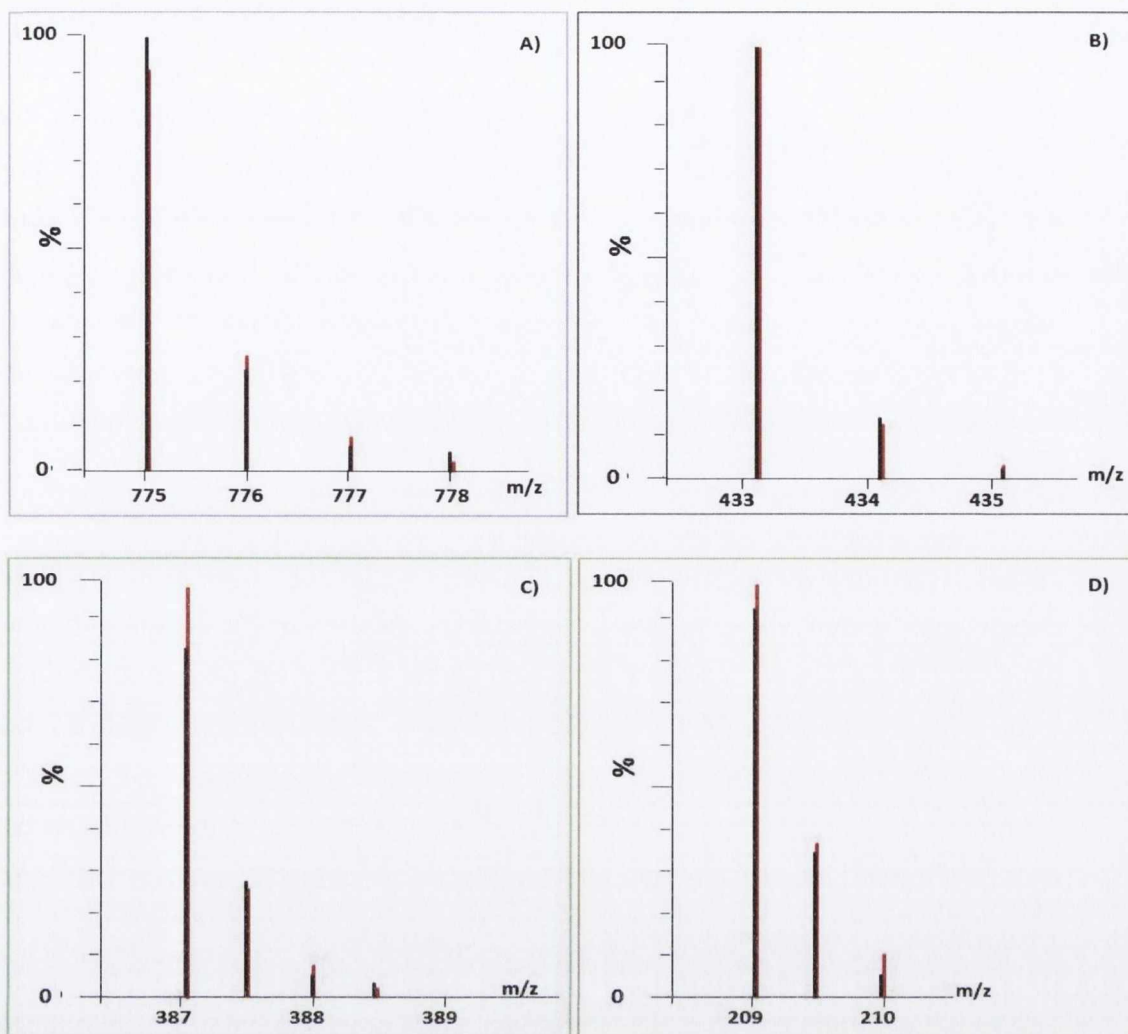


Figure 2.11: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for A) $[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA})_2]^-$ -centred at $m/z = 775.0$, B) $\{\text{H}_3[\text{Al}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA-COO})\cdot 3\text{H}_2\text{O}]\}^-$, centred at $m/z = 433.0$, C) $[\text{Al}_4(\mu\text{-O})(\mu\text{-O})(\text{hpdtA})_2]^{2-}$, centred at $m/z = 387.0$ and D) $\{\text{H}_6[\text{Al}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA-2O-COO})\cdot 4\text{H}_2\text{O}]\}^{2-}$, centred at $m/z = 209.0$ (cone voltage: 30 V).

Table 2.7: ESI-MS⁻ assignment for the signals in the reaction mixtures that led to the crystallisation of 5, 6 and 7.

m/z	Compound	Species attributed
834.1	5	$\{\text{H}_2[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA})(\text{hpdtA-O})(\text{H}_2\text{O})_4]\}^-$
775.0	5, 6 & 7	$[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA})_2]^-$
433.0	5 & 7	$\{\text{H}_3[\text{Al}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA-COO})\cdot 3\text{H}_2\text{O}]\}^-$
387.0	5, 6 & 7	$[\text{Al}_4(\mu\text{-O})(\mu\text{-O})(\text{hpdtA})_2]^{2-}$
209.0	5, 6 & 7	$\{\text{H}_6[\text{Al}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA-2O-COO})\cdot 4\text{H}_2\text{O}]\}^{2-}$
815.1	6	$\{\text{H}_3[\text{Al}_4(\mu\text{-OH})_4(\text{hpdtA})(\text{hpdtA-O})]\cdot \text{H}_2\text{O}\}^-$
983.1	7	$[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]^-$
879.0	7	$[\text{Al}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdtA})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)]^-$

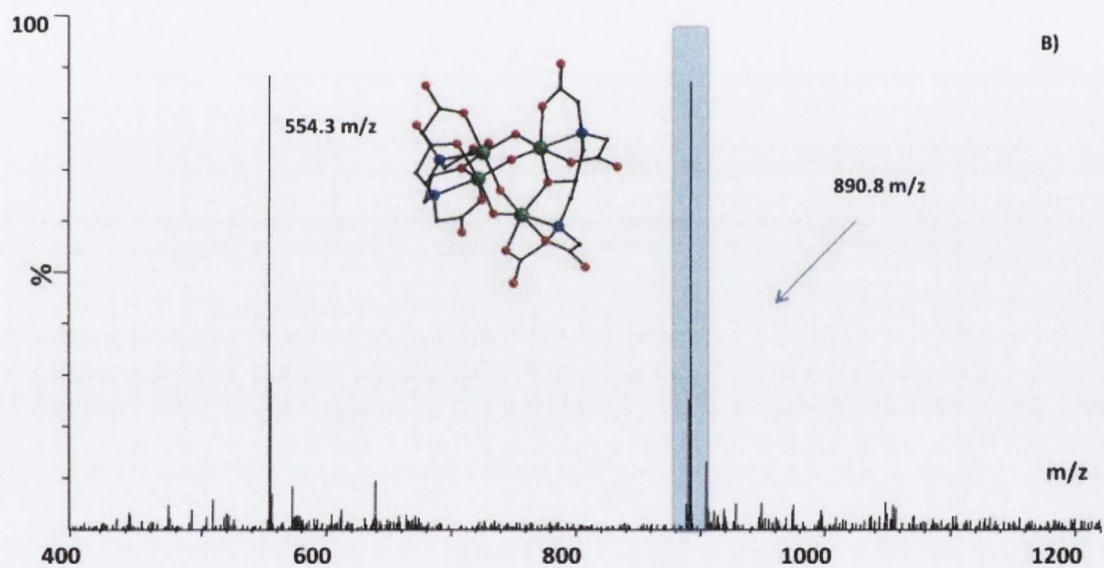
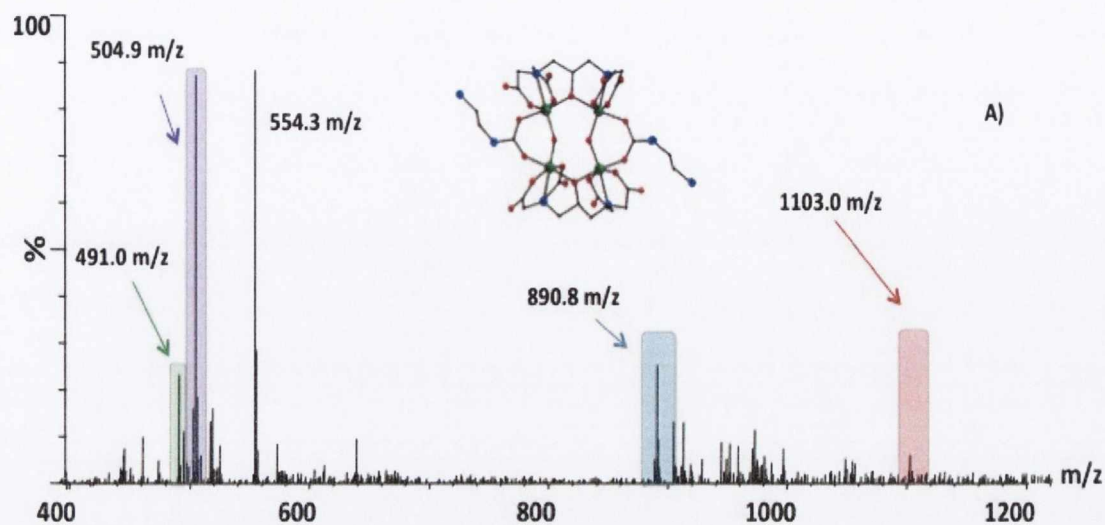
Encouraged by the stability of individual compounds in the Al^{III} *hpdta* system, our ability to identify individual species in reaction mixtures and the correlation between the results from the NMR and the ESI-MS⁻ experiments we decided to employ ESI-MS⁻ to study the stability of compounds that form in the Fe^{III} *hpdta* reaction system. To do this we prepared a stock solution of the reaction mixture by adding 0.5 moles of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.25 mmoles of *hpdta* to 50 ml deionised water. Ethylenediamine was used to dissolve the *hpdta* ligand and adjust the pH and 1.5 millilitre aliquots were used for each experiment. We recorded ESI-MS spectra at pH 4.5, 7.0 and 8.5. In addition we have also recorded the spectra of the reaction mixture at pH 8.5 twelve hours post exposure to the atmosphere.

The spectra obtained from these experiments can be observed in Figure 2.12. The presence of **3** in the reaction mixture at pH 8.5 is confirmed by the occurrence of a signal at $m/z = 1103.0$. The individual peaks within the isotopic envelope are spaced by $m/z = 1$ intervals which indicates that the signal arises from a singly negatively charged species. The signal is consistent with the molecular weight of the carbamate compound **3** with the loss of an uncoordinated oxygen atom from one of the *hpdta* carboxylate moieties. It was successfully attributed to the singly charged species $\{\text{H}_2[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})(\text{hpdta-O})(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2] \cdot \text{H}_2\text{O}\}^-$.

The signal at $m/z = 890.8$, observed in the spectra of all examined reaction mixtures is consistent with the tetranuclear species $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2]^-$ upon loss of auxiliary side chains. As mentioned above the decarboxylation or the loss of non-coordinating oxygen atoms is reported for similar lanthanide *hpdta* compounds in the literature.¹⁵² The signal at $m/z = 890.8$ indicates that although it is not possible to directly observe the planar complex $(\text{enH})[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4] \cdot n\text{H}_2\text{O}$ (**1b**) in solution, that the inherent tetranuclear core that is common to all compounds discussed here remains intact and one can use the technique to monitor the presence of the parent compounds in solution.

The signals at $m/z = 504.9$ and $m/z = 491.0$ were observed in the square planar compounds **1b** and **3**. These signals are consistent with the dinuclear species with loss of oxygen atoms and carboxylate moieties from the *hpdta* ligand. They were successfully assigned to $\{\text{H}_3[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdta-2O})4\text{H}_2\text{O}]\}^-$ and $\{\text{H}_3[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdta-COO})4\text{H}_2\text{O}]\}^-$ respectively. It is remarkable that the signals were not present in the spectra of compound **2b** or mixtures that led to its precipitation. This notable absence

suggests that these signals arise from fragmentation products of compounds that have a square planar geometry in the solid state, compounds **1b** and **3**.



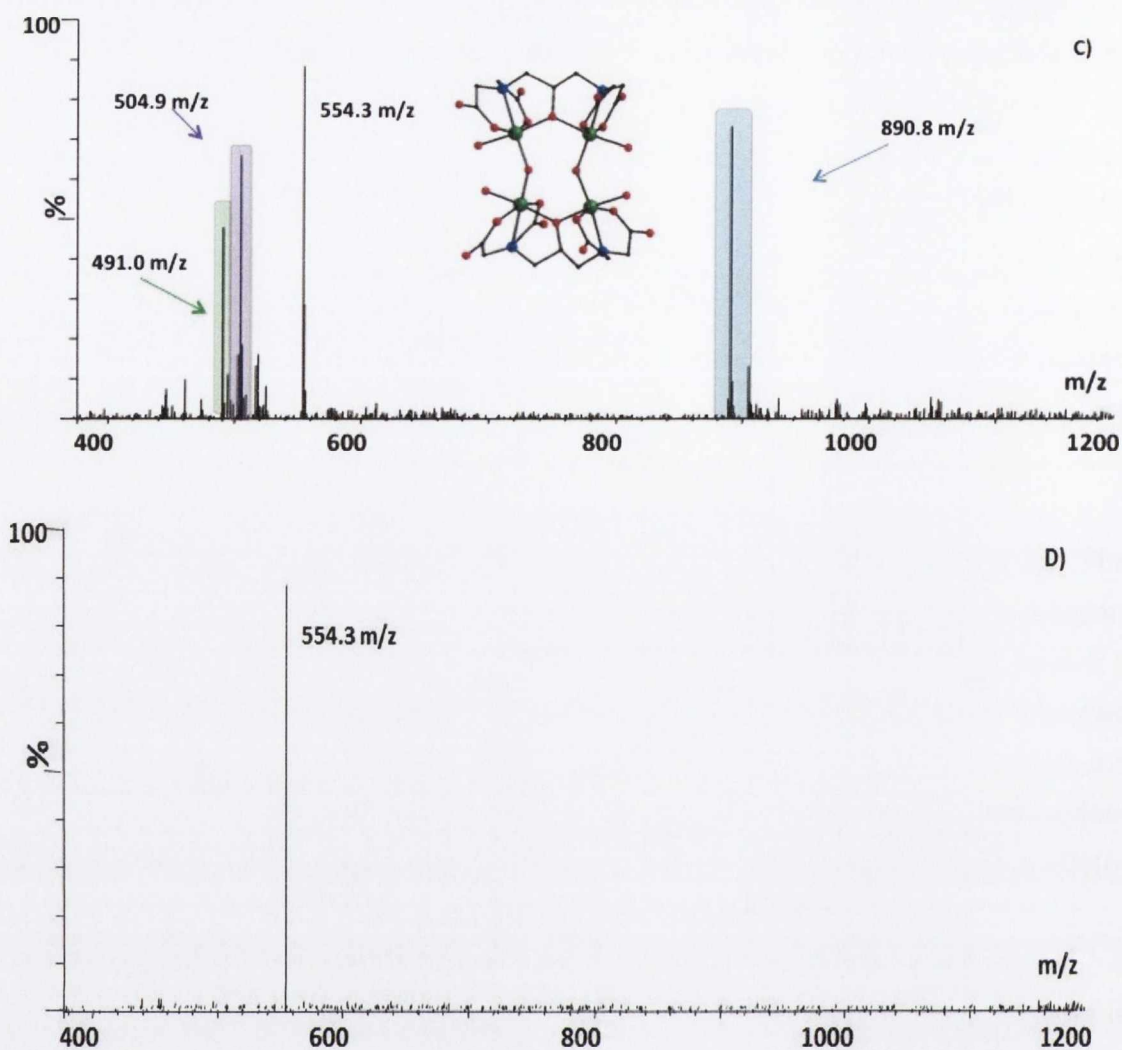


Figure 2.12: Negative-mode ESI-MS spectra for the freshly prepared reaction mixture at pH A) 8.5, B) 7.0 and C) 4.5. D) Typical spectrum representative of all three solutions above, after crystallisation of compounds (cone voltage: 30 V).

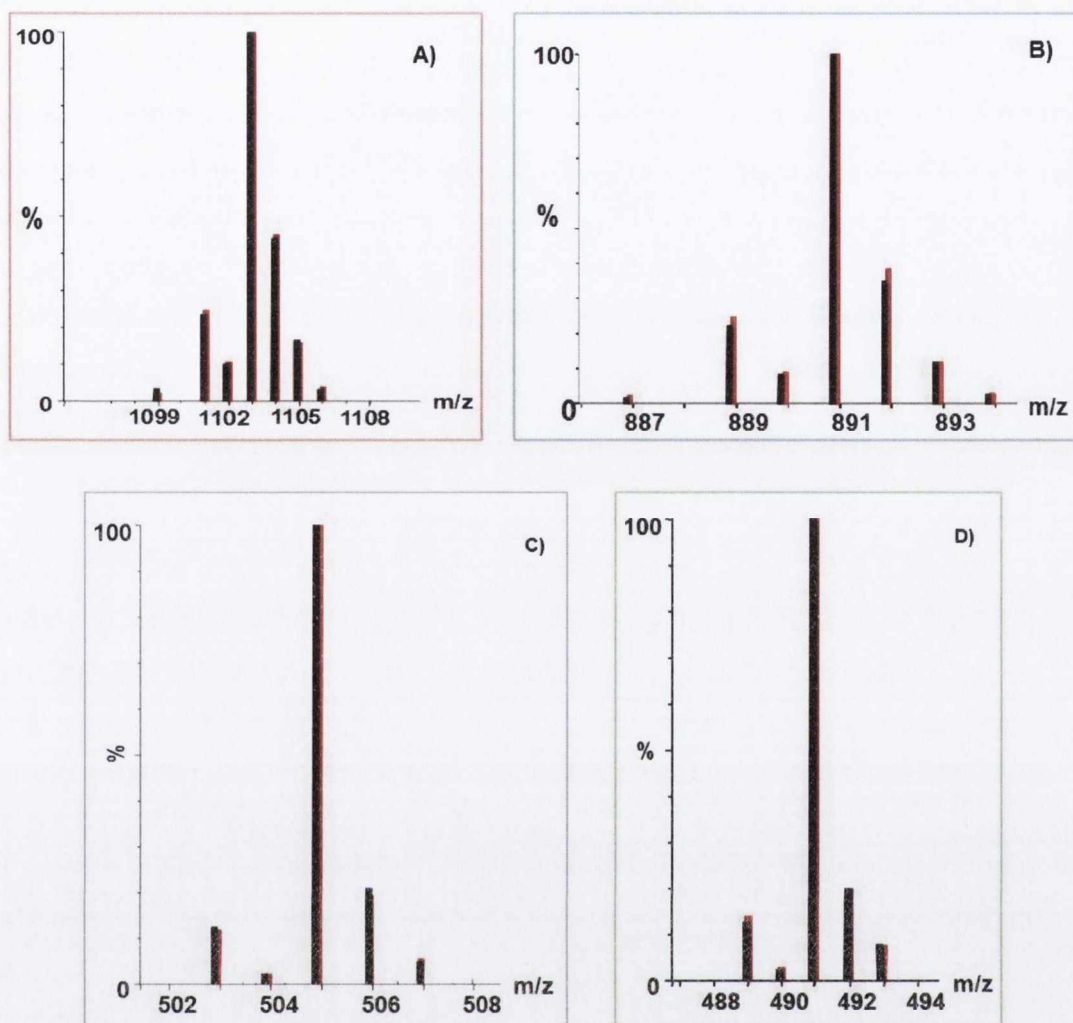


Figure 2.13: Comparison of the experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for A) $\{H_2[Fe_4(\mu-O)(\mu-OH)(hpdta)(hpdta-O)(O_2CNHC_2H_4NH_3)_2] \cdot H_2O\}$, centered at $m/z = 1103.0$, B) $[Fe_4(\mu-O)(\mu-OH)(hpdta)_2]$, centered at $m/z = 890.8$, C) $\{H_3[Fe_2(\mu-O)(\mu-OH)(hpdta-O)_2] \cdot 4H_2O\}$, centered at $m/z = 505.0$ and D) $\{H_3[Fe_2(\mu-O)(\mu-OH)(hpdta-COO)] \cdot 4H_2O\}$ centered at $m/z = 491.0$ (cone voltage: 30 V).

All three compounds crystallised successfully from the reaction mixtures and infrared analyses and P-XRD experiments confirmed the identity of **1b**, **2b** and **3** as $(enH)[Fe_4(\mu-O)(\mu-OH)(hpdta)_2(H_2O)_4] \cdot nH_2O$, $(enH_2)_{1.5}[Fe_4(\mu-O)(\mu-OH)_3(hpdta)_2] \cdot nH_2O$ and $(enH)[Fe_4(\mu-O)(\mu-OH)(hpdta)_2(O_2CNHC_2H_4NH_3)_2] \cdot 6.5H_2O$ respectively.

In order to further probe the system we decided to dissolve 20 mg of **1b**, **2b** and **3** in 1.5 ml of deionised water. Although these compounds were known to crystallise from reaction systems at different pH values we intended to see if they retained their integrity,

when dissolved in water at ca. pH=7.0. Interestingly and in-line with the previous studies, we found that the compounds did not appear to be stable in this solution.

The characteristic signal at $m/z = 1103.0$ disappeared from the spectra of **3**. While the signals at $m/z = 504.9$ and $m/z = 491.0$ disappeared from the spectra of compound **1b** and compound **3**. Despite this apparent instability the signals at $m/z = 890.0$ and $m/z = 443.8$ could still be identified in the spectra of all three compounds which suggests that the core tetranuclear compound remained intact notwithstanding the apparent decomposition of the characteristic carbamate moieties from the parent compounds. Upon further inspection it was revealed that the spectra for the compounds were essentially identical to the spectra recorded for the reaction mixture at pH 7.0 that gave rise to the precipitation of **2b** (observed in Figure 2.12B).

Motivated by this result we decided to dissolve compound **1b** and **3** in pH-adjusted solutions. Although the tetranuclear core structure appeared to be inherently stable under conditions that led to their formation, distinguishing features of the parent compounds **1b** and **3** were not observed in solution at pH 7.0. Therefore, the aim of these experiments was to investigate how the pH of solutions can influence the structural integrity of the compounds. In order to investigate this we dissolved **1b** and **3** in solutions that resembled their pH values at crystallising conditions and utilised ESI-MS to probe the effect that these solutions imposed on the structures of the compounds. **3** was dissolved in a 0.2 mM aqueous ethylenediamine solution (pH 8.5) and **1b** was dissolved in a 0.8 mM aqueous sulphuric acid solution (pH 4.5). The spectra resembled that of the reaction mixtures at pH 4.5 and pH 8.5 post exposure to the atmosphere respectively. The signal at $m/z = 1103.0$ indicates the presence of **3** while the signals at $m/z = 504.9$ and $m/z = 491.0$ indicates the presence of the square planar compound **1b**. The latter two signals were also observed in the spectra of **3** as previously seen in the reaction mixture at pH 8.5. This suggests that both **1b** and **3** remain intact under the appropriate pH conditions. Furthermore, it suggested that the tetranuclear compounds undergo core-rearrangements and interconvert upon pH adjustment into each other.

The peaks at $m/z = 504.9$ and $m/z = 491.0$ in the spectra recorded for compounds **1a**, **1b** and **3** are important peaks. They disappear from the spectra upon crystallisation of the respective compounds and they clearly identifiable when the experimental conditions are changed. Their characteristic isotopic envelopes match precisely the simulated patterns of dinuclear species, as detailed in Figure 2.13. However, one could propose two potential origins of the dinuclear species. Their presence may be a product of the

analysis whereby electrospray ionisation induces fragmentation of the square planar tetranuclear core of **1a**, **1b** and **3** within the sampling chamber. Alternatively the tetranuclear complexes may have reacted into the dinuclear species upon dissolution prior to the analyses, thus rendering their hydrolytic instability in solution. Experiments revealed a correlation between the intensity and position of the peaks, observed at $m/z = 491.0$ and $m/z = 504.9$ and the applied a cone voltage which we varied between 10 V and 150 V. This experimental observation strongly suggests that the dinuclear species were a result of ion-induced fragmentation of the square planar tetranuclear core in compounds **1a**, **1b** and **3** rather than their instability in solution. To investigate this further time-dependent ESI-MS analysis were carried out. For this purpose the compounds were dissolved in pH adjusted solution and the ESI-MS spectra of the solutions were recorded immediately and at hourly intervals. The spectra remained unchanged over 12 hours thus further suggesting that the signals result from fragmentation products of **3** during the ionisation process. The spectra re-recorded after 24 and 48 hours revealed similar results, Figure 2.14. This was further confirmed when **1b** and **3** were successfully recrystallized from the respective aqueous pH adjusted reaction mixtures.

Table 2.8: ESI-MS⁻ assignment for the signals in the reaction mixtures that led to the crystallisation of 1, 2 and 3.

m/z	Compound	Attributed Species
890.8	1a, 1b, 2a, 2b & 3	$[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt}\text{a})_2]^-$
505.0	1a, 1b & 3	$\{\text{H}_3[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdt}\text{a-2O})\cdot 4\text{H}_2\text{O}]\}^-$
491.0	1a, 1b & 3	$\{\text{H}_3[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdt}\text{a-COO})\cdot 4\text{H}_2\text{O}]\}^-$
1103.0	3	$\{\text{H}_2[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt}\text{a})(\text{hpdt}\text{a-O})(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]\cdot \text{H}_2\text{O}\}^-$

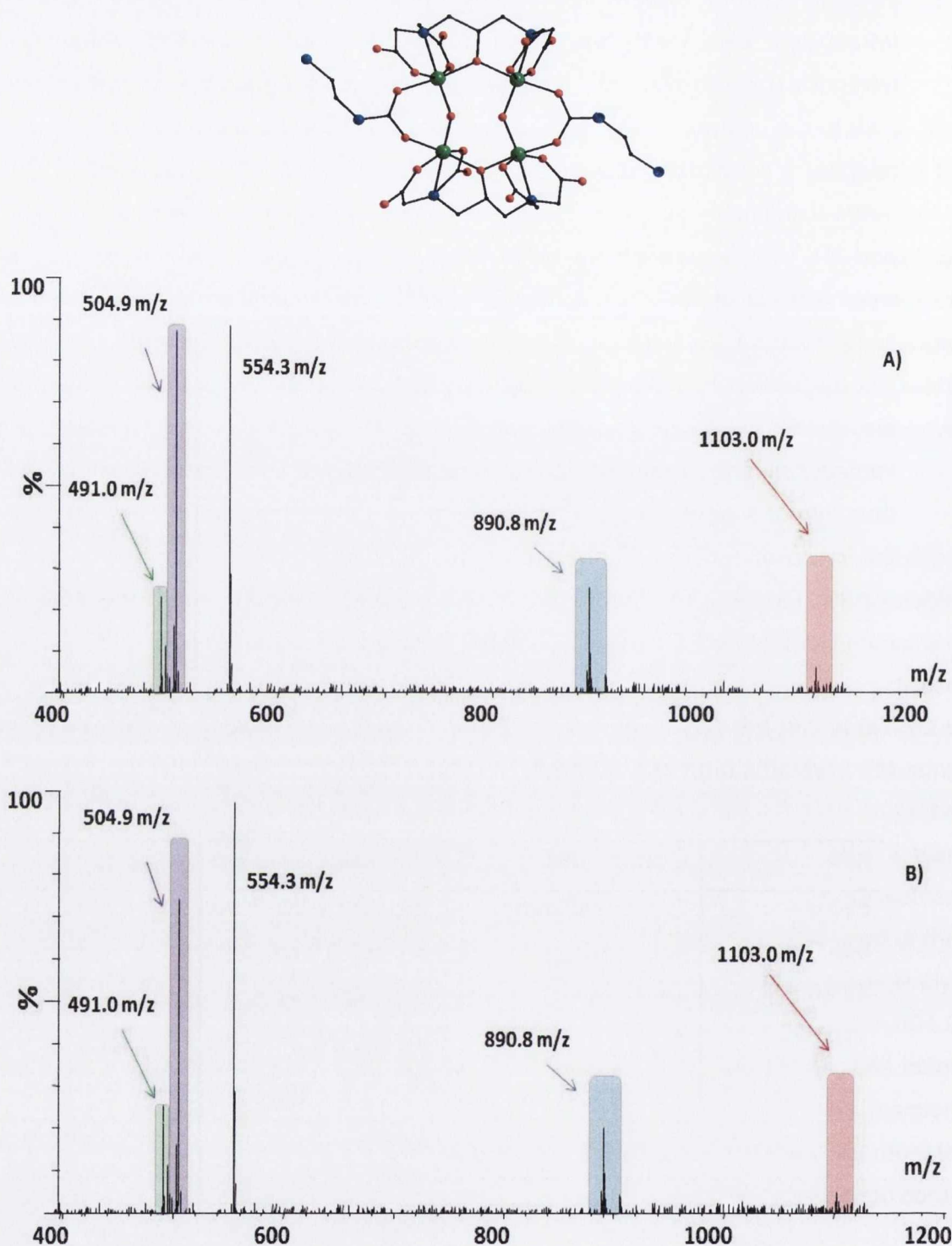
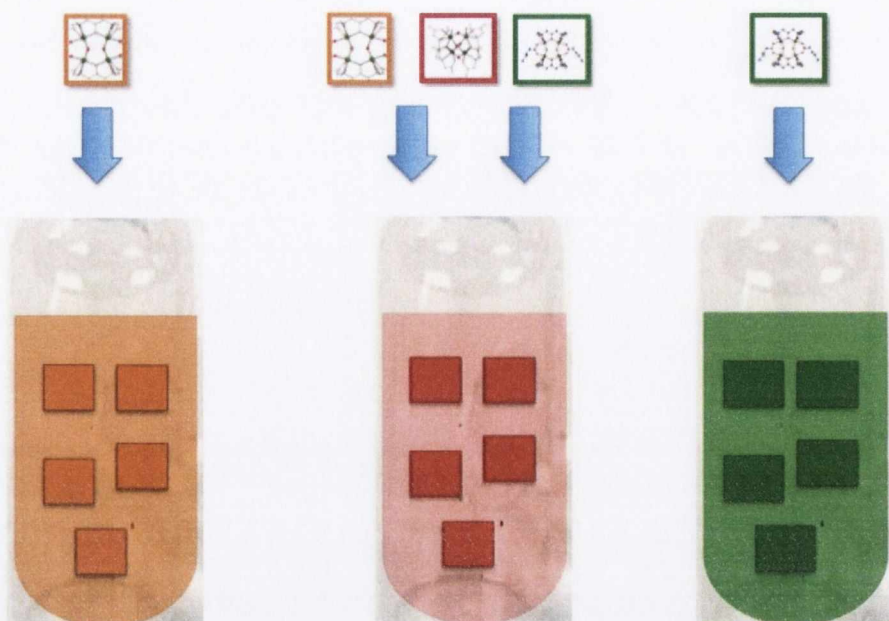


Figure 2.14: Negative-mode ESI-MS spectra for A) a fresh sample of compound 3 dissolved in aqueous ethylenediamine solution at pH 8.5. B) sample 48 hours post dissolution (cone voltage: 30 V).

A) Orange = Compound 1a or 1b, Red = compound 2a or 2b, Green = Compound 3

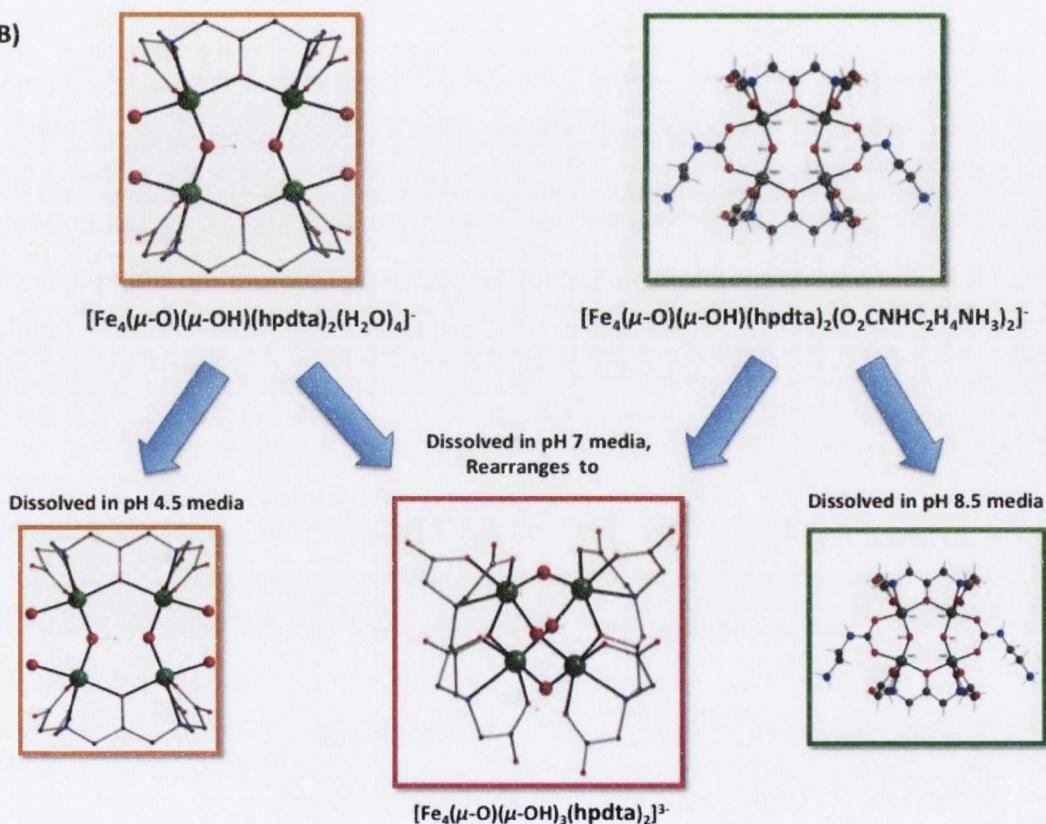


Dissolved in pH 4.5 media

Dissolved in pH 7.0 media

Dissolved in pH 8.5 media

B)



The compounds' structural integrity is retained when dissolved in appropriate pH adjusted media

Figure 2.15: A) and B) Schemes that illustrate that the compounds 1-3, orange, red and green frames, respectively, retain their structures upon dissolution in aqueous solution of appropriate pH values (matching frames), while dissolution of compounds 1 or 3 into media of pH 7.0 cause structural rearrangement to 2.

2.3.3 UV-Vis spectroscopy

The UV-Vis spectra for **1**, **2**, and **3** were recorded at concentrations of 87.5 μM using a quartz cell with 2 mm path length. The samples were dissolved in pH-adjusted media, pH 4.5, 7.0 and 8.5 respectively, in order to retain their structural integrity, as, as discussed in Section 2.3.2 the compounds were found to structurally interconvert upon pH variation. In order to examine absorbance in the charge transfer region, below 300 nm, a 2 mm cell was used. The use of a cell with larger path length or a higher concentrated solution yielded intense absorptions above 400 nm and obscured the signals observed in Figure 2.16.

The UV-Vis absorption spectra of **1a** recorded in a 0.8 mM aqueous solution of sulphuric acid (pH 4.5), displays two overlapping charge transfer absorption bands at 200 nm ($36,065 \text{ L mol}^{-1}\text{cm}^{-1}$) and 230 nm ($32,938 \text{ L mol}^{-1}\text{cm}^{-1}$) as shown in the Figure 2.8 below.¹⁵⁸ The UV-Vis absorption spectra for **2a**, recorded in deionised water at pH 7.0, displays a charge transfer absorption band at 230 nm ($41,042 \text{ L mol}^{-1}\text{cm}^{-1}$), Figure 2.16.¹⁵⁸

The UV-Vis absorption spectra for **3**, recorded in a 0.2 mM aqueous solution of ethylenediamine, display a strong charge transfer absorption band at 225 nm ($34,212 \text{ L mol}^{-1}\text{cm}^{-1}$) and two slightly obscured shoulders that result from charge transfer absorption at 305 nm ($13,162 \text{ L mol}^{-1}\text{cm}^{-1}$) and 365 nm ($6,000 \text{ L mol}^{-1}\text{cm}^{-1}$) Figure 2.17.¹⁵⁸ The two later bands, although they have high extinction coefficients, are difficult to observe. This was to be expected as the intensity of absorption was directly affected by the decreased path length of the 2mm cell we used to measure the sample (2mm vs 1cm).

The d-d transition for **3**, at ca. 475 nm ($443 \text{ L mol}^{-1}\text{cm}^{-1}$), was observed when a 0.5 mM solution of $(\text{enH})[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2] \cdot 6.5\text{H}_2\text{O}$ was dissolved in a $2 \times 10^{-1} \text{ mM}$ aqueous solution of ethylenediamine, and measured using a 1 cm cell. The observation is consistent with literature values for d-d transitions for similar Fe^{III} compounds.¹⁵⁹ The transition was not observed when $\text{NH}_4[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{H}_2\text{O})_4] \cdot 12.5\text{H}_2\text{O}$ and $(\text{pipH}_2)_{1.5}[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})_3(\text{hpdt})_2] \cdot 6\text{H}_2\text{O}$ were analysed under similar experimental conditions.

The spectra for all three compounds were re-measured after two weeks (dashed lines in figures) and only slight changes in the absorbance were observed which indicated that the compounds are stable in solution over two weeks. These results corroborate the observations in the ESI-MS and NMR studies discussed above. These analyses further

confirm that compounds **1a**, **2a** and **3** retain their integrity in solution and are stable over a period of two weeks. They are also in line with the recent literature reports, suggesting that $[\text{Fe}_4(\mu\text{-OH})_2(\text{hpdta})_2(\text{H}_2\text{O})_4]^0$, the protonated form of the $\text{NH}_4[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4] \cdot 12.5\text{H}_2\text{O}$ compound, is stable in solution.¹⁶⁰

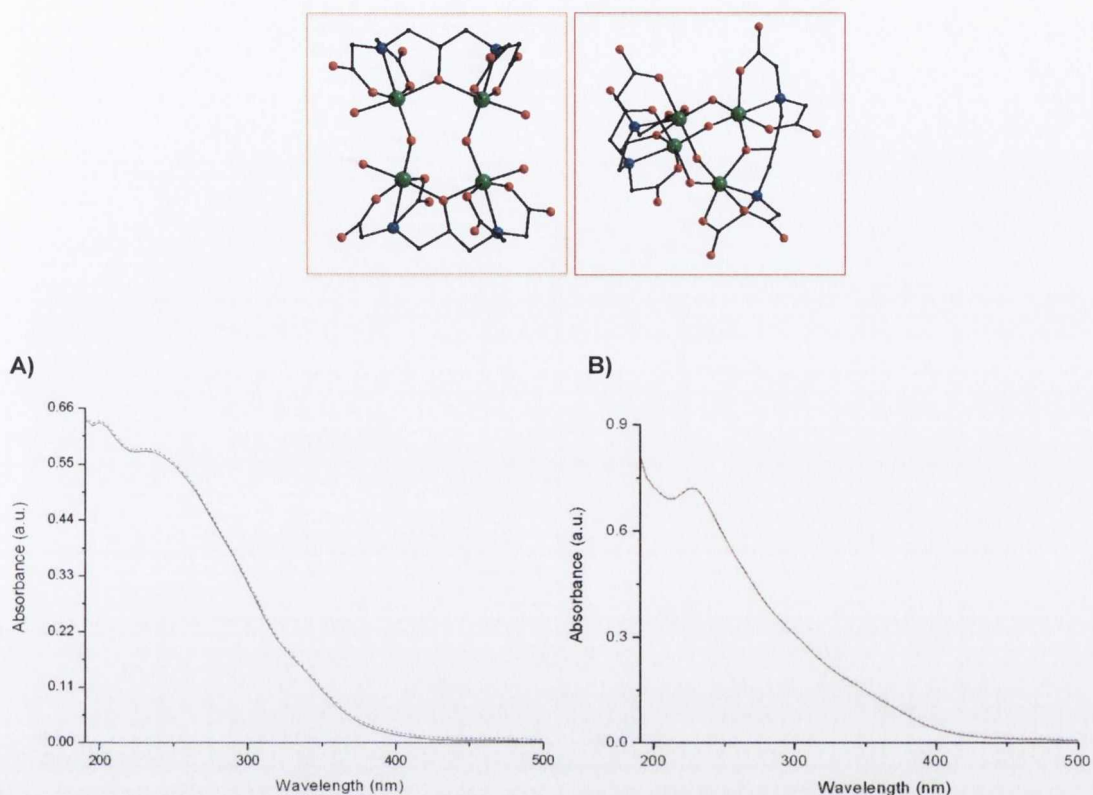


Figure 2.16: UV-Vis absorption spectra for A) a 87.5 μM solution of **1a** dissolved in an 8×10^{-1} mM aqueous solution of sulphuric acid (pH 4.5), measured using a quartz cuvette with 2 mm path length. B) a 87.5 μM aqueous solution of **2a** (pH 7.0), measured using a quartz cuvette with 2 mm path length. The structures of tetranuclear complexes in **1a** and **1b** are displayed in orange and red frames. Colour Code: C black, Fe green, H white, N blue, O red.

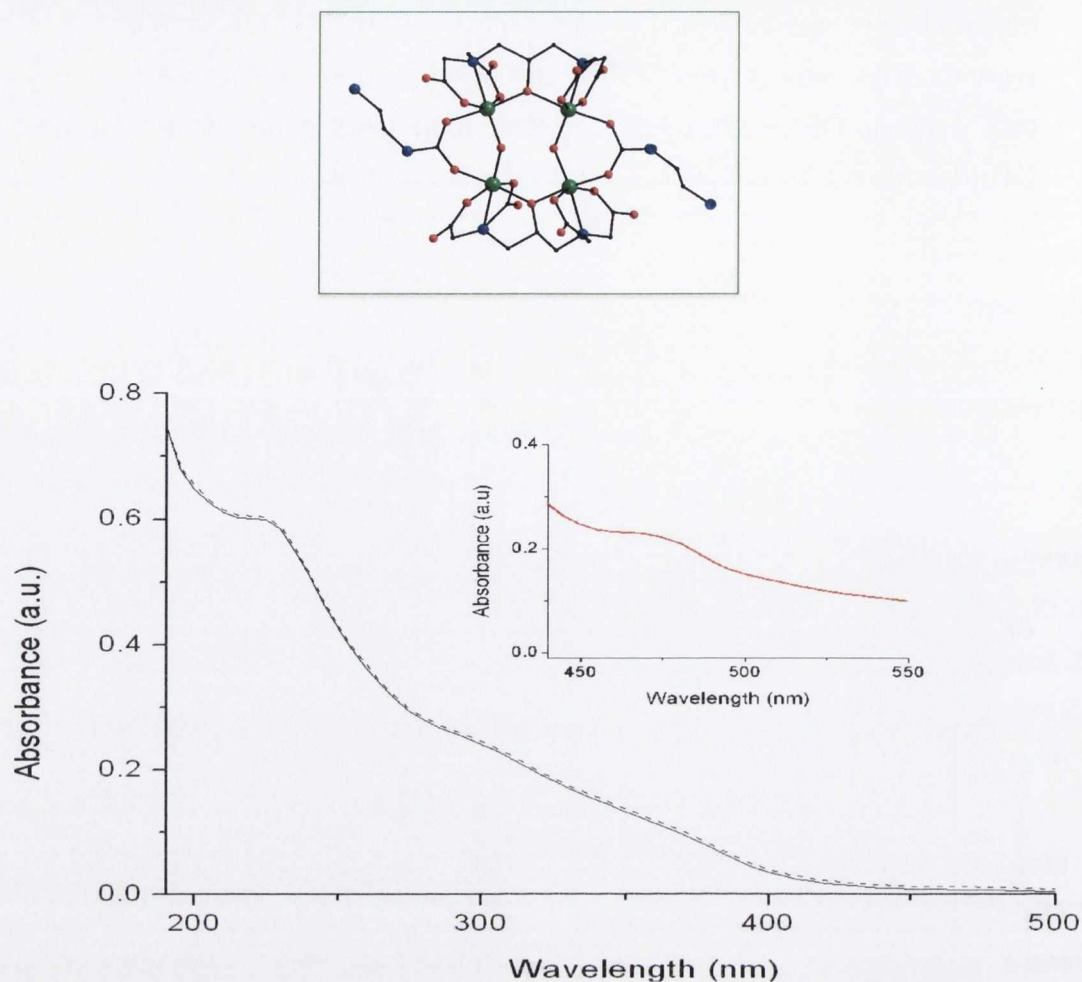


Figure 2.17: UV-Vis absorption spectra for a 87.5 μM solution 3 dissolved in a 1.5 mM aqueous ethylenediamine solution (pH 8.5), measured using a quartz cuvette (path length = 2 mm) fresh = solid line and 2 weeks old sample = dashed line. Inset = UV-Vis spectrum of a 0.5 mM solution of compound 3 measured using a quartz cell with 1 cm path length. Green frame = The tetranuclear complex in 3. Colour Code: C black, Fe green, H white, N blue, O red.

Table 2.9: Compounds 1, 2 and 3 (concentration = 87.5 μM) dissolved in a 0.8 mM aqueous solution of sulphuric acid, deionised water and 0.5 mM aqueous ethylenediamine solution respectively.

λ max (nm)	ϵ ($\text{L mol}^{-1}\text{cm}^{-1}$)	compound	transition
200	36,065	1a	charge transfer
230	32,938	1a	charge transfer
230	41,042	2a	charge transfer
225	34,212	3	charge transfer
305	13,162	3	charge transfer
365	6000	3	charge transfer
475	443*	3*	d-d transition

Chapter 3 Reactivity and Complexity in the *hpdt*a System

3.1 Introduction

The research in this chapter focuses on the synthesis and structural characterisation of novel coordination compounds based on the aqueous *hpdt*a system. It was our objective to gain a greater understanding of the coordination modes of the *hpdt*a ligand and investigate the self-assembly of Ni^{II} and V^{IV} *hpdt*a based coordination compounds. These objectives were fulfilled through successive variation of the reaction conditions that habitually lead to the formation of tetranuclear M^{III} *hpdt*a extended hybrid compounds similar to those examined in Chapter 2.

3.2 $(\text{NH}_3\text{C}_3\text{H}_6\text{NH}_3)_{0.5}\text{K}[\text{Fe}_2(\text{hpdt}a)(\text{H}_2\text{hpdt}a)] \cdot 4\text{H}_2\text{O} \cdot \text{NH}_2\text{C}_3\text{H}_6\text{NH}_2$ (**8**)

The dinuclear, Fe^{III} complex in $(\text{propylenediamineH}_2)_{0.5}\text{K}[\text{Fe}_2(\text{hpdt}a)(\text{H}_2\text{hpdt}a)] \cdot 4\text{H}_2\text{O} \cdot \text{NH}_2\text{C}_3\text{H}_6\text{NH}_2$ (**8**) is a hydrolytic side product that forms upon reacting an aqueous Fe^{III} solution with excess of $\text{H}_5\text{hpdt}a$ when the pH is adjusted to 8.0 using a propylenediamine/potassium hydroxide mixture. Light green, square shaped, crystals of **8** suitable for single-crystal X-ray diffraction experiments were obtained by co-evaporation with dimethylacetamide (Scheme 3.1). The compound crystallizes in the monoclinic space group $C2/c$ (*no.* 15). Figure 3.1 shows the structure of the dinuclear complex in **8**.

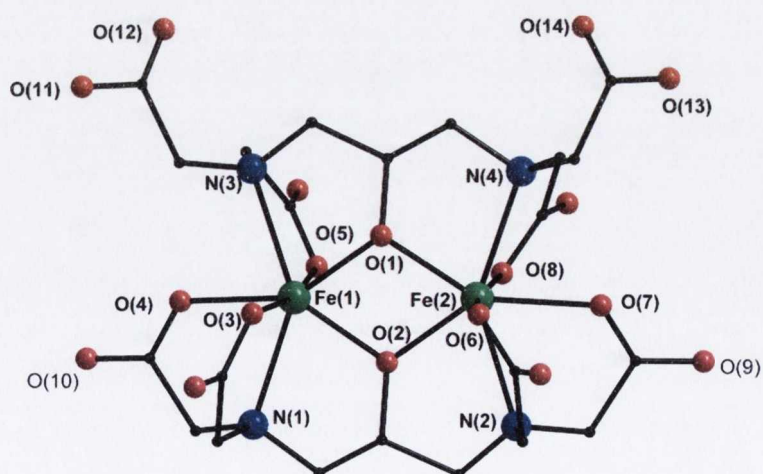
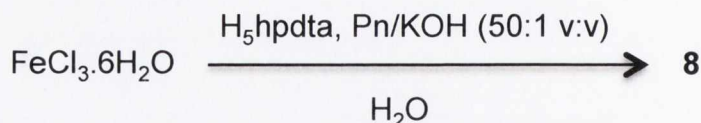


Figure 3.1: The structure of the dinuclear complex in **8**. The hydrogen atoms are omitted for clarity. Colour code: C black, Fe green, N blue, O red.



Scheme 3.1: Formation of **8**

3.2.1 Structural characterisation of **8**

The compound, which is fully represented in the asymmetric unit of the crystal structure, consists of two pentagonal-bipyramidally coordinated Fe^{III} centres stabilized by two *hpdta* ligands, a potassium counter ion that binds to two carboxylate O- donor atoms of the organic ligand, Figure 3.3, and a constitutional water molecule. It is worth noting that the two coordinating *hpdta* ligands are not identical, one *hpdta* ligand contains two protonated carboxylate moieties whilst the four carboxylate arms located on the second *hpdta* ligand are fully deprotonated. Thus all deprotonated carboxylate moieties bind to Fe^{III} centres. There are four further constitutional water molecules, a constitutional propylenediamine molecule and half of a propylene-diammonium ion present in **8**.

The two Fe centres, Fe(1) and Fe(2), are bridged by the deprotonated hydroxyl atoms O(1) and O(2) from each of the two aminocarboxylic acid ligands. The distance of 3.304(5) Å between Fe(1) and Fe(2) is consistent with the literature values for similarly coordinated Fe^{III} centres.³ Fe(1) is coordinated by the μ_2 -bridging alkoxy oxygen atoms O(1), O(2), the N-donor atoms N(1), N(3) and the carboxylate oxygen atom O(4), located on the two *hpdta* ligands, to form a distorted pentagonal plane to give $\text{Fe}^{\text{III}}\text{-O}$ and $\text{Fe}^{\text{III}}\text{-N}$ bond distances of between 1.976(9) Å and 2.132(10) Å and 2.357(23) Å and 2.395(17) Å, respectively. The coordination environment is completed by two *trans* coordinating O-donors in the apical positions, O(3) and O(5), which originate from the deprotonated carboxylic acid functionalities of the two *hpdta* ligands. The bond distances between the Fe^{III} ion and the binding carboxylate O-donors are 1.976(9) Å and 1.977(12) Å, respectively. Fe(2) is coordinated by the alkoxy atoms O(1), O(2) the N-donor atoms N(2), N(4) and $\text{O}_{\text{carboxylate}}$ atom O(7) of two *hpdta* ligands, to form the distorted pentagonal plane with $\text{Fe}^{\text{III}}\text{-O}$ and $\text{Fe}^{\text{III}}\text{-N}$ bond distances ranging from 1.972(13) Å to 2.195(19) Å and from 2.358(31) Å to 2.381(14) Å, respectively. Similar to Fe(1) the coordination environment is completed by two *trans* coordinating O-donors in the apical positions, O(6) and O(8), which originate from the deprotonated carboxylic acid functionalities of

the two *hpdta* ligands. The bond distances between the Fe^{III} ion and binding O_{carboxylate} donors are 1.983(22) Å and 1.972(13) Å, respectively.

Table 3.1: Selected bond distances for the Fe^{III} and K^I centres in 8.

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1) – O(1)	2.033(8)
	Fe(1) – O(2)	2.009(12)
	Fe(1) – N(1)	2.357(23)
	Fe(1) – O(3)	1.976(9)
	Fe(1) – O(4)	2.132(10)
	Fe(1) – N(3)	2.395(17)
	Fe(1) – O(5)	1.977(12)
Fe(2)	Fe(2) – O(1)	2.009(6)
	Fe(2) – O(2)	2.027(10)
	Fe(2) – N(2)	2.358(31)
	Fe(2) – O(6)	1.983(22)
	Fe(2) – O(7)	2.195(19)
	Fe(2) – N(4)	2.381(14)
	Fe(2) – O(8)	1.972(13)
K(1)	K(1) – O(5)	2.717(26)
	K(1) – O(8)	2.754(33)
	K(1) – O(9')	2.730(21)
	K(1) – O(1W)	2.720(17)
	K(1) – O(10')	2.695(5)

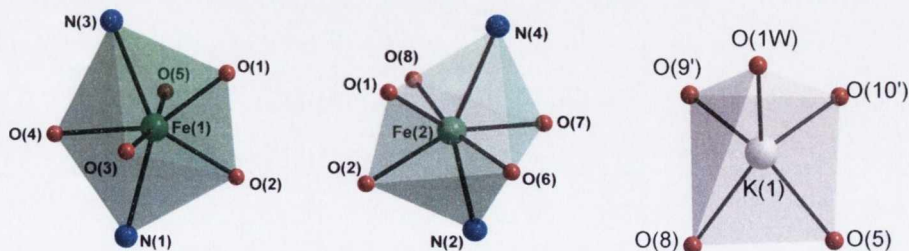


Figure 3.2: Polyhedral representations of the Fe^{III} and K^I centres in 8. The hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, K grey, N blue, O red.

The distortion within the pentagonal-bipyramidal geometry can be emphasized through examination of the bond angles between the Fe atoms and their *cis* and *trans* coordinating ligands. Taking Fe(1) as an example, the bond angles O(1)-Fe(1)-O(2), O(2)-Fe(1)-N(1), N(1)-Fe(1)-O(4), O(4)-Fe(1)-N(3) and N(3)-Fe(1)-O(1) of 68.98(14)°, 73.54(14)°, 70.39(14)°, 74.14(14)° and 74.67(13)° respectively, deviate from the ideal 72° bond angle. Similarly, the bond angles between the atoms in apical positions and atoms in the pentagonal plane highlight the distortion from the ideal geometry. These range between 78.35(14)° and 105.97(12)° varying significantly from the ideal bond angle of 90°.

Table 3.2: Selected bond angles for 8.

	Bond Angle (°)		Bond Angle (°)
O(1)-Fe(1)-O(3)	91.63(13)	N(4)-Fe(2)-O(2)	143.23(14)
O(2)-Fe(1)-O(3)	99.71(15)	N(4)-Fe(2)-O(1)	75.67(13)
O(3)-Fe(1)-O(4)	87.33(15)	N(4)-Fe(2)-O(8)	78.16(14)
O(3)-Fe(1)-N(3)	92.46(14)	O(7)-Fe(2)-O(6)	84.17(14)
N(3)-Fe(1)-O(5)	77.22(14)	O(8)-Fe(2)-O(1)	94.01(13)
O(5)-Fe(1)-O(1)	92.04(13)	O(2)-Fe(2)-N(2)	73.20(14)
N(1)-Fe(1)-O(4)	70.39(14)	O(8)-Fe(2)-O(2)	91.02(14)
N(1)-Fe(1)-O(3)	78.35(14)	O(8)-Fe(2)-O(7)	82.15(14)
O(3)-Fe(1)-N(1)	78.35(14)	O(1)-Fe(2)-O(6)	94.91(14)
O(5)-Fe(1)-N(1)	105.97(14)	O(1)W-K(1)-O(10')	90.88(13)
O(1)-Fe(1)-O(2)	68.98(14)	O(1)W-K(1)-O(5)	133.36(13)
O(2)-Fe(1)-N(1)	73.54(14)	O(1)W-K(1)-O(8)	132.97(13)
O(4)-Fe(1)-N(3)	74.14(14)	O(1)W-K(1)-O(9')	90.88(13)
N(3)-Fe(1)-O(1)	74.67(13)	O(9')-K(1)-O(10')	81.21(11)
N(4)-Fe(2)-O(6)	92.65(14)	O(8)-K(1)-O(10')	134.58(11)
N(4)-Fe(2)-N(2)	143.18(13)	O(5)-K(1)-O(9')	132.54(11)

The Fe^{III}-N and Fe^{III}-O bond distances are consistent with literature values confirming that the Fe atoms are, as expected, in a +III oxidation state.^{3, 123, 127} The assignment of

the oxidation state of the Fe atoms is further supported by charge considerations. The compound contains two Fe^{III} ions, one potassium ion and half a protonated propylenediamine molecule contributing to a charge of +8. This positive charge is counter-balanced by the 8 negative charges arising from the two aminocarboxylic acid ligands, to give a neutral compound. The two non-bonding carboxylic acid functionalities of one organic ligand remain protonated.

The potassium counterion mediates between the dinuclear complexes and interacts with the O-donor atoms of the organic ligand and constitutional water molecules. More specifically it binds to the complex through interactions to the lone pairs of carboxylate oxygen atoms, O(5) and O(8), with short distances of 2.717(18) Å and 2.754(54) Å, respectively. In addition to this, the potassium counter ion binds to O(9') and O(10') from two neighbouring complexes resulting in $\text{K}^{\text{I}}\text{-O}$ bond distances of 2.730(28) Å and 2.695(31) Å, respectively. These relatively strong interactions result in the formation of a one-dimensional polymeric assembly that extends in the direction of the crystallographic *a*-axis. The 1D assembly is characterised by an alternating arrangement of dinuclear complexes as seen in Figure 3.3. The binding geometry of the potassium counterion can be described as a highly distorted trigonal bipyramidal geometry in which the fifth coordination site is occupied by an oxygen from a constitutional water molecule, O(1W).

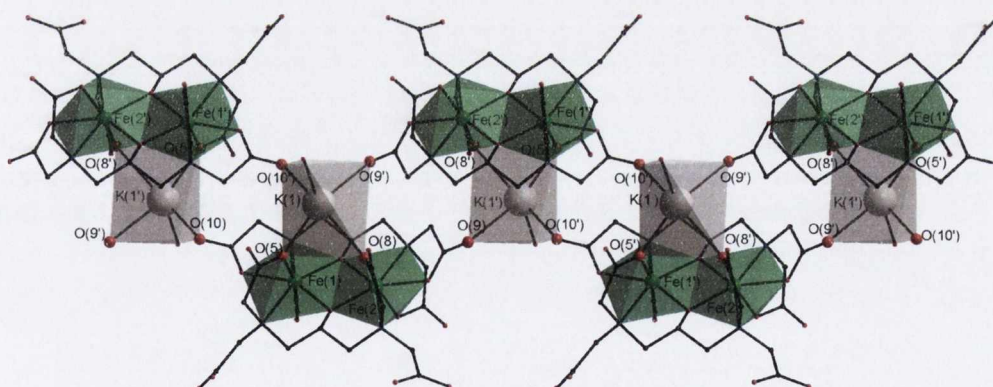


Figure 3.3: The 1D polymeric assembly in **8** that forms through $\text{K}^{\text{I}}\text{-O}$ bonds between complexes and potassium ions. The 1D assembly extends parallel to the crystallographic *a*-axis. Hydrogen atoms, propylenediamine and propylenediammonium ions and constitutional water molecules have been omitted for clarity. Polyhedral representations of the Fe^{III} and K^{I} centres in **8**. Colour Code: C black, Fe green, K grey, N blue, O red.

The structure is further stabilised in the solid state by van der Waal interactions between the organic moieties and weak H-bonds involving the non-coordinating carboxylate arms of the hpdta ligand, ammonium ions and the constitutional solvent molecules (water and amines), resulting in a lamellar structure with alternating inorganic and organic areas. Each inorganic layer has a cross-sectional thickness of *ca.* 12.17(11) Å in the [100] direction and the distance between the Fe^{III} centres in this direction is *ca.* 9.69(14) Å, Figure 3.4.

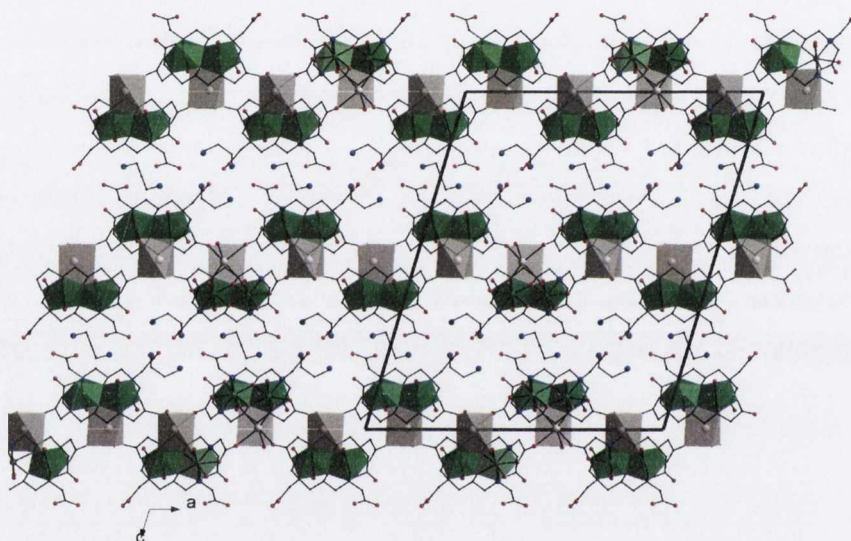


Figure 3.4: Packing structure of **8** displaying the 1D polymeric assemblies, viewed in the direction of the crystallographic *b*-axis. Polyhedral representations of the Fe^{III} and K^I centres in **8**. Hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, K grey, N blue, O red.

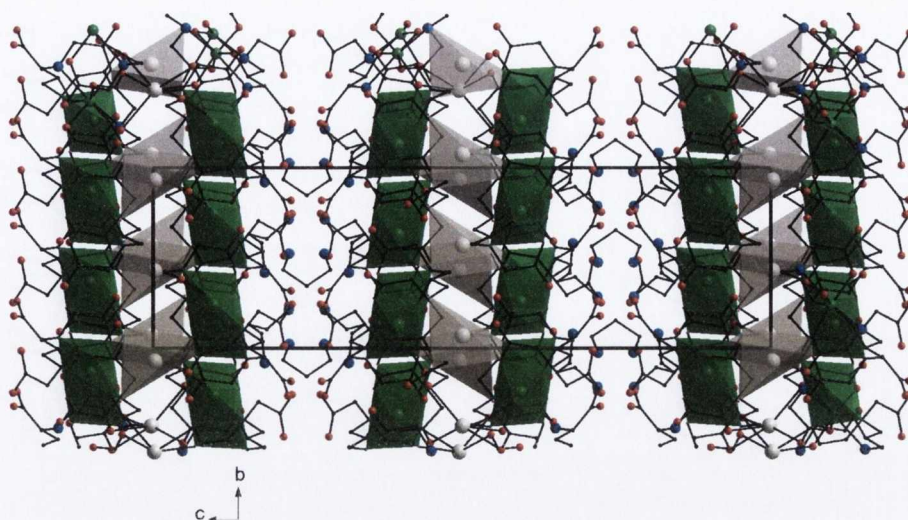


Figure 3.5: Packing diagram of 8 displaying the 1D polymeric assemblies that pack to form a lamellar structure, viewed along the crystallographic *a*-axis. Polyhedral representations of the Fe^{III} and K⁺ centres in 8. Hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, K grey, N blue, O red.

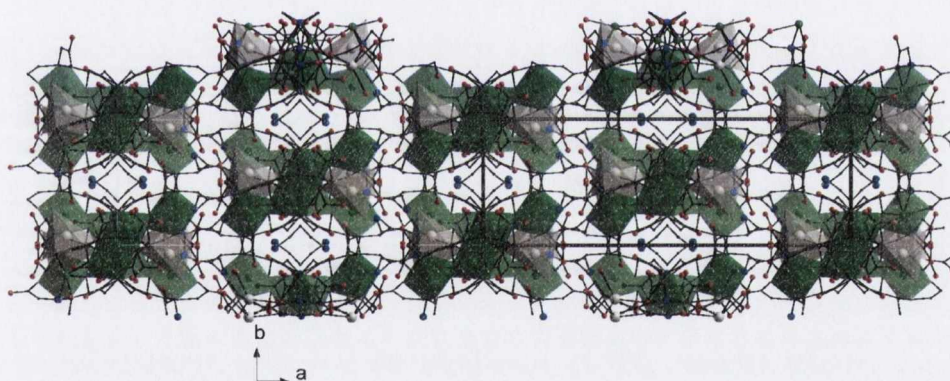


Figure 3.6: Packing structure of 8 viewed in the direction of the crystallographic *c*-axis. Polyhedral representations of the Fe^{III} and Na⁺ centres. Hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, K grey, N blue, O red.

The crystal structure refinement of examined single-crystals of **8** converged to give a final *R*₁ value of 5.44%, a goodness of fit of 1.020, a high data to parameter ratio and acceptable 'largest difference peak and hole' values supporting the provided structural model. The crystal data and structure refinement parameters are summarized in Table 3.3. A structurally related dinuclear Fe^{III}/*hpdta* complex, which crystallises in the triclinic space group *P*-1, had been previously synthesised by Schmitt *et al.*³ In this complex, the binding modes of the *hpdta* ligands is different as each of the two aminocarboxylic acid ligands retains one protonated, non-binding carboxylic acid functionality. Similar

dinuclear V^{III} and Nd^{III} complexes have been reported in the literature.¹⁶¹⁻¹⁶² Considering the formation conditions of the previously reported compounds, it appears that the presence of potassium ions are essential for the formation of **8**.

Table 3.3: Crystal data and structure refinement parameters for **8**

Compound	8
Empirical formula	C _{26.5} H ₅₀ Fe ₂ K ₁ N ₇ O ₂₂
Formula weight	963.50 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c (no.15)
Unit cell dimensions	a = 27.612(5) Å α = 90°. b = 9.1504(18) Å β = 106.35(3)°. c = 32.795(7) Å γ = 90°.
Volume	7951(3) Å ³
Z	8
Density (calculated)	1.602 Mg/m ³
Absorption coefficient	0.927 mm ⁻¹
F(000)	3955
Crystal size	0.1 x 0.5 x 0.4 mm ³
θ range for data collection	1.54 to 25.37°.
Index ranges	-33 ≤ h ≤ 32, -10 ≤ k ≤ 10, -39 ≤ l ≤ 39
Reflections collected	41846
Independent reflections	7257 [R(int) = 0.0620] on F ²
Completeness to θ = 25.37°	99.5 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	7257 / 0 / 528
Goodness-of-fit on F ²	1.020
Final R indices[I > 2σ(I)]	R1 = 0.0544, wR2 = 0.1356
R indices (all data)	R1 = 0.0720, wR2 = 0.1451
Largest diff. peak and hole	1.427 and -0.648 e.Å ⁻³

3.2.2 Physicochemical characterisation of **8**

FT-IR spectroscopy

The FT-IR spectrum for this compound (seen in Figure 3.7) exhibits the characteristic stretches for this dinuclear Fe^{III} compound that is stabilised by two iminodiacetic acid based ligands. For example a broad stretch between 3300 cm^{-1} and 2500 cm^{-1} , can be attributed to the protonated, unbound, carboxylic acid functionalities of the poly aminocarboxylic acid ligands that are engaged in H-bonds. The O-H stretches of constitutional water molecules. Alkyl C-H stretches occur below 3000 cm^{-1} . The strong asymmetric C-O stretch is observed at *ca.* 1590 cm^{-1} . The symmetric carboxylate stretches appear at *ca.* 1380 cm^{-1} .^{136 137 138} The C-N stretches occur at *ca.* 1360 cm^{-1} and *ca.* 1305 cm^{-1} and appear as two signals due to the different binding modes of the protonated and deprotonated carboxylic acid functionalities. The differences in the frequencies of the asymmetric and symmetric stretching of the coordinating carboxylate groups ($\Delta\nu$) may be used to analyse their binding modes.¹⁶³ In the FT-IR spectrum of **8**, one asymmetric C-O stretch occurs at *ca.* 1590 cm^{-1} and one symmetric stretch at *ca.* 1380 cm^{-1} . The absence of multiple asymmetric and symmetric stretches indicates that each of the carboxylate moieties partake in one type of binding to the Fe^{III} centres. The $\Delta\nu$ for **8** of *ca.* 215 cm^{-1} indicates a unidentate binding mode between the carboxylate functionalities and the Fe^{III} centres. This is consistent with the binding mode observed in the crystal structure of **8** (Figure 3.1).¹⁶³ A broad N-H stretch and an N-H wagging vibration, originating from the ammonium and amine functionalities are observed at *ca.* 3000 cm^{-1} and *ca.* 910 cm^{-1} respectively.¹³⁶⁻¹³⁸

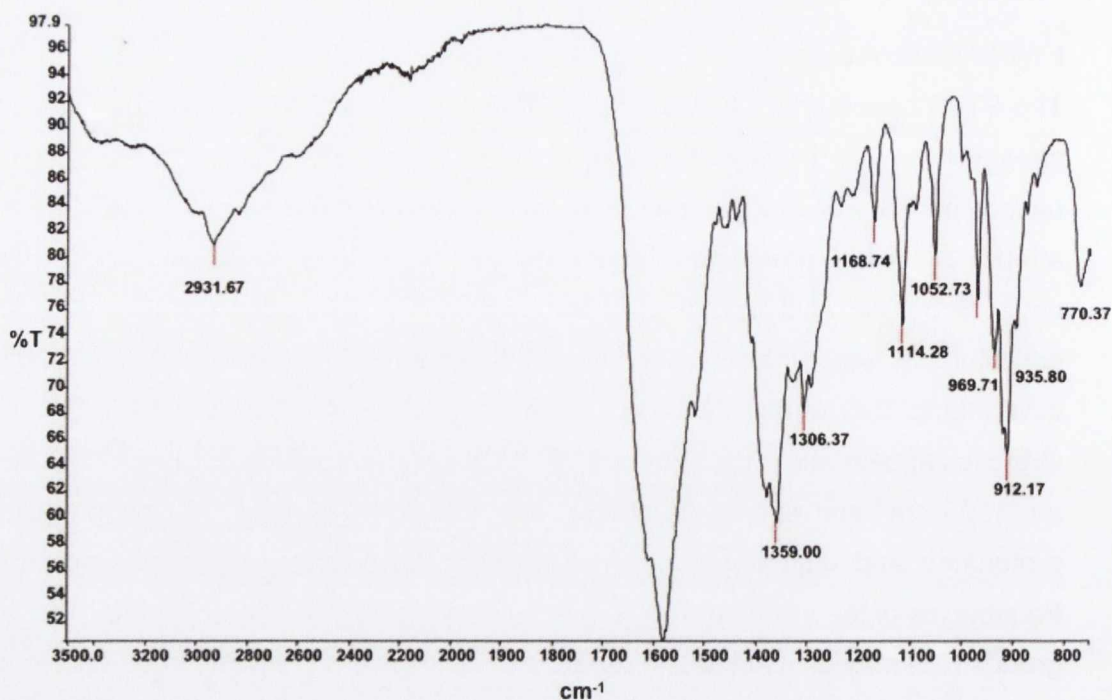


Figure 3.7: FT-IR spectrum of freshly ground microcrystals of **8** recorded using a diffuse reflectance accessory.

Table 3.4: Characteristic vibration bands observed in the FT-IR spectra of **8**.¹³⁶⁻¹³⁸

Wavenumber (cm ⁻¹)	Assignment
3000 (br) (overlapping)	O-H ν_{as} and ν_s stretches, C-H and N-H stretch
2930 (overlapping)	Carboxylic $-O^-$ stretch
1590 (s), 1380 (s)	C-O ν_{as} and ν_s stretches
1360	C-N stretch
1305	COOH stretch
910	N-H wagging (primary amide)

Thermogravimetric analysis

The thermal stability of a freshly prepared, microcrystalline sample of compound **8** was investigated using thermogravimetric analysis (TGA). The analysis was carried out in the temperature range between 35 °C and 900 °C, in an air atmosphere. The heating rate was set to 1 °C/minute. The TGA of **8** reveals a weight loss of 7.37 % in the temperature range between 35-110 °C. This thermogravimetric step can be attributed to the loss of four constitutional water molecules to form the dehydrated form of **8** (experimental weight

loss: 7.37 %, theoretical weight loss: 7.41 %). A further increase in the temperature up to ca. 270 °C produces a weight loss that occurs in a two-step process centered at ca. 230 °C and ca. 260 °C. This weight loss can be associated with the decomposition of the propylene-diammonium counterion and the Pn solvent molecule (experimental weight loss: 11.41 %, theoretical weight loss: 11.55 %). A further increase in the temperature up to ca. 610 °C gives rise to a weight loss that occurs in a two-step process centered at ca. 390 °C and ca. 590 °C. This weight loss can be associated with the loss of the *hpdta* ligands from **8** (experimental weight loss: 53.66 %, theoretical weight loss: 54.81 %). The latter weight loss centered at ca. 590 °C is thought to be associated with the formation of oxides (final experimental weight loss: 72.44 %, final theoretical weight loss: 73.77 %). The theoretical percentage masses of the proposed decomposition products were calculated as a percentage of the mass of $(\text{NH}_3\text{C}_3\text{H}_6\text{NH}_3)_{0.5}\text{K}[\text{Fe}_2(\text{hpdta})(\text{H}_2\text{hpdta})]\cdot 4\text{H}_2\text{O}\cdot \text{NH}_2\text{C}_3\text{H}_6\text{NH}_2$. These are reported in Table 3.5 and are in agreement with the experimentally observed values.

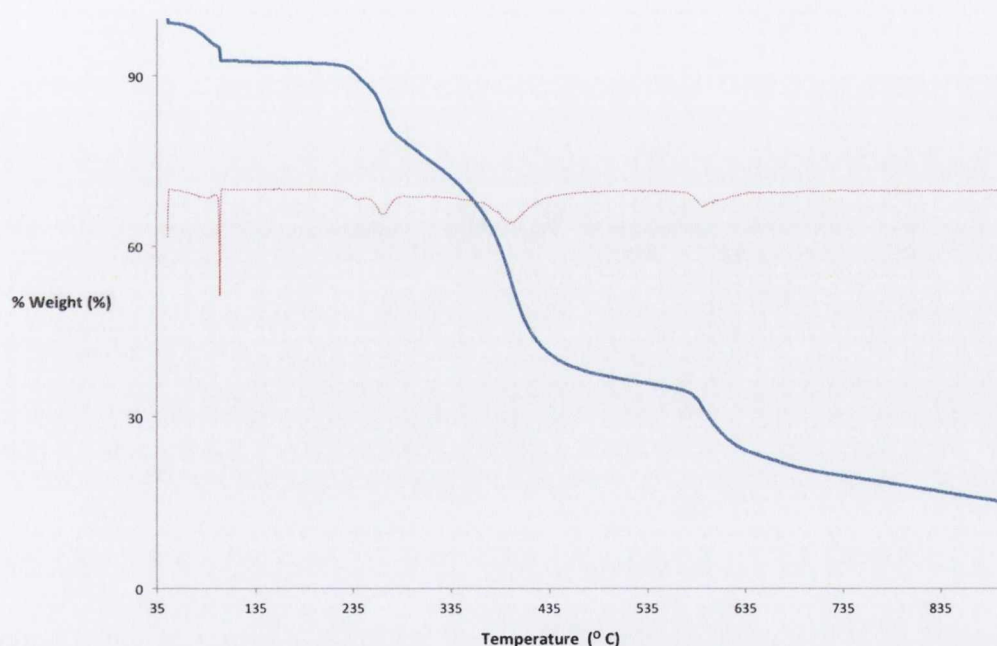


Figure 3.8: TGA curve for **8. Recorded in an air atmosphere from 35 °C to 900 °C. Heating step was set to 1 °C/minute.**

Table 3.5: Results for TGA analyses (recorded in an air atmosphere from 35 °C to 900 °C. Heating step was set to 1 °C/minute) of 8.

Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
$C_{26}H_{58}Fe_2KN_7O_{22}$	100	100	35 (Initial)
$C_{26}H_{50}Fe_2KN_7O_{18}$	92.59	92.63	35 - 110
$C_{22}H_{28}Fe_2KN_4O_{18}$	81.04	81.22	110 - 282
$KO + Fe_2O_3$	26.23	27.56	282 - 900 (Final)

Powder X-ray Diffraction

The phase purity of **8** was confirmed by recording a powder X-ray diffraction (P-XRD) pattern and comparing it to the simulated pattern. The simulated pattern was generated using the solid-state model as determined by the single-crystal X-ray diffraction experiments. The simulated and experimental patterns match, Figure 3.9, thus confirming that the solid-state model is accurate and there were no crystalline impurities within the sample.

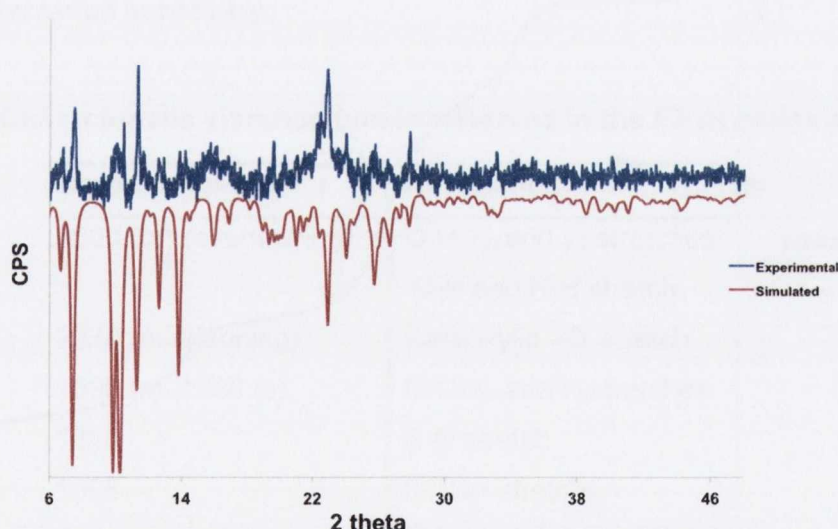


Figure 3.9: P-XRD pattern for crystals of 8 (blue) compared with a simulated pattern based on the single-crystal X-ray diffraction measurements (red).

Elemental Analysis

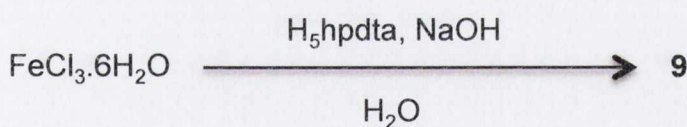
Elemental analysis was employed to further confirm the chemical formula for **8**, $C_{26}H_{44}Fe_2KN_7O_{22}$. The results, presented in Table 3.6, show a correlation between the theoretical and experimental values, thus suggesting that the constitutional assignment is correct.

Table 3.6: Theoretical and experimental elemental analysis for 8. Theoretical based on $C_{26}H_{44}Fe_2KN_7O_{22}$.

Element	Theoretical composition (%)	Experimental composition (%)
C	26.16	26.21
H	4.97	5.01
Fe	12.80	12.73
K	4.48	4.39
N	11.24	11.18

3.2.3 $Na_7[\{Fe_4(\mu-O)(\mu-OH)(hpdta)_2(CO_3)(H_2O)_2\}\{Fe_6(\mu-O)(\mu-OH)_5(hpdta)_3\}]\cdot 4H_2O$ (**9**)

The Fe^{III} complex $Na_7[\{Fe_4(\mu-O)(\mu-OH)(hpdta)_2(CO_3)(H_2O)_2\}\{Fe_6(\mu-O)(\mu-OH)_5(hpdta)_3\}]\cdot 4H_2O$ (**9**), which consists of a hexanuclear Fe^{III} complex and a tetranuclear Fe^{III} complex linked through Na^+-O bonding, is a product that forms when sodium hydroxide is used to adjust the pH of an aqueous $Fe^{III}/hpdta$ solution to 7.0 (Scheme 3.2). Dark green, rectangular crystals of **9** suitable for single-crystal X-ray diffraction experiments were obtained by co-evaporation with dimethylacetamide. The compound crystallizes in the orthorhombic space group $Im2a$. The co-crystallising hexanuclear and tetranuclear complexes in **9** can be seen in Figure 3.10.



Scheme 3.2: preparation of compound 9 (forms after 2 weeks)

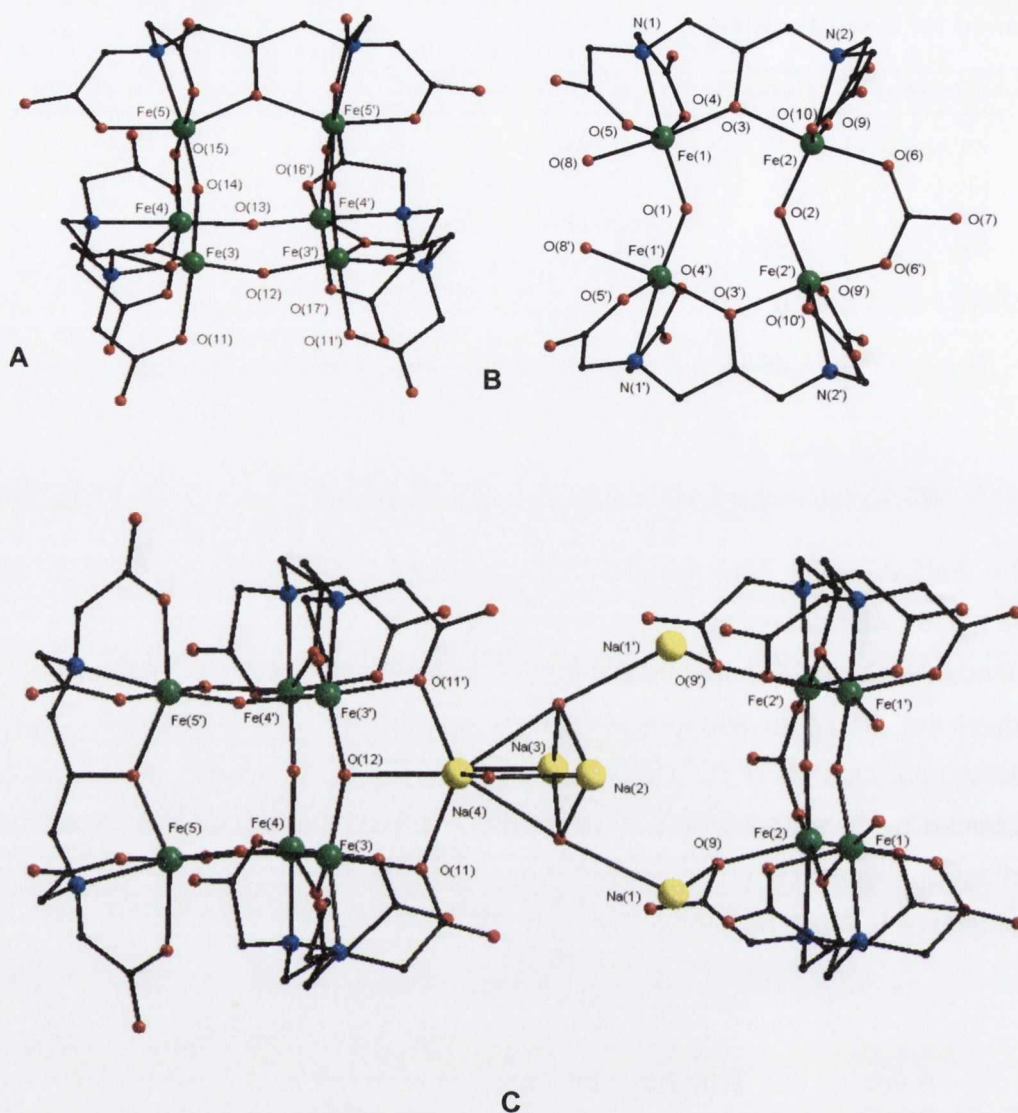


Figure 3.10: A) The hexanuclear complex $[\text{Fe}_6(\mu\text{-O})(\mu\text{-OH})_5(\text{hpdta})_3]^{4-}$ in **9**, B) the tetranuclear complex $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{CO}_3)(\text{H}_2\text{O})_2]^{3-}$ in **9**. C) The two Fe^{III} complexes in **9** linked through $\text{Na}^+\text{-O}$ bonding. Constitutional water molecules and the hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, N blue, Na yellow, O red.

3.2.4 Structural characterisation of **9**

The overall structure of **9** can be described as consisting of tetra- and hexanuclear Fe^{III} complexes linked through a series of $\text{Na}^+\text{-O}$ bonds. The latter bonds involve the sodium ions $\text{Na}(1)\text{-Na}(4)$ and symmetry equivalents, constitutional water molecules, the $\text{O}_{\text{carboxylate}}$ atoms $\text{O}(9)$, $\text{O}(11)$, their symmetry equivalents and an oxygen atom ($\text{O}(12)$) that derives from a bridging hydroxo moiety. An inversion centre is located in the centre of the tetranuclear complex whilst the full hexanuclear oxo-cluster is generated through the symmetry operation of a mirror plane.

The tetranuclear complex within **9** can be described as composed of two symmetry-related dinuclear sub-units, containing one fully deprotonated *hpdta* ligand bound to two Fe^{III} centres, Fe(1), Fe(2) and symmetry equivalents, that are linked by μ_2 -bridging alkoxo O atoms, O(3) and O(3'), of the organic ligands. These dinuclear subunits are further linked *via* a bridging oxo/hydroxo moiety, O(1) and O(2), to form a square planar tetranuclear complex.

The overall hexanuclear complex can be described as composed of three dinuclear subunits, each stabilized by one fully deprotonated *hpdta* ligand that bridges two Fe^{III} centres by μ_2 -bridging alkoxo O atoms, O(22), O(23) and symmetry equivalents. Two of the subunits are linked *via* oxo and hydroxo bridging ligands, O(12) and O(13) to form a square plane containing four octahedrally coordinated Fe^{III} atoms, Fe(3), Fe(4) and symmetry equivalents. The third dinuclear sub unit caps the square Fe₄ unit and is linked through four bridging hydroxo ligands, O(14), O(15) and symmetry equivalents.

Within the hexanuclear complex the closest distances between Fe(3) and its neighbouring Fe^{III} atoms, Fe(3'), Fe(4) and Fe(5) are 3.605(2) Å, 3.500(3) Å and 3.656(3) Å, respectively. The distances between Fe(4) and its neighbouring Fe atoms Fe(5) and Fe(5') are 3.665(3) Å and 3.656(3) Å, respectively. The distances between Fe(4') and its neighbouring atoms Fe(5) and Fe(5') are 3.665(3) Å and 3.505(3) Å whilst the distances between Fe(3') and its neighbouring Fe^{III} atoms Fe(3) and Fe(5') are 3.605(3) Å and 3.656(3) Å. The distance between Fe(5) and Fe(5') is 3.730(3) Å. Each of these Fe^{III} atoms are octahedrally coordinated by the O_{carboxylate} and N- donor atoms of the deprotonated iminodiacetic acid functionalities of the *hpdta* ligands surrounding Fe(3-5) and symmetry equivalents, in *facial* fashions. The coordinating sites *trans* to the N-donors, for Fe(3), Fe(4) and symmetry equivalents, are occupied by oxygen atoms of the bridging oxo-hydroxo moiety, O(12) and O(13). Their Fe^{III}-O bonds are 1.918(13) Å and 1.824(12) Å long. The short O(12)...O(13) distance of 2.60 Å is characteristic of a strong intramolecular H-bond thus confirming the assignment of the oxo/hydroxo moiety in the square plane of the hexanuclear complex. The remaining two coordination sites of Fe(5) are provided by two bridging hydroxo ligands, O(14) and O(15). These hydroxo moieties link Fe(5) to the planar {Fe₄} unit and complete the distorted octahedral coordination environments of Fe(3) and Fe(4). The Fe^{III}-OH bond distances involving the bridging hydroxo groups agree very well with literature values and vary between 1.913(44) Å and 2.040(48) Å.

The structure of the tetranuclear complex in **9** is almost identical to that contained in compound **4**. However, it is only stabilized by one CO_3^{2-} ligand. The second CO_3^{2-} ligand is formally replaced by two coordination water molecules that bind to Fe(1) and the symmetry generated Fe(1') atom to give $\text{Fe}^{\text{III}}\text{-O}$ bond distances of 2.008(20) Å. Each of the Fe^{III} centres, have similar coordination environments to those seen in complex **4**. The bond distances and $\text{Fe}^{\text{III}}\text{-Fe}^{\text{III}}$ distances observed in this tetranuclear complex are consistent with those observed in **4**. For example, the distances between Fe(1) and its neighbouring Fe^{III} atoms, Fe(2) and Fe(1'), of 3.738(3) Å and 3.416(2) Å, respectively correspond to the distances between Fe(1) and its neighbouring Fe atoms in **4**. The assignment of the oxo/hydroxo moiety of the tetranuclear complex is confirmed through the characteristically short intramolecular H-bond distance between O(1)...O(2) of 2.31 Å.

The distorted octahedral coordination environments are exemplified in the bond angles O(2)-Fe(2)-O(6), O(16)-Fe(4)-N(4) and O(12)-Fe(3)-O(23) of 97.98(30)°, 75.64(38)° and 101.82(25)° which deviate from the ideal 90° angle. Slight deviations for the ideal angle are observed for the bond angles O(1)-Fe(1)-O(8), O(23)-Fe(3)-O(14) and O(15)-Fe(5)-O(22) of 92.90(29)°, 87.41(41)° and 89.83(38)°. Deviations from the linear modal are observed for bond angles O(2)-Fe(2)-N(2), O(12)-Fe(3)-N(3), O(23)-Fe(4)-O(16) and O(21)-Fe(5)-O(22)° which are characterised by values of 170.63(28)°, 163.52(23)°, 155.63(44)° and 153.02(26)°. Other selected bond lengths and angles involving the Fe^{III} centres in **9** are summarised in Table 3.7 and Table 3.8.

Table 3.7: Selected bond distances for 9

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1)-N(1)	2.156(10)
	Fe(1)-O(1)	1.837(26)
	Fe(1)-O(4)	2.000(36)
	Fe(1)-O(3)	2.021(73)
	Fe(1)-O(8)	2.008(32)
	Fe(1)-O(5)	2.058(42)
Fe(2)	Fe(2)-N(2)	2.232(50)
	Fe(2)-O(2)	1.853(65)
	Fe(2)-O(9)	2.042(34)
	Fe(2)-O(10)	2.059(14)

	Fe(2)-O(6)	1.949(19)
	Fe(2)-O(3)	2.083(76)
Fe(3)	Fe(3)-O(12)	1.918(13)
	Fe(3)-O(23)	1.931(60)
	Fe(3)-O(14)	1.979(43)
	Fe(3)-O(11)	2.077(34)
	Fe(3)-O(18)	2.002(3)
	Fe(3)-N(3)	2.225(13)
Fe(4)	Fe(4)-O(13)	1.824(12)
	Fe(4)-O(15)	1.982(45)
	Fe(4)-O(23)	2.01(56)
	Fe(4)-O(16)	2.026(35)
	Fe(4)-O(24)	2.078(29)
	Fe(4)-N(4)	2.246(57)
Fe(5)	Fe(5)-O(14)	1.913(44)
	Fe(5)-O(20)	2.032(39)
	Fe(5)-O(21)	2.037(65)
	Fe(5)-O(15)	2.040(48)
	Fe(5)-O(22)	2.058(65)
	Fe(5)-N(5)	2.201(22)

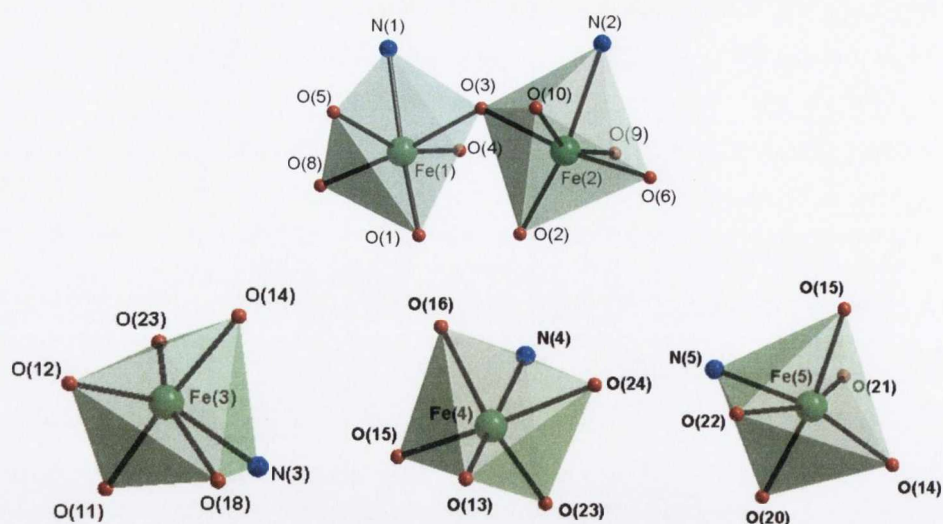


Figure 3.11: Polyhedral representations of the Fe^{III} centres in **9**. The hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, N blue, O red.

Table 3.8: Selected bond angles for compound **9**.

	Bond Angle ($^{\circ}$)		Bond Angle ($^{\circ}$)
O(1)-Fe(1)-O(4)	103.91(25)	O(14)-Fe(3)-O(11)	176.04(39)
O(1)-Fe(1)-O(8)	92.90(29)	O(12)-Fe(3)-N(3)	163.52(23)
O(4)-Fe(1)-O(8)	90.88(37)	O(23)-Fe(3)-N(3)	81.45(35)
O(1)-Fe(1)-O(3)	92.62(24)	O(14)-Fe(3)-N(3)	98.21(35)
O(4)-Fe(1)-O(3)	88.70(31)	O(11)-Fe(3)-N(3)	78.57(34)
O(8)-Fe(1)-O(3)	174.40(36)	O(13)-Fe(4)-O(15)	91.47(31)
O(1)-Fe(1)-O(5)	101.35(30)	O(13)-Fe(4)-O(23)	101.43(25)
O(4)-Fe(1)-O(5)	154.73(44)	O(15)-Fe(4)-O(23)	88.21(42)
O(8)-Fe(1)-O(5)	87.42(45)	O(13)-Fe(4)-O(16)	102.53(26)
O(3)-Fe(1)-O(5)	90.58(39)	O(15)-Fe(4)-O(16)	86.75(42)
O(1)-Fe(1)-N(1)	173.53(29)	O(23)-Fe(4)-O(16)	155.63(44)
O(4)-Fe(1)-N(1)	78.59(35)	O(13)-Fe(4)-O(24)	100.45(34)
O(8)-Fe(1)-N(1)	93.03(41)	O(15)-Fe(4)-O(24)	167.94(39)
O(3)-Fe(1)-N(1)	81.41(37)	O(23)-Fe(4)-O(24)	87.62(41)
O(5)-Fe(1)-N(1)	76.34(39)	O(16)-Fe(4)-O(24)	92.41(41)
O(2)-Fe(2)-O(6)	97.98(30)	O(13)-Fe(4)-N(4)	176.56(33)
O(2)-Fe(2)-O(9)	104.26(29)	O(15)-Fe(4)-N(4)	91.33(44)
O(6)-Fe(2)-O(9)	88.69(41)	O(23)-Fe(4)-N(4)	80.66(38)
O(2)-Fe(2)-O(10)	100.96(25)	O(16)-Fe(4)-N(4)	75.64(38)
O(6)-Fe(2)-O(10)	87.86(41)	O(24)-Fe(4)-N(4)	76.83(46)

O(9)-Fe(2)-O(10)	154.78(38)	O(14)-Fe(5)-O(20)	87.52(45)
O(2)-Fe(2)-O(3)	90.71(23)	O(14)-Fe(5)-O(21)	98.31(40)
O(6)-Fe(2)-O(3)	171.24(37)	O(20)-Fe(5)-O(21)	92.22(42)
O(9)-Fe(2)-O(3)	88.06(35)	O(14)-Fe(5)-O(15)	100.71(44)
O(10)-Fe(2)-O(3)	91.62(34)	O(20)-Fe(5)-O(15)	171.29(45)
O(2)-Fe(2)-N(2)	170.63(28)	O(21)-Fe(5)-O(15)	89.43(43)
O(6)-Fe(2)-N(2)	90.00(44)	O(14)-Fe(5)-O(22)	108.32(28)
O(9)-Fe(2)-N(2)	80.72(38)	O(20)-Fe(5)-O(22)	84.82(31)
O(10)-Fe(2)-N(2)	74.31(34)	O(21)-Fe(5)-O(22)	153.02(26)
O(3)-Fe(2)-N(2)	81.45(38)	O(15)-Fe(5)-O(22)	89.83(38)
O(12)-Fe(3)-O(23)	101.82(25)	O(14)-Fe(5)-N(5)	159.32(48)
O(12)-Fe(3)-O(14)	98.08(26)	O(20)-Fe(5)-N(5)	74.38(50)
O(23)-Fe(3)-O(14)	87.41(41)	O(21)-Fe(5)-N(5)	72.99(42)
O(12)-Fe(3)-O(11)	85.26(25)	O(15)-Fe(5)-N(5)	97.97(47)
O(23)-Fe(3)-O(11)	89.82(40)	O(22)-Fe(5)-N(5)	80.41(34)

The relatively short bond distances indicate that the Fe atoms are in the +III oxidation state. The assignment of oxidation states is confirmed through charge considerations of the anionic complexes. The hexanuclear structure as seen in Figure 3.10, containing six Fe^{III} ions, three fully deprotonated ligands, the bridging oxo-hydroxo motif and the four hydroxo bridging moieties, has a charge of -4. The tetranuclear complex as seen in Figure 3.10, containing four Fe^{III} ions, two fully deprotonated ligands, the carbonate group and the bridging oxo-hydroxo ligand, has a charge of -3. Altogether, seven Na⁺ cations counter-balance the negative charges. However, these counter ions are disordered whereby the atom positions of Na(1-4) and symmetry equivalents are only half occupied.

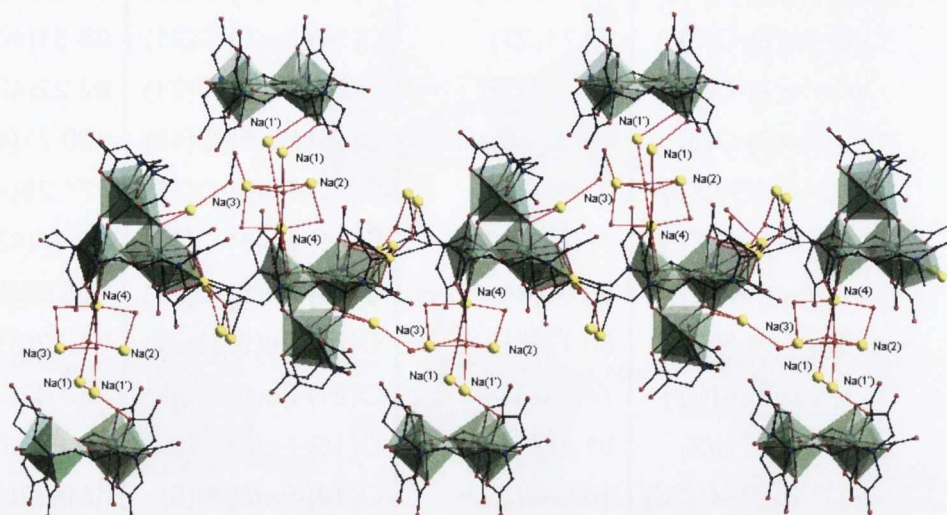


Figure 3.12: The hexanuclear and tetranuclear complexes in **9** aggregating through $\text{Na}^+\text{-O}$ and $\text{Na}^+\text{-O}_{\text{carboxylate}}$ bonds, highlighted in red, to form a 1D network. Polyhedral representation of the Fe^{III} centres. The hydrogen atoms and constitutional water molecules have been omitted for clarity. Colour Code: C black, Fe green, N blue, Na yellow, O red.

The tetranuclear and hexanuclear Fe^{III} complexes in **9** aggregate *via* the Na^+ counter ions and water molecules to give a one dimensional network structure. All sodium atoms are as expected five or six coordinated and reveal typical $\text{Na}^+\text{-O}$ bond distances ranging between 2.263(14) Å to 2.411(15) Å. Figure 3.10 and Figure 3.12 indicate how the transition metal complexes assemble in the crystal structure involving these sodium ions, carboxylate oxygen atoms from the *hpdt*a ligands and constitutional water molecules. Intermolecular interactions arrange the complexes and counter ions in **9** to form sheets that extend parallel to the crystallographic *bc*-plane. One needs to consider that both, Na^+ ions and water molecules are highly disordered. This disorder (especially that of the disordered solvent molecules) and the small size of the single-crystals results in a high *R*1 value of *ca.* 14.5% of the structure. Despite the high *R*1 value, the refined structure has a goodness of fit of 1.052, a high data to parameter ratio and acceptable 'largest difference peak and hole' values supporting the provided structural model. Elemental analysis further confirms the constitution of **9**. When the PLATON routine SQUEZE is used to account for the extended disordered parts of the structure, the *R*1 value drops below 7%.

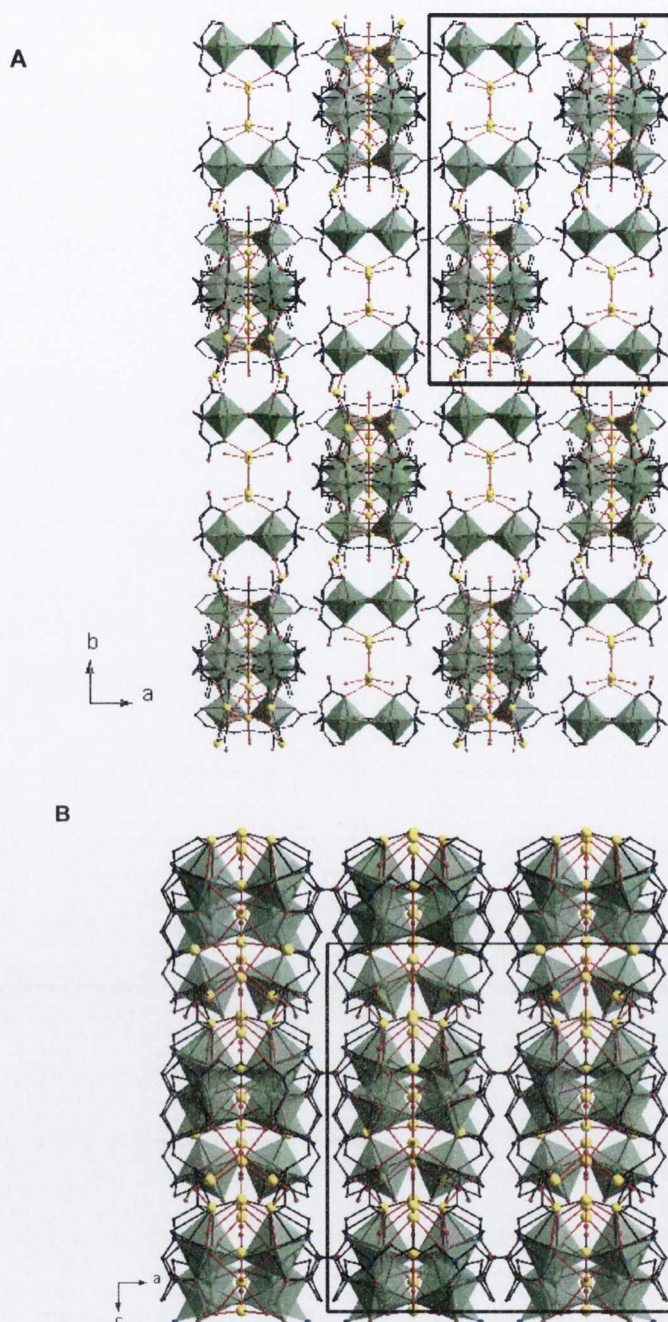


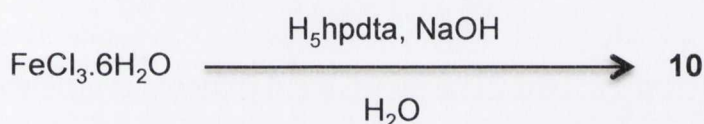
Figure 3.13: The packing structures of **9** viewed along the crystallographic A) *c*-axis and B) *b*-axis. Polyhedral representation of the Fe^{III} centres. The hydrogen atoms and constitutional water molecules have been omitted for clarity. Colour Code: C black, Fe green, N blue, Na yellow, O red.

Table 3.9: Crystal data and structure refinement parameters for 9

Identification code	9
Empirical formula	$C_{56}Fe_{10}H_{78}N_{10}Na_7O_{62}$
Formula weight	2602.62 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Im2a</i>
Unit cell dimensions	$a = 20.251(4)$ Å $b = 30.984(6)$ Å $c = 21.742(4)$ Å
Volume	13642(5) Å ³
Z	4
Density (calculated)	1.455 Mg/m ³
Absorption coefficient	1.171 mm ⁻¹
F(000)	5871
Crystal size	0.1 x 0.15 x 0.2 mm ³
Φ range for data collection	1.20 to 25.08°
Index ranges	-22 ≤ h ≤ 24, -35 ≤ k ≤ 36, -25 ≤ l ≤ 25
Reflections collected	39591
Independent reflections	12438 [R(int) = 0.0492]
Completeness to θ = 25.08°	99.6 %
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	12438/1/809
Goodness-of-fit on F ²	1.052
Final R indices [I > 2σ(I)]	R1 = 0.1449, wR2 = 0.2960
R indices (all data)	R1 = 0.1785, wR2 = 0.3118
Largest diff. peak and hole	1.001 and -1.091 e.Å ⁻³

3.3 Na[Fe₃(H₂O)₂(μ-O)(C₉H₅N₂O₇)₂]-6H₂O (**10**)

The trinuclear centrosymmetric Fe^{III} complex [Fe₃(H₂O)₂(μ-O)(C₉H₁₁N₂O₇)₂]⁻ contained in **3**, in which the Fe^{III} atoms are coordinated to the donor atoms of two partially decomposed *hpdta* ligands is an unexpected decomposition product. The complex forms when an aqueous Fe^{III}/*hpdta* solution is treated with sodium hydroxide in the presence of [2,18-dipropanoato(2-)-Fe^{III}] (**L2**) and allowed to reflux for five days (Scheme 3.3). Both aminocarboxylic acid ligands in **10** are decomposition products of the *hpdta* ligand and form through the cleavage of an acetate moiety. Dark red, cubic crystals of **10** suitable for single-crystal X-ray diffraction were reproducibly obtained by co-evaporation of the resulting solution with dimethylacetamide. The complex crystallises in the monoclinic space group *P*2₁/*n*. Figure 3.14 shows the structure of the trinuclear complex in **10**.



Scheme 3.3: preparation of compound **10** (refluxed at 110 °C for 5 days)

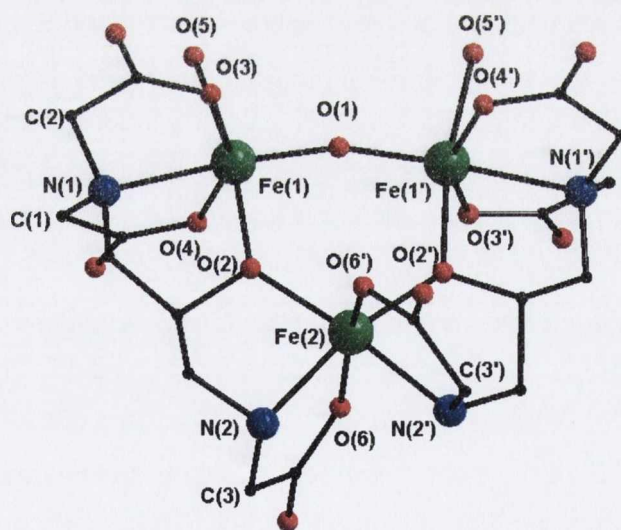


Figure 3.14: The structure of the trinuclear complex in **10**. The hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, N blue, O red.

3.3.1 Structural characterisation of **10**

The structure and symmetry of the trinuclear complex in **10**, is characterised by a central mirror plane. The complex contains three octahedrally coordinated Fe^{III} centres, Fe(1), Fe(1') and Fe(2). The atoms Fe(1) - Fe(2) and Fe(1') - Fe(2) are bridged by the alkoxo atom O(2') of the organic aminocarboxylic acid ligands while Fe(1) and Fe(1') are bridged by a bridging μ_2 -oxo ligand. The respective distances between Fe(1) and its neighbouring Fe^{III} atoms, Fe(2) and Fe(1'), are 3.648(2) Å and 3.517(4) Å while the distance between Fe(2) and its neighbouring Fe^{III} atoms Fe(1) and the symmetry equivalent Fe(1') atom is 3.648(2) Å. Fe(1) binds to the two oxygen atoms, O(3) and O(4), from the two deprotonated carboxylic acid groups of the iminodiacetic acid moieties. The bond distances between the O_{carboxylate} atoms and Fe(1) of 2.010(17) Å and 2.051(12) Å, respectively, are similar to comparable Fe^{III}-O bond distances observed in the literature.^{3, 123, 127} The third coordination site of Fe(1) is occupied by a nitrogen donor, N(1), to give Fe^{III}-N bond distance of 2.232(6) Å. These three atoms bind together in a *facial* arrangement to Fe(1). The distorted octahedral coordination sphere is completed by the alkoxo atom O(2), the bridging oxo ligand O(1) and an oxygen atom from a water ligand O(5). The Fe^{III}-O bond lengths are 2.041(5) Å for Fe(1)-O(2), 1.782(27) Å for Fe(1)-O(1) and 2.109(5) Å for Fe(1)-O(5). The short Fe(1)-O(1) bond distance is characteristic of a bond distance involving an Fe^{III} centre and an oxo ligand.³ Fe(1') is generated through symmetry operations and it has an identical coordination environment to Fe(1). Fe(2) is coordinated by the N- and O- donor atoms from the two decomposition products of the *hpdta* ligands, O(2), O(2'), N(2) and N(2'), to form a distorted square planar arrangement with Fe^{III} bond distances of 1.968(5) Å for the Fe(2)-O(2) and 2.208(5) Å for the Fe(2)-N bonds. The octahedral coordination environment of Fe(2) is completed by two *trans* coordinating O-donors in the apical positions, O(6) and O(6'), which originate from the deprotonated carboxylic acid functionalities of the aminocarboxylic acid ligands to give Fe^{III}-O_{carboxylate} bond distances of 2.008(6) Å.

The distortion within the octahedral coordination geometries in **3** can be emphasized through examination of the bond angles between the Fe^{III} atoms and the *cis* and *trans* coordinated atoms. Taking Fe(2) as an example, the bond angles O(2')-Fe(2)-N(2) and O(6)-Fe(2)-O(6'), of 167.48(8)° and 164.18(13)°, deviate from the ideal 180° bond angle. Similarly, the bond angles between the *cis* coordinated atoms within the octahedral coordination sphere highlight the distortion from the ideal geometry. These range between 78.76(14)° and 92.79(12)° varying significantly from the expected bond angle of 90°.

The Fe-N and Fe-O bond distances confirm that the Fe atoms are in a +III oxidation state. This can also be deduced through charge consideration of the anionic complex. The compound contains three Fe^{III} ions, and a Na⁺ ion contributing to a charge of +10. This positive charge is counter balanced by 8 negative charges arising from the two aminocarboxylic acid ligands, and two negative charges derived from the oxo bridge.

Table 3.10: Selected bond distances for the Fe^{III} and Na⁺ centres in 10.

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1)-O(1)	1.782(2)
	Fe(1)-O(3)	2.010(17)
	Fe(1)-O(2)	2.041(5)
	Fe(1)-O(4)	2.051(12)
	Fe(1)-O(5)	2.109(5)
	Fe(1)-N(1)	2.232(6)
Fe(2)	Fe(2)-O(6)	2.008(6)
	Fe(2)-N(2)	2.208(5)
	Fe(1)-O(1)	1.782(2)
	Fe(2)-O(2)	1.968(5)
Na(1)	Na(1)-O(7)	1.967(14)
	Na(1)-O(1)	2.564(25)
	Na(1)-O(5)	2.439(10)

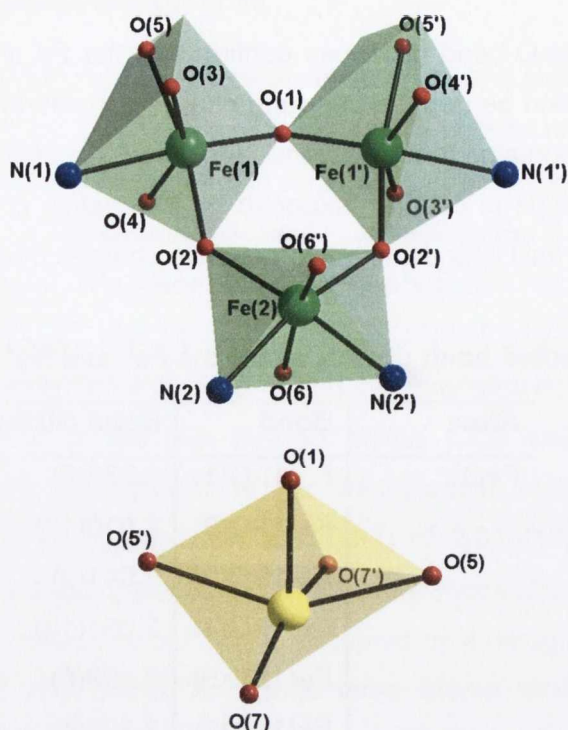


Figure 3.15: Polyhedral representations of the Fe^{III} and Na^+ centres in **10**. The hydrogen atoms have been omitted for clarity. Na yellow, O red.

Table 3.11: Selected bond angles for compound **10**.

	Bond Angle (°)		Bond Angle (°)
O(1)-Fe(1)-O(3)	101.10(16)	O(1)-Fe(1)-N(1)	175.24(15)
O(1)-Fe(1)-O(2)	94.58(14)	O(3)-Fe(1)-N(1)	78.07(21)
O(3)-Fe(1)-O(2)	91.80(16)	O(2)-Fe(1)-N(1)	80.79(19)
O(1)-Fe(1)-O(4)	105.19(16)	O(4)-Fe(1)-N(1)	76.43(21)
O(3)-Fe(1)-O(4)	152.29(18)	O(5)-Fe(1)-N(1)	89.33(21)
O(2)-Fe(1)-O(4)	94.66(16)	O(2)-Fe(2)-O(6)	96.54(15)
O(1)-Fe(1)-O(5)	95.29(15)	O(2)-Fe(2)-N(2)	82.76(15)
O(3)-Fe(1)-O(5)	85.60(18)	O(6)-Fe(2)-N(2)	78.76(16)
O(2)-Fe(1)-O(5)	170.11(18)	O(6)-Fe(2)-O(6')	164.18(13)
O(4)-Fe(1)-O(5)	83.43(18)	O(2')-Fe(2)-N(2)	78.76(14)

The sodium counter ion, Na(1), in **10** adopts a distorted square pyramidal binding geometry. Its equatorial plane is occupied by an oxygen atom from a solvent water molecule O(7) and an oxygen atom, O(5), from a second water molecule and their symmetry equivalents, O(7') and O(5'). The Na^+ -O bond distances are 1.967(14) Å and

2.439(10) Å respectively. The inner binding sphere is completed by the oxo ligand O(1) with a Na⁺-O bond length of 2.564(25) Å.

Compound **10** is stabilised in the solid state by weak H-bonds between the Fe^{III} complex and constitutional water molecules. The H-bonds are characterised by donor-acceptor distances that range between 2.709(40) Å and 3.568(18) Å. The prevailing H-bonds occur between the O_{carboxylate} atoms of the *hpdta* ligands and two oxygen atoms, O(7) and O(7'), of water molecules that hydrate sodium counterion. Inter-molecular H-bonding interactions between the oxygen atom O(7) and the coordinating carboxylate oxygen O(4) further contribute to the stabilisation of **10** in the solid state.—The packing arrangements of the complexes in **10** are shown in Figure 3.16 to Figure 3.18.

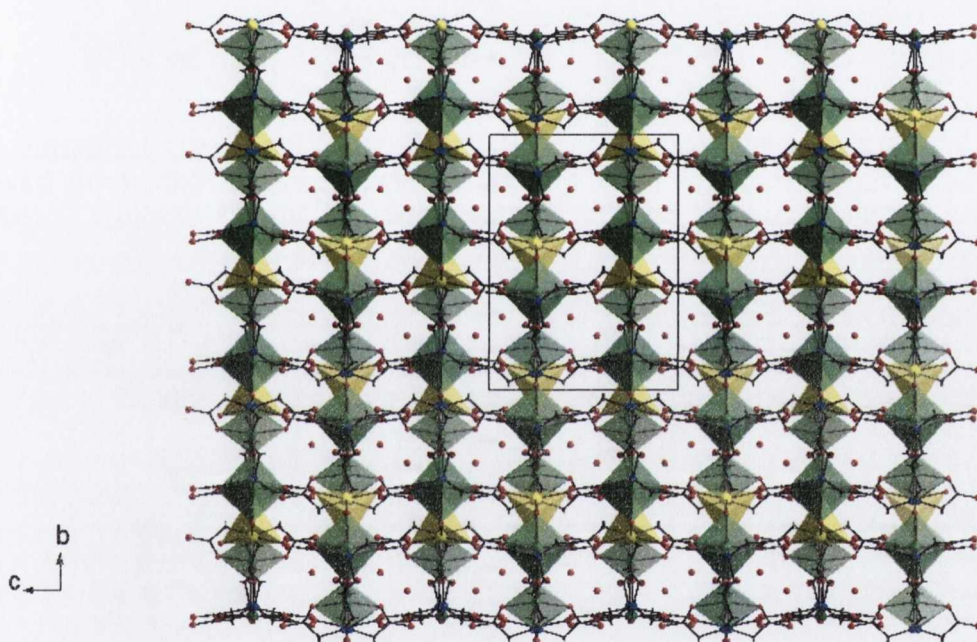


Figure 3.16: Packing diagram of **10** displaying the extension of assemblies along the crystallographic b- and c-axis. Viewed along the crystallographic a-axis. Polyhedral representations of the Fe^{III} and Na⁺ centres. Hydrogen atoms have been omitted for clarity. Colour code: C black, Fe green, N blue, Na yellow, O red.

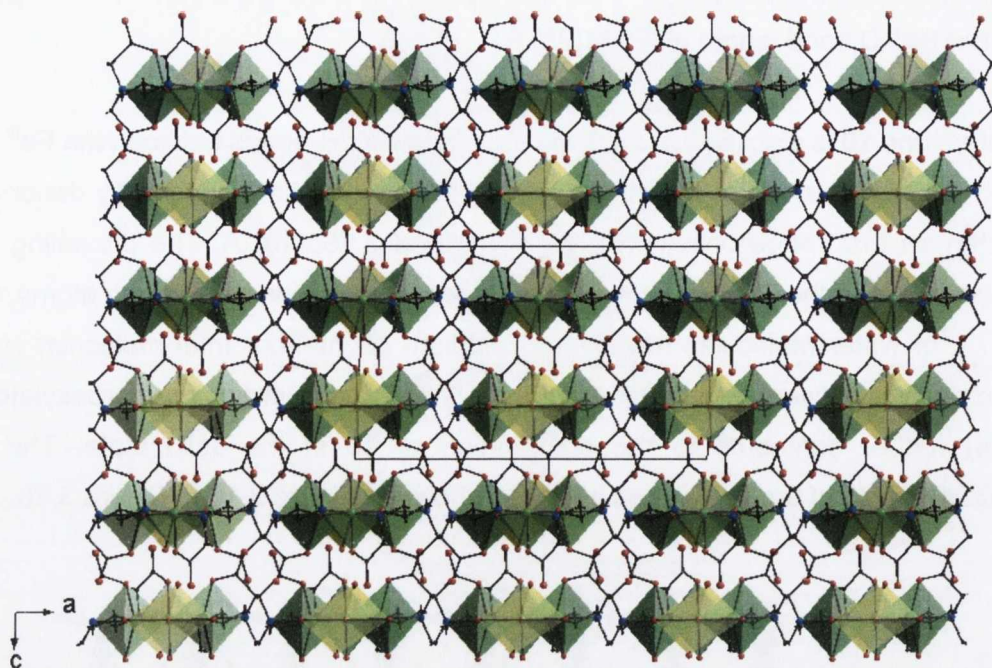


Figure 3.17: Packing structure of 10, viewed along the crystallographic *b*-axis. Polyhedral representations of the Fe^{III} and Na^+ centres, Hydrogen atoms have been omitted for clarity. Colour code: C black, Fe green, N blue, Na yellow, O red.

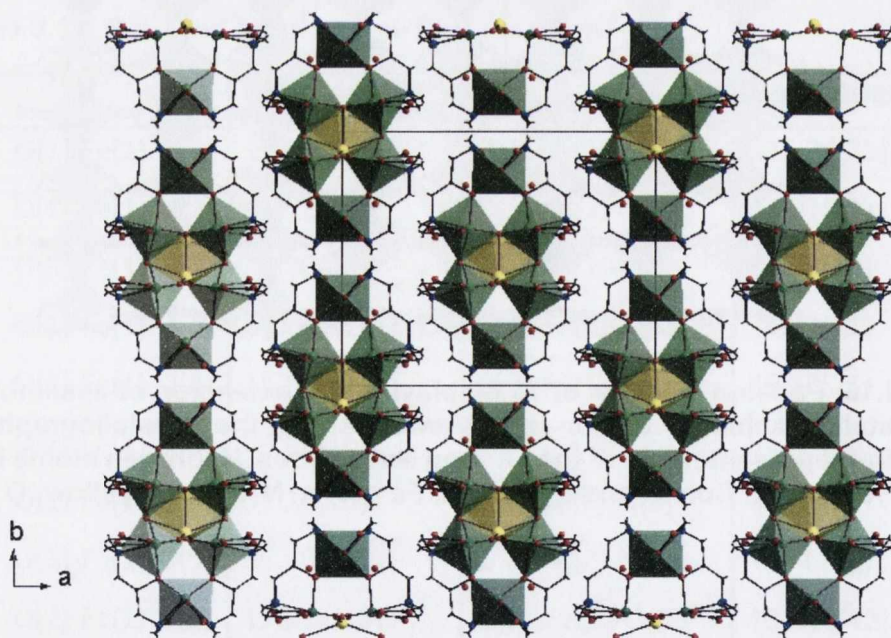


Figure 3.18: Packing diagram of 10, with polyhedral representations of the Fe^{III} and Na^+ centres. Viewed along the crystallographic *c*-axis. Hydrogen atoms have been omitted for clarity. Colour code: C black, Fe green, N blue, Na yellow, O red.

The crystal structure refinement of **10** is characterised by a final R1 value of 6.55%, a goodness of fit of 1.051, a high data to parameter ratio and an acceptable ‘largest difference peak and hole’ values supporting the provided structural model. The crystal data and structure refinement parameters for examined single-crystals of **10** are summarized in Table 3.12.

Table 3.12: Crystal data and structure refinement parameters for 10

Compound	10	
Empirical formula	C ₁₈ H ₃₈ Fe ₃ N ₄ NaO ₂₃	
Formula weight	869.03 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	<i>a</i> = 18.374(4) Å	α = 90°.
	<i>b</i> = 15.003(3) Å	β = 93.01(3)°.
	<i>c</i> = 11.064(2) Å	γ = 90°.
Volume	3045.8(11) Å ³	
Z	3	
Density (calculated)	1.849 Mg/m ³	
Absorption coefficient	1.517 mm ⁻¹	
F(000)	1720	
Crystal size	0.1 x 0.5 x 0.4 mm ³	
Φ range for data collection	11.75 to 25.00°.	
Index ranges	-21 ≤ <i>h</i> ≤ 21, -17 ≤ <i>k</i> ≤ 17, -13 ≤ <i>l</i> ≤ 13	
Reflections collected	11574	
Independent reflections	2598 [R(int) = 0.0372] on F ²	
Completeness to θ= 25.00°	97.1 %	
Refinement method	Full-matrix least-squares	
Data/restraints/parameters	2598 / 0 / 224	
Goodness-of-fit on F ²	1.051	
Final R indices[<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0655, wR2 = 0.1941	
R indices (all data)	R1 = 0.0894, wR2 = 0.2518	
Largest diff. peak and hole	2.044 and -1.501 e.Å ⁻³	

3.3.2 Physicochemical characterisation of **10**

FT-IR spectroscopy

The FT-IR spectrum for this compound (seen in Figure 3.19) exhibits the characteristic stretches that are expected for the observed compound that contains a trinuclear Fe^{III} oxo-bridged complex that is stabilised by iminodiacetic acid based ligands. The broad band centered at *ca.* 3340 cm⁻¹ can be attributed to symmetrical and asymmetrical O-H stretching vibrations of the crystallization water molecules engaged in H-bonds. The asymmetric and symmetric stretches that originate from the deprotonated and coordinating carboxylic acid functionalities appear at *ca.* 1615 cm⁻¹ and *ca.* 1380 cm⁻¹. The asymmetric Fe^{III}-O stretch of the bridging oxo ligand appears at *ca.* 815 cm⁻¹.¹⁶⁴ The frequency differences of the asymmetric and symmetric stretches of the carboxylate groups, ($\Delta\nu$), may be used to determine its binding mode.¹⁶³ In the FT-IR spectrum of **10**, there is one asymmetric C-O stretch at *ca.* 1615 cm⁻¹ and a symmetric stretch at *ca.* 1380 cm⁻¹. The absence of multiple asymmetric and symmetric stretches indicates that each of the carboxylate moieties is engaged in a similar type of binding. The $\Delta\nu$ for **10** of *ca.* 235 cm⁻¹ indicates that the carboxylate functional groups in **10** adopt the unidentate binding mode which is consistent with the coordination of the carboxylate moieties observed in the crystal structure of **10** (Figure 3.14).¹⁶³ The unusually sharp stretches at *ca.* 2970 cm⁻¹ and *ca.* 970 cm⁻¹, have been assigned to asymmetric C-H stretches involving sp³ hybridized C atoms and N-H vibrations.

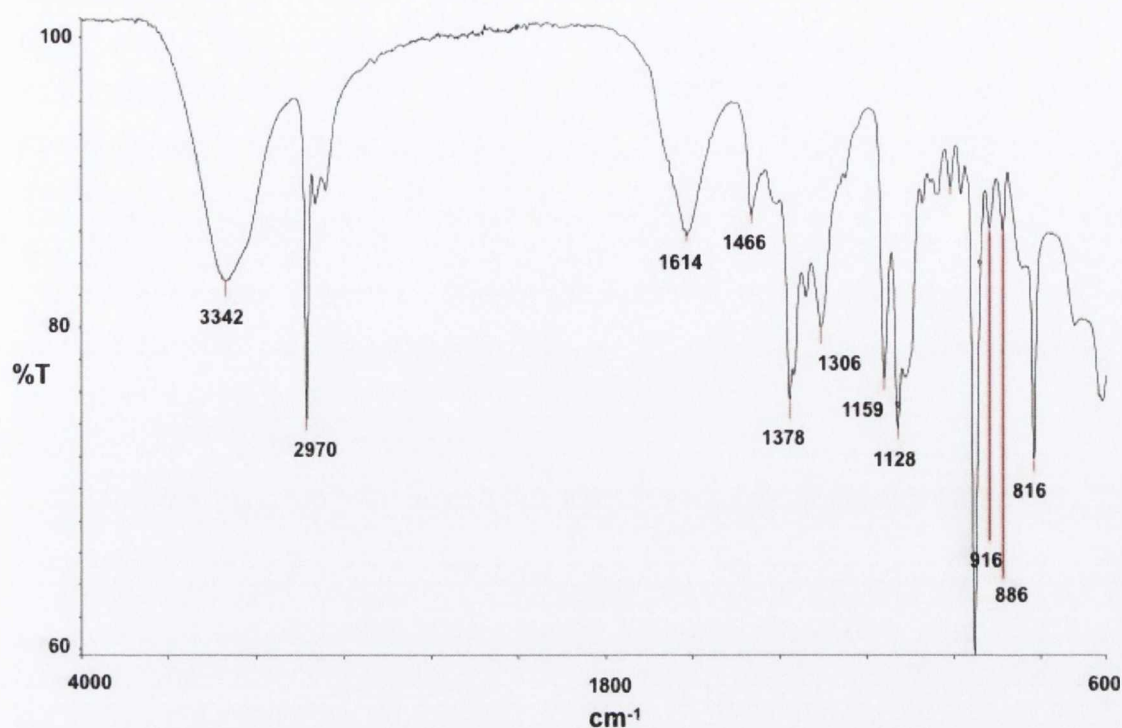


Figure 3.19: FT-IR spectrum of freshly ground microcrystals of **10** recorded using a diffuse reflectance accessory.

Table 3.13: Characteristic vibrational bands observed in the FT-IR spectra of **10**.¹³⁶⁻¹³⁸

Wavenumber (cm ⁻¹)	Assignment
3340	O-H ν_s and ν_{as} stretches and N-H stretch
2970	Asymmetric sp^3 hybridized C-H stretch and N-H stretches
1615, 1380,	C-O ν_{as} and ν_s stretches
1305	-OH stretching
1355	C-N
970	N-H bend
815	Fe ^{III} -O stretch

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to establish the thermal stability of compound **10**. The analysis was carried out in the temperature range between 30 °C and 880 °C, in an air atmosphere. The heating rate was set to 1 °C/minute. The TGA of **10** reveals a weight loss of 12.29 % in the temperature range 30-110 °C. This thermogravimetric step can be attributed to the loss of six constitutional water molecules (experimental weight loss: 12.29 %, theoretical weight loss: 12.43 %). A second weight

loss of 3.67 % in the temperature range between 110-200 °C can be attributed to the loss of the two coordinating water molecules (e.g. see O (5) and O(5') in Figure 3.14), (experimental weight loss: 3.67 %, theoretical weight loss: 4.14 %). A further increase in the temperature up to ca. 620 °C gives rise to a weight loss that occurs in a two-step process centered at ca. 390 °C and ca. 575 °C. This weight loss can be associated with oxidative decomposition of the *hpdta* ligands from **10** (experimental weight loss: 57.83 %, theoretical weight loss: 59.61 %). The formation of oxides occurs above 620 °C (final experimental weight loss: 73.77 %, final theoretical weight loss: 76.17 %). The theoretical mass percentages of the proposed decomposition products were calculated as a percentage of the mass of $\text{Na}[\text{Fe}_3(\text{H}_2\text{O})_2(\mu\text{-O})(\text{C}_9\text{H}_5\text{N}_2\text{O}_7)_2]\cdot 6\text{H}_2\text{O}$. These are reported in Table 3.14 and are in agreement with the experimentally observed values.

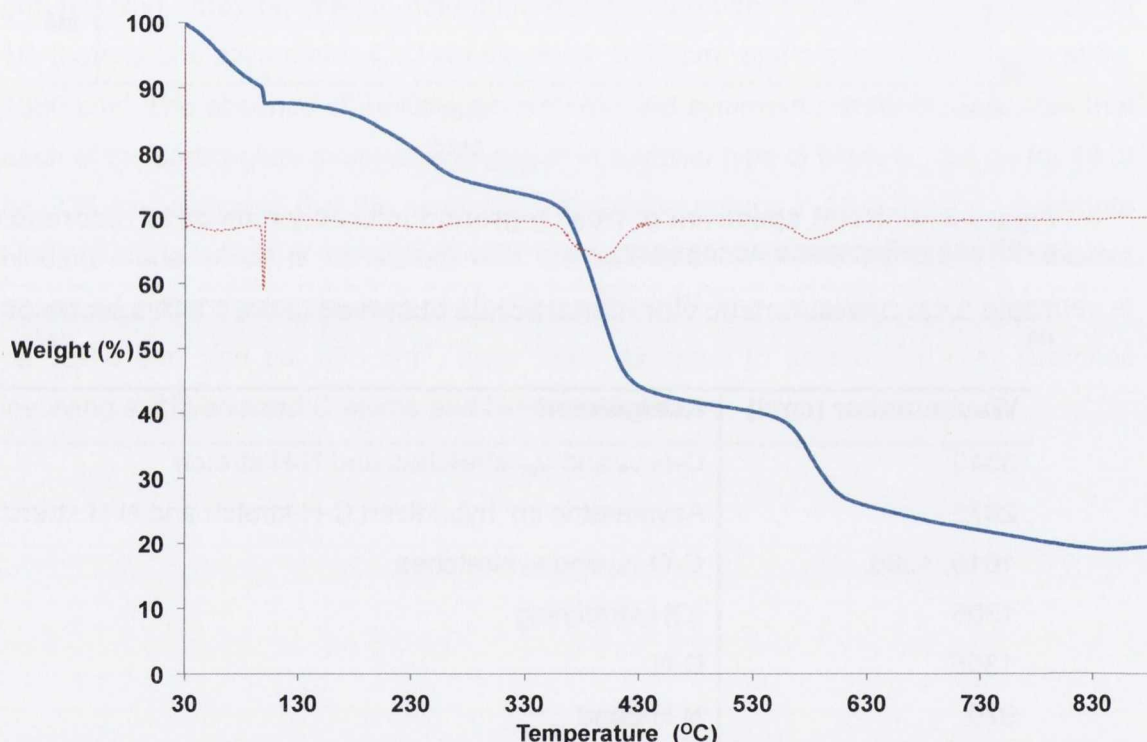


Figure 3.20: TGA curve for **10**. Recorded in an air atmosphere from 30 °C to 880 °C. Heating step was set to 1 °C/minute.

Table 3.14: Results for TGA analyses (recorded in an air atmosphere from 30 °C to 880 °C. Heating step was set to 1 °C/minute) of **10**.

Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
$\text{C}_{18}\text{H}_{38}\text{Fe}_3\text{N}_4\text{NaO}_{23}$	100	100	35 (Initial)
$\text{C}_{18}\text{H}_{26}\text{Fe}_3\text{N}_4\text{NaO}_{17}$	87.57	87.71	35 - 110
$\text{C}_{18}\text{H}_{22}\text{Fe}_3\text{N}_4\text{NaO}_{15}$	83.43	84.04	110 - 200
Na^+ & Fe^{III} oxides	24.44	26.73	200 - 620

Additional Characterisations:

A powder X-ray diffraction (P-XRD) pattern of **10** was recorded. The experimental pattern was consistent with the simulated pattern as determined by the single-crystal X-ray diffraction experiments. This verified the accuracy of the solid-state model and confirmed the absence of crystalline impurities from the sample. The results from elemental analysis, presented in Table 3.15, reveal a good correlation between the theoretical and experimental values. This further establishes the phase-purity of **10** and confirms that the chemical formula, $C_{18}H_{38}Fe_3N_4NaO_{23}$, is correct.

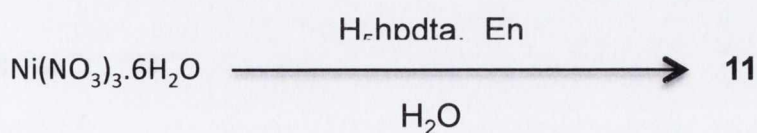
Table 3.15: Theoretical and experimental elemental analysis for 10. Theoretical based on $C_{18}H_{38}Fe_3N_4NaO_{23}$.

Element	Theoretical composition (%)	Experimental composition (%)
C	24.89	25.01
H	4.41	4.41
Fe	19.28	19.33
N	6.45	6.62

3.4 The Ni^{II} hpdta system

3.4.1 $enH_2[Ni(H_1hpdta)] \cdot 2H_2O$ (**11**)

The mononuclear centrosymmetric Ni^{II} complex $[Ni(Hhpdta)]^{2-}$ within **11**, consists of a Ni^{II} centre coordinated to one *hpdta* ligand. The Ni^{II} complex forms when ethylenediamine is used to adjust the pH of an aqueous Ni^{II}/*hpdta* solution to 8.5 (Scheme 3.4). Light purple, plate-like crystals of **11** suitable for single-crystal X-ray diffraction were obtained by co-evaporation with dimethylacetamide. The complex crystallizes in the triclinic space group *P*-1. Figure 3.21 shows the structure of the mononuclear complex in **11**.



Scheme 3.4: preparation of compound 11.

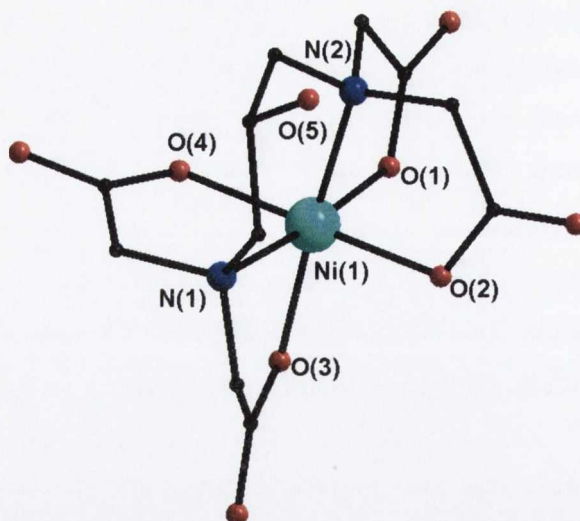


Figure 3.21: The structure of the mononuclear complex in **11**. The hydrogen atoms are omitted for clarity. Colour code: C black, N dark blue, Ni light blue, O red.

3.4.2 Structural characterisation of **11**

The asymmetric unit of **11** is defined by one nickel centre coordinated, in a distorted octahedral geometry by the donor atoms of a partially deprotonated *hpdt*a ligand, a doubly protonated ethylenediamine counter ion and two solvent water molecules.

The Ni^{II} centre, Ni(1), binds to three carboxylate oxygen atoms, O(1), O(2) and O(4) in a *meridional* fashion to give Ni^{II}-O bond distances of 2.032(12) Å [Ni(1)-O(1)], 2.030(10) Å [Ni(1)-O(2)] and 2.060(14) Å [Ni(1)-O(4)]. A N-donor, N(1), of the iminodiacetic acid ligand, binds to the Ni centre at a distance of 2.086(16) Å. The distorted octahedral coordination sphere of Ni(1) is completed by the *trans* coordinating carboxylate oxygen atom O(3), and the N-donor atom N(2) that bind, as shown in Figure 3.21, at the apical positions with bond distances of 2.025(9) Å and 2.073(4) Å, respectively. The Ni^{II}-N and Ni^{II}-O bond lengths are in line with the literature values for Ni^{II}-O bonds structurally related Ni^{II} complexes.¹⁶⁵ Selected bond distances and bond angles involving the Ni^{II} centre in **11** are presented in Table 3.16. and Table 3.17. Distortion from the ideal 90° bond angle is exemplified through observation of the angles O(3)-Ni(1)-O(1) of 98.78(15)° and the N(2)-Ni(1)-N(1) angle of 97.09(16)°. Moderate distortion in the equatorial plane is characterised by the bond angles O(2)-Ni(1)-O(1), O(1)-Ni(1)-O(4) O(2)-Ni(1)-N(1) and O(4)-Ni(1)-N(1) of 91.33(15)°, 91.40(15)°, 94.34(16)° and 82.89(16)°, respectively. Furthermore, the most significant deviation from 180° involves the carboxylate O-donor atom O(1) for the observed bond angle O(1)-Ni(1)-N(1) of 174.20(15)°.

Table 3.16: Selected bond distances for the Ni^{II} centres in **11**.

Atom	Bond	Bond Distance (Å)
Ni(1)	Ni(1)-O(3)	2.025(9)
	Ni(1)-O(2)	2.030(10)
	Ni(1)-O(1)	2.032(12)
	Ni(1)-O(4)	2.060(14)
	Ni(1)-N(2)	2.073(4)
	Ni(1)-N(1)	2.086(16)

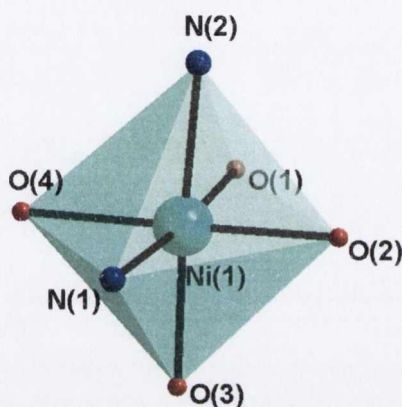


Figure 3.22: Polyhedral representation of the Ni^{II} centre in **11**. The hydrogen atoms have been omitted for clarity. Colour Code: C black, N blue, Ni light blue, O red.

Table 3.17: Selected bond angles for compound **11**.

	Bond Angle (°)		Bond Angle (°)
O(3)-Ni(1)-O(1)	98.78(15)	O(1)-Ni(1)-N(2)	82.25(15)
O(2)-Ni(1)-O(1)	91.33(15)	O(4)-Ni(1)-N(2)	94.22(15)
O(3)-Ni(1)-O(4)	89.54(14)	O(3)-Ni(1)-N(1)	82.26(15)
O(2)-Ni(1)-O(4)	176.57(15)	O(2)-Ni(1)-N(1)	94.34(16)
O(1)-Ni(1)-O(4)	91.40(15)	O(1)-Ni(1)-N(1)	174.20(15)
O(3)-Ni(1)-N(2)	176.08(16)	O(4)-Ni(1)-N(1)	82.89(16)
O(2)-Ni(1)-N(2)	84.10(16)	N(2)-Ni(1)-N(1)	97.09(16)

Compound **11** is stabilised in the solid state primarily by hydrogen bond interactions to form a 1D sheet in the crystallographic *bc*-plane, Figure 3.23. The interactions occur between the non-coordinating O-donor atoms of the carboxylate arms of the *hpdta* ligand, constitutional water molecules and the ethylene-diammonium counterion.

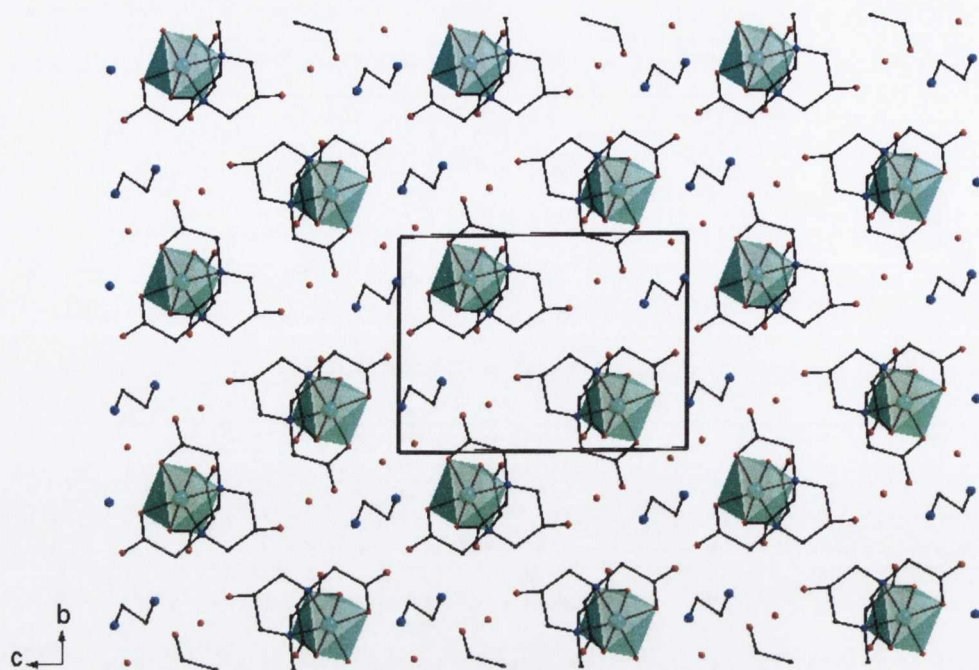


Figure 3.23: Packing structure of **11** viewed in the direction of the crystallographic *a*-axis. Polyhedral representations of the Ni^I centres. Hydrogen atoms have been omitted for clarity. Colour Code: C black, N blue, Ni blue, O red.

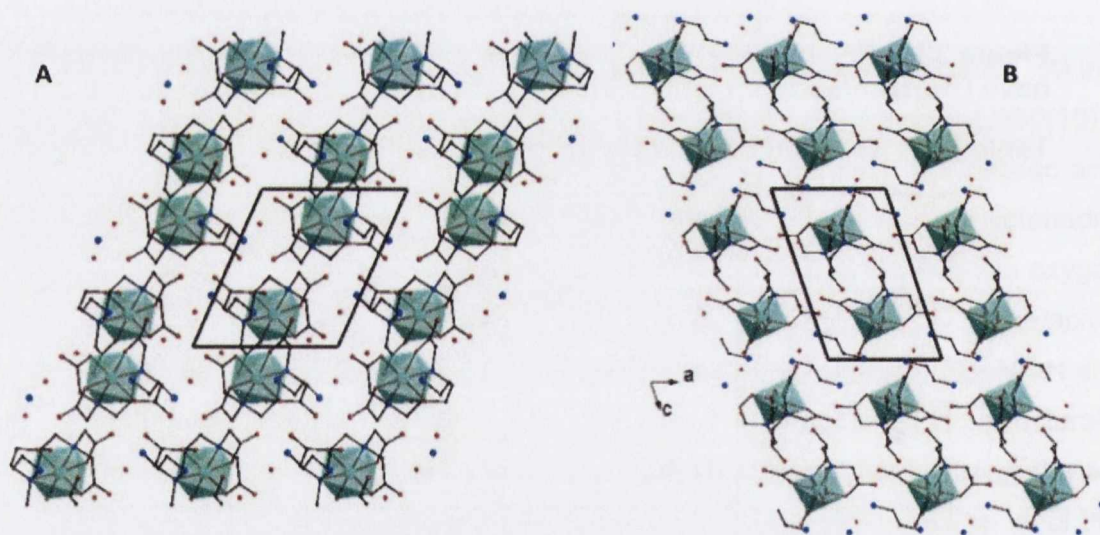


Figure 3.24: Packing structure of **11** viewed along the crystallographic A) *c*-axis and B) the crystallographic *b*-axis. Hydrogen atoms have been omitted for clarity. Colour Code: C black, N blue, Ni blue, O red.

The refinement of the crystal structure of **11** converges to give a final *R*₁ value of 5.56%, a goodness of fit of 1.063, a high data to parameter ratio and an acceptable 'largest difference peak and hole' values supporting the provided structural model. The crystal data and structure refinement parameters are summarized in Table 3.18.

Table 3.18: Crystal data and structure refinement parameters for 11

Compound	11
Empirical formula	C ₁₀ H ₂₆ N ₄ NiO ₁₁
Formula weight	437.03g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 8.8062(18) Å α = 82.61(3)°. <i>b</i> = 9.946(2) Å β = 70.21(3)°. <i>c</i> = 12.817(3) Å γ = 65.53(3)°.
Volume	961.3(4) Å ³
<i>Z</i>	2
Density (calculated)	1.336 Mg/m ³
Absorption coefficient	1.050 mm ⁻¹
<i>F</i> (000)	384
Crystal size	0.25 x 0.35 x 0.4 mm ³
Φ range for data collection	1.69 to 25.08°.
Index ranges	-10 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 11, -15 ≤ <i>l</i> ≤ 15
Reflections collected	10220
Independent reflections	3407 [<i>R</i> (int ¹⁶⁵) = 0.0165] on <i>F</i> ²
Completeness to θ = 25.08°	99.5 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	3407 / 0 / 120
Goodness-of-fit on <i>F</i> ²	1.063
Final <i>R</i> indices[<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0556, <i>wR</i> 2 = 0.1410
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0566, <i>wR</i> 2 = 0.1420
Largest diff. peak and hole	1.132 and -0.863 e.Å ⁻³

3.4.3 Physicochemical characterisation of 11

FT-IR spectroscopy

The FT-IR spectrum for **11** is similar to the spectra of the previously discussed compounds **1-10**. The spectral similarities are not surprising given that the main characteristics of the FT-IR spectra arise from the coordinating *hpdta* ligand. For the

case of **11** the O-H stretches of water molecules engaged in H-bonds appear at *ca.* 3380 cm^{-1} . The broad signals above 3000 cm^{-1} result further from N-H vibrations of the ethylene-diammonium counter ions.

The stretches at *ca.* 1595 cm^{-1} and *ca.* 1395 cm^{-1} are attributed to asymmetric and symmetric carboxylate stretches, respectively. The weak stretch at *ca.* 1440 cm^{-1} is difficult to assign however, it is expected to originate from N-H bonds. The frequency differences of the asymmetric and symmetric carboxylate stretches ($\Delta\nu$) are indicative of the binding mode of the *hpdta* ligand.¹⁶³ In **11**, there is one asymmetric C-O stretch, at *ca.* 1600 cm^{-1} and a symmetric stretch at *ca.* 1395 cm^{-1} . The absence of multiple asymmetric and symmetric stretches suggests that all carboxylate functionalities bind in a similar fashion to the central Ni^{II} ion. The $\Delta\nu$ of *ca.* 200 cm^{-1} indicates that the carboxylate groups in **11** adopt the unidentate binding mode which is consistent with the binding mode observed in the crystal structure of **11** (Figure 3.21).¹⁶³

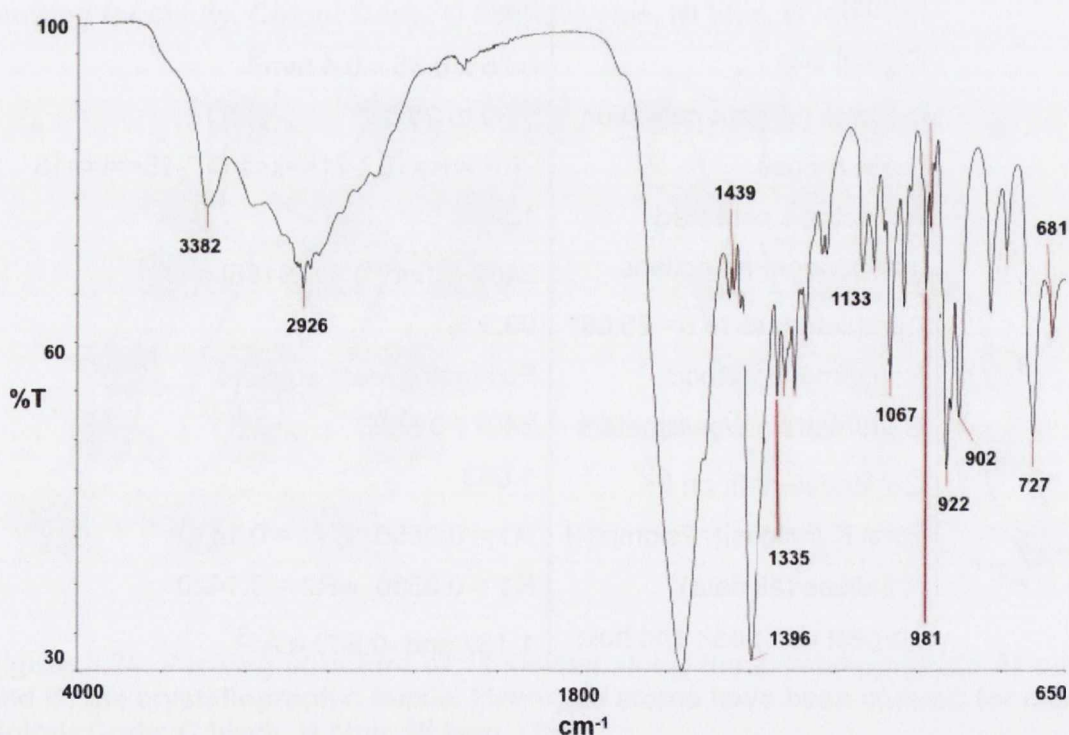


Figure 3.25: FT-IR spectrum of freshly ground microcrystals of **11** recorded using a diffuse reflectance accessory.

Table 3.19: Characteristic vibrational bands observed in the FT-IR spectra of **11.**¹³⁶⁻¹³⁸

Wavenumber (cm ⁻¹)	Assignment
3380	O-H ν_s and ν_{as} stretches
1600, 1395	C-O ν_{as} and ν_s stretches
1440	N-H stretch
1335, 1315	C-N
1305	-OH stretch
920	N-H bend
900	Out of plane -OH stretch

Thermogravimetric analysis

The thermal stability of **11** was characterised using thermogravimetric analysis (TGA). The analysis was carried out in the temperature range between 25 °C and 900 °C, in an air atmosphere. The heating rate was set to 5 °C/minute. The TGA of **11** reveals a weight loss of 7.88 % in the temperature range 25-85 °C. This thermogravimetric step can be attributed to the loss of the two constitutional water molecules (experimental weight loss: 7.88 %, theoretical weight loss: 8.23 %). A second weight loss of 77.43 % occurs when the temperature is increased to 470 °C. The three steps overlap each other and result in peaks in the TGA derivative curve centered at *ca.* 310 °C, *ca.* 365 °C and *ca.* 430 °C respectively. The peak centered at *ca.* 310 °C may be attributable to the loss of the ethylene-diammonium counterion, (experimental weight loss: 17.38 %, theoretical weight loss: 17.39 %) while the losses centered at *ca.* 365 °C and *ca.* 430 °C are attributable to the decomposition of the *hpdta* ligand and formation of Ni^{II} oxides (experimental weight loss: 60.05 %, theoretical weight loss: 60.87 %). The theoretical mass percentages of the proposed decomposition products were calculated as a percentage of the mass of enH₂[Ni(Hhpdta)].·2H₂O. These are reported in Table 3.20 and are in agreement with the experimentally observed values.



Figure 3.26: TGA curve for **11**. Recorded in an air atmosphere from 25 °C to 900 °C. Heating step was set to 5 °C/minute.

Table 3.20: Results for TGA analysis (recorded in an air atmosphere from 25 °C to 900 °C. Heating step was set to 5 °C/minute) of **11**.

Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
$C_{10}H_{26}N_4NiO_{11}$	100	100	25 (Initial)
$C_{10}H_{22}N_4NiO_9$	91.76	92.12	25 - 85
$C_7H_{10}N_2NiO_9$	74.37	74.73	85 - 340
NiO_2	13.51	14.70	340 – 900 (Final)

Powder X-ray Diffraction

A P-XRD experiment was performed to confirm the phase purity of the bulk sample of **11**. The results were compared with the simulated pattern as determined by the single-crystal X-ray diffraction experiments of **11**. The results, presented in Figure 3.27, suggest that crystals of **11** are phase pure and the refined structural model is accurate. The absence of reflections in the P-XRD pattern can be explained by the crystal habit. **11** forms thin, plate-like crystals, thus, some particular crystal planes may be not present in the recorded pattern. The loss of constitutional water molecules upon grinding the sample in preparation of the powder X-ray analysis, most likely explains the differences between experimental and calculated X-ray powder pattern.

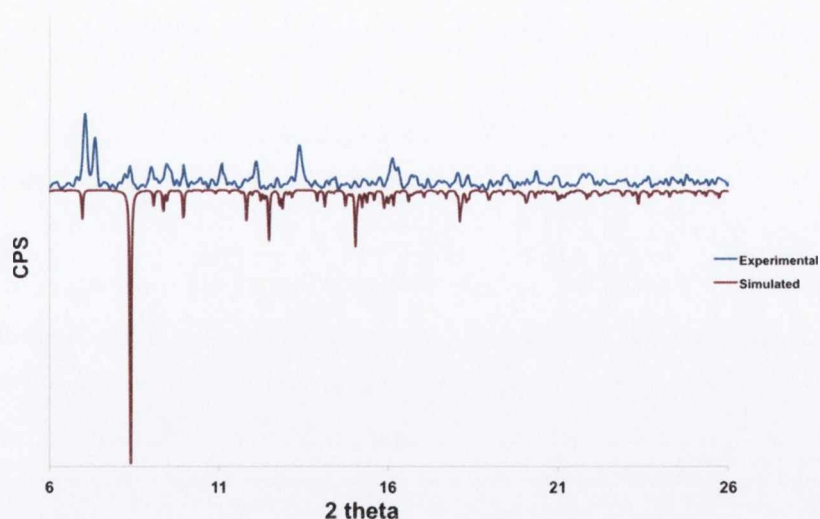


Figure 3.27: P-XRD pattern for crystals of **11** (blue) compared with a simulated pattern based on the single-crystal X-ray diffraction measurements (red)

Elemental Analysis

The chemical formula for **11**, $\text{C}_{10}\text{H}_{26}\text{N}_4\text{NiO}_{11}$ was further confirmed using elemental analysis. The results, presented in Table 3.21, show a good correlation between the theoretical and experimental values.

Table 3.21: Theoretical and experimental elemental analysis for 11. Theoretical based on $\text{C}_{10}\text{H}_{26}\text{N}_4\text{NiO}_{11}$.

Element	Theoretical composition (%)	Experimental composition (%)
C	27.48	27.78
H	6.00	5.91
N	12.82	12.66
Ni	13.43	13.12

3.5 The V^{III} *hpdt*a system

The formation of *hpdt*a containing V^{III} compounds was investigated herein. V^{III} *hpdt*a analogues were of particular interest due to the $\text{V}^{\text{III}}/\text{V}^{\text{II}}$ redox potential of -0.26 V (vs SHE). The potential was desirable compared to Fe^{III} *hpdt*a systems that require a reduction potential of $+0.77\text{ V}$ (vs SHE).^{166 167 168} The redox potentials provide an insight into the potential energy requirements to facilitate the electrochemical reduction of fixed CO_2 . For example the dinuclear Fe^{III} compound **8** would require an electric potential of -1.296 V (vs. SHE) to catalyse the proton-assisted, two electron reduction of carbon

dioxide to carbon monoxide and water. Replacing the Fe^{III} compound with a dinuclear V^{III} analogue reduces the energy requirement, or electric potential (E°), to 0.266 V (vs. SHE).¹¹

Inspiration for this work was drawn from reports in the literature detailing the isolation of a dinuclear V^{III} *hpdta* compounds that is structurally related to **8**.^{1, 3, 169-170, 171} It was our aim to modify the reaction conditions to investigate the formations of a tetranuclear V^{III} *hpdta* compound. The development of a system that distributes the reduction equivalents over four V^{III} centres combined with a low activation energy would be a step towards a more efficient model system for the four electron, proton assisted, reduction of carbon dioxide to produce methanol.

With this in mind it was our aim to investigate the formation of tetranuclear V^{III} *hpdta* compounds. The protocol involved the reaction of aqueous *hpdta* and VCl_3 solutions using ethylenediamine, sodium hydroxide or propylenediamine to deprotonate the ligand and adjust the pH to values in the range 2.5 to 9.5. Each experiment was performed in degassed solutions under atmospheric conditions and repeated under nitrogen in the absence and presence of DMA and methanol. Some systems were further treated with carbon dioxide, or sodium hydrogen carbonate, benzoic acid or acetic acid to promote the crystallisation process of desired complexes.

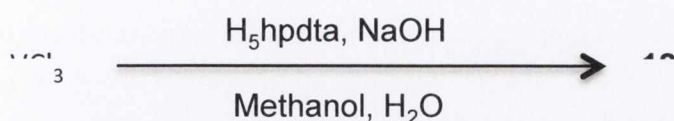
The studies revealed the requirement of atmospheric conditions and the subsequent oxidation of the V^{III} ions to obtain crystalline products. Under these conditions the colour of reaction mixture changes from green to a blue colour indicative of the oxidation to V^{IV} . Single-crystals of a compound containing the $[\text{V}_4(\mu\text{-O})_2(\text{hpdta})_2(\text{O})_4]^{2+}$ complex could be obtained over a wide range of reaction conditions. Variations of the reaction conditions influenced the quality and rate of formation of the compound, rather than the nature of the structure of the complex. It was concluded that the tetranuclear V^{IV} complex in **12** is the most inherently stable complex under the applied conditions.

The reaction that led to the most suitably sized crystals for single-crystal X-ray diffraction experiments is described below.

3.5.1 $\text{Na}_8[\text{V}_4(\mu\text{-O})_2(\text{hpdta})_2(\text{O})_4]\cdot 3\text{H}_2\text{O}$ (**12**)

The tetranuclear, V^{IV} complex in $\text{Na}_8[\text{V}_4(\mu\text{-O})_2(\text{hpdta})_2(\text{O})_4]\cdot 3\text{H}_2\text{O}$ (**12**) is an oxidation product that forms upon reacting a degassed aqueous *hpdta* ligand solution with a

degassed aqueous VCl_3 solution when 3 ml methanol is added to the reaction mixture and sodium hydroxide is used to adjust the pH to 4.0. Blue-silver, square shaped crystals of **12** suitable for single-crystal X-ray diffraction were obtained after fifteen days upon exposure to the atmosphere and co-evaporation with dimethylacetamide. The compound crystallizes in the monoclinic space group $C2/c$ (no. 15). Figure 3.28 shows the structure of the tetranuclear complex in **12**.



Scheme 3.5: Preparation of compound 12.

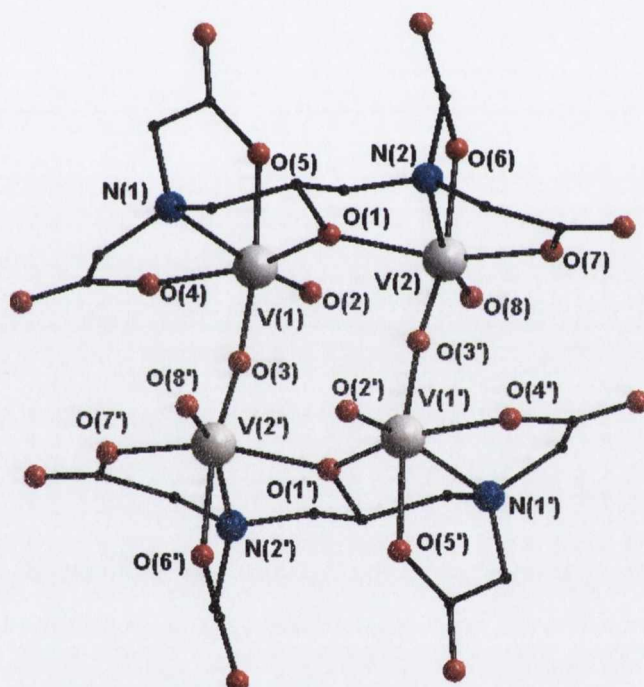


Figure 3.28: The structure of the tetranuclear complex in 12. The hydrogen atoms are omitted for clarity. Colour code: C black, V^{IV} grey, N blue, O red.

3.5.2 Structural characterisation of 12

Each of the four V^{IV} centres in **12** adopts a distorted octahedral coordination geometry with distances of 3.622(88) Å and 3.723(26) Å between $\text{V}(1)\text{-V}(2)$ and $\text{V}(1)\text{-V}(2')$, respectively. The asymmetric unit contains half of the tetranuclear complex in **12**, including the two vanadium centres, $\text{V}(1)$ and $\text{V}(2)$, a coordinating, bridging *hpdta* ligand and three O^{2-} oxo groups, $\text{O}(2)$, $\text{O}(8)$ and $\text{O}(3)$. The complex is completed by symmetry operations. The octahedral coordination environment of the $\text{V}(1)$ centre is formed by the

carboxylate O-donor O(4), the alkoxy O-donor O(1), the O²⁻ oxo group O(2), the N-donor N(1) and reveal V-O bond distances of 2.001(3) Å, 2.025(8) Å and 1.612(10) Å, respectively while the V-N bond distance is 2.288(13) Å. The shorter V-O bond distance of 1.612(10) Å between V(1) and O(2) is consistent with literature values for V^{IV}=O bonds and illustrates the double bond character of this bond.^{172,173} The O_{carboxylate}-donor atom O(5) and the μ_2 -O-donor atom O(3), occupy the apical positions of the octahedra as shown in Figure 3.29 giving distances of 2.033(16) Å and 1.929(4) Å, respectively. The V(2) centre displays a similar coordination environment to the V(1) centre. The equatorial planes as shown in Figure 3.29 are formed by O-donor atoms O(7), O(8), O(1) and the N-donor atom N(2) to give bond distances of 2.008(7) Å, 1.618(10) Å, 2.018(12) Å and 2.276(5) Å, respectively. The apexes of the distorted octahedra are occupied by the O_{carboxylate}-donor atom O(6) and the μ_2 -O-donor atom generated by symmetry, O(3'). The corresponding V-O bond lengths are 2.058(14) Å and 1.803(3) Å, respectively.

The distortion from ideal octahedral coordination geometries can be illustrated through examination of the bond angles. The bond angles involving the V centres and the atoms located at the apical positions are 164.28(27)° for O(3)-V(1)-O(5) and 164.19(28)° for O(3')-V(2)-O(6) thus deviating considerably from the ideal 180°. Similarly, the bond angles of 101.26(21)°, 86.74(23)°, 88.27(22)°, 98.55(24)° and 82.66(23)° for O(2)-V(1)-O(4), O(3)-V(1)-O(1), O(3)-V(1)-N(1), O(8)-V(2)-O(7) and O(1)-V(2)-O(6) respectively, deviate greatly from the ideal 90°. Moderate deviations from the ideal 90° angle include 91.39(25)°, 91.13(26)° and 90.61(23)° for O(2)-V(1)-O(5), O(8)-V(2)-O(6) and O(7)-V(2)-O(6) respectively. A list of selected bond angles can be found in Table 3.23.

Bond valence sum analysis confirms that all four V atoms in **12** adopt the oxidation state +IV.⁴¹ The V^{IV}-N and V^{IV}-O bond distances are in agreements with the V^{IV} oxidation state.^{172,173 and 174} The assignment is further supported by charge considerations. The compound contains four V^{IV} and five Na⁺ ions, contributing to a charge of +21. This positive charge is counter-balanced by the two fully deprotonated *hpdt*a ligands, the two bridging oxygen atoms, O(3), O(3') and the four O²⁻ oxygen donors, O(2), O(8) and symmetry equivalents, to give the neutral compound **12**.

Table 3.22: Selected bond distances for the V^{IV} centres in 12.

Atom	Bond	Bond Distance (Å)	BVS	Assigned Oxidation state
V(1)	V(1)-O(2)	1.612(10)	4.1605	4
	V(1)-O(3)	1.929(4)		
	V(1)-O(4)	2.001(3)		
	V(1)-O(1)	2.025(8)		
	V(1)-O(5)	2.033(16)		
	V(1)-N(1)	2.288(13)		
V(2)	V(2)-O(8)	1.618(10)	3.9572	4
	V(2)-O(3')	1.803(3)		
	V(2)-O(7)	2.008(7)		
	V(2)-O(1)	2.018(12)		
	V(2)-O(6)	2.058(14)		
	V(2)-N(2)	2.276(5)		

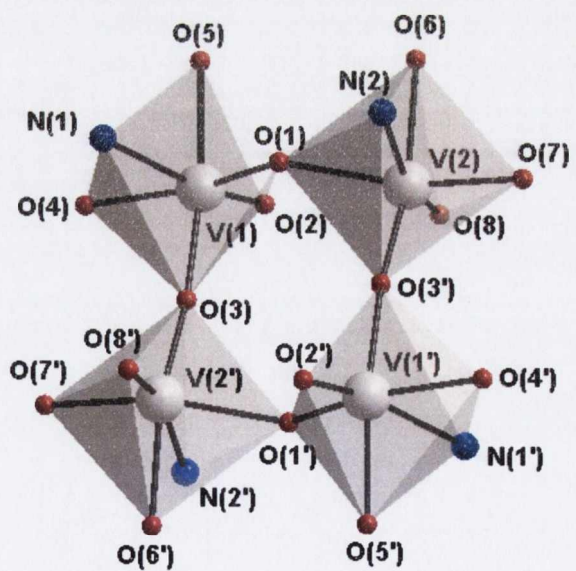


Figure 3.29: Polyhedral representations of the V^{IV} centres in 12. The hydrogen atoms have been omitted for clarity. Colour Code: C black, N blue, O red, V^{IV} grey.

Table 3.23: Selected bond angles for compound 12.

	Bond Angle (°)		Bond Angle (°)
O(2)-V(1)-O(3)	103.95(24)	O(5)-V(1)-N(1)	76.73(22)
O(2)-V(1)-O(4)	101.26(21)	O(8)-V(2)-O(7)	98.55(24)
O(3)-V(1)-O(4)	86.96(25)	O(8)-V(2)-O(1)	106.84(24)
O(2)-V(1)-O(1)	105.61(21)	O(7)-V(2)-O(1)	153.80(17)
O(3)-V(1)-O(1)	86.74(23)	O(8)-V(2)-O(6)	91.13(26)
O(4)-V(1)-O(1)	153.13(20)	O(7)-V(2)-O(6)	90.61(23)
O(2)-V(1)-O(5)	91.39(25)	O(1)-V(2)-O(6)	82.66(23)
O(3)-V(1)-O(5)	164.28(27)	O(8)-V(2)-N(2)	164.78(24)
O(4)-V(1)-O(5)	93.46(24)	O(7)-V(2)-N(2)	75.00(19)
O(1)-V(1)-O(5)	85.83(23)	O(1)-V(2)-N(2)	78.8(2)
O(2)-V(1)-N(1)	167.04(22)	O(6)-V(2)-N(2)	75.37(21)
O(3)-V(1)-N(1)	88.27(22)	O(3')-V(2)-O(6)	164.19(28)
O(1)-V(1)-N(1)	78.99(19)		

The structure is characterised in the solid state by van der Waal interactions and interactions between the uncoordinated oxygen atoms of the carboxylate moieties, the solvent water molecules and the Na⁺ counter ions. The sodium ions are disordered and they adopt distorted octahedral binding environments. The Na⁺-O bond distances vary between *ca.* 2.2 Å and *ca.* 2.5 Å. The packing arrangement of **12** can be seen in Figure 3.30 and Figure 3.31.

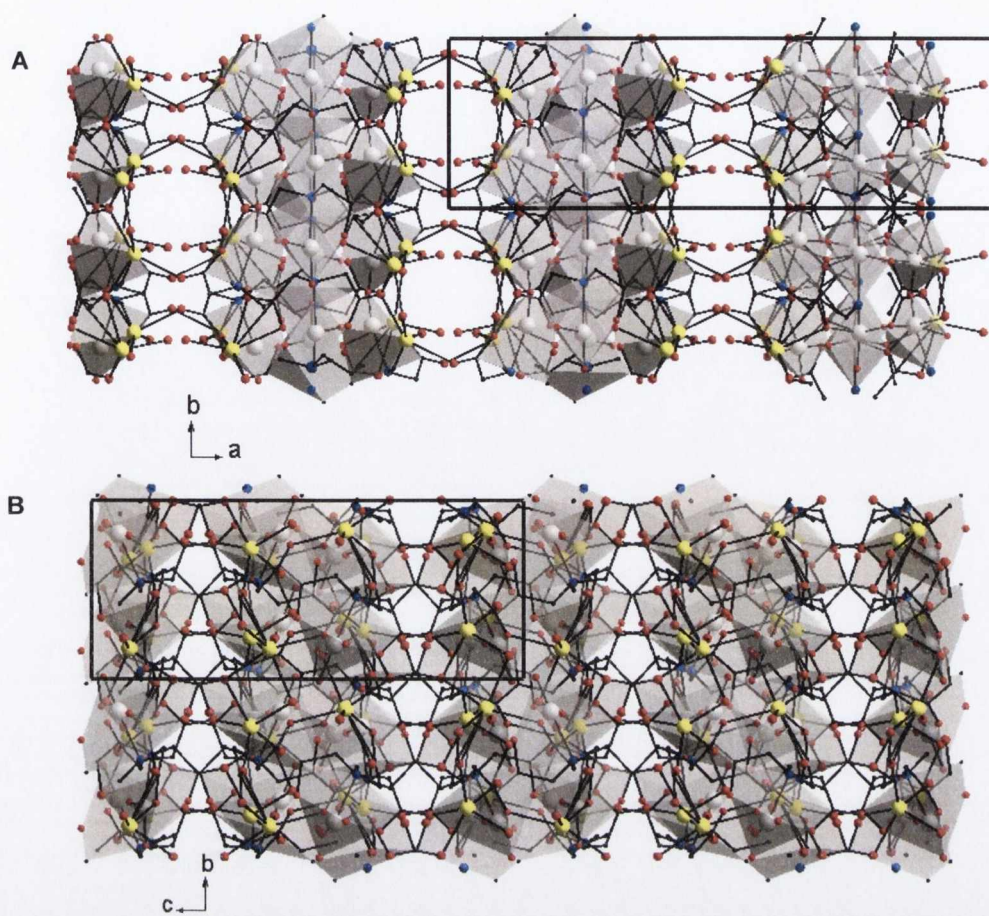


Figure 3.30: Packing diagram of 12, with polyhedral representations of the V^{IV} centres. Viewed along the crystallographic A) c -axis , B) a -axis. Hydrogen atoms have been omitted for clarity. Colour code: C black, N blue, Na yellow, O red, V^{IV} grey.

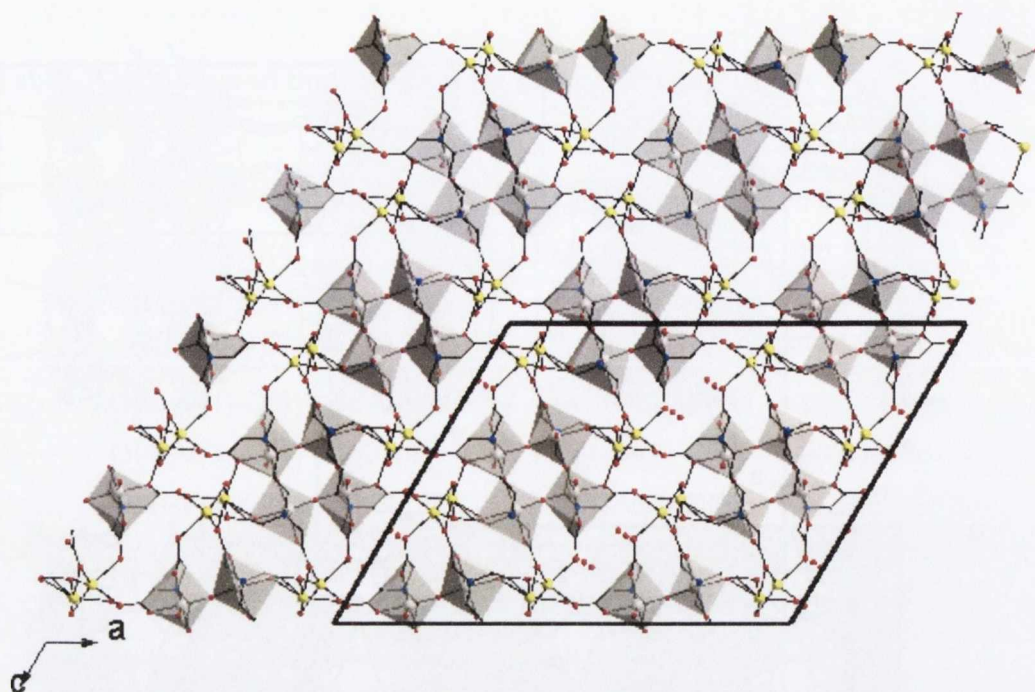


Figure 3.31: Packing diagram of **12, with polyhedral representations of the V^{IV} centres, view along the crystallographic b -axis. Hydrogen atoms have been omitted for clarity. Colour Code: C black, N blue, Na yellow, O red, V^{IV} grey.**

The crystal structure refinement of **12** is converged at a final $R1$ value of 7.44%, a goodness of fit of 1.017, an acceptable data to parameter ratio and 'largest difference peak and hole' values supporting the provided structural model. The crystal data and structure refinement parameters are summarized in Table 3.24.

Table 3.24: Crystal data and structure refinement parameters for 12

Compound	12
Empirical formula	C ₁₄ H ₂₄ N ₄ Na ₅ O ₂₇ V ₄
Formula weight	999.06g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 28.034(6) Å α = 90°. b = 7.5510(15) Å β = 120.46(3)°. c = 21.257(4) Å γ = 90°.
Volume	3896.2(11) Å ³
Z	4
Density (calculated)	2.017 Mg/m ³
Absorption coefficient	1.429 mm ⁻¹
F(000)	2304
Crystal size	0.2 x 0.4 x 0.3 mm ³
Φ range for data collection	1.69 to 25.00°.
Index ranges	-33 ≤ h ≤ 33, -7 ≤ k ≤ 8, -25 ≤ l ≤ 17
Reflections collected	15157
Independent reflections	5720 [R(int) = 0.0452] on F ²
Completeness to θ = 25.00°	99.2 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	5720 / 0 / 299
Goodness-of-fit on F ²	1.017
Final R indices [I > 2σ(I)]	R1 = 0.744, wR2 = 0.1933
R indices (all data)	R1 = 0.824, wR2 = 0.2306
Largest diff. peak and hole	0.768 and -0.957 e.Å ⁻³

3.5.3 Physicochemical characterisation of 12

FT-IR spectroscopy

Compound **12** exhibits the characteristic FT-IR stretch associated with *hpdta* coordination compounds. The broad band at ca. 3330 cm⁻¹ identifies the O-H stretches arising from the constitutional water molecules present in **12**. The strong asymmetric and symmetric stretches arising from the carboxylate moieties appear at ca. 1634 cm⁻¹,

ca. 1610 cm^{-1} , ca. 1370 cm^{-1} and ca. 1340 cm^{-1} , respectively. The signals at 1320 cm^{-1} and ca. 1270 cm^{-1} may be attributable to the C-N stretches. The former C-N stretch partly overlaps with the discussed, C-O stretches at ca. 1370 cm^{-1} and ca. 1340 cm^{-1} . The characteristic $\text{V}^{\text{IV}}=\text{O}$ stretch does not clearly emerge in the spectrum for **12**. It has been extensively investigated in the literature and is reported to resonate as a band at ca. 1000 cm^{-1} , with several examples of its appearance between ca. 990 cm^{-1} and ca. 885 cm^{-1} .¹⁷⁵

The frequency differences of the asymmetric and symmetric carboxylate stretches ($\Delta\nu$) may be used to determine the binding mode of the carboxylate functionality.¹⁶³ In the case of **12**, there are two asymmetric C-O stretches at ca. 1635 cm^{-1} and ca. 1610 cm^{-1} and there are two symmetric stretches at ca. 1370 cm^{-1} and ca. 1340 cm^{-1} . The corresponding $\Delta\nu$ values for **12** are ca. 260 cm^{-1} and ca. 270 cm^{-1} indicating that both carboxylate functional groups adopt the unidentate binding modes. This is consistent with the crystal structure of **12** (Figure 3.28).¹⁶³ It is probable that the two resonances for the C-O binding arises from the symmetry of the coordinations cluster in which the donor atoms of the iminodiacetic acid functions of the *hpdta* ligands adopt facial arrangements. The tendency of some carboxylate functionalities to engage in H-bonds may also affect the IR-spectrum of **12**.

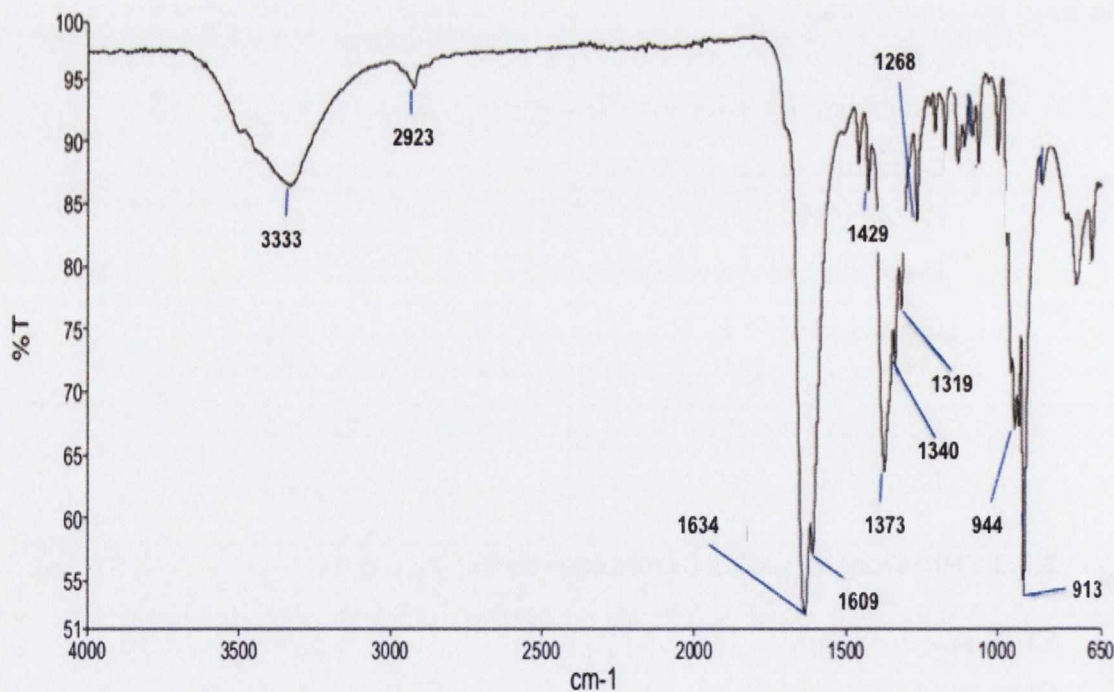


Figure 3.32: FT-IR spectrum of freshly ground microcrystals of **12** recorded using a diffuse reflectance accessory.

Table 3.25:Characteristic vibrational bands observed in the FT-IR spectra of **12.**¹³⁶⁻¹³⁸

Wavenumber (cm ⁻¹)	Assignment
3330 (br)	O-H ν_s + ν_{as} stretches and N-H stretch
1635 (s), 1610 (s)	Asymmetric C-O stretch
1370 (s), 1340 (s)	Symmetric C-O stretch
1320, 1270	C-N stretch

Thermogravimetric analysis

The thermal stability of **12** was characterised by thermogravimetric analysis (TGA). The analysis was carried out in the temperature range between 30 °C and 900 °C, in an air atmosphere. The heating rate was set to 10 °C/minute with an isothermal step at 100 °C for 15 minutes. The TGA of **12** reveals a weight loss of 5.04 % in the temperature range between 30-100 °C. This thermogravimetric step can be attributed to the loss of the three constitutional water molecules (experimental weight loss: 5.04 %, theoretical weight loss: 5.55 %). A further increase in the temperature up to 760 °C produces a weight loss that occurs in a two-step process centered at *ca.* 340 °C and *ca.* 525 °C. This weight loss can be associated with the oxidative decomposition of the *hpdt*a ligands and the formation of metal oxides (experimental weight loss: 51.40 %, theoretical weight loss: 50.08 %), (final experimental weight loss: 56.44 %, final theoretical weight loss: 55.63 %). The theoretical mass percentages of the proposed decomposition products were calculated as a percentage of the mass of $\text{Na}_5[\text{V}_4(\mu\text{-O})_2(\text{hpdt})_2(\text{O})_4]\cdot 3\text{H}_2\text{O}$. These are reported in Table 3.26 and are in agreement with the experimentally observed values.

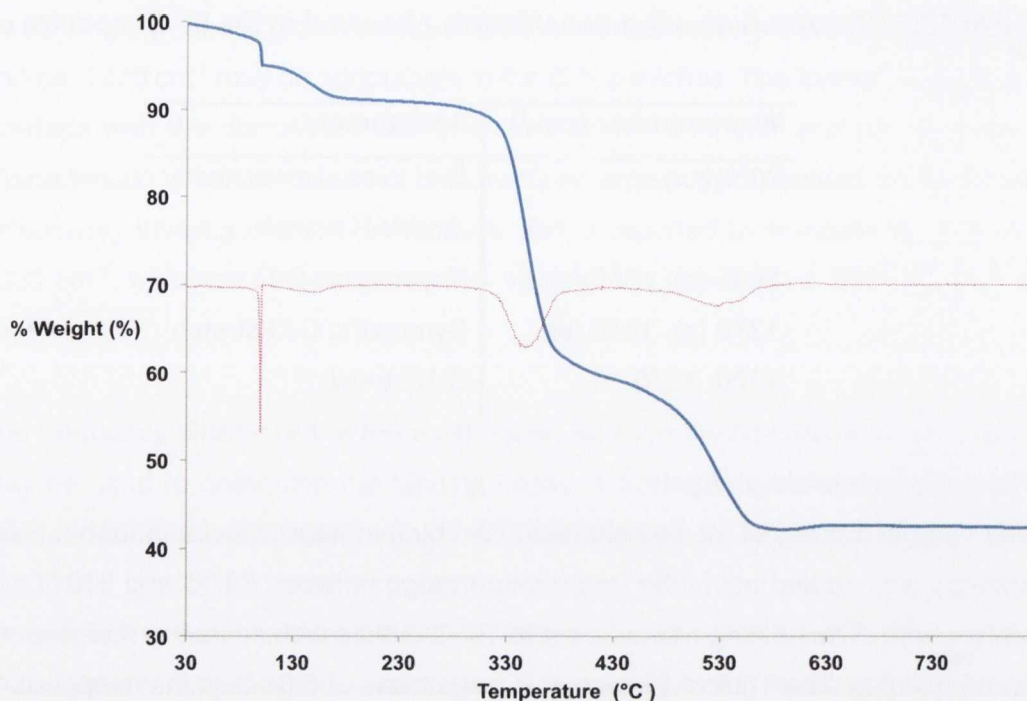


Figure 3.33: TGA curve for **12**. Recorded in an air atmosphere from 30°C to 900 °C. Heating step was set to 10 °C/minute with an isothermal step at 100°C for 15 minutes.

Table 3.26: Results for TGA analysis (recorded under atmospheric conditions from 30 °C to 900 °C. Heating step was set to 10 °C/minute with an isothermal step at 100°C for 15 minutes) of **12**.

Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
$C_{14}H_{24}N_4Na_5O_{27}V_4$	100	100	30 (Initial)
$C_{14}H_{18}N_4Na_5O_{24}V_4$	94.35	94.97	30 - 100
Ligand decomposition	44.37	43.56	100 - 900

Elemental Analysis

The assigned chemical formula for **12**, $C_{14}H_{24}N_4Na_5O_{27}V_4$ was confirmed using elemental analysis. The results, presented in Table 3.27, show a good correlation between the theoretical and experimental values. These results coupled with the P-XRD results confirm the phase-purity of **12**.

Table 3.27: Theoretical and experimental elemental analysis for 12. Theoretical based on C₁₄H₂₄N₄Na₅O₂₇V₄.

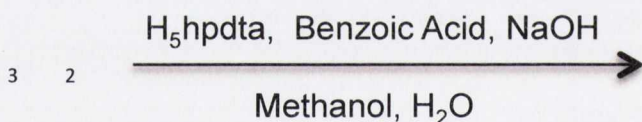
Element	Theoretical composition (%)	Experimental composition (%)
C	16.83	16.88
H	2.42	2.45
N	5.61	5.57
Na	11.51	11.46

Chapter 4 Carboxylate Binding Studies to Produce Octanuclear Coordination Clusters

The objective of these studies was to provide an understanding of the tetranuclear M^{III} *hpdt*a compounds' affinity towards carboxylate bearing ligands. It was also our intention to acquire novel coordination compounds that are stabilized by carboxylate bearing ligands. In doing so, we have provided an insight into their carbonate or carbamate binding reactivity's and developed a synthetic methodology to prepare unprecedented Fe^{III} coordination compounds that form in the presence of carboxylated ligands.

4.1 $\text{Na}_3[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2\}(\text{OOC}\text{C}_6\text{H}_5)_2]\cdot 12\text{H}_2\text{O}\cdot\text{DMF}$ (**13**)

The tetranuclear Fe^{III} complex in $\text{Na}_3[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2\}(\text{OOC}\text{C}_6\text{H}_5)_2]\cdot 12\text{H}_2\text{O}\cdot\text{DMF}$ (**13**) is formed when aqueous Fe^{III} solutions are reacted with H_5hpdt a, benzoic acid (**L3**) and when sodium hydroxide is used to adjust the pH to 7.5 (Scheme 4.1). Brown, reflective, plate-like crystals of **13** suitable for single-crystal X-ray diffraction measurements were obtained by co-evaporation with dimethylformamide. The compound crystallizes in the triclinic space group *P*-1. Figure 4.1 shows the structure of the tetranuclear complex in **13**.



Scheme 4.1: Formation of 13

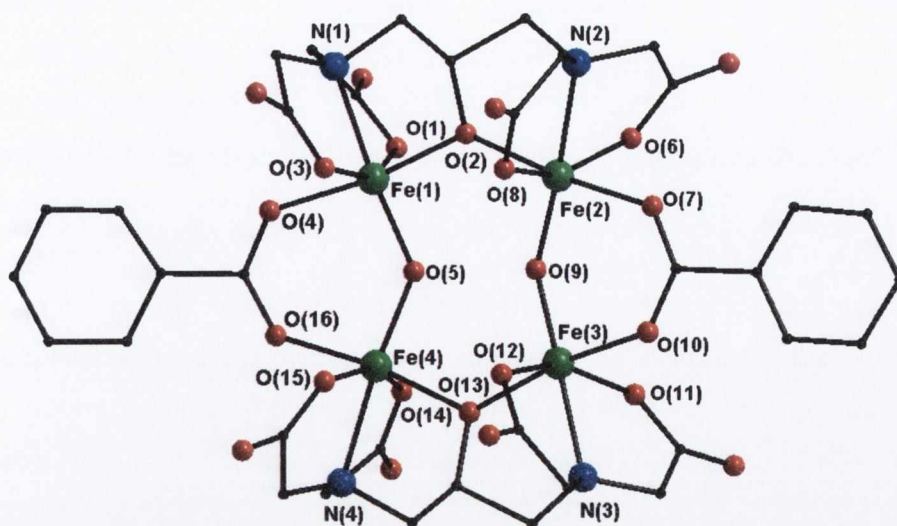


Figure 4.1: The structure of the tetranuclear complex in **13**. The hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, N blue, O red.

4.1.1 Structural characterisation of **13**

The square planar tetranuclear Fe^{III} compound, **13**, is coordinated by two fully deprotonated *hpdta* ligands, bridging oxo/hydroxo moieties (originating from two deprotonated water molecules) and two benzoate ligands. The benzoate ligands bind in a *syn, syn*, bidentate bridging mode to Fe(1) and Fe(4), and Fe(2) and Fe(3), respectively. The four Fe^{III} centres in **13**, Fe(1), Fe(2), Fe(3) and Fe(4), are in a comparable coordination environment and adopt distorted octahedral coordination geometries. Fe(1)/Fe(2) and Fe(3)/Fe(4) are bridged by the alkoxo oxygen atoms, O(2) and O(13), of two *hpdta* ligands. The distances between Fe(1)-Fe(2) and Fe(3)-Fe(4) are *ca.* 3.8 Å. The Fe(1)-Fe(4) and Fe(2)-Fe(3) distances along the oxo/hydroxo moieties are *ca.* 3.4 Å in length.

The Fe^{III} ion, Fe(1), is coordinated by an alkoxo oxygen atom O(2), and two carboxylate oxygen atoms, O(1) and O(3) and shows Fe^{III} -O distances of 2.035(13) Å, 2.07(22) Å and 2.064(26) Å, respectively. The equatorial plane is completed by an oxygen atom, O(4), located on the auxiliary benzoate ligand. The Fe(1)-O(4) bond length is 2.084(14) Å. The apical positions of the coordination environment as visualised in Figure 4.2 are occupied by the N-donor atom, N(1), and the bridging O-donor atom O(5), to give bond distances of 2.170(20) Å and 1.856(18) Å, respectively. The Fe^{III} -O and Fe^{III} -N bond lengths are comparable to those observed in **8**, **9** and **10** and are consistent those reported for Fe^{III} compounds in the literature.^{1-3, 123, 139, 169, 176} The distortion from ideal octahedral coordination geometry for Fe(1) is exemplified through examination of the bond angles. For example the bond angles N(1)-Fe(1)-O(5) and O(4)-Fe(1)-O(2) are 174.80(95)° and 171.63(92)° thus deviating from the ideal angle of 180°. Significant deviations from 90° angles are observed

for O(5)-Fe(1)-O(3), N(1)-Fe(1)-O(1), N(1)-Fe(1)-O(3), O(5)-Fe(1)-O(1), O(5)-Fe(1)-O(4) and N(1)-Fe(1)-O(2) of 104.91(86)°, 77.77(90)°, 77.87(84)°, 99.81(89)°, 96.57(91)° and 84.08(87)° respectively. Minor deviations are observed for the bond angles O(5)-Fe(1)-O(2), O(4)-Fe(1)-N(1) and O(2)-Fe(1)-O(1) of 91.48(85)°, 87.98(89)° and 92.84(84)° respectively.

The remaining Fe^{III} ions in **13**, Fe(2), Fe(3) and Fe(4) adopt similar coordination environments. They are coordinated to nitrogen and oxygen donor atoms of the fully deprotonated *hpdta* ligands and O-donor atoms of the bridging ligands. The donor atoms of the iminodiacetic acid functionalities of the *hpdta* ligand surround the ions in *meridional* fashions. The Fe^{III}-O and Fe^{III}-N bond distances, range from 1.856(18) Å to 2.086(25) Å and from 2.170(20) Å to 2.216(14) Å, respectively. Deviations for the ideal 180° angle of an octahedral coordination sphere can be observed for the bond angles O(14)-Fe(4)-O(15), O(12)-Fe(3)-O(11) and O(8)-Fe(2)-O(6) of 155.80(96)°, 154.64(91)° and 153.00(88)°, respectively. Significant deviances from the 90° angle are observed for the bond angles O(15)-Fe(4)-N(4), O(11)-Fe(3)-N(3) and O(6)-Fe(2)-N(2) of 78.72(29)°, 76.91(28)° and 76.30(26)° respectively. Other selected bond lengths and bond angles involving the Fe^{III} centres in **13** are summarised in Table 4.1 and

Table 4.2. The four distorted octahedral coordination polyhedra in the tetranuclear complex in **13** share common vertices.

Table 4.1: Selected bond distances for the Fe^{III} centres in **13**.

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1)-O(5)	1.856(18)
	Fe(1)-O(2)	2.035(13)
	Fe(1)-O(3)	2.064(26)
	Fe(1)-O(1)	2.067(21)
	Fe(1)-O(4)	2.084(14)
	Fe(1)-N(1)	2.170(20)
Fe(2)	Fe(2)-O(9)	1.862(11)
	Fe(2)-O(2)	2.067(16)
	Fe(2)-O(8)	2.065(26)

	Fe(2)-O(7)	2.074(16)
	Fe(2)-O(6)	2.078(20)
	Fe(2)-N(2)	2.173(15)
Fe(3)	Fe(3)-O(9)	1.871(10)
	Fe(3)-O(12)	2.039(24)
	Fe(3)-O(10)	2.046(14)
	Fe(3)-O(11)	2.074(23)
	Fe(3)-O(13)	2.085(13)
	Fe(3)-N(3)	2.195(14)
Fe(4)	Fe(4)-O(5)	1.863(11)
	Fe(4)-O(14)	2.003(23)
	Fe(4)-O(16)	2.023(14)
	Fe(4)-O(13)	2.054(16)
	Fe(4)-O(15)	2.086(25)
	Fe(4)-N(4)	2.216(14)

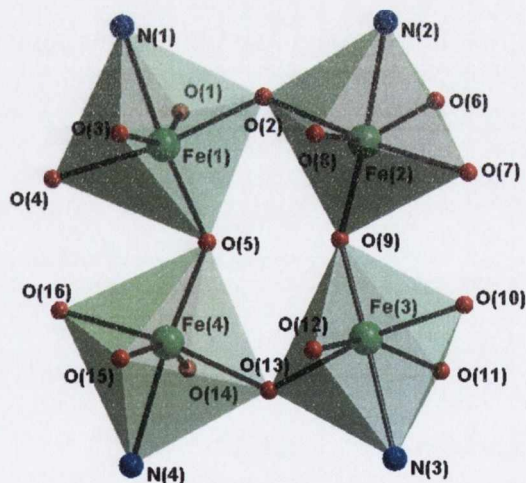


Figure 4.2: Polyhedral representation of the Fe^{III} centres in 13. The hydrogen and carbon atoms have been omitted for clarity. Colour Code: Fe green, N blue, O red.

Table 4.2: Selected bond angles for compound 13.

	Bond Angle (°)		Bond Angle (°)
O(5)-Fe(1)-O(2)	91.48(25)	O(9)-Fe(3)-O(12)	105.61(86)
O(5)-Fe(1)-O(3)	104.91(26)	O(9)-Fe(3)-O(10)	95.56(84)
O(2)-Fe(1)-O(3)	90.00(22)	O(12)-Fe(3)-O(10)	88.85(83)
O(5)-Fe(1)-O(1)	99.81(29)	O(9)-Fe(3)-O(11)	99.39(87)
O(2)-Fe(1)-O(1)	92.84(24)	O(12)-Fe(3)-O(11)	154.64(91)
O(3)-Fe(1)-O(1)	155.04(28)	O(10)-Fe(3)-O(11)	84.52(84)
O(5)-Fe(1)-O(4)	96.57(31)	O(9)-Fe(3)-O(13)	93.94(82)
O(2)-Fe(1)-O(4)	171.63(32)	O(12)-Fe(3)-O(13)	87.17(80)
O(3)-Fe(1)-O(4)	85.72(22)	O(10)-Fe(3)-O(13)	170.39(87)
O(1)-Fe(1)-O(4)	88.07(28)	O(11)-Fe(3)-O(13)	95.39(88)
O(5)-Fe(1)-N(1)	174.80(35)	O(9)-Fe(3)-N(3)	174.57(91)
O(2)-Fe(1)-N(1)	84.08(27)	O(12)-Fe(3)-N(3)	78.43(89)
O(3)-Fe(1)-N(1)	77.87(24)	O(10)-Fe(3)-N(3)	88.10(87)
O(1)-Fe(1)-N(1)	77.77(30)	O(11)-Fe(3)-N(3)	76.91(88)
O(4)-Fe(1)-N(1)	87.98(29)	O(13)-Fe(3)-N(3)	82.54(86)
O(5)-Fe(4)-O(14)	98.97(30)	O(9)-Fe(2)-O(2)	90.87(81)
O(5)-Fe(4)-O(16)	95.70(29)	O(9)-Fe(2)-O(8)	104.89(82)
O(14)-Fe(4)-O(16)	87.9(9)	O(2)-Fe(2)-O(8)	88.44(80)
O(5)-Fe(4)-O(13)	92.51(26)	O(9)-Fe(2)-O(7)	95.98(85)
O(14)-Fe(4)-O(13)	92.54(27)	O(2)-Fe(2)-O(7)	173.10(92)
O(16)-Fe(4)-O(13)	171.61(33)	O(8)-Fe(2)-O(7)	89.00(86)
O(5)-Fe(4)-O(15)	104.89(31)	O(9)-Fe(2)-O(6)	101.74(25)
O(14)-Fe(4)-O(15)	155.80(36)	O(2)-Fe(2)-O(6)	95.58(26)
O(16)-Fe(4)-O(15)	85.84(27)	O(8)-Fe(2)-O(6)	153.00(28)
O(13)-Fe(4)-O(15)	90.38(30)	O(7)-Fe(2)-O(6)	83.86(24)
O(5)-Fe(4)-N(4)	174.11(32)	O(9)-Fe(2)-N(2)	173.69(30)
O(14)-Fe(4)-N(4)	77.84(29)	O(2)-Fe(2)-N(2)	83.40(26)

O(16)-Fe(4)-N(4)	89.17(27)	O(8)-Fe(2)-N(2)	77.68(25)
O(13)-Fe(4)-N(4)	82.74(27)	O(7)-Fe(2)-N(2)	89.80(28)
O(15)-Fe(4)-N(4)	78.72(29)	O(6)-Fe(2)-N(2)	76.30(26)

The charge of the negative tetranuclear complex in **13** is compensated by sodium counter cations. The sodium ions in **13** are partially hydrated/solvated and bind to the carboxylate O-donors of the coordinating *hpdta* ligands. The sodium ions are disordered and they adopt distorted octahedral or trigonal bipyramidal binding environments. The Na⁺-O bond distances vary between *ca.* 2.3 Å and *ca.* 2.8 Å. The counter ions and their symmetry equivalents locate between the tetranuclear transition metal complexes and connect these in the solid state.

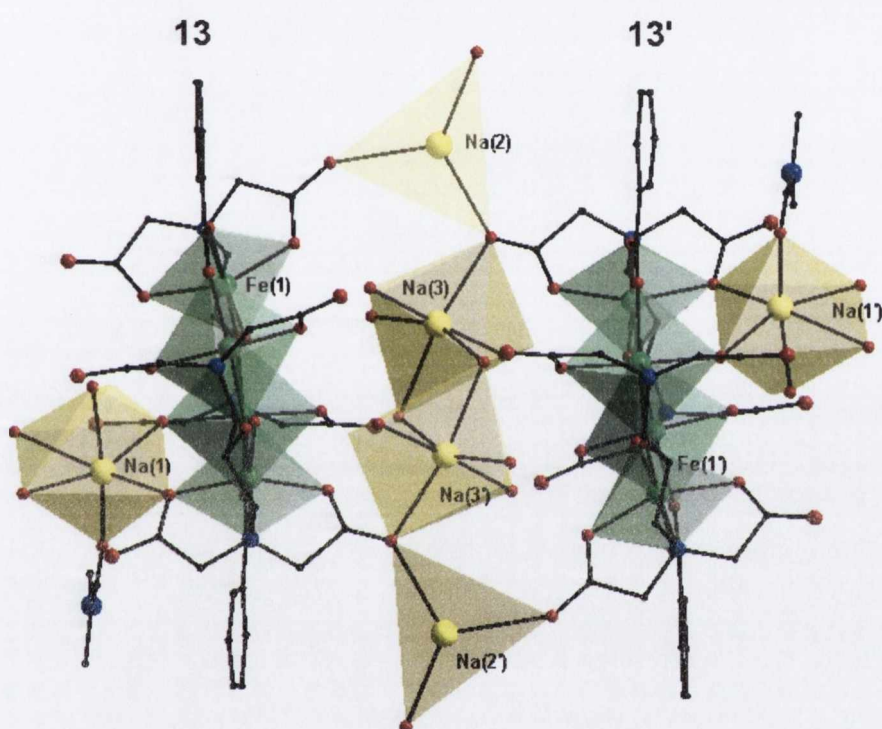


Figure 4.3: Packing view of **13, whereby two parallel aligned tetranuclear complexes are linked via Na⁺-O bonds, with polyhedra representations of the Fe^{III} and Na⁺ centres. The hydrogen atoms and constitutional water molecules have been omitted for clarity. Colour Code: C black, Na yellow, Fe green, N blue, O red.**

13 aggregates via its counter ions into 2D polymeric networks that extend into the crystallographic *b*- and *c*-axes. This aggregation is supported by weak London forces, van der Waal forces and ion-dipole interactions. The packing structure of **13** further reveals π - π interactions between benzoate ligands resulting in distances of *ca.* 3.2 Å between the centroids of two antiparallel benzene rings. The π - π stacking between the benzene rings can be observed when the structure is viewed along the crystallographic *b*-axis, Figure 4.4.

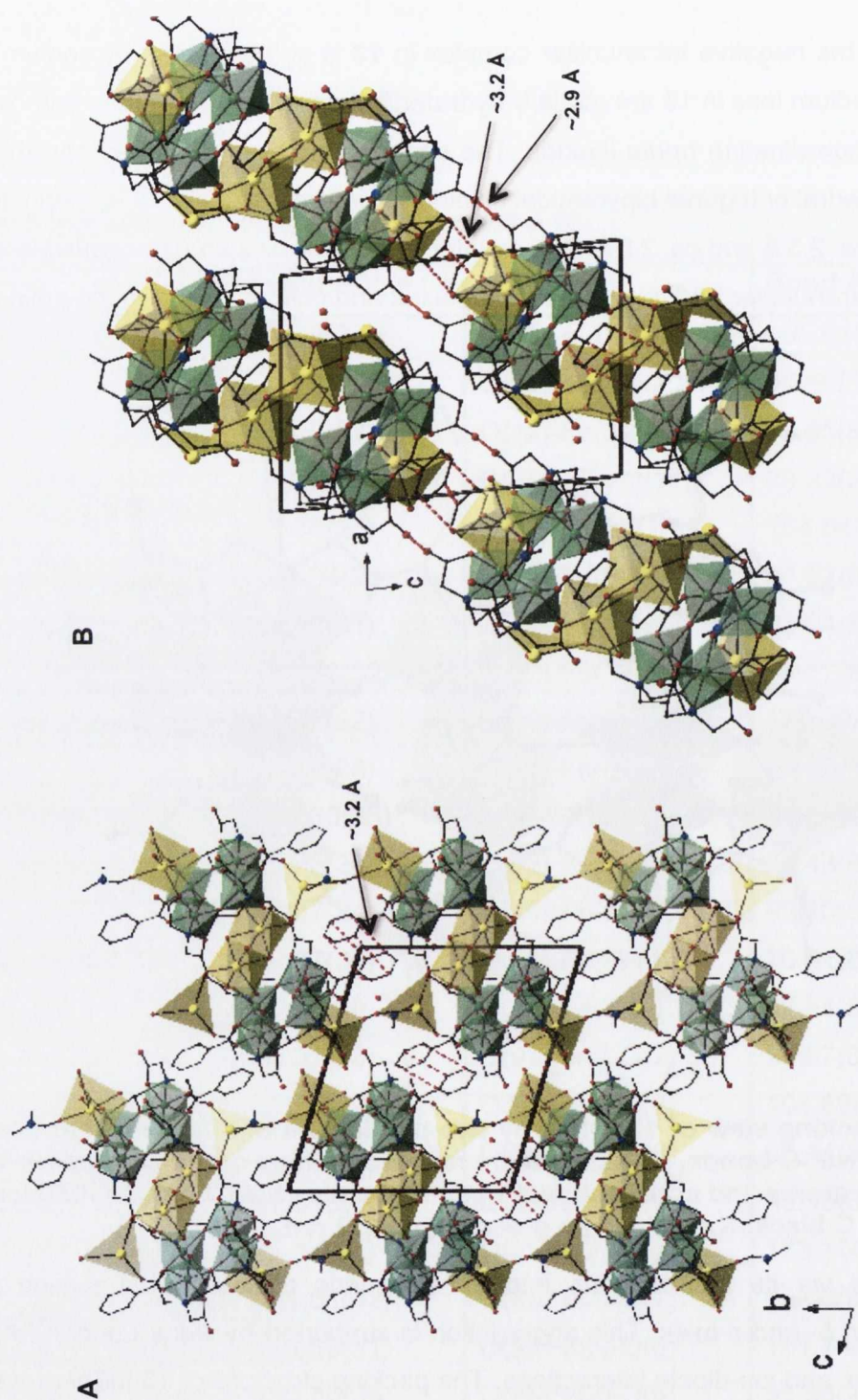


Figure 4.4: Packing structure of 13, viewed along the A) crystallographic *a*-axis and B) crystallographic *b*-axis; Polyhedral representations of the Fe^{III} and Na⁺ centres and interactions highlighted in red dashed bonds. The hydrogen atoms have been omitted for clarity. Colour Code: C black, Na yellow, Fe green, N blue, O red

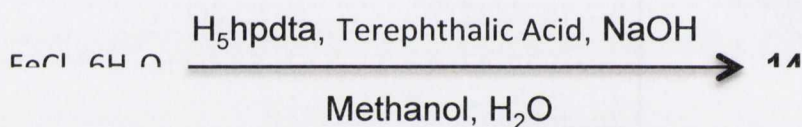
When viewing the crystallographic data in Table 4.3, one needs to consider that the atoms were refined isotropically and that both the Na⁺ atoms and twelve water molecules are highly disordered. This disorder (especially that of the disordered solvent molecules) is reflected by a high R1 value of ca. 14.92% for the refined crystallographic data of examined single crystals of **13**. The refined structure has a goodness of fit of 1.025, a high data to parameter ratio and acceptable ‘largest difference peak and hole’ values supporting the provided structural model. Elemental analysis further confirms the constitution of **13**.

Table 4.3: Crystal data and structure refinement parameters for 13

Compound	13	
Empirical formula	C ₃₉ H ₆₈ Fe ₄ N ₅ Na ₃ O ₃₇	
Formula weight	1491.32 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 11.73(7) Å	α = 73.48(18)°.
	<i>b</i> = 15.37(12) Å	β = 83.80(14)°.
	<i>c</i> = 17.71(13) Å	γ = 88.45(16)°.
Volume	3044(38) Å ³	
<i>Z</i>	2	
Density (calculated)	1.226 Mg/m ³	
Absorption coefficient	9.942 mm ⁻¹	
<i>F</i> (000)	1118	
Crystal size	0.4 x 0.1 x 0.2 mm ³	
Φ range for data collection	2.62 to 46.48°.	
Index ranges	-7 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 16	
Reflections collected	6534	
Independent reflections	4447 [<i>R</i> (int) = 0.0672] on <i>F</i> ²	
Completeness to θ = 25.08°	83.9 %	
Refinement method	Full-matrix least-squares	
Data/restraints/parameters	4447 / 0 / 356	
Goodness-of-fit on <i>F</i> ²	1.025	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1492, <i>wR</i> 2 = 0.3558	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2565, <i>wR</i> 2 = 0.4160	
Largest diff. peak and hole	1.063 and -1.077 e.Å ⁻³	

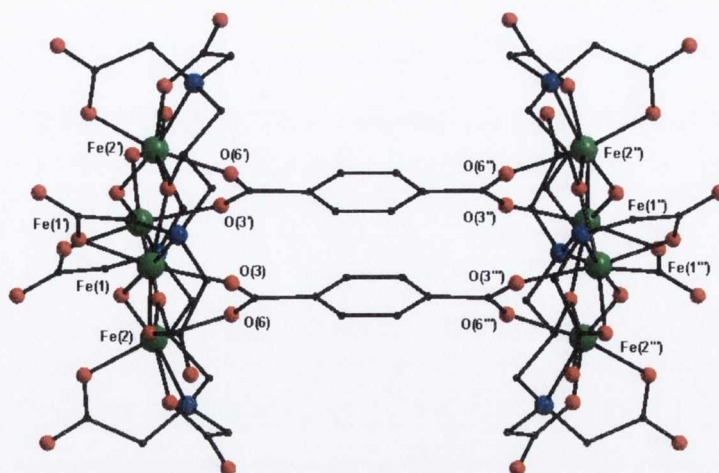
4.2 $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdt}\text{a})_2\}_2(\text{OOC}\text{C}_6\text{H}_4\text{COO})_2]\cdot 43\text{H}_2\text{O}$ (**14**)

$\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdt}\text{a})_2\}_2(\text{OOC}\text{C}_6\text{H}_4\text{COO})_2]\cdot 43\text{H}_2\text{O}$ (**14**) contains two rectangular tetranuclear Fe^{III} complexes linked *via* two deprotonated terephthalic acid ligands, (**L4**), to form the octanuclear Fe^{III} complex $[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdt}\text{a})_2\}_2(\text{OOC}\text{C}_6\text{H}_4\text{COO})_2]^{8-}$. The basic structure is comparable to **13** as its formation relies on the affinity of the tetranuclear Fe^{III} sub-units towards carboxylate-bearing ligands. The isolation of **14** is important as it is the first instance where the tetranuclear compounds coordinate to bifunctional ligands to form octanuclear species. **14** forms in a nitrogen atmosphere from aqueous *hpdt*a/ Fe^{III} reaction systems upon the addition of a methanol solution of **L4** and sodium hydroxide to adjust the pH (Scheme 4.2). Variations of the co-ligand concentration influenced the quality of the crystals and the rate of formation of the compound, rather than the nature of the complex. Green-red, rectangular crystals of **14** suitable for single-crystal X-ray diffraction measurements were obtained by co-evaporation with dimethylacetamide (DMA). The centrosymmetric compound crystallizes in the monoclinic space group $C2/m$. The structure of the octanuclear complex in **14** is illustrated in Figure 4.5.



Scheme 4.2: Formation of 14 under a nitrogen atmosphere.

A



B

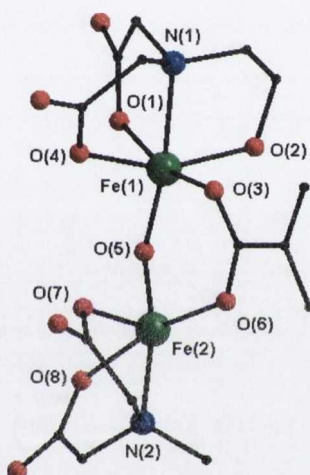


Figure 4.5: A) The octanuclear complex and B) the asymmetric unit in **14. The sodium counter ions, hydrogen atoms and constitutional water molecules of **14** have been omitted for clarity. Colour Code: C black, Fe green, N blue, O red.**

4.2.1 Structural characterisation of **14**

The octanuclear complex in **14** consists of two tetranuclear Fe^{III} sub-units linked via two dicarboxylate ligands, **L4**. In contrast to the complex in **13**, the tetranuclear sub-units are less regular and the bridging O^{2-} ligands are not strictly contained within the Fe_4 plane. The distance between Fe(1) and Fe(2'), and Fe(2) and Fe(1') in **14** is 3.625(79) Å. Conversely, the distance between Fe(1) and Fe(2), and Fe(1') and Fe(2') is 3.232(9) Å. This latter distance is considerably shorter than observed in other related tetranuclear complexes.^{3, 123-124, 127} This effect can be attributed to the coordinating dicarboxylate (**L4**) ligands that have, in comparison to the benzoate in **13**, rotated 90° with respect to the Fe_4 plane.

It appears that the linking dicarboxylate ligands impose a steric strain on the tetranuclear units. This and the modified reaction conditions result in less symmetric tetranuclear units than in **13** and other related complexes. In comparison to **13** the O-H...O bridging motif has been replaced by two bridging O²⁻ ligands. Also in contrast to **13** the carboxylate O-donor and N-donor atoms of the iminodiacetic acid moieties of the *hpdta* ligand adopt *facial* arrangements. This rearrangement facilitates the described binding mode of the dicarboxylate ligands.

The symmetry independent unit in **14** consists of two Fe^{III} iron centres, Fe(1) and Fe(2) coordinated to nitrogen and oxygen donor atoms located on two half *hpdta* ligands, two oxygen donor atoms, O(3) and O(6) from **L4** and an oxygen atom from a bridging oxo group, O(5). The asymmetric unit additionally contains a sodium counterion, Na(1), and three constitutional water molecules, O(1-3)_w. Each of the Fe^{III} centres in **14** adopt a distorted octahedral coordination environment. For example Fe(1) is coordinated by the carboxylate oxygen atoms, O(1), O(4), an alkoxo oxygen atom O(2) and the N-donor atom N(1) of a *hpdta* ligand; the corresponding Fe^{III}-O distances are 2.049(13) Å, 2.066(15) Å and 2.007(13) Å, respectively, and the Fe^{III}-N distance is 2.211(15) Å, respectively. The equatorial plane of the octahedral coordination environment of Fe(1) as shown in Figure 4.6 is completed by the O_{carboxylate} donor atom O(3) of **L4** and a bridging oxo O-donor atom O(5) to give Fe^{III}-O distances of 2.061(13) Å and 1.803(12) Å, respectively. Fe(2) is coordinated to the N-donor atom N(2), the carboxylate oxygen atoms O(7) and O(8), and the symmetry generated alkoxy atom O(2') each located on the *hpdta* ligand to give Fe^{III}-O distances of 2.079(15) Å, 2.052(14) Å and 2.003(15) Å, respectively and an Fe^{III}-N bond length of 2.234(14) Å. The octahedral inner binding sphere is completed by a carboxylate oxygen atom O(6) of **L4** and the bridging oxo O-donor atom O(5). The latter O-donors result in Fe^{III}-O bond lengths of 2.027(14) Å and 1.803(12) Å, respectively.

The distorted octahedral coordination environment can be exemplified through examination of the bond angles. For example, deviation from the linear modal is observed for the bond angles O(4)-Fe(1)-O(2), N(2)-Fe(2)-O(5), N(1)-Fe(1)-O(5) and O(7)-Fe(2)-O(2') of 156.01(5)°, 168.60(5)°, 171.81(6)° and 153.96(5)°, correspondingly. Deviations from the typical 90° angle are apparent for the respective bond angles O(3)-Fe(1)-N(1), O(2)-Fe(1)-N(1), O(7)-Fe(2)-O(5) and O(6)-Fe(2)-O(5) of 84.72(5)°, 80.59(6)°, 96.32(6)° and 98.67(5)°. Additional selected bond lengths and angles involving the Fe^{III} and Na⁺ centres in **14** are summarised in Table 4.4 and Table 4.5.

Table 4.4: Selected bond distances for the Fe^{III} and Na⁺ centres in 14.

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1)-O(5)	1.803(12)
	Fe(1)-O(2)	2.007(13)
	Fe(1)-O(1)	2.049(13)
	Fe(1)-O(3)	2.061(13)
	Fe(1)-O(4)	2.066(15)
	Fe(1)-N(1)	2.211(15)
Fe(2)	Fe(2)-O(5)	1.803(12)
	Fe(2)-O(2')	2.003(15)
	Fe(2)-O(6)	2.027(14)
	Fe(2)-O(8)	2.052(14)
	Fe(2)-O(7)	2.079(15)
	Fe(2)-N(2)	2.234(14)
Na(1)	Na(1)-O(2)w	2.324(4)
	Na(1)-O(4)	2.403(16)
	Na(1)-O(3)w	2.415(2)
	Na(1)-O(1)w	2.444(2)
	Na(1)-O(10''')	2.447(17)

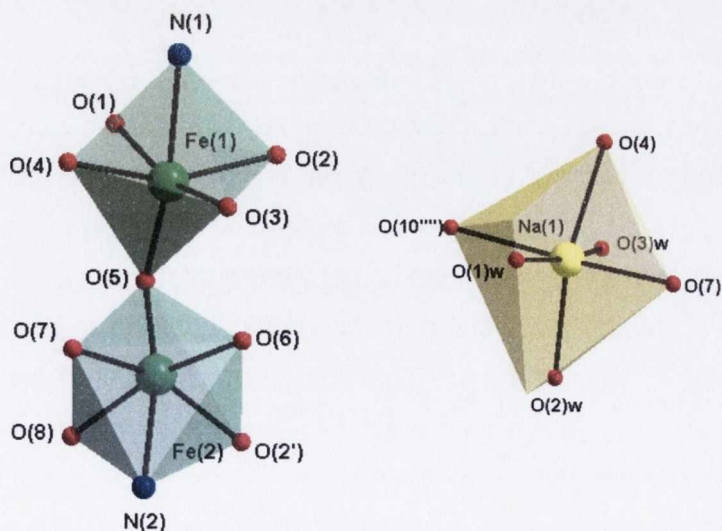


Figure 4.6: Polyhedral representations of the Fe^{III} and Na⁺ centres in 14. Colour Code: Fe green, N blue, Na yellow, O red.

Table 4.5: Selected bond angles for compound 14.

	Bond Angle (°)		Bond Angle (°)
O(5)-Fe(1)-O(2)	105.11(6)	O(6)-Fe(2)-O(7)	87.04(5)
O(5)-Fe(1)-O(1)	94.64(6)	O(8)-Fe(2)-O(7)	91.51(5)
O(2)-Fe(1)-O(1)	88.54(5)	O(5)-Fe(2)-N(2)	168.60(5)
O(5)-Fe(1)-O(3)	101.21(5)	O(2')-Fe(2)-N(2)	80.48(5)
O(2)-Fe(1)-O(3)	87.69(5)	O(6)-Fe(2)-N(2)	87.09(5)
O(1)-Fe(1)-O(3)	164.15(5)	O(8)-Fe(2)-N(2)	78.77(5)
O(5)-Fe(1)-O(4)	98.84(6)	O(7)-Fe(2)-N(2)	74.04(5)
O(2)-Fe(1)-O(4)	156.01(5)	O(2)w-Na(1)-O(4)	167.97(8)
O(1)-Fe(1)-O(4)	90.95(6)	O(2)w-Na(1)-O(3)w	85.65(9)
O(3)-Fe(1)-O(4)	86.29(5)	O(4)-Na(1)-O(3)w	88.99(7)
O(5)-Fe(1)-N(1)	171.81(6)	O(2)w-Na(1)-O(1)w	97.84(8)
O(2)-Fe(1)-N(1)	80.59(6)	O(4)-Na(1)-O(1)w	89.09(6)
O(1)-Fe(1)-N(1)	79.47(6)	O(3)w-Na(1)-O(1)w	170.89(8)
O(3)-Fe(1)-N(1)	84.72(5)	O(2)w-Na(1)-O(10''')	95.55(8)
O(4)-Fe(1)-N(1)	75.74(6)	O(4)-Na(1)-O(10''')	95.06(5)
O(5)-Fe(2)-O(2')	109.57(5)	O(3)w-Na(1)-O(10''')	88.50(8)
O(5)-Fe(2)-O(6)	98.67(5)	O(1)w-Na(1)-O(10''')	82.80(6)
O(2')-Fe(2)-O(6)	86.38(5)	O(2)w-Na(1)-O(7)	90.01(8)
O(5)-Fe(2)-O(8)	95.71(6)	O(4)-Na(1)-O(7)	81.01(5)
O(2')-Fe(2)-O(8)	88.71(5)	O(3)w-Na(1)-O(7)	105.20(8)
O(6)-Fe(2)-O(8)	165.62(5)	O(1)w-Na(1)-O(7)	83.28(6)
O(5)-Fe(2)-O(7)	96.32(6)	O(10''')-Na(1)-O(7)	165.59(6)
O(2')-Fe(2)-O(7)	153.96(5)		

The octanuclear complex in **14** carries a charge of -8 that is compensated by eight sodium ions. The sodium ions in **14** bind to the carboxylate O-donors, O(4), O(7), O(10) and symmetry equivalents, of the coordinating *hpdta* ligands. The sodium ions are disordered and they adopt generally distorted octahedral binding environments. The Na⁺-O bond distances vary between *ca.* 2.3 Å and 2.5 Å. Selected bond lengths and bond angles involving Na⁺-O bonds are summarised in Table 4.4 and Table 4.5. The Na⁺ counter ions and symmetry equivalents locate between the tetranuclear transition metal complexes to form two-dimensional sheets that extend parallel to the *ab*-plane. The organic dicarboxylate moieties that connect the tetranuclear subunits pillar between these sheets to give a honeycomb-type network structure containing channels of *ca.* 19.8 Å in cross section diameter, Figure 4.7A.

Channels that extend into the crystallographic *a*-axis are characterized by internal diameters of ca. 10 Å and void spaces with diameters of ca. 7.4 Å between the channels, Figure 4.7B.

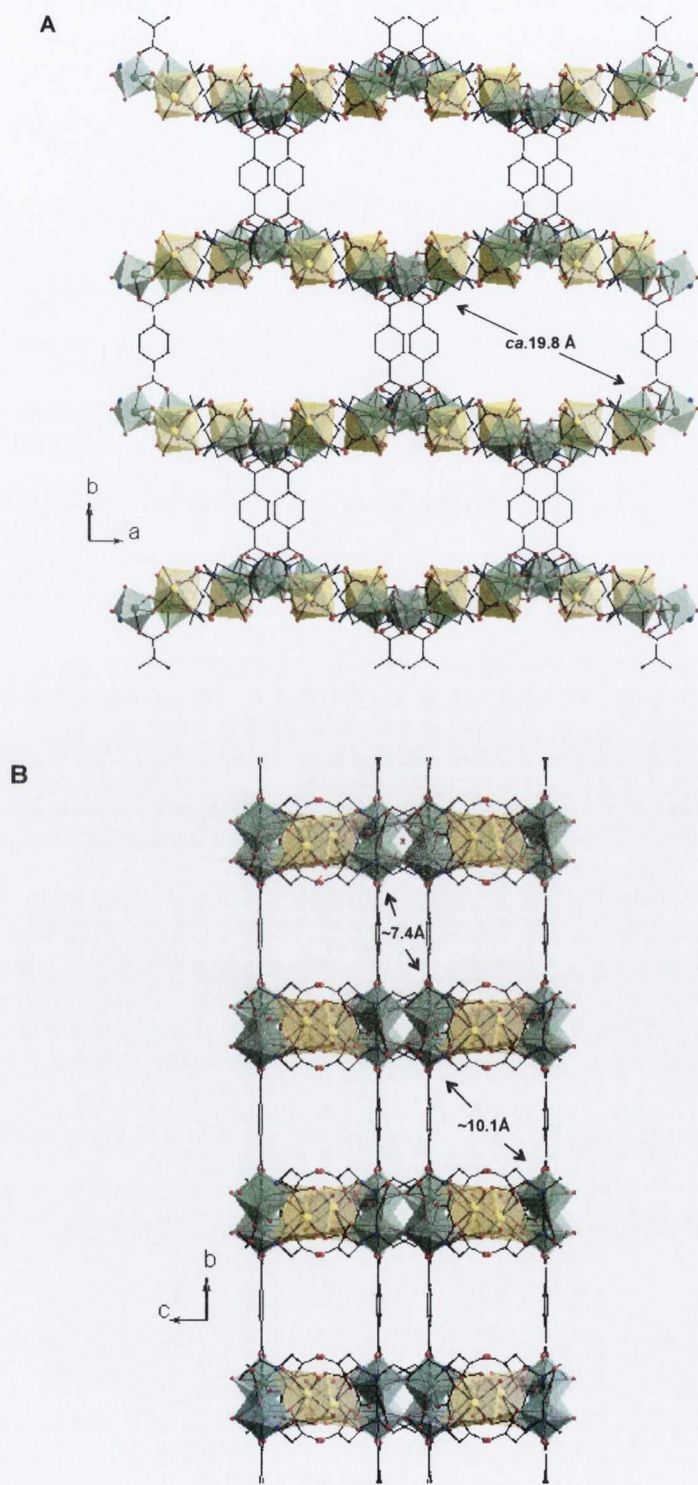


Figure 4.7: View of the Na⁺-O mediated lamellar structure in 14. Viewed along the crystallographic A) *c*-axis and B) *a*-axis. Polyhedral representations of the Fe^{III} and Na⁺ centres. The hydrogen atoms and constitutional water molecules have been omitted for clarity. Colour Code: C black, Fe green, N blue, Na yellow, O red.

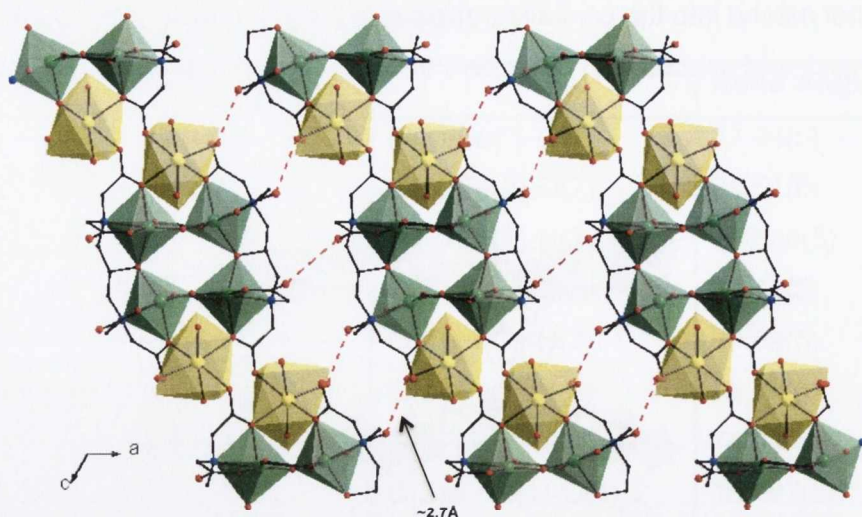


Figure 4.8: Viewed along the crystallographic *b*-axis. Polyhedral representations of the Fe^{III} and Na^+ centres. Colour Code: C black, Fe green, N blue, Na yellow, O red.

The crystal data and structure refinement parameters for **14** are detailed in Table 4.6. The R value of 3.7 %, goodness of fit of 1.037 and acceptable 'largest difference peak and hole' values confirm the accuracy of the structural model.

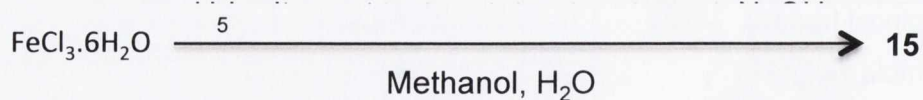
Table 4.6: Crystal data and structure refinement parameters for **14**

Compound	14	
Empirical formula	C ₆₀ H ₁₄₆ Fe ₈ N ₈ Na ₈ O ₉₁	
Formula weight	3066.32g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/m	
Unit cell dimensions	a = 23.976(5) Å	α = 90°.
	b = 25.774(5) Å	β = 119.92(3)°.
	c = 13.343(3) Å	γ = 90°.
Volume	7147(3) Å ³	
Z	2	
Density (calculated)	1.117 Mg/m ³	
Absorption coefficient	0.874 mm ⁻¹	
F(000)	2440	
Crystal size	0.3 x 0.2 x 0.2 mm ³	
Φ range for data collection	1.580 to 28.447°.	
Index ranges	-32<=h<=32, -34<=k<=34, -17<=l<=17	
Reflections collected	48879	
Independent reflections	9154 [R(int) = 0.0474] on F ²	
Completeness to θ = 25.08°	99.8 %	
Refinement method	Full-matrix least-squares	
Data/restraints/parameters	9154 / 0 / 316	
Goodness-of-fit on F ²	1.037	
Final R indices[I>2sigma(I)]	R1 = 0.0373, wR2 = 0.1074	
R indices (all data)	R1 = 0.0421, wR2 = 0.1106	
Largest diff. peak and hole	0.818 and -0.333 e.Å ⁻³	

4.3 Na₈[{Fe₄(μ-O)₂(hpdta)₂]₂(OOCCH₁₂H₁₆COO)₂·35H₂O (**15**)

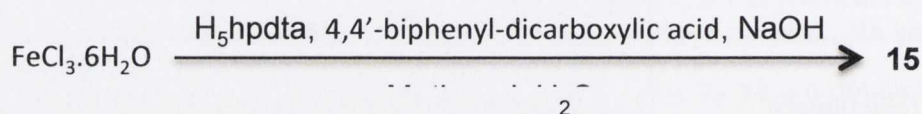
The octanuclear Fe^{III} complex in Na₈[{Fe₄(μ-O)₂(hpdta)₂]₂(OOCCH₁₂H₁₆COO)₂·35H₂O (**15**) is structurally related to the complex in **14**. It was prepared under a nitrogen atmosphere via a modified synthetic approach using an aqueous FeCl₃ solution, *H₅hpdta* and 4,4'-biphenyl-dicarboxylic acid (**L5**) as starting materials. The compound formed when a methanol solution

of L5 was added to the reaction mixture and sodium hydroxide was used to adjust the pH to



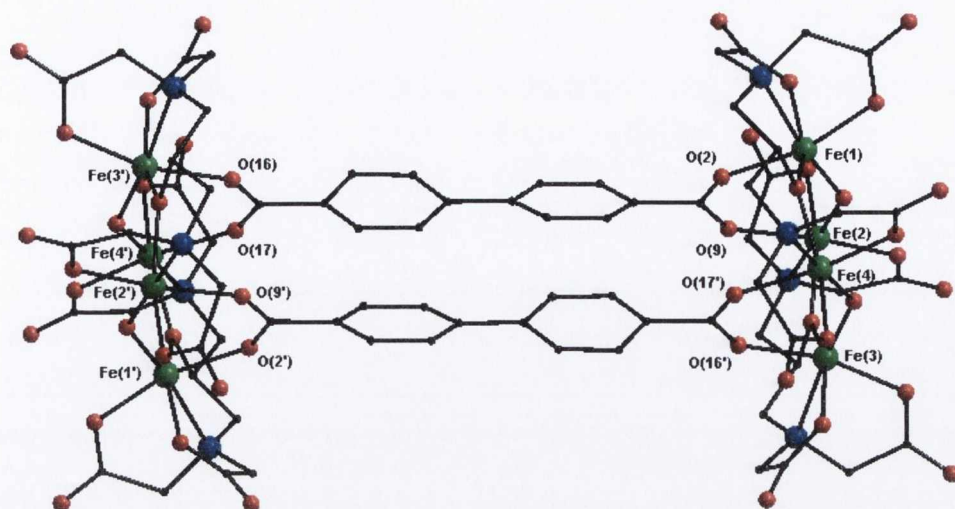
8.0 (

Scheme 4.3). Dark green-brown, rectangular crystals of **15** suitable for single-crystal X-ray diffraction were obtained by co-evaporation with dimethylformamide (DMF). The compound crystallizes in the triclinic space group *P*-1. Figure 4.9A shows the structure of the octanuclear complex in **15**.



Scheme 4.3: Formation of 15 under a nitrogen atmosphere.

A



B

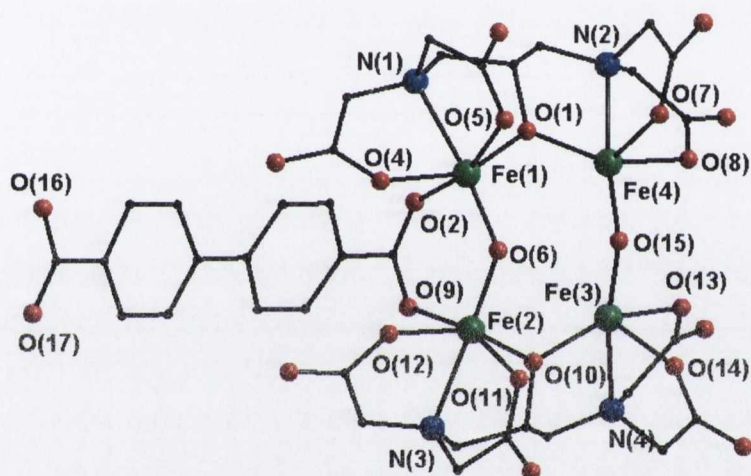


Figure 4.9: A) The octanuclear complex and B) the asymmetric unit in **15**. The sodium counter ions, hydrogen atoms and constitutional water molecules have been omitted for clarity. Colour Code: C black, Fe green, N blue, O red.

4.3.1 Structural characterisation of **15**

Compound **15** is comparable to **14** in that it contains two tetranuclear sub-units bridged by two dicarboxylate ligands, Figure 4.9A. The increased size of the 4,4'-biphenyl-dicarboxylate ligand extends the distance between two Fe^{III} metal centres in the distinct tetranuclear sub-units in **15** to ca. 15.1 Å as compared to 10.6 Å in **14**. The asymmetric unit of **15**, seen in Figure 4.9B, contains a tetranuclear sub-unit and a coordinating 4,4'-biphenyl-dicarboxylic acid ligand. The tetranuclear sub-unit is stabilised by two deprotonated *hpdta* ligands. The Fe^{III} ions, Fe(1)-Fe(2) and Fe(3)-Fe(4) are bridged by μ -bridging oxo moieties, O(6) and O(15). The asymmetric unit also contains three sodium counter ions and eighteen

constitutional water molecules, one of which is disordered across two locations. The octanuclear complex displayed in Figure 4.9A is formed by two symmetry equivalent units.

The eight Fe^{III} centres in **15**, Fe(1)-Fe(4) and symmetry equivalents, adopt distorted octahedral coordination environments as observed in previously described Fe^{III} compounds. However, as observed in **14**, the tetranuclear sub-unit in **15** is less regular and the O²⁻ bridging ligands are not contained within the Fe₄ plane as compared to the tetranuclear compound in **13** and in previously discussed, structurally related, compounds.² The distance between the alkoxo bridged Fe^{III} centres Fe(1)-Fe(4), Fe(2)-Fe(3) and symmetry equivalents are 3.643(11) Å and 3.655(44) Å, respectively. Considerably shorter distances of 3.286(43) Å and 3.261(37) Å are observed between the oxo bridged Fe(1)-Fe(2) and Fe(3)-Fe(4) Fe^{III} pairs and symmetry equivalents. The shorter distances are characteristic of octanuclear Fe^{III} complexes connected through polycarboxylate ligands. As observed in **14**, this effect is caused by the coordinating carboxylate moieties that have rotated *ca.* 90° in comparison to the coordinating benzoate ligands in **13** resulting in the repositioning of the Fe^{III} atoms.

The Fe^{III} centres in **15**, all have similar coordination environments. The N- and O-donor atoms from the *hpdta* ligands, surround the centres in a *facial* arrangement, the remaining coordination sites are completed by oxygen atoms from the bidentate bridging carboxylate moieties and the μ -bridging O²⁻ ligands. The O-donor atoms situated in the equatorial plane of the distorted octahedral environment of Fe(1), as shown in Figure 4.9B, form Fe^{III}-O bond of 2.008(12) Å [Fe(1)-O(1)], 2.071(10) Å [Fe(1)-O(5)], 2.077(15) Å [Fe(1)-O(4)] and 2.025(11) Å [Fe(1)-O(2)]. The apical position are occupied by N(1) and a bridging oxo O-donor atom, O(6), to give bond distances ranging between 2.223(1) Å and 1.814(7) Å. The short Fe(1)-O(6) bond length unambiguously identifies a bridging oxo moiety. Similarly, the O- and N-donor atoms from the *hpdta* ligand, O(10), O(11) O(12) and N(3), coordinate to Fe(2) to give bond lengths of 2.013(11) Å, 2.078(15) Å, 2.078(11) Å and 2.240(7) Å. The octahedral coordination environment is completed by the carboxylate oxygen atom O(9) located on **L5** and a bridging oxo moiety, O(6), to give bond distances of 2.051(3) Å and 1.814(8) Å. Fe(3) and Fe(4) and symmetry equivalents are in comparable coordination environments with Fe^{III}-N bond distances ranging between 2.216(7) Å and 2.219(19) Å and Fe^{III}-O bond distances of 2.003(1) Å to 2.088(5) Å.

Selected bond distances and angles are detailed in Table 4.7 and Table 4.8. The deviation for the ideal octahedral geometry can be observed by bond angle analysis. In particular the angles N(1)-Fe(1)-O(6), N(2)-Fe(4)-O(15), N(4)-Fe(3)-O(15) and N(3)-Fe(2)-O(6) of 168.46(25)°, 173.16(25)°, 170.48(26)° and 173.70(27)° show a slight deviation from ideal linearity. The angles O(4)-Fe(1)-O(1) and O(2)-Fe(1)-O(5) of 154.36(23)° and 163.04(22)°

further highlight the deviation from the ideal 180° angle. The bond angle N(1)-Fe(1)-O(4) of 73.50(23)° reveals the most significant deviation from the ideal 90° angle while the angles 89.21(22)° [O(5)-Fe(1)-O(1)], 88.34(23)° [O(4)-Fe(1)-O(5)], 90.44(21)° [O(11)-Fe(2)-O(10)], 87.15(19)° [O(14)-Fe(3)-O(13)] and 79.31(25)° [N(2)-Fe(4)-O(7)] deviate moderately from 90°.

Table 4.7: Selected bond distances for Fe^{III} centres in 15.

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1)-O(6)	1.814(7)
	Fe(1)-O(1)	2.008(12)
	Fe(1)-O(2)	2.025(11)
	Fe(1)-O(5)	2.071(10)
	Fe(1)-O(4)	2.077(15)
	Fe(1)-N(1)	2.223(5)
Fe(2)	Fe(2)-O(6)	1.814(8)
	Fe(2)-O(10)	2.013(11)
	Fe(2)-O(9)	2.051(3)
	Fe(2)-O(11)	2.078(15)
	Fe(2)-O(12)	2.078(11)
	Fe(2)-N(3)	2.240(7)
Fe(3)	Fe(3)-O(15)	1.812(10)
	Fe(3)-O(10)	2.014(5)
	Fe(3)-O(16')	2.035(13)
	Fe(3)-O(14)	2.066(18)
	Fe(3)-O(13)	2.083(16)
	Fe(3)-N(4)	2.216(7)
Fe(4)	Fe(4)-O(15)	1.806(1)
	Fe(4)-O(1)	2.003(8)
	Fe(4)-O(7)	2.041(17)
	Fe(4)-O(17')	2.053(3)
	Fe(4)-O(8)	2.088(5)
	Fe(4)-N(2)	2.219(19)

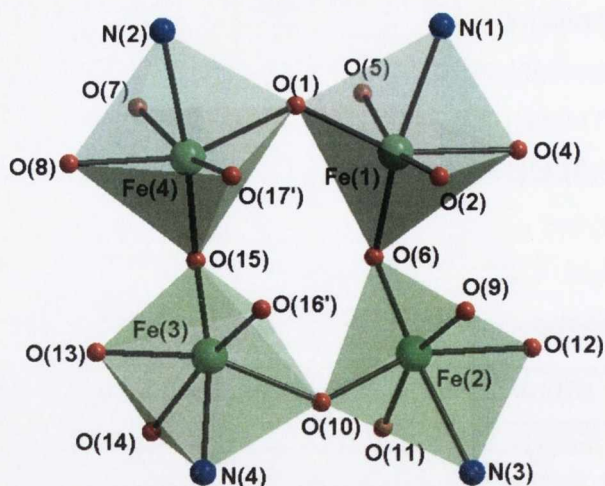


Figure 4.10: Polyhedral representations of the Fe^{III} centres in 15. Colour Code: C black, Fe green, N blue, O red.

Table 4.8: Selected bond angles for compound 15.

	Bond Angle ($^{\circ}$)		Bond Angle ($^{\circ}$)
N(1)-Fe(1)-O(6)	168.46(25)	N(4)-Fe(3)-O(15)	170.48(26)
O(2)-Fe(1)-O(5)	163.04(22)	O(16')-Fe(3)-O(14)	164.21(19)
O(4)-Fe(1)-O(1)	154.36(23)	O(10)-Fe(3)-O(13)	154.93(21)
N(1)-Fe(1)-O(5)	78.31(26)	N(4)-Fe(3)-O(13)	74.69(23)
N(1)-Fe(1)-O(1)	81.01(23)	N(4)-Fe(3)-O(14)	79.69(23)
N(1)-Fe(1)-O(2)	84.74(24)	N(4)-Fe(3)-O(16)	84.63(26)
N(1)-Fe(1)-O(4)	73.50(23)	N(4)-Fe(3)-O(10)	80.54(24)
O(6)-Fe(1)-O(5)	97.75(24)	O(15)-Fe(3)-O(14)	97.00(22)
O(6)-Fe(1)-O(1)	109.95(22)	O(15)-Fe(3)-O(13)	96.31(24)
O(6)-Fe(1)-O(2)	98.97(21)	O(15)-Fe(3)-O(16')	98.18(24)
O(5)-Fe(1)-O(1)	89.21(22)	O(15)-Fe(3)-O(10)	108.62(24)
O(1)-Fe(1)-O(2)	87.71(22)	O(14)-Fe(3)-O(13)	87.15(19)
O(2)-Fe(1)-O(4)	87.25(22)	O(13)-Fe(3)-O(16')	86.89(21)
O(4)-Fe(1)-O(5)	88.34(23)	O(16')-Fe(3)-O(10)	86.97(22)
N(3)-Fe(2)-O(6)	173.70(27)	O(10)-Fe(3)-O(14)	92.29(20)
O(9)-Fe(2)-O(11)	162.31(18)	N(2)-Fe(4)-O(15)	173.16(25)
O(12)-Fe(2)-O(10)	155.39(21)	O(1)-Fe(4)-O(8)	156.15(21)
O(6)-Fe(2)-O(11)	98.33(25)	O(17)-Fe(4)-O(7)	163.99(21)
O(11)-Fe(2)-O(6)	98.33(25)	N(2)-Fe(4)-O(7)	79.31(25)
O(6)-Fe(2)-O(10)	104.95(23)	N(2)-Fe(4)-O(8)	75.19(24)

O(6)-Fe(2)-O(9)	98.76(24)	N(2)-Fe(4)-O(17')	84.68(24)
O(6)-Fe(2)-O(12)	99.57(25)	N(2)-Fe(4)-O(1)	81.11(24)
N(3)-Fe(2)-O(11)	78.90(26)	O(15)-Fe(4)-O(7)	95.88(24)
N(3)-Fe(2)-O(10)	80.82(23)	O(15)-Fe(4)-O(8)	100.02(22)
N(3)-Fe(2)-O(9)	83.64(26)	O(15)-Fe(4)-O(17')	100.07(21)
N(3)-Fe(2)-O(12)	74.78(24)	O(17')-Fe(4)-O(15)	100.07(21)
O(11)-Fe(2)-O(10)	90.44(21)	O(15)-Fe(4)-O(1)	103.82(22)
O(10)-Fe(2)-O(9)	89.56(21)	O(7)-Fe(4)-O(8)	89.09(23)
O(9)-Fe(2)-O(12)	84.73(21)	O(8)-Fe(4)-O(17')	86.70(22)
O(12)-Fe(2)-O(11)	87.94(21)	O(17')-Fe(4)-O(1)	88.49(22)

The octanuclear complex $[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdt})_2\}_2\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})\}_2]^{8-}$ in **15** carries an overall charge of $-\text{VIII}$. This is compensated by eight sodium counter ions, Na(1)-Na(4) and symmetry equivalents, linked to $\text{O}_{\text{carboxylate}}$ donor atoms of the *hpdt* ligand and O donor atoms of constitutional water molecules. The sodium ions are partially hydrated/solvated and bind to the carboxylate O-donors of the coordinating *hpdt* ligands. The sodium ions are disordered and they adopt generally highly distorted octahedral or trigonal bipyramidal binding environments. The $\text{Na}^+\text{-O}$ bond distances vary between *ca.* 2.4 Å and *ca.* 2.9 Å. The extensive network of $\text{Na}^+\text{-O}$ bonds link the octanuclear sub-units into polymeric chains, Figure 4.11. The chains are stabilised by inter-molecular H-bonding and weak van der Waal forces to form a 2D lamellar structure with clearly defined inorganic and organic areas, Figure 4.12. The organic areas contain **L5**, coordinating carboxylate moieties and the carbon-nitrogen backbone of the *hpdt* ligands. The inorganic layers extend across *ca.* 13.51 Å and are composed of Fe^{III} and Na^+ centres and auxiliary O- donor atoms.

Interestingly we found that an almost identical structure to **15** was isolated by slightly modifying the synthetic procedure that led to **15**. The reaction was carried out under atmospheric conditions, using an aqueous sodium hydroxide solution to adjust the pH to 7.0 and upon adding excess of 4,4'-biphenyl-dicarboxylic acid (**L5**). Light green-square, crystals of the compound were observed, amongst green powders, in the crystallisation vessel six days post co-evaporation with dimethylacetamide. The single crystal X-ray diffraction data was poor as the crystals were very small and difficult to measure. However, it was possible to identify the core structure from the collected data and the compound is undoubtedly composed of octanuclear complexes that pack differently to **15**. Images of the structure (**15a**) can be seen in the appendix.

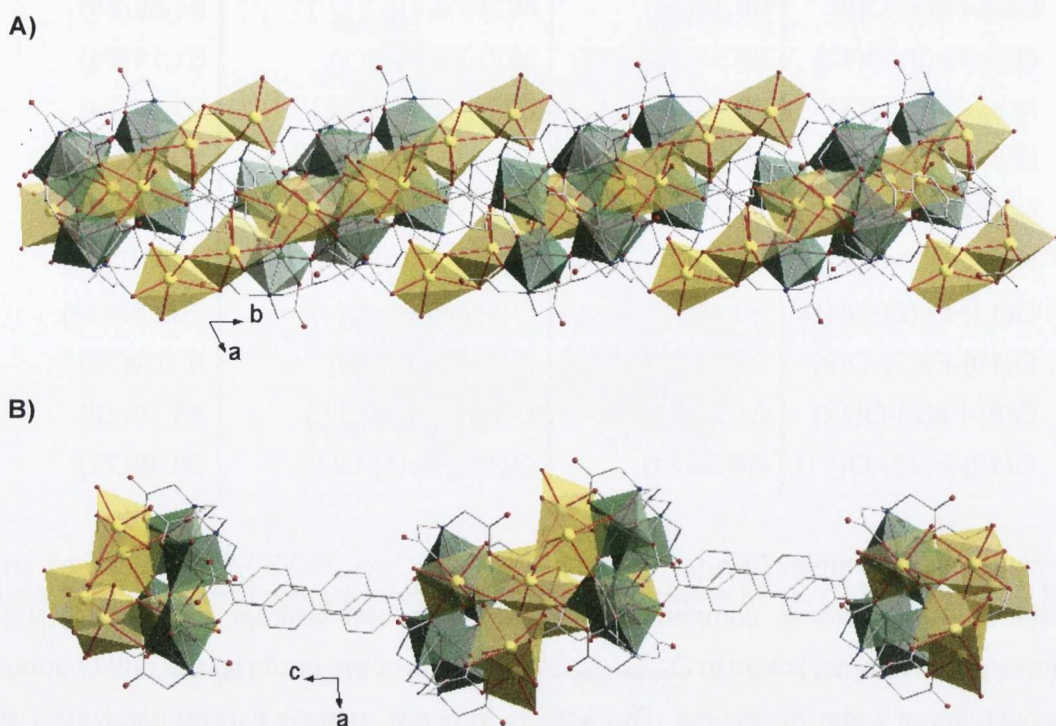


Figure 4.11: Polyhedral representations of the Na^+ -O mediated polymeric chains in **15** viewed in the direction of the crystallographic A) c -axis, B) b -axis. The hydrogen atoms and constitutional water molecules have been omitted for clarity. Colour Code: C light grey, Fe green, N blue, Na yellow, O red.

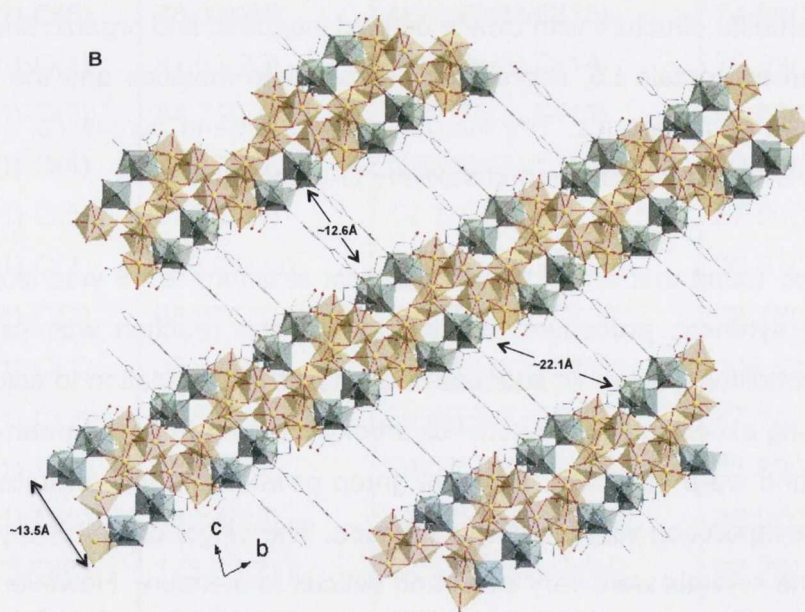


Figure 4.12: The layered lamellar packing structure of **15**. Viewed along the crystallographic a -axis. Polyhedral representations of the Fe^{III} and Na^+ centres. The hydrogen atoms and constitutional water molecules have been omitted for clarity. C light grey, Fe green, N blue, Na yellow, O red.

The crystal structure refinement of examined single crystals of **15** is characterised by a final R1 value of 8.39 %, a goodness of fit of 0.993, a high data to parameter ratio and acceptable ‘largest difference peak and hole’ values supporting the provided structural model. The crystal data and structure refinement parameters are summarized in Table 4.9.

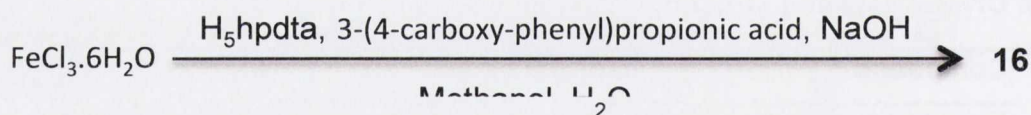
Table 4.9: Crystal data and structure refinement parameters for 15

Compound	15	
Empirical formula	$\text{C}_{72}\text{H}_{139}\text{Fe}_8\text{N}_8\text{Na}_8\text{O}_{85}$	
Formula weight	$2831.32\text{ g mol}^{-1}$	
Temperature	$150(2)\text{ K}$	
Wavelength	$0.71073\text{ \AA}$	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 12.624(3)\text{ \AA}$	$\alpha = 75.52(3)^\circ$
	$b = 13.302(3)\text{ \AA}$	$\beta = 85.76(3)^\circ$
	$c = 22.737(4)\text{ \AA}$	$\gamma = 62.53(3)^\circ$
Volume	$3276.2(12)\text{ \AA}^3$	
Z	1	
Density (calculated)	1.334 Mg/m^3	

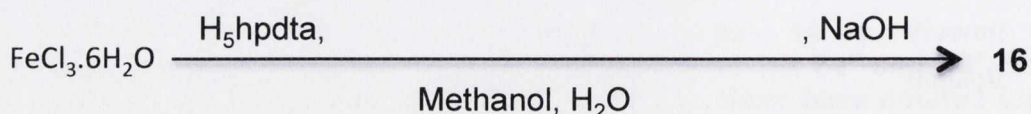
Absorption coefficient	0.968 mm ⁻¹
F(000)	1296
Crystal size	0.23 x 0.10 x 0.14 mm ³
Φ range for data collection	0.93 to 25.00°
Index ranges	-15<= <i>h</i> <=14, -15<= <i>k</i> <=15, -27<= <i>l</i> <=27
Reflections collected	34968
Independent reflections	11505 [R(int) = 0.0536] on F ²
Completeness to θ= 25.08°	100.0 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	11505 / 0 / 784
Goodness-of-fit on F ²	0.993
Final R indices[I>2σ(I)]	R1 = 0.0839, wR2 = 0.2512
R indices (all data)	R1 = 0.1138, wR2 = 0.2796
Largest diff. peak and hole	2.324 and -0.642 e.Å ⁻³

4.4 Na₁₀[{Fe₄(μ-O)₂(hpdta)₂}₂(OOCCH₈H₈COO)₂]Cl₂·26H₂O (**16**)

The coordination compound Na₁₀[{Fe₄(μ-O)₂(hpdta)₂}(OOCCH₈H₈COO)₂]Cl₂·26H₂O (**16**), consists of two tetranuclear Fe^{III} complexes that are linked through two deprotonated 3-(4-carboxy-phenyl)propionate ligands as observed in **15**. It forms by reacting an aqueous FeCl₃ solution with H₅hpdta and 3-(4-carboxy-phenyl)propionic acid (L6) upon adjusting the pH to 7.0 with sodium hydroxide (



Scheme 4.4). Light green, square crystals of **16** suitable for single-crystal X-ray diffraction measurements were obtained by co-evaporation with dimethylacetamide. The compound crystallises in the monoclinic space group C2/c. Figure 4.13A shows the octanuclear complex within the crystal structure of **16**. **16** was exclusively isolated from reaction mixtures that contained Cl⁻ anions.



Scheme 4.4: Preparation of compound 16

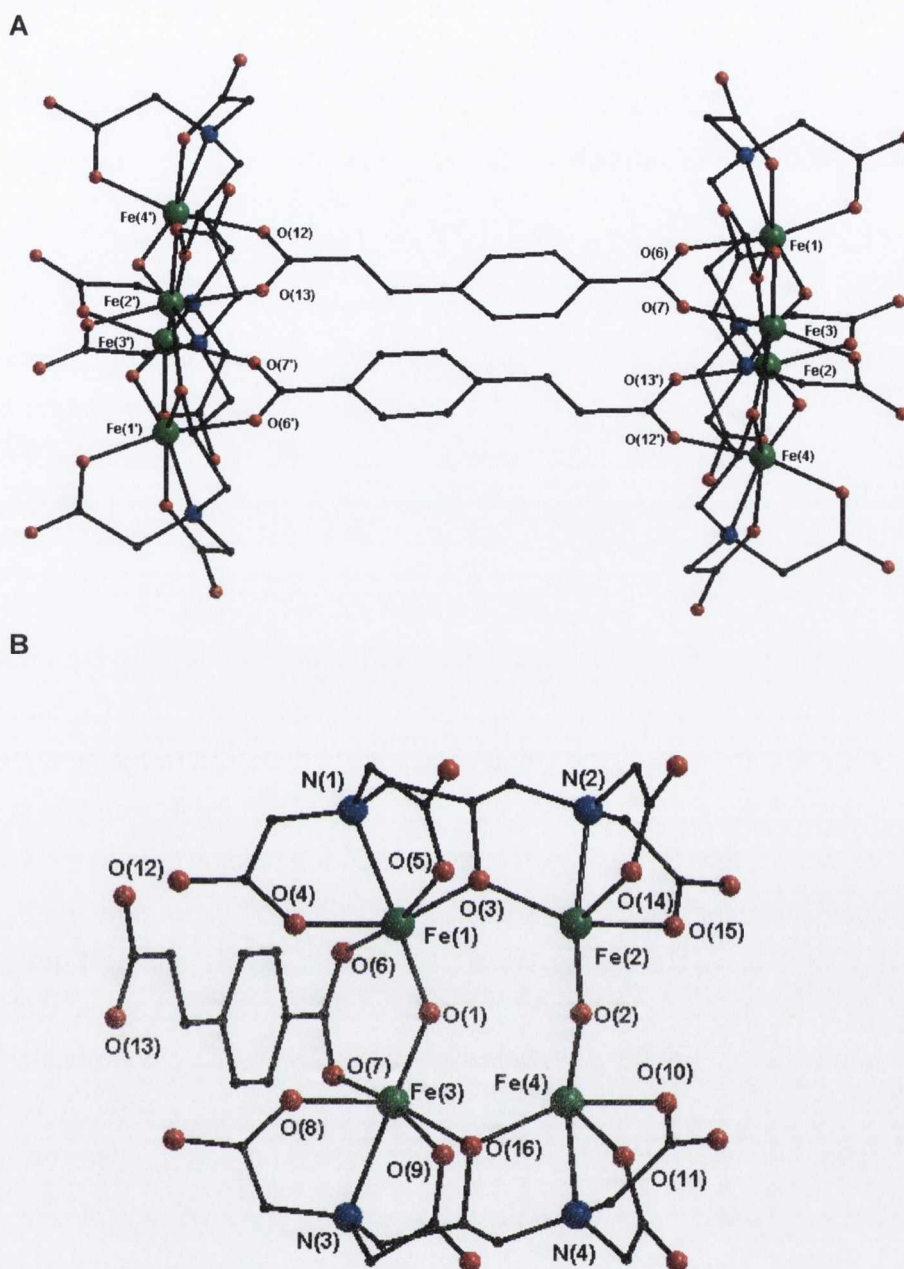


Figure 4.13: A) The octanuclear complex and B) the asymmetric unit in **16. The sodium counter ions, hydrogen atoms and constitutional water molecules have been omitted for clarity. Colour Code: C black, Fe green, N blue, O red.**

4.4.1 Structural characterisation of **16**

The asymmetric unit of **16**, Figure 4.13A, consists of one tetranuclear complex linked to one fully deprotonated 3-(4-carboxy-phenyl)propionic acid ligand through the oxygen atoms O(6) and O(7) that bridge between Fe(1) and Fe(3). The complete molecular entity is generated by a symmetry operation involving an inversion centre to give an octanuclear complex in which two Fe₄ units are linked to each other through two deprotonated 3-(4-carboxy-phenyl)propionic acid ligands (Figure 4.13A). The tetranuclear Fe₄ sub-structure in **16** is related to the previously discussed structures where each of the Fe atoms resides in a

distorted octahedral coordination environment. The distance between Fe(1) and Fe(2), and, Fe(3) and Fe(4) in **16** is *ca.* 3.64 Å. Conversely, the distance between Fe(1) and Fe(3) and Fe(2) and Fe(4) is *ca.* 3.24 Å. This latter distance is considerably shorter than observed in other related tetranuclear complexes.^{3, 123-124, 127}

The coordination in the tetranuclear unit is comparable to the coordination observed in **13-15**. Fe(1) and Fe(2), and, Fe(3) and Fe(4) are bridged by the alkoxo atoms O(3) and O(16) from *hpdta* ligands. Fe(1) and Fe(3) are bridged by a μ -oxo moiety, O(1), whilst Fe(2) and Fe(4) are bridged by a μ -oxo moiety O(2) resulting in a rectangular arrangement of the Fe^{III} centres. The identity of the oxo moieties was unambiguously confirmed by the short Fe^{III}-O distances of 1.797(56) Å for Fe(1)-O(1), 1.805(15) Å for Fe(3)-O(1), 1.805(28) Å for Fe(2)-O(2) and 1.805(15) Å for Fe(4)-O(2).

Within the tetranuclear unit Fe(1) binds to the oxygen atoms O(4) and O(5) that derive from the two-deprotonated carboxylic acid groups of the *hpdta* ligand, to give average Fe^{III}-O bond distances of *ca.* 2.070(11) Å. A third coordination site is occupied by the nitrogen donor atom, N(1), to form a Fe^{III}-N bond of 2.234(53) Å in length. These three atoms bind together in a *facial* arrangement to the Fe(1). The distorted octahedral binding sphere is completed by the deprotonated hydroxyl oxygen atom of the ligand O(3), an oxygen atom from a bridging oxo moiety O(1) and an oxygen atom from the deprotonated carboxylic acid group of **L6**, O(6). The Fe^{III}-O bond lengths range between 1.797(56) Å for Fe(1)-O(1) and 2.038(22) Å for Fe(1)-O(6). The atoms Fe(2), Fe(3) and Fe(4) are found in a comparable coordination environment to Fe(1) displaying Fe^{III}-O bond distances which range between 1.805 (28) Å and 2.062(28) Å for Fe(2)-O(2) and Fe(2)-O(14), respectively; 1.805(15) Å and 2.025(19) Å for Fe(3)-O(1) and Fe(3)-O(7), respectively, and 1.805(15) Å and 2.011(24) Å for Fe(4)-O(2) and Fe(4)-O(16), respectively. These distances are consistent with those observed in complexes **13-15**.

The distortion from ideal octahedral coordination geometries is exemplified through analysis of the bond angles. The most considerable deviations from the linear arrangement are observed for the bond angles O(4)-Fe(1)-O(3), O(5)-Fe(1)-O(6) and N(1)-Fe(1)-O(1) of 154.79(18)°, 166.41(19)° and 168.9(2)°, respectively. Considerable deviations from the 90° angle could be observed for the angles O(1)-Fe(1)-O(3), N(1)-Fe(1)-O(4), O(14)-Fe(2)-N(2) and N(3)-Fe(3)-O(9) of 107.51(18)°, 74.64(20)°, 78.95(19)° and 78.48(20)°, respectively. While subtle divergence from 90° are observed for the bond angles N(1)-Fe(1)-O(6), O(10)-Fe(4')-O(11) and O(1)-Fe(3)-O(9) with values of 87.81(19)°, 88.36(18)° and 93.37(18)°, respectively. Other selected bond lengths and bond angles involving the Fe^{III} centres in **16** are listed in Table 4.10 and Table 4.11.

The Fe^{III}-N and Fe^{III}-O bond distances confirm that the Fe atoms are in the +III oxidation state. This can also be deduced through charge consideration of the anionic complex. The -8 charge of the $[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdt})_2\}_2\{\text{OOC}\text{C}_6\text{H}_5\text{COO}\})_2]^{8-}$ complex and the -2 charge of the two Cl anions is compensated by ten Na⁺ cations.

Table 4.10: Selected bond distances for the Fe^{III} centres in 16.

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1)-O(1)	1.797(56)
	Fe(1)-O(3)	2.008(34)
	Fe(1)-O(6)	2.038(22)
	Fe(1)-O(5)	2.055(45)
	Fe(1)-O(4)	2.084(29)
	Fe(1)-N(1)	2.234(53)
Fe(2)	Fe(2)-O(2)	1.805(28)
	Fe(2)-O(3)	2.006(32)
	Fe(2)-O(15)	2.054(27)
	Fe(2)-O(14)	2.062(28)
	Fe(2)-O(13')	2.063(16)
	Fe(2)-N(2)	2.232(37)
Fe(3)	Fe(3)-O(1)	1.805(15)
	Fe(3)-O(16)	2.008(14)
	Fe(3)-O(7)	2.025(19)
	Fe(3)-O(9)	2.047(24)
	Fe(3)-O(8)	2.083(16)
	Fe(3)-N(3)	2.235(22)
Fe(4)	Fe(4)-O(2)	1.805(15)
	Fe(4)-O(16)	2.011(24)
	Fe(4)-O(12')	2.013(24)
	Fe(4)-O(11)	2.038(29)
	Fe(4)-O(10)	2.107(13)
	Fe(4)-N(4)	2.228(26)

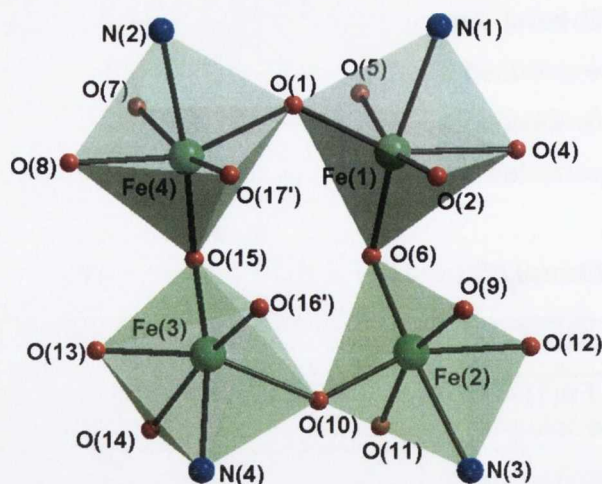


Figure 4.14: Polyhedral representation of the Fe^{III} centres in 16. Colour Code: Fe green, N blue, O red.

Table 4.11: Selected bond angles for compound 16.

	Bond Angle ($^{\circ}$)		Bond Angle ($^{\circ}$)
O(1)-Fe(1)-O(3)	107.51(18)	O(3)-Fe(2)-N(2)	80.85(18)
O(1)-Fe(1)-O(6)	100.04(18)	O(15)-Fe(2)-N(2)	75.03(17)
O(3)-Fe(1)-O(6)	88.32(18)	O(14)-Fe(2)-N(2)	78.95(19)
O(1)-Fe(1)-O(5)	93.43(18)	O(2)-Fe(2)-Fe(4')	140.24(13)
O(3)-Fe(1)-O(5)	89.33(18)	O(3)-Fe(2)-Fe(4')	80.65(12)
O(6)-Fe(1)-O(5)	166.41(19)	O(15)-Fe(2)-Fe(4')	81.25(12)
O(1)-Fe(1)-O(4)	97.70(18)	O(1)-Fe(3)-O(16)	104.85(18)
O(3)-Fe(1)-O(4)	154.79(18)	O(16)-Fe(3)-O(7)	88.38(18)
O(6)-Fe(1)-O(4)	87.57(18)	O(1)-Fe(3)-O(9)	93.37(18)
O(5)-Fe(1)-O(4)	88.88(18)	O(16)-Fe(3)-O(9)	88.78(18)
O(1)-Fe(1)-N(1)	168.9(2)	O(7)-Fe(3)-O(9)	165.98(19)
O(3)-Fe(1)-N(1)	80.36(21)	O(1)-Fe(3)-O(8)	100.25(19)
O(6)-Fe(1)-N(1)	87.81(19)	O(16)-Fe(3)-O(8)	154.87(18)
O(5)-Fe(1)-N(1)	78.60(19)	O(7)-Fe(3)-O(8)	85.83(19)
O(4)-Fe(1)-N(1)	74.64(20)	O(9)-Fe(3)-O(8)	90.97(19)
O(3)-Fe(1)-Fe(3)	115.30(13)	O(1)-Fe(3)-N(3)	170.42(20)
O(6)-Fe(1)-Fe(3)	75.60(12)	O(16)-Fe(3)-N(3)	80.23(20)
O(5)-Fe(1)-Fe(3)	117.36(13)	O(7)-Fe(3)-N(3)	87.52(20)
O(4)-Fe(1)-Fe(3)	87.65(12)	O(9)-Fe(3)-N(3)	78.48(20)
N(1)-Fe(1)-Fe(3)	156.30(15)	O(8)-Fe(3)-N(3)	75.11(22)
O(2)-Fe(2)-O(3)	105.75(18)	O(16)-Fe(3)-Fe(1)	111.16(12)

O(2)-Fe(2)-O(15)	98.65(18)	O(7)-Fe(3)-Fe(1)	75.74(12)
O(3)-Fe(2)-O(15)	155.58(18)	O(9)-Fe(3)-Fe(1)	118.01(12)
O(2)-Fe(2)-O(14)	94.35(18)	O(8)-Fe(3)-Fe(1)	91.05(15)
O(3)-Fe(2)-O(14)	89.56(18)	N(3)-Fe(3)-Fe(1)	159.11(15)
O(15)-Fe(2)-O(14)	89.55(19)	O(2)-Fe(4)-O(12')	81.26(14)
O(2)-Fe(2)-O(13')	141.66(13)	O(16)-Fe(4)-O(12')	78.68(14)
O(3)-Fe(2)-O(13')	87.08(13)	O(12')-Fe(4)-O(11)	80.45(14)
O(15)-Fe(2)-O(13')	74.08(13)	O(12')-Fe(4)-O(10)	73.70(14)
O(2)-Fe(2)-N(2)	170.70(19)	O(12')-Fe(4)-N(4)	72.95(14)

The sodium ions in **16** are partially hydrated/solvated and bind to the carboxylate O-donors of the coordinating *hpdta* ligands. The sodium ions are disordered and they adopt distorted octahedral or trigonal bipyramidal binding environments. The Na⁺-O bond distances reveal typical Na⁺-O bond distances that range between 2.455(20) Å and 2.864(12) Å. The octanuclear Fe^{III} complexes in **16** aggregate *via* the Na⁺-O bonds to form polymeric chains, Figure 4.15. The polymeric chains link via weak van der Waal interactions and inter-molecular H-bonding between coordinated O_{carboxylate} atoms of *hpdta* ligands and constitutional water molecules, to form a 3D structure shown with view in the crystallographic *ab*, *bc* and *ac*-planes in Figure 4.16 and Figure 4.17.

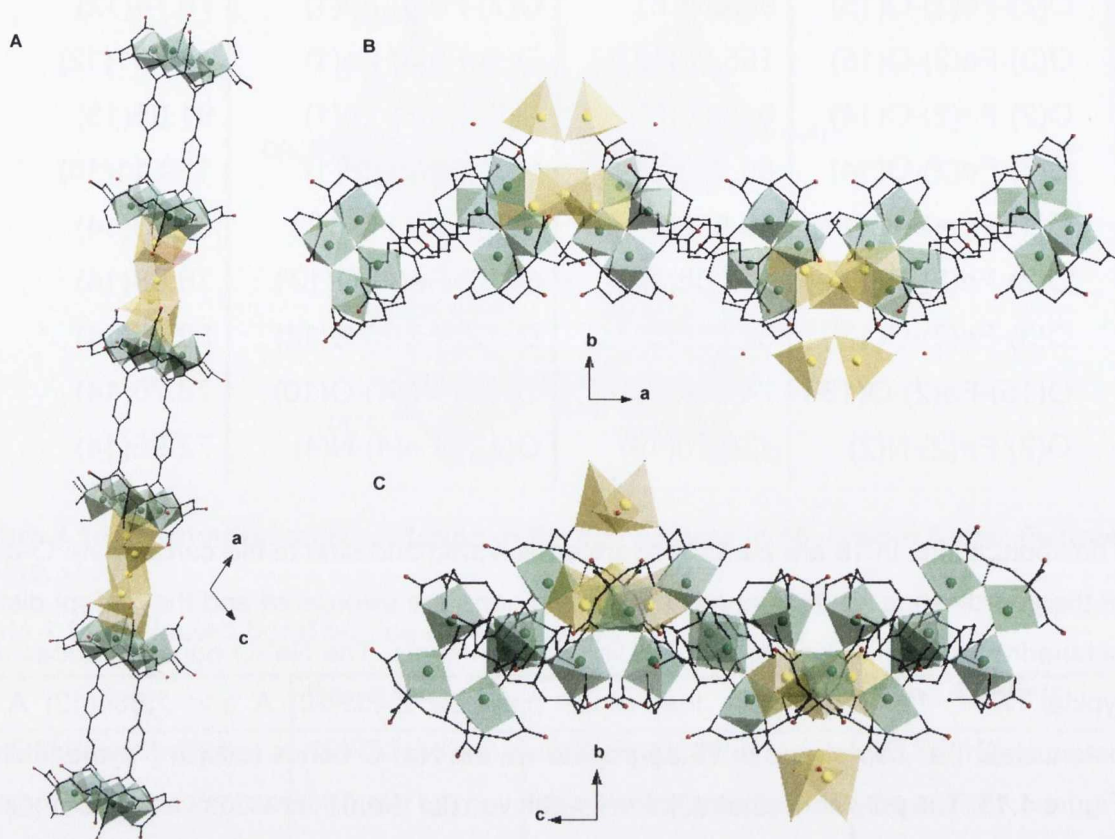


Figure 4.15: Perspective view of the Na⁺-O mediated chains of 16 viewed along A) the crystallographic *b*-axis B) crystallographic *c*-axis and C) crystallographic *a*-axis. Polyhedral representations of the Fe^{III} and Na⁺ centres. Hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, N blue, Na yellow, O red.

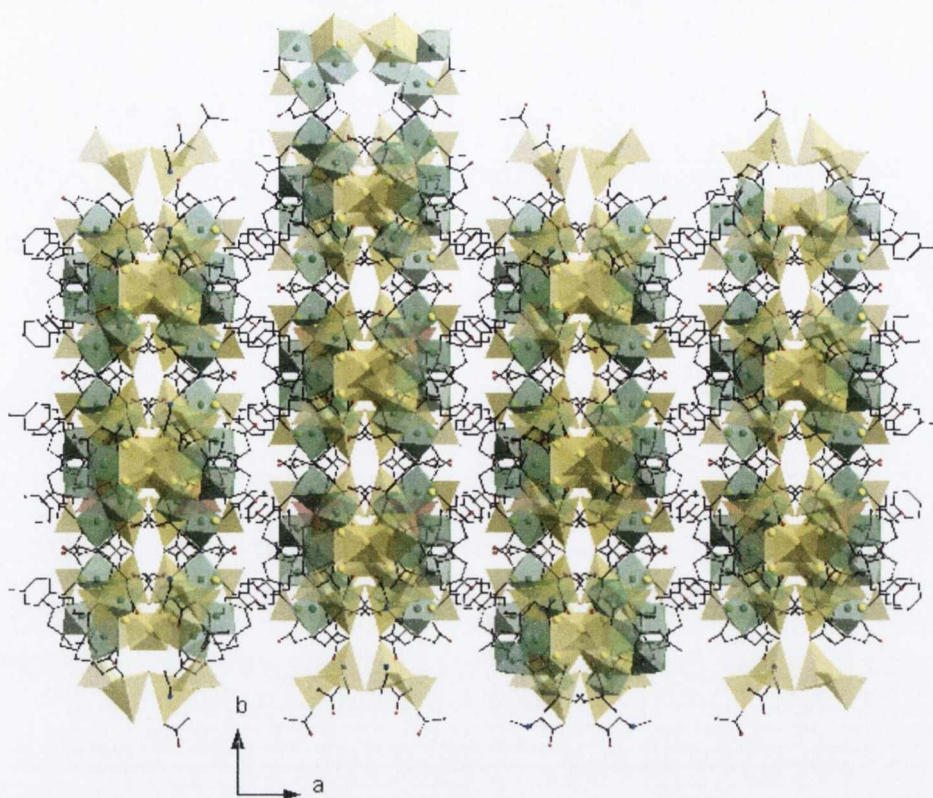


Figure 4.16: Packing structure of **16** viewed along the crystallographic *c*-axis. Polyhedra representation of the Fe^{III} and Na^+ centres. Hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, N blue, Na yellow, O red.

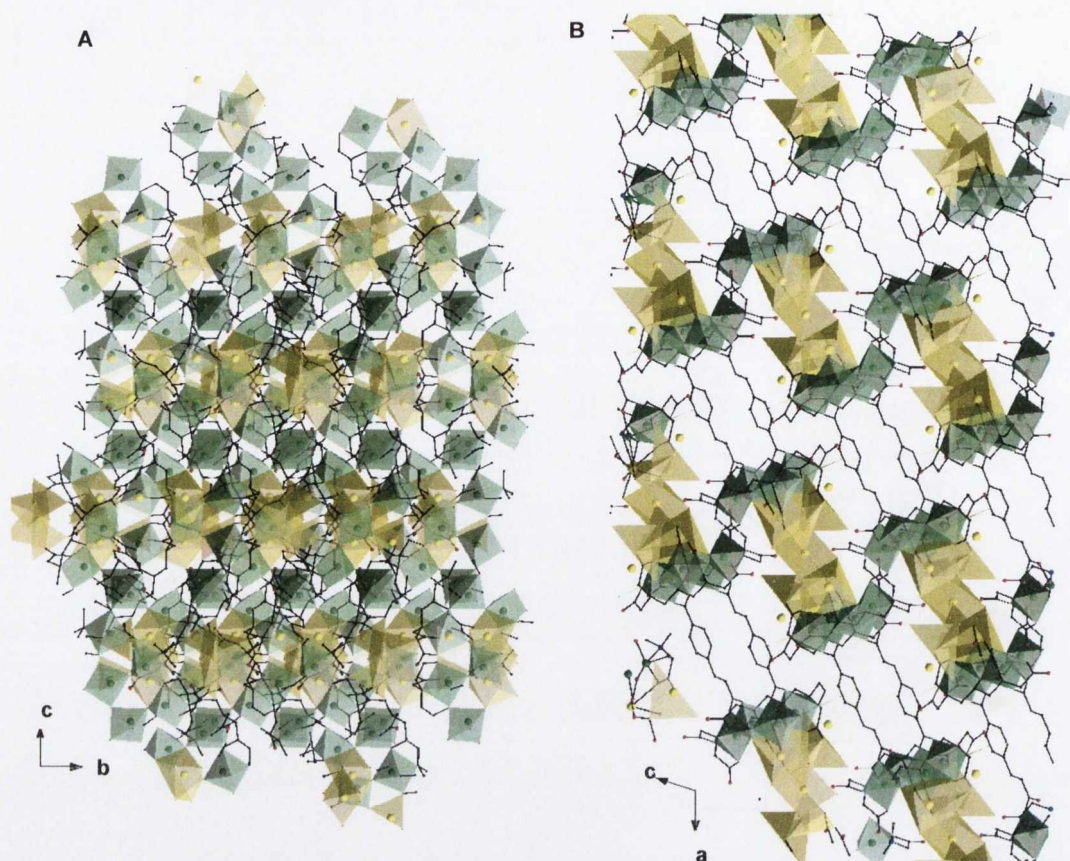


Figure 4.17: Packing structure of **16**, viewed along the crystallographic A) *a*-axis and B) *b*-axis. Polyhedral representations of the Fe^{III} and Na⁺ centres. Hydrogen atoms have been omitted for clarity. Colour Code: C black, Fe green, N blue, Na yellow, O red.

The crystal structure refinement of examined single crystals of **16** reveals a final R1 value of 8.00%, a goodness of fit of 1.043, a high data to parameter ratio and an acceptable 'largest difference peak and hole' values which support the structural assignment.

Table 4.12: Crystal data and structure refinement parameters for 16

Compound	16
Empirical formula	C ₆₄ H ₁₂₁ Cl ₂ Fe ₈ N ₈ Na ₁₀ O ₇₆
Formula weight	2966.21 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 35.993(7) Å α = 90°. b = 13.774(3) Å β = 108.23(3)°. c = 23.962(5) Å γ = 90°.
Volume	11283(4) Å ³
Z	4
Density (calculated)	1.553 Mg/m ³
Absorption coefficient	1.175 mm ⁻¹
F(000)	5319
Crystal size	0.2 x 0.1 x 0.15 mm ³
Φ range for data collection	1.59 to 25.07°.
Index ranges	-42<=h<=31, -16<=k<=16, -28<=l<=28
Reflections collected	32106
Independent reflections	9963 [R(int) = 0.0348] on F ²
Completeness to θ= 25.08°	99.4 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	9963 / 0 / 692
Goodness-of-fit on F ²	1.043
Final R indices[I>2sigma(I)]	R1 = 0.0800, wR2 = 0.2293
R indices (all data)	R1 = 0.0944, wR2 = 0.2402
Largest diff. peak and hole	1.081 and -0.829 e.Å ⁻³

4.5 Physicochemical properties of compounds 13-16

FT-IR spectroscopy

The FT-IR spectra recorded for **13-16** display the characteristic vibrational bands that are expected for the observed compounds that contain Fe^{III} ions coordinated by iminodiacetic

acid-based ligands. Each spectrum exhibits broad asymmetric and symmetric O-H stretches that are derived from constitutional water molecules. In the spectrum of **13** these are centered at *ca.* 3340 cm^{-1} . They appear at *ca.* 3385 cm^{-1} in the spectra of **14-16**. The asymmetric stretches originating from the deprotonated and coordinating carboxylic acid functionalities of the hpdta ligands occur at *ca.* 1635 cm^{-1} and *ca.* 1605 cm^{-1} in the spectra of **13** and **14-16**, respectively. The symmetric carboxylate stretches resonate at *ca.* 1385 cm^{-1} , and in the range 1370 cm^{-1} -1380 cm^{-1} for **13** and **14-16**, respectively. The asymmetric and symmetric stretches arising from the deprotonated carboxylate moieties of **L2-L6**, appear at *ca.* 1590 cm^{-1} and *ca.* 1435 cm^{-1} , in the spectrum for **13** and in the range between *ca.* 1535 cm^{-1} and *ca.* 1540 cm^{-1} , and between *ca.* 1430 cm^{-1} and *ca.* 1435 cm^{-1} in the spectra of compounds **14-16**, respectively. The frequency differences of the symmetric and asymmetric stretches of the carboxylate groups, ($\Delta\nu$), may be used to determine its binding mode. For example in **13** the $\Delta\nu$ value for the first set of asymmetric and symmetric carboxylate stretches is *ca.* 250 cm^{-1} reflecting their unidentate coordination modes within **13**. The second $\Delta\nu$ value of *ca.* 155 cm^{-1} is attributable to the carboxylate moieties of the benzoate ligands that coordinate to Fe^{III} centres in a syn, syn bidentate bridging fashion, Figure 4.1. In each spectrum the C-N stretching vibrations appear at in the range *ca.* 1320 cm^{-1} to 1325 cm^{-1} and the -OH bending vibrations appear at *ca.* 910 cm^{-1} . The FT-IR spectra and details of the assignments can be seen in Figure 4.18 and Table 4.13.

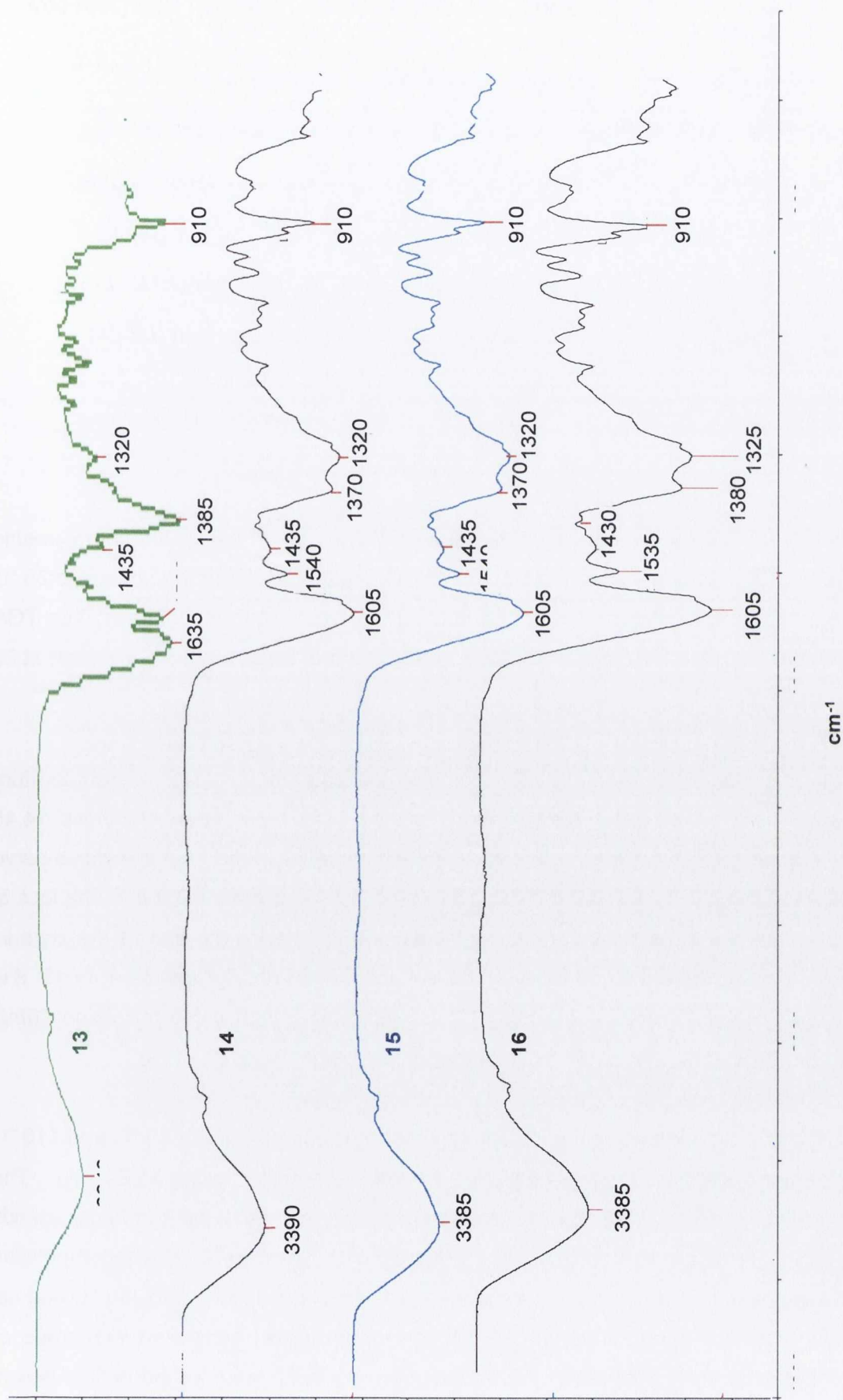


Figure 4.18: FT-IR spectra of freshly ground microcrystals of compounds 13-16, recorded using a diffuse reflectance accessory.

Table 4.13: Characteristic vibrational bands observed in the FT-IR spectra of compounds 13-16.¹³⁶⁻¹³⁸

Wavenumber (cm ⁻¹) compounds 13-16 res.	Assignment
ca. 3340, 3390, 3385 & 3385	O-H $\nu_s + \nu_{as}$ stretches
ca. 1635, 1605, 1605 & 1605	ν_{as} C-O stretch (<i>hpdt</i> a)
ca. 1385, 1370, 1370 & 1380	ν_s C-O stretch (<i>hpdt</i> a)
ca. 1590, 1540, 1540 & 1535	ν_{as} C-O stretch (L2-L6)
ca. 1435, 1435, 1435 & 1430	ν_s C-O stretch (L2-L6)
ca. 1320, 1320, 1320 & 1325	C-N stretch
ca. 910	bending -OH vibrations

Thermogravimetric analysis

The thermal stability of compounds **13-16** was characterised using thermogravimetric analyses (TGA). The analyses were performed in the temperature range between 25 °C and 900 °C, in an air atmosphere. The heating rate was set to 5 °C/minute. The TGA experiments for 15 and 16 were recorded with isothermal steps (each 15 minutes) at 25 °C and 110 °C.

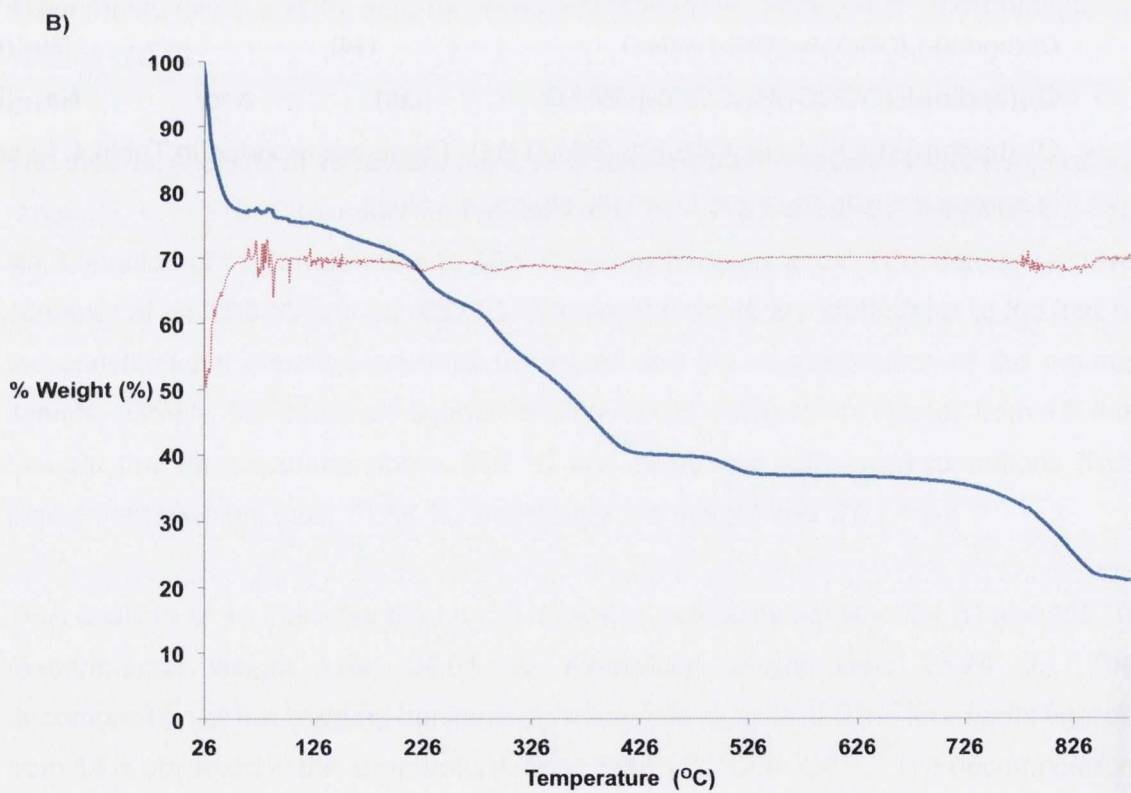
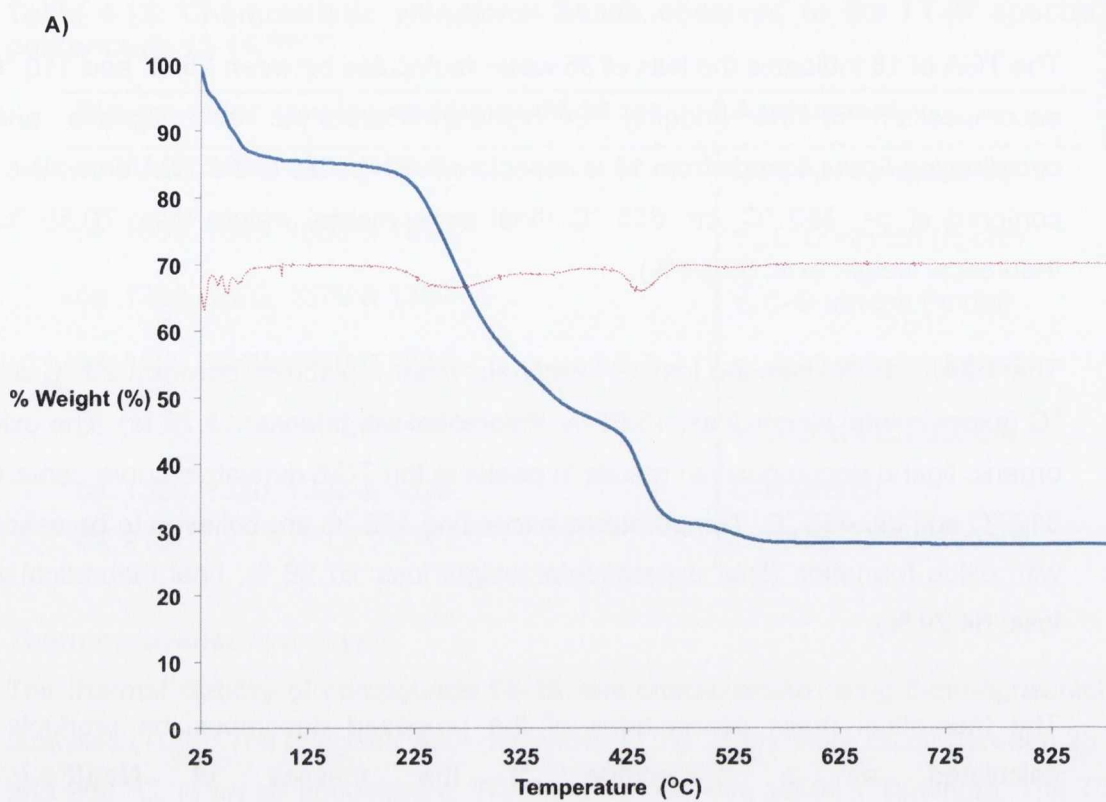
The thermal analysis of **13** reveals the loss of twelve water molecules in the temperature range 25 °C to 110 °C (experimental weight loss: 14.46 %, theoretical weight loss: 14.48 %). Elevation of the temperature to 590 °C results in peaks in the TGA derivative curve centered at ca. 260 °C and ca. 430 °C. The weight losses are attributable to the loss of the constitutional dimethylacetamide molecule and the decomposition of the organic ligands, namely, the benzoate ligands and the coordinating *hpdt*a ligands from **13**. It is thought that temperatures above 590 °C are associated with oxide formations (final experimental weight loss: 71.84 %, final theoretical weight loss: 70.74 %).

TGA analysis of **14** indicates the loss of 43 water molecules between 25 °C and 110 °C (experimental weight loss: 24.61 %, theoretical weight loss: 25.24 %). The decomposition of the bridging benzene dicarboxylate ligands and the four *hpdt*a ligands from **14** is observed in the temperature range from 110 °C to 530 °C. The decomposition results in peaks in the TGA derivative curve centered at ca. 285 °C, ca. 380 °C and ca. 500 °C. The loss centered at ca. 530 °C is thought to be associated with oxide or carbonate formation (final experimental weight loss: 78.30 %, final theoretical weight loss: 77.33 %).

The TGA of **15** indicates the loss of 35 water molecules between 25 °C and 110 °C. The decomposition of the bridging 4,4'-biphenyl-dicarboxylic acid ligands and the coordinating *hpdta* ligands from **15** is associated with peaks in the TGA derivative curve centered at *ca.* 380 °C, *ca.* 655 °C (final experimental weight loss: 70.55 %, final theoretical weight loss: 69.39 %).

The TGA of **16** reveals the loss of twenty-six water molecules between 25 °C and 110 °C (experimental weight loss: 15.99 %, theoretical weight loss: 15.78 %). The oxidative organic ligand decomposition results in peaks in the TGA derivative curve centered *ca.* 312 °C and *ca.* 455 °C. Temperatures exceeding 455 °C are believed to be associated with oxide formation (final experimental weight loss: 67.96 %, final theoretical weight loss: 64.29 %).

The theoretical mass percentages of the proposed decomposition products were calculated as a percentage of the masses of $\text{Na}_3[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2\}(\text{OOC}\text{C}_6\text{H}_5)_2] \cdot 12\text{H}_2\text{O} \cdot \text{DMF}$ (**13**), $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_6\text{H}_4\text{COO})_2] \cdot 43\text{H}_2\text{O}$ (**14**), $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})_2] \cdot 35\text{H}_2\text{O}$ (**15**) and $\text{Na}_{10}[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\text{Cl}_2 \cdot 26\text{H}_2\text{O}$ (**16**). These are reported in Table 4.14 and are in agreement with the experimentally observed values.



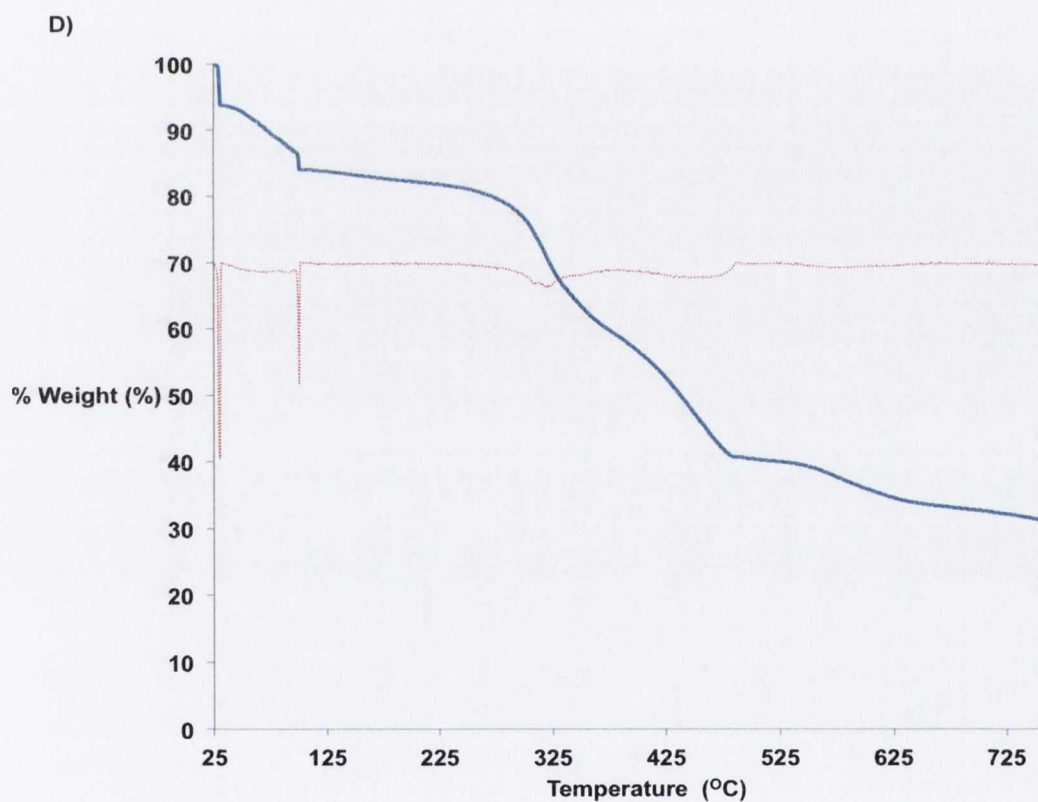
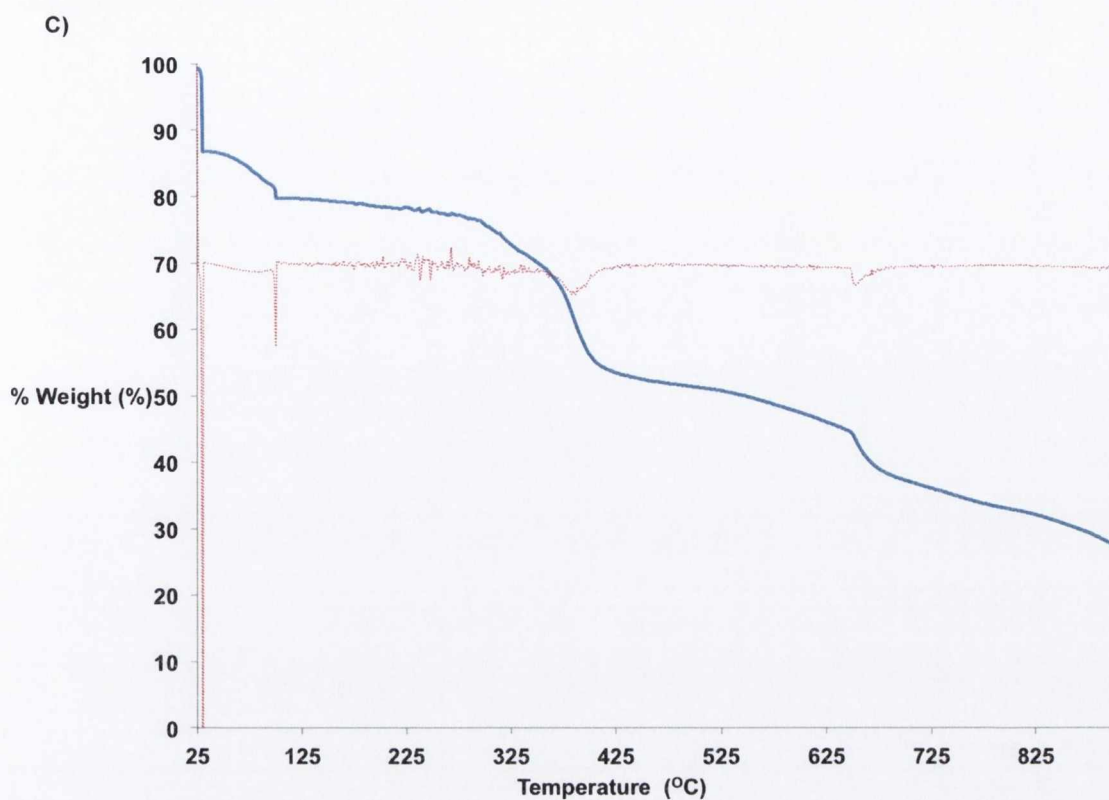


Figure 4.19: TGA curves for A) 13, B) 14, C) 15 and D) 16. Recorded in an air atmosphere from 25 °C to 900 °C. Heating step was set to 5 °C/minute. The TGA experiments for 15 and 16 were recorded with isothermal steps at 25 °C and 110 °C for 15 minutes.

Table 4.14: Results for TGA analyses (recorded in air atmospheres from 25 °C to 900 °C. Heating step was set to 5 °C/minute of 13-16. The TGA experiments for 15 and 16 were recorded with isothermal steps at 25 °C and 110 °C for 15 minutes.

	Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
13	C ₃₉ H ₆₇ Fe ₄ N ₅ Na ₃ O ₃₇	100	100	25 (Initial)
	C ₃₉ H ₄₃ Fe ₄ N ₅ Na ₃ O ₂₅	85.51	85.54	25 - 110
	Ligand decomposition & oxide formation	29.26	28.16	110 - 900 (Final)
14	C ₆₀ H ₁₄₆ Fe ₈ N ₈ Na ₈ O ₉₁	100	100	25 (Initial)
	C ₆₀ H ₆₀ Fe ₈ N ₈ Na ₈ O ₄₈	74.76	75.39	25 - 110
	Ligand decomposition & oxide formation	22.67	21.70	110 - 900 (Final)
15	C ₇₂ H ₁₃₉ Fe ₈ N ₈ Na ₈ O ₈₅	100	100	25 (Initial)
	C ₇₂ H ₆₉ Fe ₈ N ₈ Na ₈ O ₅₀	79.71	79.77	25 - 110
	Ligand decomposition & oxide formation	30.61	29.45	110 - 900 (Final)
16	C ₆₄ H ₁₂₁ Cl ₂ Fe ₈ N ₈ Na ₁₀ O ₇₆	100	100	25 (Initial)
	C ₆₄ H ₆₉ Cl ₂ Fe ₈ N ₈ Na ₁₀ O ₅₀	84.22	84.00	25 - 110
	Ligand decomposition & oxide formation	35.71	32.04	110 - 900 (Final)

Elemental Analysis

Elemental analyses were employed to further confirm the chemical formulae of **13-16**, $\text{C}_{39}\text{H}_{68}\text{Fe}_4\text{N}_5\text{Na}_3\text{O}_{37}$, $\text{C}_{60}\text{H}_{78}\text{Fe}_8\text{N}_8\text{Na}_8\text{O}_{57}$, $\text{C}_{72}\text{H}_{139}\text{Fe}_8\text{N}_8\text{Na}_8\text{O}_{85}$ and $\text{C}_{64}\text{H}_{121}\text{Cl}_2\text{Fe}_8\text{N}_8\text{Na}_{10}\text{O}_{76}$, respectively. The results, presented in Table 4.15, show a correlation between the theoretical and experimental values, thus suggesting that the constitutional assignments are correct and further confirm the purities of the samples.

Table 4.15: Theoretical and experimental elemental analyses for 13-17. Theoretical based on $C_{39}H_{68}Fe_4N_5Na_3O_{37}$, $C_{60}H_{78}Fe_8N_8Na_8O_{57}$, $C_{72}H_{139}Fe_8N_8Na_8O_{85}$, and $C_{64}H_{121}Cl_2Fe_8N_8Na_{10}O_{76}$, respectively.

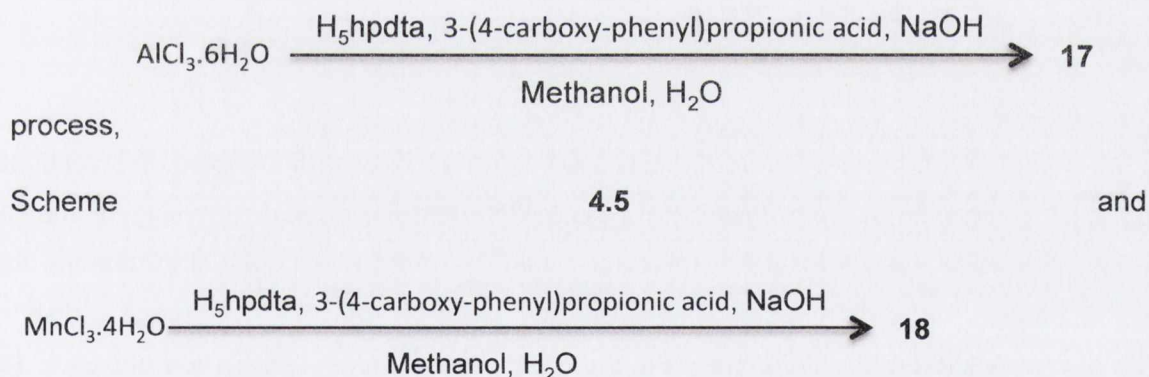
	Element	Theoretical composition (%)	Experimental composition (%)
13	C	31.41	31.43
	H	4.60	4.62
	Fe	14.98	14.95
	N	4.70	4.68
	Na	4.62	4.59
14	C	29.37	29.32
	H	3.20	3.17
	Fe	18.21	18.24
	N	4.57	5.54
	Na	7.49	7.46
15	C	27.83	27.85
	H	4.51	4.47
	Fe	14.38	14.36
	N	3.61	3.56
	Na	5.92	5.95
16	C	25.92	26.01
	H	4.11	4.16
	Fe	15.06	15.10
	N	3.78	3.83
	Na	7.75	7.69

4.6 The synthesis of Al and Mn analogues of compound 16

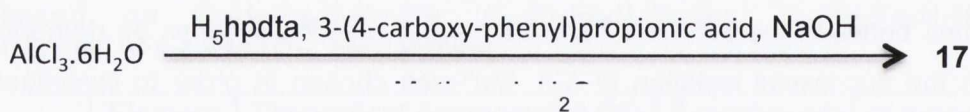
In consecutive experiments the synthetic protocol that led to the formation of the octanuclear Fe^{III} compound **16** was modified by varying the metal salts added to the system. The co-ligand used in these investigations was 3-(4-carboxy-phenyl) propionic acid (**L6**), containing two carboxylic acid groups. The aim of the investigations was to explore the effects of the metal ions in on the self-assembly process. The Al^{III} and Mn^{II}

ions were employed in these studies. The rationale behind the selection arose from the similarities between the Al^{III} *hpdta* and Fe^{III} *hpdta* reaction systems as demonstrated through the successful isolation of **1-5**. Mn^{II} was chosen in order to investigate the behaviour of divalent ions in the examined reaction system. Mn^{II} was considered to be a suitable divalent cation due to the high stability of the high-spin, +II oxidation state. Thus the Mn^{III} ion has the tendency to disproportionate into Mn^{II} and Mn^{IV} . However it has the tendency to form *in-situ* as it is reported to be stabilised in distorted octahedral coordination environment comparable to those observed in compounds **13-16**. Furthermore the previous isolation of mixed-valence tetranuclear $\text{Mn}^{\text{II/III/IV}}\text{-Ca}^{\text{III}}$ compounds in pursuance of the fact that a naturally occurring Mn_4CaO_n cluster acts as a catalyst for the evolution of oxygen from water in the photosystem-II, motivated us to investigate the Mn^{II} or Mn^{III} *hpdta* system.¹⁷⁷

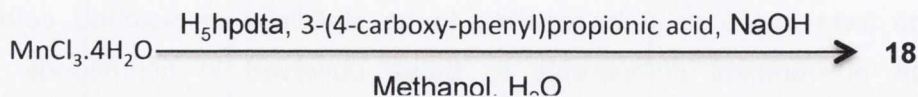
The reactions were carried out using a modified approach to the methodology described for **16**. Aqueous solutions of *hpdta* were reacted with aqueous solutions of metal salts. L6 was introduced to the solutions via a 0.25mM solution of sodium hydroxide and additional sodium hydroxide was used to adjust the pH of the reaction mixtures to 7.0. DMA was added to the reaction mixtures in an attempt to promote the crystallisation



Scheme 4.6. Despite the sequential alteration of the reaction conditions it was not possible to successfully isolate crystalline material suitable for single-crystal diffraction analysis. However, elemental analyses, TGA and FT-IR analyses strongly suggest that Mn and Al^{III} complexes form, whose structures are similar to those of the previously discussed Fe complexes **13-16**. The Al^{III} compound, **17** formed a white precipitate immediately following the addition of DMA to the reaction mixture. Similarly a dark brown precipitate of a Mn compound, **18**, forms within 48 hours.



Scheme 4.5: Preparation of compound 17



Scheme 4.6: Preparation of compound 18

4.6.1 Physicochemical characterisation of compounds 17 and 18

The characterisations of **17** and **18** are based on the assumption that the Al^{III} , Mn^{II} and Fe^{III} ions behave similarly in the *hpdta*-**L6** system. It was expected that the tetranuclear complexes would self-assemble and react with two equivalents of **L6** to form octanuclear complexes as observed in **16**. This assumption was justified by the similarities of the coordination environments in a plethora of $\text{M}^{\text{III}}/\text{hpdta}$ complexes reported in the literature.^{1-4, 122, 125, 152, 169, 178-179} The tetranuclear $\text{Mn}^{\text{II}}/\text{hpdta}$ complex previously described in the literature further supported our assumption that a Mn^{II} analogue of **16** forms under the applied reaction conditions.¹⁷⁷

FT-IR

The first step in the successful characterization of **17** and **18** involved an investigation of their central ion coordination modes. FT-IR was employed to investigate the binding modes of the carboxylates moieties within **17** and **18**. The resulting spectra, seen in Figure 4.20, were compared with the spectrum of **16**. The spectra display the characteristic vibrational bands that are expected for isostructural complexes of **16**. The average $\Delta\nu$ value for the first set of asymmetric and symmetric carboxylate stretches in **17** and **18** is *ca.* 225 cm^{-1} indicating that the deprotonated *hpdta* carboxylate functionalities bind in a unidentate coordination mode.¹⁶³ The $\Delta\nu$ value the second type of carboxylate moieties is *ca.* 105 cm^{-1} indicating that **L6** coordinates to Fe^{III} centres and engages in a *syn-syn bidentate*-bridging mode.¹⁶³ These values and the IR spectra further indicate that the coordination environments in **17** and **18** are comparable to those observed in previously discussed Fe^{III} coordination compounds. The assignments of the stretches for **17** and **18** can be seen in Table 4.16. All recoded FT-IR spectra are almost identical and compare very well with those of the corresponding Fe species.

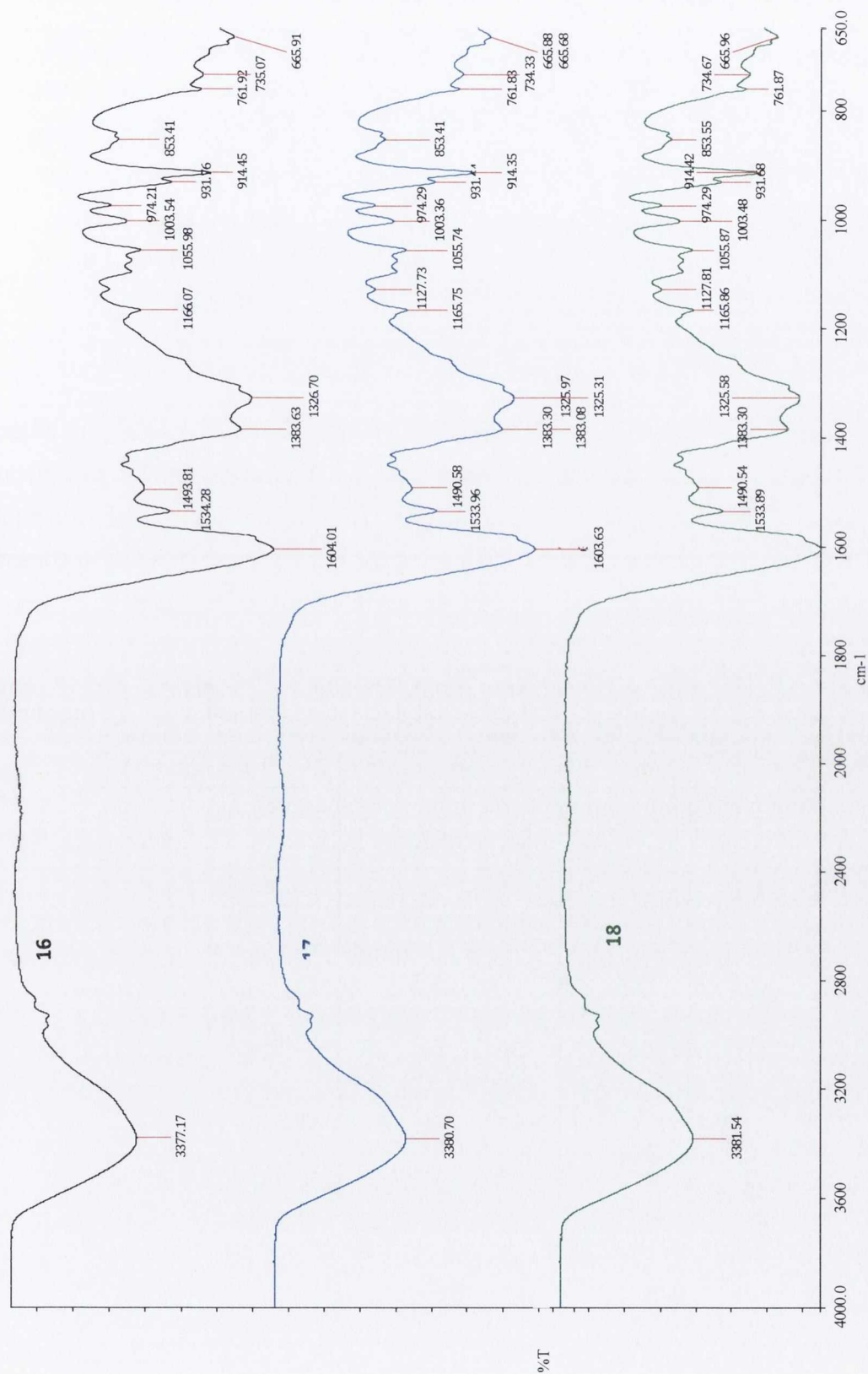


Figure 4.20: FT-IR Spectra displaying the characteristic absorptions for compounds 17 and 18 compared with 16. Recorded using a diffuse reflectance sampling accessory.

Table 4.16: Characteristic vibrational bands observed in the FT-IR spectra of compounds 16-18 respectively.¹³⁶⁻¹³⁸

Wavenumber (cm ⁻¹) compounds 16-19 res.	Assignment
ca. 3380 (br)	O-H $\nu_s + \nu_{as}$ stretches
2925, 2930 & 2930	Carboxylic $-\text{O}^-$ stretch
1605, 1605 & 1610 (s)	ν_{as} C-O stretch (<i>hpdt</i> a)
1380 (s)	ν_s C-O stretch (<i>hpdt</i> a)
1535	ν_{as} C-O stretch (L6)
1430	ν_s C-O stretch (L6)
ca. 1325	C-N stretch

Chemical Analysis

The chemical formulae, $[\text{C}_{64}\text{H}_{147}\text{Al}_8\text{N}_8\text{Na}_8\text{O}_{89}]$ and $[\text{C}_{64}\text{H}_{119}\text{Mn}_8\text{N}_8\text{Na}_8\text{O}_{75}]$, of **17** and **18** were further confirmed through elemental analysis. The experimental and theoretical values are consistent, as seen in Table 4.17, thus confirming the constitutional assignments. The oxidation state of the Mn centres in **18** was assigned to +II considering the starting MnCl_2 material and the complex described in the literature.¹⁷⁷

Table 4.17: Theoretical and experimental elemental analysis for 17 and 18. Theoretical based on $[\text{C}_{64}\text{H}_{147}\text{Al}_8\text{N}_8\text{Na}_8\text{O}_{89}]$ and $[\text{C}_{64}\text{H}_{119}\text{Mn}_8\text{N}_8\text{Na}_8\text{O}_{75}]$, respectively.

	Element	Theoretical (%)	Experimental (%)
17	C	26.95	26.93
	H	5.19	5.21
	N	3.93	4.02
	Na	6.45	6.44
18	C	27.22	27.85
	H	4.25	4.27
	N	3.97	3.96
	Na	6.51	6.49

Thermogravimetric analysis

The TGA analysis was carried out on freshly prepared samples of **17** and **18** in the temperature range between 25 °C and 900 °C, in an air atmosphere. The heating rate was set to 5 °C/minute with isothermal steps at 25 °C and 110 °C (15 minutes). An additional isothermal step was added at 350 °C for 15 minutes in the TGA analysis of **18**.

Analysis of a sample of **17** reveals the loss of 39 water molecules in the temperature range from 25 °C to 110 °C (experimental weight loss: 24.41 %, theoretical weight loss: 24.61 %). Whilst the TGA analysis of **18** reveals a loss of 25 water molecules (experimental weight loss: 16.00 %, theoretical weight loss: 15.94 %). The oxidative ligand decomposition from **17** results in peaks centered at *ca.* 350 °C, *ca.* 385 °C, followed by a steady decrease in weight between 425 °C and 660 °C. The organic ligand decomposition for **18** results in peaks centered at *ca.* 358 °C and *ca.* 375 °C, followed by an accumulative weight loss between 430 °C and 660 °C. The formation of oxides is believed to occur in temperatures above 660 °C. Final experimental weight loss: 74.84 %, final theoretical weight loss: 74.79 % for **17**. Final experimental weight loss: 73.53 %, final theoretical weight loss: 73.00 % for **18**.

The theoretical mass percentages of the proposed decomposition products were calculated as a percentage of the mass of $\text{Na}_8[\{\text{Al}_4(\mu\text{-O})_2(\text{hpdt})_2\}_2(\text{OCC}_8\text{H}_8\text{COO})_2] \cdot 39\text{H}_2\text{O}$ and $\text{Na}_8[\{\text{Mn}_4(\mu\text{-O})_2(\text{hpdt})_2\}_2(\text{OCC}_8\text{H}_8\text{COO})_2] \cdot 25\text{H}_2\text{O}$. These are reported in Table 4.18 and are in agreement with the experimentally observed values.

Table 4.18: Results for TGA analysis (recorded in an air atmosphere from 25 °C to 900 °C. Heating step was set to 5 °C/minute with isothermal steps at 25 °C and 110 °C for 15 minutes) of 17 and 18. An additional isothermal step was added at 350 °C for 15 minutes in the TGA analysis of 18.

	Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
17	C ₆₄ H ₁₄₇ Al ₈ N ₈ Na ₈ O ₈₉	100	100	25 (Initial)
	C ₆₄ H ₆₉ Al ₈ N ₈ Na ₈ O ₅₀	75.39	75.59	25 - 110
	Ligand decomposition and oxide formation	25.21	25.16	110 - 900 (Final)
18	C ₆₄ H ₁₁₉ Mn ₈ N ₈ Na ₈ O ₇₅	100	100	25 (Initial)
	C ₆₄ H ₆₉ Mn ₈ N ₈ Na ₈ O ₅₀	84.05	84.00	25 - 110
	Ligand decomposition and oxide formation	27.00	26.47	110 - 900 (Final)

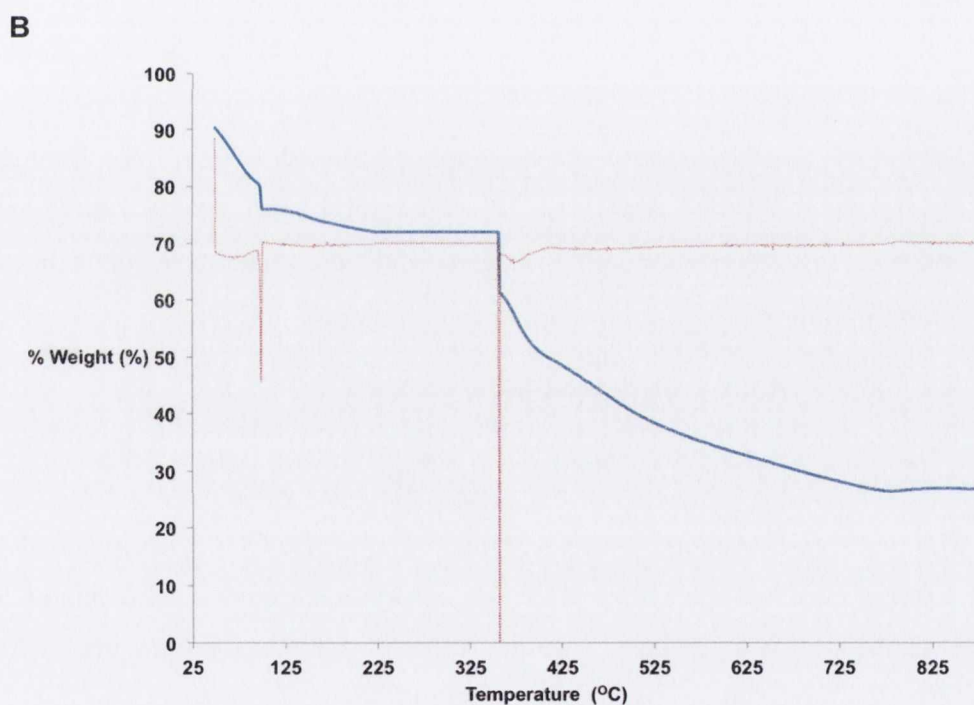
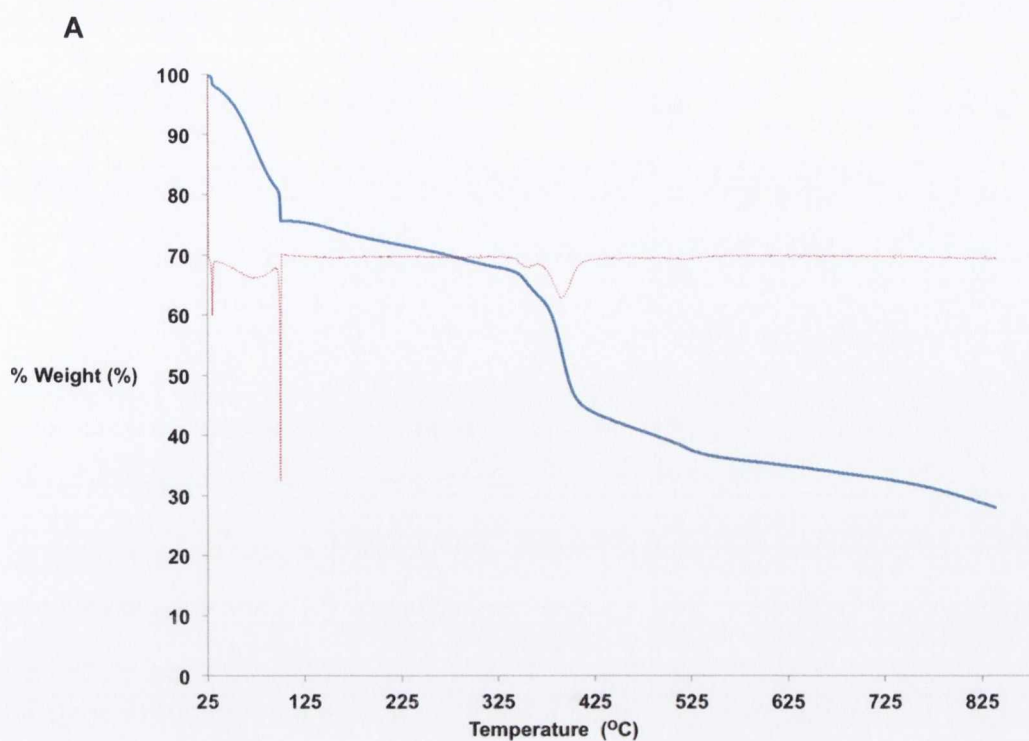


Figure 4.21: TGA curve for A) 17 and B) 18. Recorded in an air atmosphere from 25 °C to 900 °C. Heating step was set to 5 °C/minute with isothermal steps at 25 °C and 110 °C for 15 minutes). An additional isothermal step was added at 350 °C for 15 minutes in the TGA analysis of 18.

Chapter 5 Fixation and potential activation of atmospheric CO₂ to form carbamate and carbonate Fe^{III} *hpdta* complexes

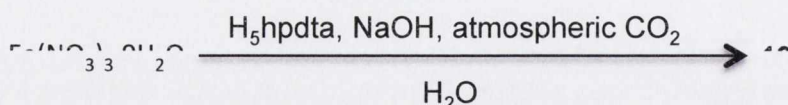
5.1 Introduction

As mentioned in the introduction, CO₂ is a greenhouse gas and the role of increasing atmospheric CO₂ concentrations on global warming is well established. It is believed that the CO₂ problem could be partially alleviated by the development of artificial photochemical systems that could economically fix CO₂ and transform it into fuels or useful chemicals. This research addresses the question of how the tetranuclear Fe^{III} *hpdta* complexes, that have a high affinity towards carboxylate bearing ligands, fix atmospheric carbon dioxide. The compound's ability to reversibly release CO₂ is examined in these studies. Additionally, their capacity to scavenge electrons from the MLCT excited state of [Ru(bpy)₃]²⁺ and their electrochemical redox characteristics are explored. This research is the first occasion where the photophysical and electrochemical properties of the transition metal *hpdta* systems have been examined and allows for an evaluation of the compound's potential applications as catalysts in the reduction of CO₂.

5.2 The Fixation of Atmospheric CO₂

5.2.1 {Na}₅[Fe^{III}₄(μ-O)(μ-OH)(*hpdta*)₂(CO₃)₂]·15H₂O (**19**)

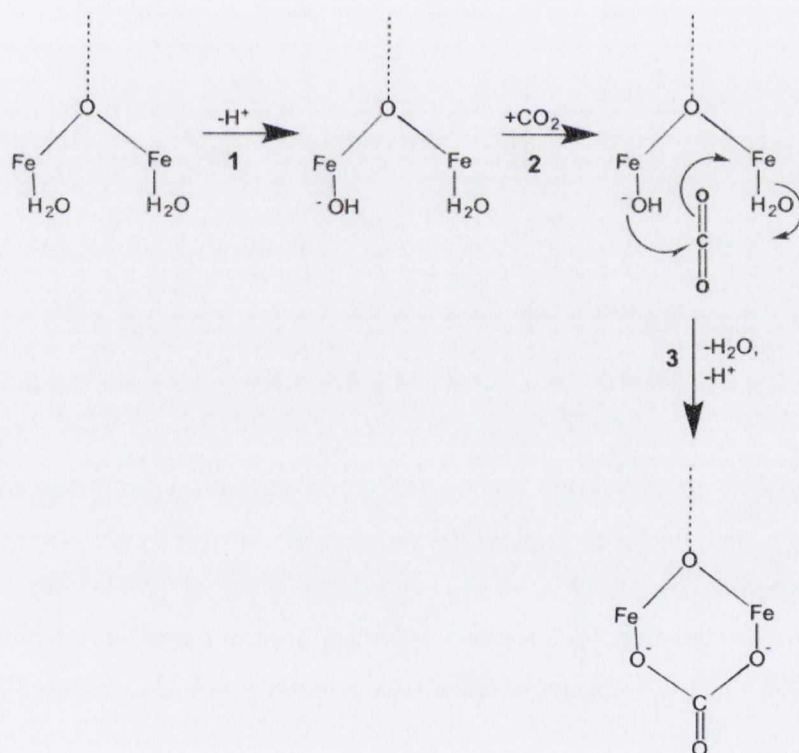
The novel coordination compound {Na}₅[Fe^{III}₄(μ-O)(μ-OH)(*hpdta*)₂(CO₃)₂]·15H₂O (**19**) is isolated from reactions between the polyaminocarboxylic acid ligand, *H₅hpdta* and Fe(NO₃)₃·9H₂O using NaOH to adjust the pH to 8.5 (



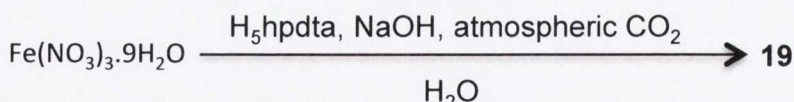
Scheme 5.2). Dark green, rectangular shaped crystals of **19** suitable for single-crystal X-ray diffraction measurements were obtained by co-evaporation with dimethylacetamide. The tetranuclear complex in **19** is shown in Figure 5.1. It is stabilized by two fully deprotonated *hpdta* ligands and two carbonate ligands, atom labels C(1), O(6-8) and their symmetry equivalents. The CO₃²⁻ ligands bind in a *syn, syn*, bidentate bridging

mode to Fe(1)-Fe(2') and Fe(2)-Fe(1'). Comparable tetranuclear Fe^{III} complexes have been explored in the past. However, this is the first occasion where the tetranuclear compound has been stabilised without addition of a carbonate-containing reactant to the reaction mixture.^{2, 180} These carbonate groups are important as they are thought to be formed by the hydration of atmospheric CO₂ at the metal sites and their presence demonstrates CO₂ fixation. **19** does not form when the reaction is pursued under an inert atmosphere.

The reaction pathway for the fixation of CO₂ is comparable to that of carbonic anhydrase.¹⁸¹⁻¹⁸⁷ The proposed reaction route, detailed in Scheme 5.1, reinforces the pathway described by Schmitt *et al.* for the formation of carbon dioxide trapping carbamate compounds.² The first step involves deprotonation of an auxiliary water ligand to form a coordinated hydroxo moiety (**1** in Scheme 5.1). In the second step the hydroxo moiety nucleophilically attacks a dissolved carbon dioxide molecule, which in step three disengages a water molecule from a neighbouring Fe^{III} ion to form the bidentate bridging (bi)carbonate molecule (**2** and **3** in Scheme 5.1).



Scheme 5.1: Proposed reaction mechanism for the fixation of CO₂ at the Fe^{III} centres in **19**.²



Scheme 5.2: Preparation of 19

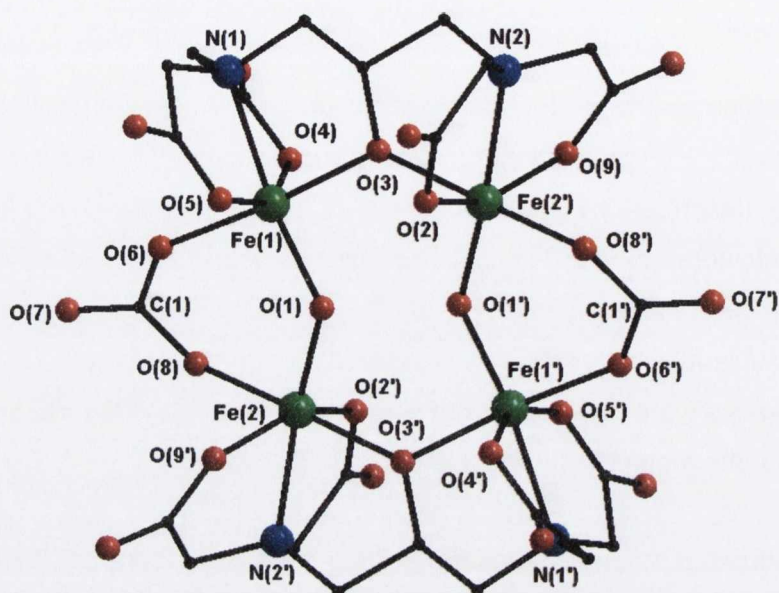


Figure 5.1: The structure of the tetranuclear complex in 19. The hydrogen atoms have been omitted for clarity. Colour code: C black, Fe green, N blue, O red.

5.2.2 Structural characterisation of 19

The carbonate complex **19** crystallises in the triclinic crystal system in the space group *P*-1. The asymmetric unit consists of two Fe^{III} centres, Fe(1) and Fe(2) and one deprotonated *hpdta* ligand. The overall complex can be described as consisting of two dinuclear units, in which the two Fe^{III} centres are linked by a μ_2 -bridging alkoxo O atom of the organic molecule. The two dinuclear building blocks are linked *via* bridging oxo/hydroxo moieties (originating from two deprotonated water molecules) to form a square planar tetranuclear complex. An inversion centre is located in the centre of the tetranuclear complex.

Fe(1) is separated from its neighbouring Fe^{III} atoms, Fe(2) and Fe(2'), by 3.421(46) Å and 3.763(44) Å. The values are consistent with those found in the literature.³ Each of the Fe^{III} centres in **19** are in similar environments displaying distorted octahedral coordination geometries. The O_{carboxylate}-donor and N-donor atoms from the two

iminodiacetic acid functionalities of the *hpdta* molecules bind to the Fe^{III} ions in a *meridional* fashion.

The oxidation state of each Fe ion centre can be determined by an analysis of the Fe^{III} bond lengths and coordination environments. For Fe(1), two coordination sites are occupied by the two oxygen atoms, O(4) and O(5), that derive from two deprotonated carboxylic acid groups of the *hpdta* molecule. The Fe(1)-O_{carboxylate} bond distances are 2.051(9) Å and 2.049(2) Å, respectively. A third coordination site is occupied by a N-donor atom, N(1), to give Fe^{III}-N bond distance of 2.21(14) Å. The three atoms bind in a *meridional* arrangement to the Fe(1) cation. The corresponding Fe(2')-O and Fe(2')-N bonds display distances of 2.063(22) Å, 2.024(3) Å and 2.197(13) Å, respectively. The distorted octahedral coordination spheres of both Fe^{III} ions are completed by the deprotonated O_{hydroxyl} atom of the organic molecule O(3), an oxygen atom from a bridging oxo/hydroxo moiety, O(1) and O(1'), and an oxygen atom from the bridging carbonato group, O(6) and O(8'). The Fe^{III}-O bond lengths are 2.063(23) Å for Fe(1)-O(3), 1.845(12) Å for Fe(1)-O(1), 1.995(11) Å for Fe(1)-O(6), 2.054(7) Å for Fe(2')-O(3), 1.839(8) Å for Fe(2')-O(1') and 2.001(21) Å for Fe(2')-O(8'). These relatively short bond distances indicate that the Fe atoms are in the +III oxidation state.

The distortion from ideal octahedral coordination geometry can be observed through examination of the bond angles. The most significant deviations from the linear modal is seen for the bond angles O(5)-Fe(1)-O(4) and O(2)-Fe(2')-O(9) of 153.49(21)° and 152.45(22)°. Minor deviations of 7.3° and 3.8° are seen for the angles N(1)-Fe(2)-O(1), O(3)-Fe(2')-O(8') of 172.67(18)°, 176.18(16)°. Divergence for the ideal 90° angle is exemplified in the *cis* angles O(5)-Fe(1)-N(1) and N(2)-Fe(2)-O(2) of 78.59(21)° and 78.67(19)°. Further non-conformities are seen for the bond angles N(1)-(Fe1)-O(3) of 81.63°, N(2)-Fe(2')-O(3) of 81.75(14)° and O(4)-Fe(1)-N(1) of 76.06(18)°. Minor deviations are characterised by the bond angles O(1')-Fe(2')-O(3) and O(1)-Fe(1)-O(3) with values of 90.38° and 91.79(16)°. Other selected bond distances and angles involving the Fe^{III} centres in **19** are summarised in **Table 5.1** and **Table 5.2**.

Table 5.1: Selected bond distances for the Fe^{III} centres in 19.

Atom	Bond	Bond Distance (Å)
Fe(1)	Fe(1)-O(1)	1.845(12)
	Fe(1)-O(6)	1.995(11)
	Fe(1)-O(5)	2.049(2)

Fe(2')	Fe(1)-O(4)	2.051(9)
	Fe(1)-O(3)	2.063(23)
	Fe(1)-N(1)	2.21(14)
	Fe(2')-O(1')	1.839(8)
	Fe(2')-O(8')	2.001(21)
	Fe(2')-O(2)	2.024(3)
	Fe(2')-O(3)	2.054(7)
	Fe(2')-O(9)	2.063(22)
	Fe(2')-N(2)	2.197(13)

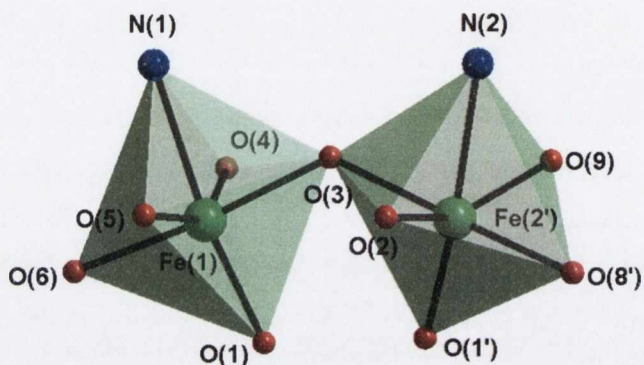


Figure 5.2: Polyhedral representations of the Fe^{III} centres in 19. The *hpdta* ligand has been omitted for clarity. Colour code: Fe green, N blue, O red.

Table 5.2: Selected bond angles for compound 19.

	Bond Angle (°)		Bond Angle (°)
O(1')-Fe(1)-O(6)	93.19(18)	O(5)-Fe(1)-N(1)	78.59(21)
O(1')-Fe(1)-O(5)	104.48(24)	O(4)-Fe(1)-N(1)	76.06(18)
O(6)-Fe(1)-O(5)	86.43(22)	O(3)-Fe(1)-N(1)	81.63(14)
O(1')-Fe(1)-O(4)	101.61(21)	O(1')-Fe(2')-O(8')	92.36(17)
O(6)-Fe(1)-O(4)	87.54(18)	O(1')-Fe(2')-O(2)	91.52(13)
O(5)-Fe(1)-O(4)	153.49(21)	O(1')-Fe(2')-O(3)	89.46(13)
O(1')-Fe(1)-O(3)	91.79(16)	O(1')-Fe(2')-O(9)	90.91(13)
O(6)-Fe(1)-O(3)	173.05(16)	O(1')-Fe(2')-N(2)	97.63(13)
O(5)-Fe(1)-O(3)	87.63(19)	O(2)-Fe(2')-O(9)	152.45(22)
O(4)-Fe(1)-O(3)	96.20(16)	O(3)-Fe(2')-O(8')	176.18(16)
O(1')-Fe(1)-N(1)	172.67(18)	N(2)-Fe(2')-O(1')	170.65(18)
O(6)-Fe(1)-N(1)	93.65(16)	O(2)-Fe(2')-O(1')	106.41(22)

The assignment of the oxidation state in **19** is confirmed through charge considerations of the anionic complex. The core complex as seen in Figure 5.1, containing four Fe^{III} ions, two fully deprotonated *hpdta* molecules, the two carbonate groups and the bridging oxo/hydroxo moiety, has a charge of -5. The charge of the complex is compensated by five Na⁺ cations to give a neutral compound. The counter-ions are disordered whereby the atom positions of Na(1), Na(3), Na(4) and symmetry equivalents are only half occupied in the crystal structure.

The Na⁺ ions are disordered and adopt octahedral coordination environments. They are coordinated to the tetranuclear Fe^{III} complex in **19** via O_{carbonate} and O_{carboxylate} atoms and reveal typical Na⁺-O bond distances of 2.436(29) Å to 2.812(47) Å. The extensive Na⁺-O inter-molecular bonding congregate units of **19** into a 2D polymeric network. **19** is further characterised in the solid state by bonds between constitutional water molecules and O_{carboxylate} atoms of *hpdta* molecules that separated by distances of ca. 2.30 Å to ca. 3.35 Å.

The crystal structure of **19** reveals highly disordered Na⁺ ions and water molecules, thus obtaining elevated R1 and GOF values of 14.5 % and 1.88, respectively. Therefore it was necessary to use the PLATON routine SQUEZE** to account for the extended disorder in the final refinement of the crystal structure, see Table 5.3.

** The PLATON SQUEZE routine removes all of the electron density that arises from disordered solvent molecules.

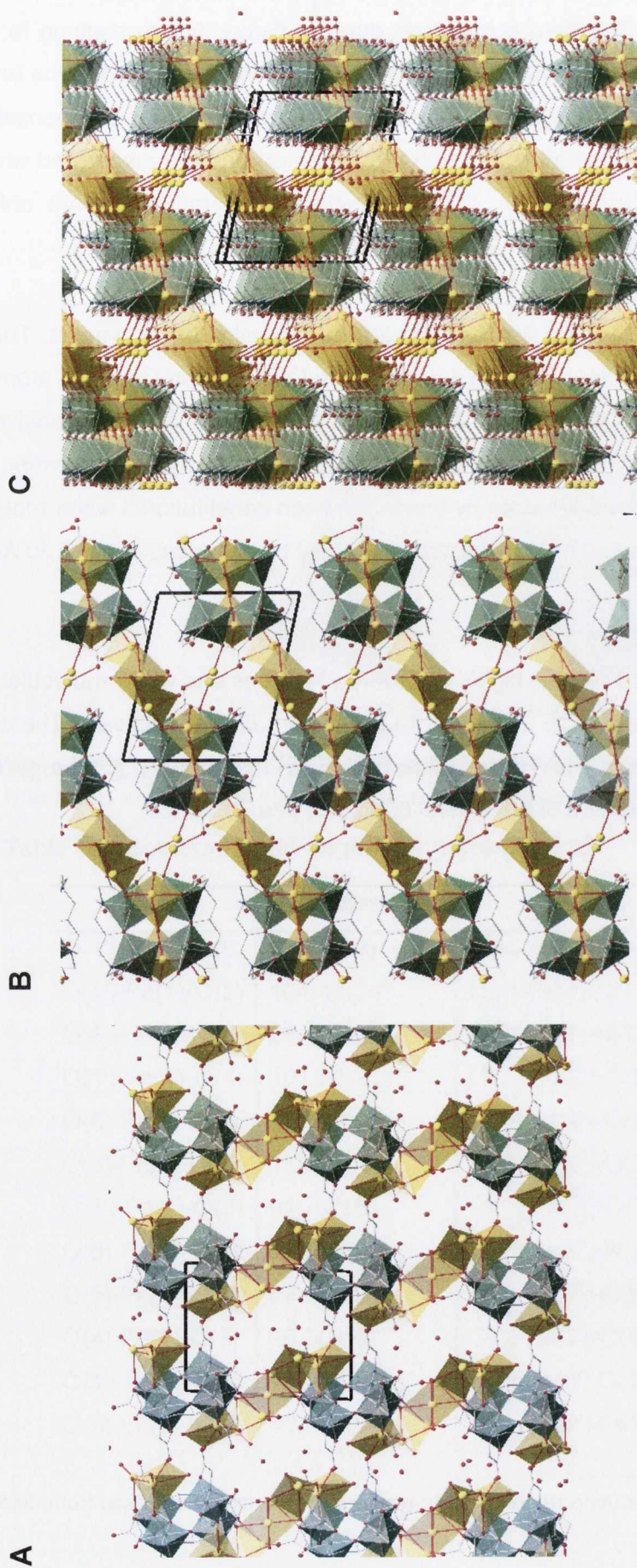


Figure 5.3: Packing structures of 19 viewed along the A) crystallographic *a*-axis. B) Cross sectional view and C) Perspective view of 19 that extend into the crystallographic *a*-axis. Polyhedral representations of the Fe^{III} and the Na^+ centres. The hydrogen atoms have been omitted for clarity. Colour code: C light grey, Na yellow, Fe green, O red.

Due to the high degree of disorder and a weakly diffracting crystal, it was not possible to satisfactorily locate all of the hydrogen atoms; H-atoms of the *hpdta* molecule were refined using the HFIX command. It is worth noting that in **19**, the bridging oxo/hydroxo moieties in the centre of the complex appear crystallographically equivalent. However, the very short O(1)-O(1') contact of 2.409(37) Å unambiguously confirms the presence of a H-bond. This is in agreement with reported related complexes.^{1, 3, 123}

Table 5.3: Squeezed crystal data and structure refinement parameters for 19

Compound	19
Empirical formula	C ₂₄ H ₅₇ Fe ₄ N ₄ Na ₅ O ₄₁
Formula weight	1396.04g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71075 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 10.804(5) Å α = 78.26(3)°. <i>b</i> = 11.655(4) Å β = 88.00(3)°. <i>c</i> = 12.814(6) Å γ = 64.85(2)°.
Volume	1427.6(11) Å ³
Z	1
Density (calculated)	1.204 Mg/m ³
Absorption coefficient	1.071 mm ⁻¹
F(000)	523
Crystal size	0.35 x 0.10 x 0.24 mm ³
Φ range for data collection	1.63 to 25.00°.
Index ranges	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -15 ≤ <i>l</i> ≤ 15
Reflections collected	33805
Independent reflections	5020 [R(int) = 0.0583] on F ²
Completeness to θ = 25.00°	99.7 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	5020 / 0 / 268
Goodness-of-fit on F ²	1.036
Final R indices[<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0752, wR2 = 0.2312
R indices (all data)	R1 = 0.0846, wR2 = 0.2404
Largest diff. peak and hole	1.349 and -0.994 e.Å ⁻³

5.2.3 Physicochemical characterisation of 19

FT-IR spectroscopy

The FT-IR spectrum of **19**, Figure 5.4, exhibits the characteristic stretches for *hpdta* coordinated Fe^{III} compounds as observed in the FT-IR spectra of compounds **1-4**, **8**, **10** and **13-16**. The symmetric and asymmetric -OH stretching is observed at ca. 3375 cm^{-1} . The frequencies of the asymmetric and symmetric carboxylate stretches at ca. 1610 cm^{-1} and ca. 1320 cm^{-1} , vary by ca. 285 cm^{-1} . The $\Delta\nu$ indicates a unidentate binding mode, Figure 5.1.¹⁶³ The characteristic FT-IR stretch that relates to the bidentate carbonate ligand appears at ca. 1480 cm^{-1} .¹⁴¹⁻¹⁴²

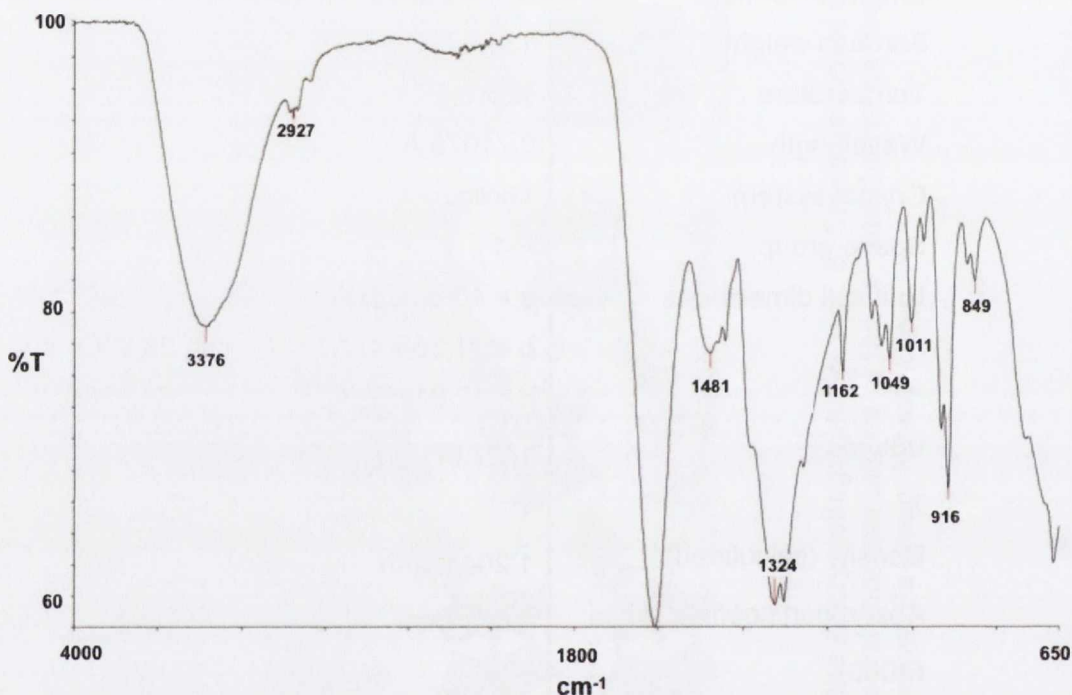


Figure 5.4: FT-IR spectrum of freshly ground microcrystals of **19** recorded using a diffuse reflectance accessory.

Table 5.4: The characteristic FT-IR vibrations, and corresponding assignments, for **19**.^{136-138, 188}

Wavenumber (cm^{-1})	Assignment(s)
3375	O-H ν_s and ν_{as} stretches
1610	$\nu_{as}\text{COO}^-$
1325	$\nu_s\text{COO}^-$
1480	CO_3^{2-} ν_{as} stretch ¹⁴¹⁻¹⁴²
915	Out of plane -OH stretch

Thermogravimetric analysis

The thermal degradation pathway of **19** was investigated using TGA. The analysis was performed in the temperature range between 25 °C and 900 °C under atmospheric conditions. The heating rate was set to 1 °C/minute with an isothermal step at 25 °C and 100 °C for 15 minutes. The loss of fifteen water molecules from **19** is observed in the temperature range from 25 °C to 110 °C (experimental weight loss: 19.68 %, theoretical weight loss: 19.34 %). Increasing the temperature to 311 °C results in the loss of the carbonate side groups (experimental weight loss: 8.64 %, theoretical weight loss: 8.60 %). A further increase in temperature to 570 °C gives rise to the oxidative ligand decomposition resulting in peaks in the TGA derivative curve centered at *ca.* 375 °C, *ca.* 465 °C and *ca.* 560 °C. It is believed that Na and Fe oxides form at temperatures exceeding 570 °C (final experimental weight loss: 63.47 %, final theoretical weight loss: 63.07 %).

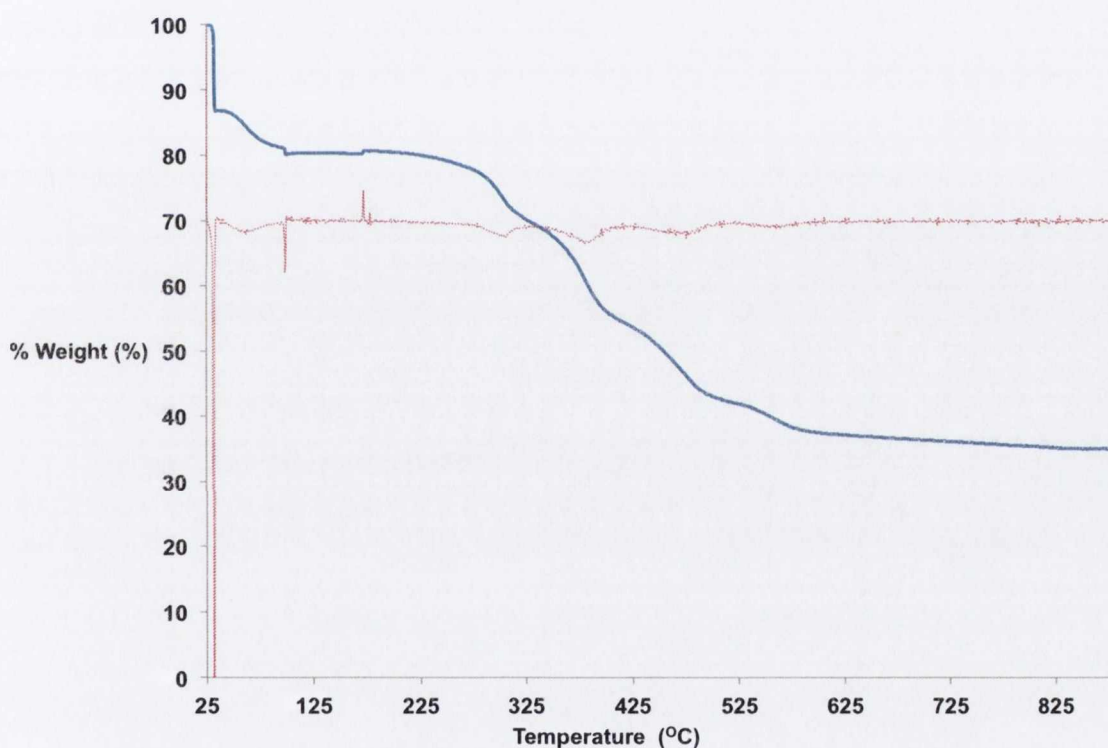


Figure 5.5: TGA curve for **19**. recorded in atmospheric conditions from 25 °C to 900 °C.

Table 5.5: Results for TGA analysis (recorded in an air atmosphere from 25 °C to 900 °C.

Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
C ₂₄ H ₅₇ Fe ₄ N ₄ Na ₅ O ₄₁	100	100	25 (Initial)
C ₂₄ H ₂₇ Fe ₄ N ₄ Na ₅ O ₂₆	80.65	80.32	30 - 110
C ₂₂ H ₂₇ Fe ₄ N ₄ Na ₅ O ₂₀	72.06	71.69	110 - 311
Ligand decomposition ^{††}	36.86	36.53	311-900 (final)

Powder X-ray Diffraction

Powder X-ray diffraction experiments were used to investigate the phase purity of **19**. Pristine crystals of **19** were ground to a powder for the analysis. The resultant pattern, seen in blue in Figure 5.6, matches the simulated pattern, seen in red in Figure 5.6. The simulated pattern was generated using the ‘un-squezzed’ crystallographic information file (CIF) for **19**. The correspondence between the two patterns suggests the phase purity of **19** and further establishes the accuracy of the refined structural model as determined by the single-crystal X-ray diffraction experiments. The absence of minor peaks from the measured powder pattern is attributed to the loss of constitutional water molecules during the grinding process.

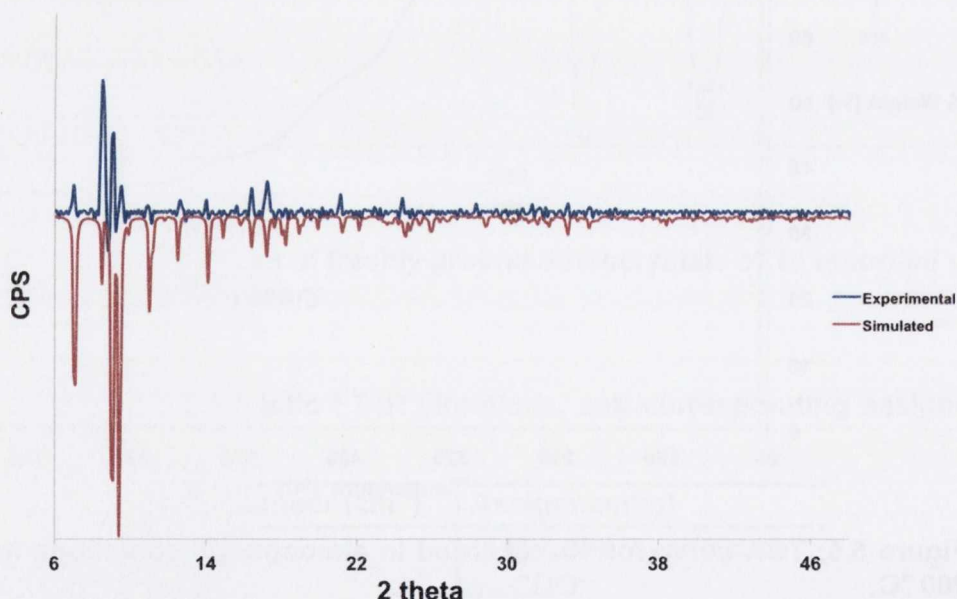


Figure 5.6: P-XRD pattern for crystals of **19 (blue) compared with a simulated pattern based on the single-crystal X-ray measurements (red)**

Elemental Analysis

^{††} and oxide formation

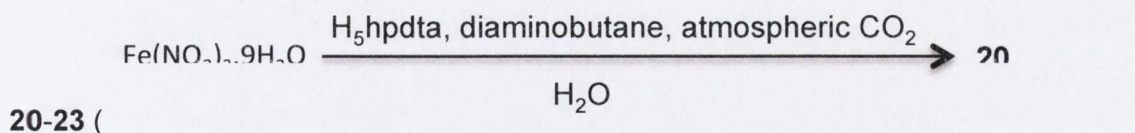
The chemical formula for **19**, C₂₄H₅₇Fe₄N₄Na₅O₄₁, was further investigated using elemental analysis. The matching theoretical and experimental values, Table 3.27, confirm the accuracy of the constitutional assignments and further suggests the phase purity of **19**.

Table 5.6: Theoretical and experimental elemental analysis for 19. Theoretical based on $C_{24}H_{57}Fe_4N_4Na_5O_{41}$.

Element	Theoretical composition (%)	Experimental composition (%)
C	20.65	20.59
Fe	16.00	16.08
H	4.12	4.15
N	4.01	3.98
Na	8.23	8.29

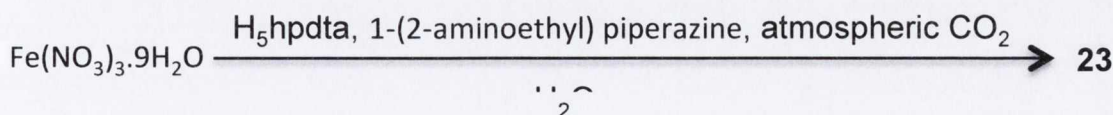
5.2.4 Synthesis of related carbon dioxide fixing carbamate compounds 20-23

In these studies we investigated the formation of a series of carbamate compounds $(\text{NH}_2\text{C}_4\text{H}_8\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_4\text{H}_8\text{NH}_3)_2]\cdot 10\text{H}_2\text{O}$ (**20**), $(\text{NH}_2\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHNNH}_3)_2]\cdot 9\text{H}_2\text{O}$ (**21**), $(\text{NH}_2\text{C}_6\text{H}_{12}\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_6\text{H}_{12}\text{NH}_3)_2]\cdot 9\text{H}_2\text{O}$ (**22**) and $(\text{NHC}_2\text{H}_4\text{NC}_4\text{H}_8\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NC}_4\text{H}_8\text{NH}_2)_2]\cdot 8\text{H}_2\text{O}$ (**23**). The procedures used to prepare these compounds were adapted from a typical procedure for comparable hydrolytic reactions described by Schmitt *et al.*¹²³ 1,4-Diaminobutane, hydrazine, hexamethylenediamine and 1-(2-aminoethyl) piperazine were used to adjust the pH of the aqueous $\text{Fe}^{\text{III}}/\text{hpdta}$ reaction mixtures to *ca.* 8.5 resulting in formation of compounds



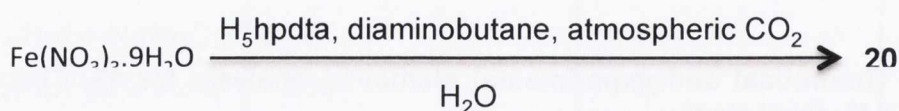
Scheme

5.3

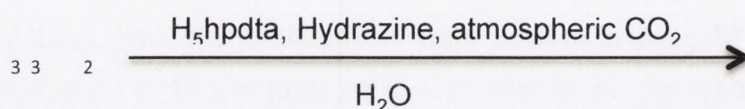


Scheme 5.6). Despite extensive modifications of the reaction systems it was not possible to isolate suitably sized crystals for single-crystal X-ray diffraction experiments. **20-23** precipitated as green powders from their reaction mixtures within two days of

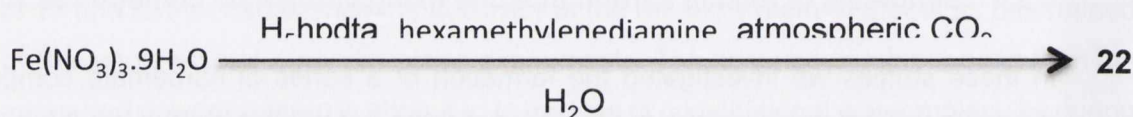
preparation. Their formations were investigated using FT-IR, chemical analysis and TGA.



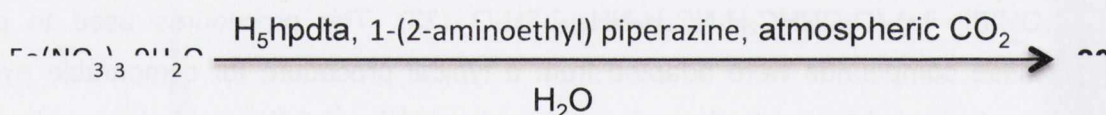
Scheme 5.3: Preparation of 20



Scheme 5.4: Preparation of 21



Scheme 5.5: Preparation of 22

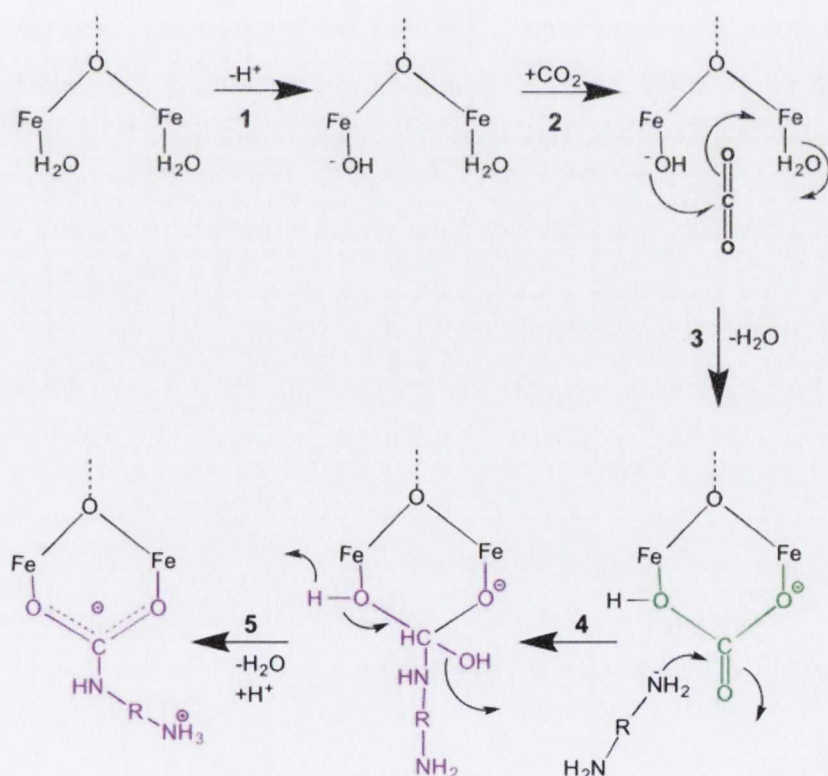


Scheme 5.6: Preparation of 23

5.2.5 Physicochemical characterisation of 20-23

It was anticipated that **20-23** (highlighted in purple in Scheme 5.7) would form tetranuclear compounds with coordination environments similar to those observed in **1-4**, **13-17** and **19**. It was expected that the protolytic activation of a coordinating water molecule would promote a series of nucleophilic attacks resulting in the coordination of a dissolved carbon dioxide molecule to an Fe^{III} centre in the form of a bicarbonate molecule (Steps 1 and 2 in Scheme 5.7). The molecule is expected to displace a water molecule from a neighbouring Fe^{III} atom to form a bidentate coordinating (bi)carbonate bridging molecule (Step 3 in Scheme 5.7). The subsequent step is envisaged to involve a nucleophilic attack on the activated carbonate molecule resulting in the formation of C-

N bonds between the carbonate molecule and diamine molecule (Step 4 in Scheme 5.7). The elimination of a second water molecule results in the carbamic acid/carbamate ligand. The auxiliary ligand is reported to bind to the Fe centres in a zwitterionic form upon protonation of the unreacted amine group (Step 5 in Scheme 5.7).² These assumptions are supported by the extensive research into Fe^{III} *hpdta* based coordination compounds that readily form tetranuclear species under the given reaction conditions. Moreover, our previous studies have shown that the tetranuclear Fe^{III} compounds have a high affinity towards carboxylate bearing molecules as demonstrated through the successful isolation and structural characterisations of compounds **13-16**. It has also been effectively demonstrated that the synthetic methodology utilised in this research results in the fixation of carbon dioxide molecules through the isolation of compounds **3** and **7**. Through the isolation of related Al^{III} and Fe^{III} carbon dioxide trapping compounds, **3** and **7**, it has been established that the base can be interchanged to form carbon dioxide fixing analogues suggesting that the key component in the fixation of carbon dioxide is the tetranuclear metal compound in solution rather than the hydrolysing agent added to the reaction.²



Scheme 5.7: The proposed reaction pathway for the fixation of carbon dioxide and the formation of carbamate coordinating molecules.

FT-IR spectroscopy

The identity and coordination modes of compounds **20-23** was confirmed through FT-IR spectroscopy. The infrared spectrum of the reference tetranuclear Fe^{III} carbamate compound (enH)[Fe₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₂H₄NH₃)₂].6.5H₂O (**3**) and the spectra for the complexes **20-23** (seen in Figure 5.7), are similar. The asymmetric and symmetric -OH stretching appears in the range *ca.* 3330 cm⁻¹ to *ca.* 3375 cm⁻¹. The broad range is attributable to the solvent water molecules associated with compounds **3** and **20-23**. The asymmetric carboxylate stretch, which forms part of the, previously discussed, characteristic 'triplet' stretch for carbamate compounds appears at *ca.* 1615 cm⁻¹, *ca.* 1620 cm⁻¹, *ca.* 1615 cm⁻¹, *ca.* 1615 cm⁻¹ and *ca.* 1620 cm⁻¹ in the spectra of **3** and **20-23**. The N-H deformation arising from the singly protonated nitrogen atom on the zwitterionic carbamate is present in each spectrum appearing at *ca.* 1510 cm⁻¹, *ca.* 1510 cm⁻¹, *ca.* 1500 cm⁻¹, *ca.* 1500 cm⁻¹ and *ca.* 1505 cm⁻¹ in the spectra of **3** and **20-23** respectively.¹⁸⁸ The symmetric carboxylate stretches for the six compounds appear at *ca.* 1375 cm⁻¹, *ca.* 1365 cm⁻¹, *ca.* 1365 cm⁻¹, *ca.* 1365 cm⁻¹ and *ca.* 1370 cm⁻¹ respectively. The energy differences between the asymmetric and symmetric stretches for the six compounds are in the range *ca.* 240 cm⁻¹ to *ca.* 255 cm⁻¹ indicating that the hpdta carboxylate functionalities coordinate in a unidentate bridging mode for compounds **20-23**. The values are comparable to those observed for the tetranuclear Fe^{III} hpdta compound **3**. A noteworthy difference in the spectra is the absence of the NH⁺ deformation arising from the protonated nitrogen carbamate zwitterions, that is typically observed at *ca.* 1560 cm⁻¹, from the spectrum of **23**.¹⁸⁸ This was expected as the diamino piperazine derivative in **23** is unlikely to form a zwitterionic species that contains a primary amide functionality. The NH⁺ deformation is also absent in the infrared spectrum of the Ga^{III} compound (pipH)[Ga₄(μ-O)(μ-OH)(hpdta)₂(O₂CNC₄H₈NH₃)].14H₂O, which forms through CO₂ fixation and contains a similar piperazine molecule.^{3, 123} The assignment of selected stretches in the FT-IR spectra of **3** and **20-23** can be seen in Table 5.7.

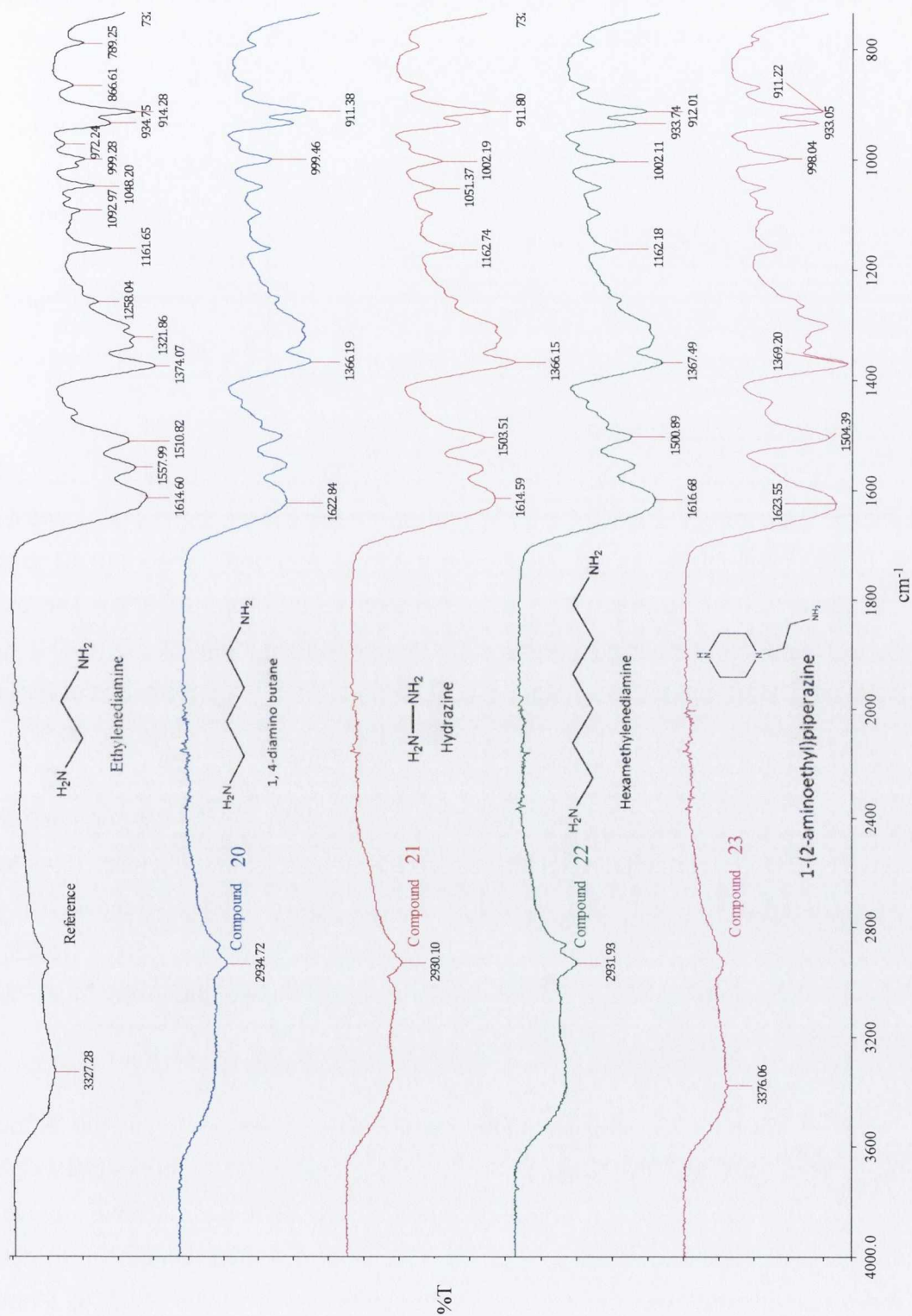


Figure 5.7: FT-IR Spectra displaying the characteristic vibrations for 3 and 20-23. Recorded using a diffuse reflectance sampling accessory.

Table 5.7: The characteristic FT-IR absorptions, and corresponding assignments, for compounds **3 and **20-23**.**^{136-138, 188}

Wavenumber (cm ⁻¹) compounds 3 and 20-23 res.	Assignment(s)
3327, 3329, 3336, 3365, 3376	O-H ν_s and ν_{as} stretches
1614, 1622, 1614, 1616, 1623	ν_{as} COO ⁻
1374, 1366, 1366, 1367, 1369	ν_s COO ⁻
1557, 1556, 1561, 1559	NH ₃ ⁺ deformation 1° amine ¹⁸⁸
1510, 1507, 1503, 1500, 1504	N-H deformation (1° amine) ¹⁸⁸
ca. 910	N-H wagging (1° and 2° amine) ¹⁸⁹

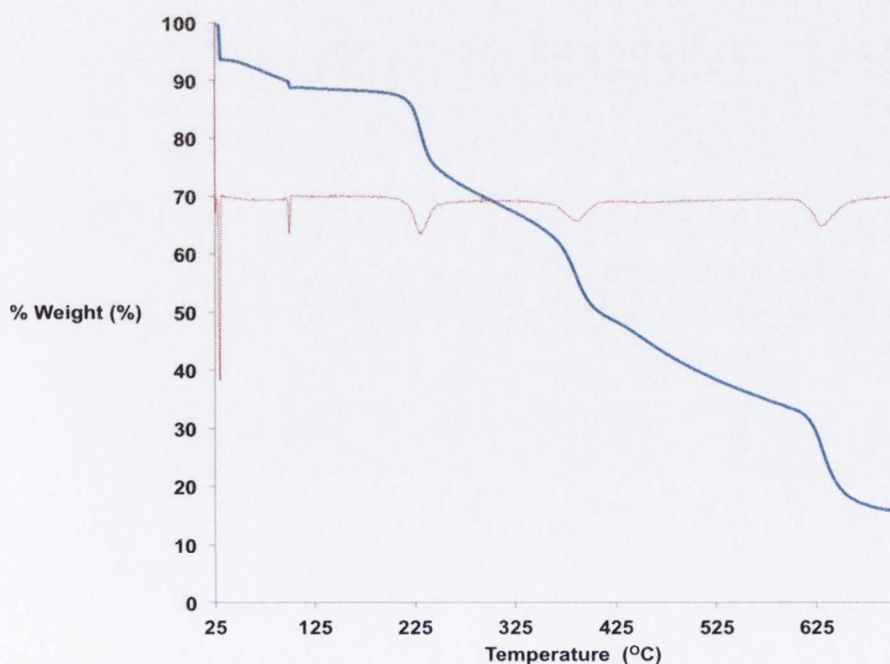
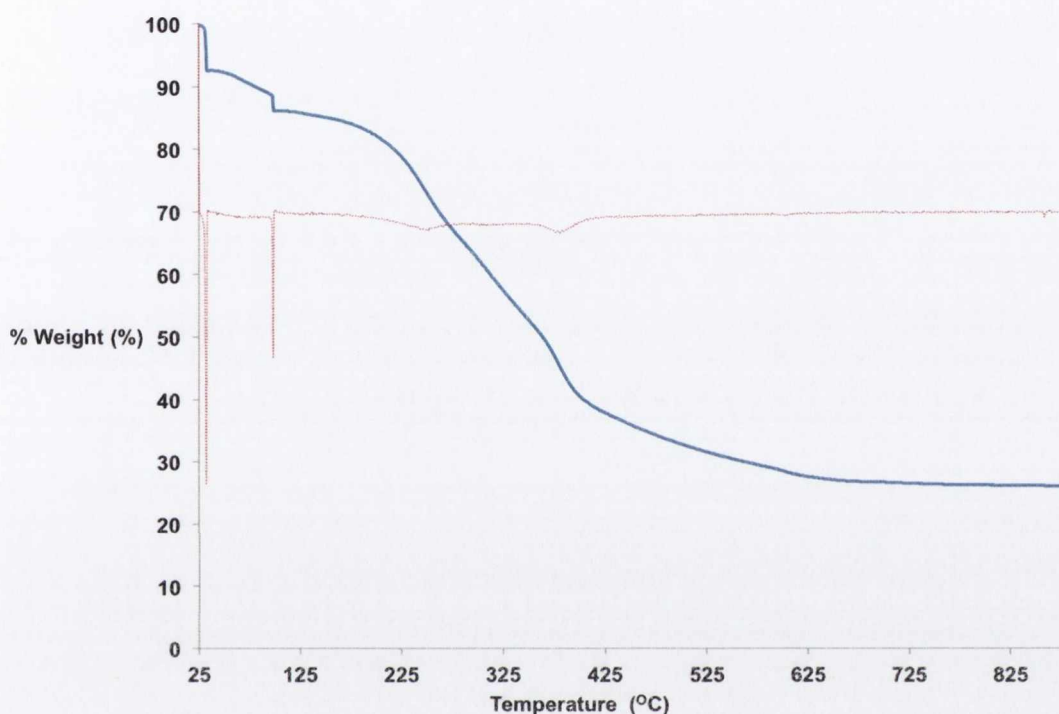
Thermogravimetric analysis

The loss of 10 water molecules is observed from **20** in the temperature range 25 °C to 110 °C (experimental weight loss: 13.59 %, theoretical weight loss: 13.48%). The auxiliary carbamate moieties decompose in the temperature range 110 °C to 280 °C (experimental weight loss: 19.77 %, theoretical weight loss: 19.79 %). The oxidative *hpdta* ligand decomposition occurs in the temperature range 280 °C to 550 °C. It is believed that temperatures exceeding 550 °C gives rise to the formation of Fe^{III} oxides (Final experimental weight loss: 76.02 %, final theoretical weight loss: 76.00 %).

The TGA curve for **21** reveals the loss of 9 water molecules in the temperature range 25 °C to 110 °C (experimental weight loss: 13.49 %, theoretical weight loss: 13.44 %). The oxidative organic ligand decomposition occurs in a two-step process across the temperature range 110 °C to 550 °C. Temperatures exceeding 550 °C result in the formation of metal oxide material (final experimental weight loss: 74.36 %, final theoretical weight loss: 73.70 %).

The TGA profile for **22** establishes the loss of 9 water molecules within the temperature range from 24 °C to 110 °C, (experimental weight loss: 11.04 %, theoretical weight loss: 10.87 %). Further increase in temperature to 625 °C gives rise to oxidative organic ligand decomposition centred at ca. 230 °C, ca. 380 °C and ca. 625 °C in the TGA derivative curve, (experimental weight loss: 71.95 %, theoretical weight loss: 71.92 %). Metal oxide formation is expected to occur in the temperature range 725 °C - 900 °C (experimental weight gain: 4.35 %, theoretical weight gain: 4.29 %). Final experimental weight loss: 82.99 %, final theoretical weight loss: 82.79 %.

The loss of 8 water molecules from **23** is observed in the temperature range 25 °C to 110 °C (experimental weight loss: 9.54 %, theoretical weight loss 9.52 %). The oxidative organic ligand decomposition occurs in the temperature range 110 °C to 550 °C and results in peaks in the TGA derivative curve centred at *ca.* 250 °C and *ca.* 380 °C. At temperatures exceeding 550 °C metal oxides would be expected to form (final experimental loss: 78.79 %, theoretical weight loss: 78.80%).



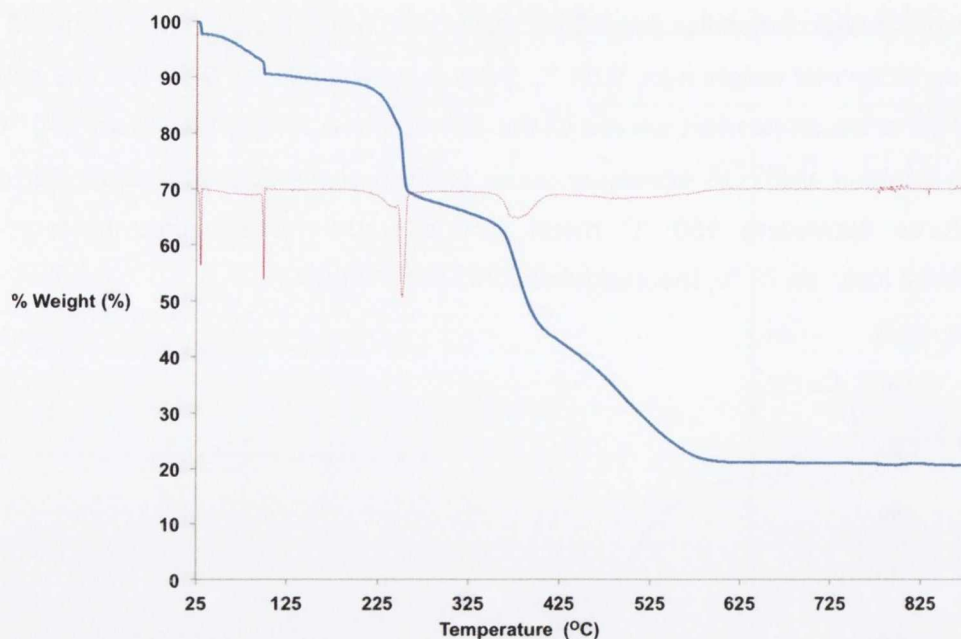


Figure 5.8: TGA curve for A) 21, B) 22 and C) 23. Recorded in atmospheric conditions from 25 °C-900 °C. A heating step was set to 1 °C/minute with an isothermal step at 25 °C and 100 °C for 15 minutes.

Table 5.8: Results for TGA analysis (recorded in an air atmosphere from 25 °C to 900 °C. Linear heating step was set to 1 °C/minute) of 20-23.

	Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
20	C ₃₆ H ₈₄ Fe ₄ N ₁₀ O ₃₄	100	100	25 (Initial)
	C ₃₆ H ₆₄ Fe ₄ N ₁₀ O ₂₄	86.52	85.41	25 - 110
	C ₂₂ H ₂₇ Fe ₄ N ₄ O ₂₀	66.72	66.64	110 – 280
	Ligand decomposition and oxide formation	23.99	23.98	280 – 900 (final)
21	C ₂₄ H ₅₈ Fe ₄ N ₁₀ O ₃₃	100	100	25 (Initial)
	C ₂₄ H ₄₀ Fe ₄ N ₁₀ O ₂₄	86.56	86.51	25 – 110
	Ligand decomposition and oxide formation	26.50	26.23	110 – 900 (final)
22	C ₄₂ H ₉₄ Fe ₄ N ₁₀ O ₃₃	100	100	25 (Initial)
	C ₄₂ H ₇₆ Fe ₄ N ₁₀ O ₂₄	89.13	88.96	25 – 110
	Ligand decomposition and oxide formation	21.42	21.30	110 – 900
23	C ₄₂ H ₈₉ Fe ₄ N ₁₃ O ₃₂	100	100	25 (initial)
	C ₄₂ H ₇₃ Fe ₄ N ₁₃ O ₂₄	90.47	90.46	25 – 110
	Ligand decomposition and oxide formation	21.12	21.20	110 - 900

Chemical analysis:

Chemical analysis was performed on bulk samples of **20-23** to further confirm their constitutional assignment of $C_{36}H_{84}Fe_4N_{10}O_{34}$, $C_{24}H_{58}Fe_4N_{10}O_{33}$, $C_{42}H_{94}Fe_4N_{10}O_{33}$ and $C_{42}H_{89}Fe_4N_{13}O_{32}$ respectively. Table 3.9 shows the corresponding theoretical and experimental values, thus confirming the constitutional assignments and the phase purity of **20-23**.

Table 5.9: Theoretical and experimental elemental analysis for 20-23. Theoretical based on $C_{36}H_{84}Fe_4N_{10}O_{34}$, $C_{24}H_{58}Fe_4N_{10}O_{33}$, $C_{42}H_{94}Fe_4N_{10}O_{33}$ and $C_{42}H_{89}Fe_4N_{13}O_{32}$, respectively.

	Element	Theoretical composition (%)	Experimental composition (%)
20	C	30.35	30.33
	H	5.94	5.88
	Fe	15.68	15.64
	N	9.83	9.70
21	C	23.28	23.16
	H	4.72	4.64
	Fe	18.04	18.06
	N	11.31	11.25
22	C	33.84	33.77
	H	6.36	6.29
	Fe	14.99	15.04
	N	9.40	9.36
23	C	33.37	33.34
	H	5.93	5.90
	Fe	14.78	14.73
	N	12.05	12.08

Table 5.10: Comparison of the percentage yields of 20-23 over four days. Day 4 = final % yield.

	20	21	22	23
Day 1 (%)	ca. 30	ca. 20	ca. 20	ca. 25
Day 2 (%)	ca. 45	ca. 35	ca. 30	ca. 40
Day 4 (%)	ca. 50	ca. 45	ca. 45	ca. 50

5.3 Reversible capture and release of CO₂ utilising the carbon dioxide trapping compounds 3 and 20-23

As previously mentioned, the tetranuclear coordination compounds **3** and **20-23** are stabilized through auxiliary molecules that derive from the fixation of carbon dioxide. As demonstrated by Schmitt *et al.* the fixation occurs at high pH values whereas at lower values the $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{H}_2\text{O})_4]^-$ species is formed. With this knowledge we investigated the possibility of releasing the absorbed CO₂ by lowering the pH of the system containing **3** from 8.5 to 4.5. We also investigated the uptake of the CO₂ when the pH was readjusted to 8.5 using ethylenediamine, as illustrated in Figure 5.9.

These investigations were performed in a gas-tight mass spectrometry vial that was sealed with a septum and a layer of parafilm. The headspace samples were obtained by insertion of a gas tight glass syringe through the septum. We monitored the absorption/desorption behaviour by comparison of the relative intensities of the O₂ (31.99 m/z) and CO₂ (43.99 m/z) signals of the headspace samples. Figure 5.11A displays the relative intensities of O₂ and CO₂ that naturally exists in the atmosphere. The experiments were performed in quintuplet in order to investigate the presence of **1** and **3** in solution. Their presence was confirmed through ESI-MS⁻ analyses of the solutions contained in the GC-MS vial after each pH adjustment. As previously discussed, **3** is characterised in solution using ESI-MS⁻ via the isotopic envelope at 1103.0 m/z. The isotopic envelopes at 891.0 m/z, 504.9 m/z and 490.1 m/z are assignable to $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2]^-$, $\{\text{H}_3[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})\text{-}2\text{O})\cdot 4\text{H}_2\text{O}\}^-$ and $\{\text{H}_3[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})\text{-COO})\cdot 4\text{H}_2\text{O}\}^-$ indicating the presence of **1** in solution.

5.3.1 Uptake and release of CO₂ in liquid aqueous and solid systems containing tetranuclear Fe^{III}/hpdt complexes

The uptake and release of CO₂ by the tetranuclear complexes $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{H}_2\text{O})_4]^-$ and $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]^-$ was observed in

aqueous solutions (summarized in Figure 5.9).¹⁹⁰ To investigate this behaviour we dissolved **3** at basic pH values in deionised H₂O. Upon acidification the gas chromatography mass spectrometry headspace analyses, which were performed after 2 and 24 hours, clearly identify the release of CO₂. Figure 5.9B illustrates the release of CO₂ that is identified through the dramatic increase in the intensity of the peak at 43.99 m/z. CO₂ absorption subsequently occurs upon addition of ethylenediamine. This result is shown in Figure 5.9C where the intensity of the CO₂ peak at 43.99 m/z dramatically decreases. Further acidification leads to the re-release of CO₂ that is characterised by an increase in intensity at 43.99 m/z in the recorded spectrum. All solids of the carbamate compound **3** release CO₂ upon treatment with diluted aqueous sulphuric acid. GC-MS head space analysis of the headspace when **3** was dissolved in deionised water, pH 7.0, and aqueous H₂SO₄ solutions ranging in concentration from 0.47 mM, pH 5.5, and 0.26 mM, pH 2.0, reveal an increase in the peak intensity at 43.99 m/z for the solutions that contained acidic media, Figure 5.10C-E. This further demonstrates the role acid plays in the CO₂ releasing process.

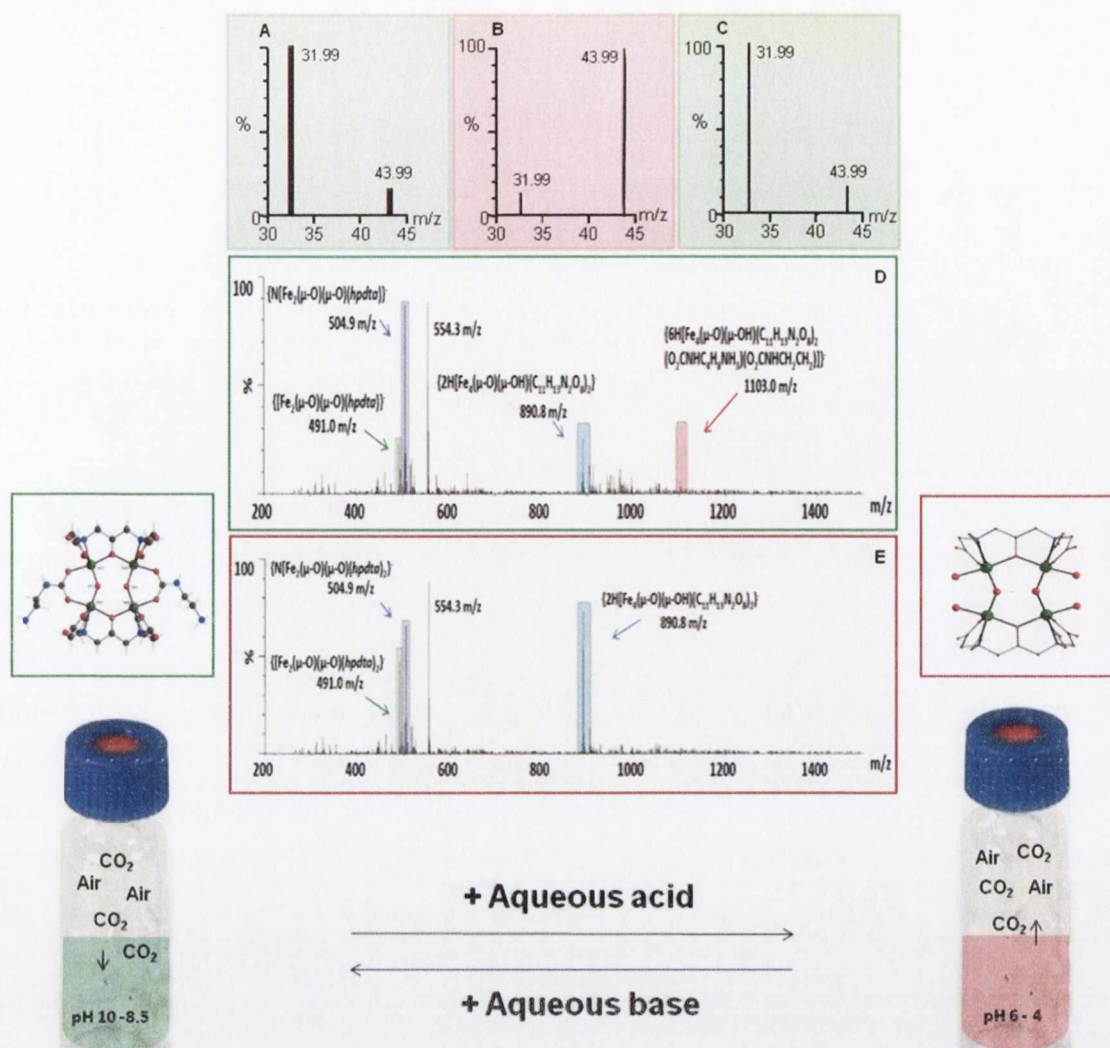


Figure 5.9: Treating 3, observed in the green box, with acid causes the release of CO₂ and the formation of 1, observed in the red box. Readjusting the pH, by addition of a base, results in the uptake of CO₂ and the reformation of 3. In this schematic, compound 3 takes the form of $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]^-$ when dissolved in an aqueous en solution at pH values greater than 8.5 (green solution), and compound 1 takes the form of $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4]^-$ when aqueous acid solution is added to reduce the pH of the system to values lower than 6 (red solution). A)-C) = GC-MS recorded for the headspace analysis following A) the dissolution of compound 3 in 1 ml 0.15 mM aqueous en solution. B) the addition of 0.06 μl of 33 % (v/v) aqueous H₂SO₄ solution to adjust the pH of the system to 4. C) the subsequent addition of 0.1 μl of a 75 % (v/v) aqueous en solution to adjust the pH of the system to 9.0. D) and E) display the ESI-MS recorded for the solutions at pH values of 9.0 and 4.0 respectively. The signal appearing at 1103.0 m/z in D characterises the presence of 3 in solution. The signals at 891.0 m/z, 504.9 m/z and 490.1 m/z in E characterise the presence of the tetranuclear core and confirms the presence of 1 in solution.

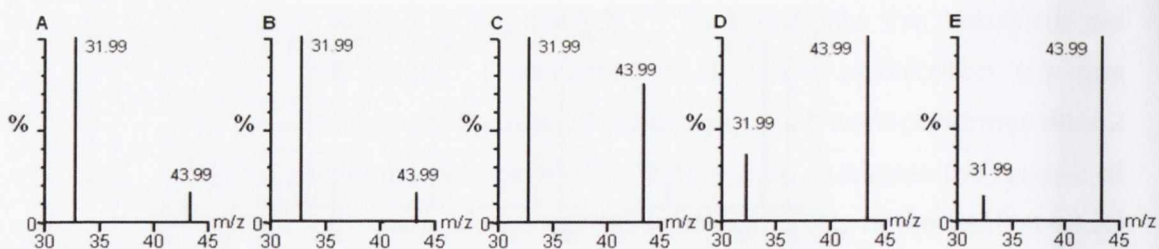


Figure 5.10: Gas chromatography Mass spectra (GC-MS) recorded for the headspace of GC-MS vial containing 50 mg of **3 dissolved in 1 ml of: A) 0.15 mM aqueous en solution, pH 9.5, B) deionised water, pH = 7, C) 0.47 mM aqueous H₂SO₄ solution, pH 5.5, D) 0.40 mM aqueous H₂SO₄ solution, pH 4 and E) 0.26 mM aqueous H₂SO₄ solution, pH 2.0.**

The experiments were repeated in the absence of metal compounds. The experiments at representative concentrations show no uptake and release of CO₂ and clearly underline the role of the metal complexes for the fixation of CO₂, Figure 5.11C-D. We confirmed that acidification of a solution of the tetrahedral complex **2**, which contains no receptor sites and does not fix carbon dioxide, did not result in increased concentrations of CO₂ in the headspace of the mass spectrometry vial, Figure 5.11E. The experiment was also repeated using varying concentrations of **3**. In this experiment the intensity of the CO₂ peak was observed to increase in response to the increasing concentrations of **3** (Figure 5.12). The correlation between the **3**'s initial concentration in solution and the release of CO₂ post acidification, further emphasise the importance of **3** in this process. Similar analyses of aqueous diamine solutions containing compounds **20-23** confirm their reversible CO₂ capture and release capabilities. Figure 5.13 illustrates the release of CO₂ from the solutions containing **19**, **20** and **22** post acidification using 0.06 µl of a 33 % (v/v) aqueous H₂SO₄ solution, pH 9.5 to 4.0.

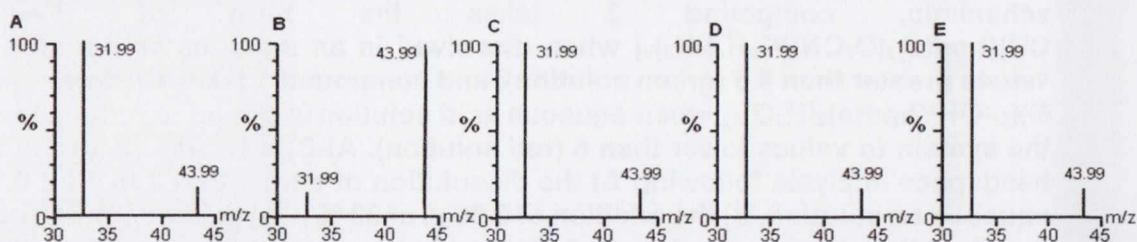


Figure 5.11: GC-MS spectra showing the O₂ : CO₂ ratio (31.99 m/z : 43.99 m/z) recorded for: A) 5 µl of a conventional air sample, B) 5 µl of a pure CO₂ standard, headspace analyses of GC-MS vial following the addition of 0.06 µl of a 33 % (v/v) aqueous H₂SO₄ solution to a system containing 1 ml of 0.15 mM aqueous en solution (C), 1 ml of deionised water (D) and **2 dissolved in 1 ml of 0.15 mM aqueous en solution (E).**

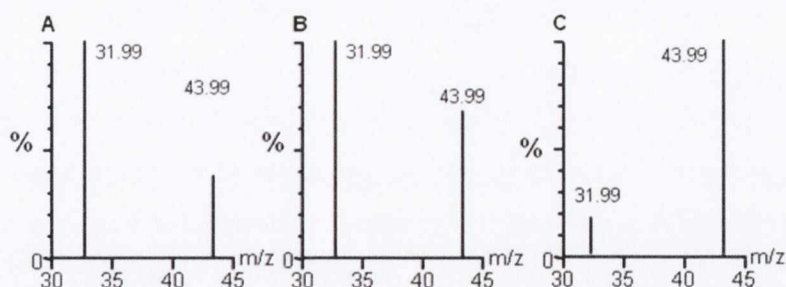


Figure 5.12: GC-MS spectra recorded for the headspace of GC-MS vial following the addition of 0.06 μl of a 33 % (v/v) aqueous H_2SO_4 solution to a system containing x mg of **3** dissolved in 1 ml of 0.15 mM aqueous en solution. A) x = 10 mg, B) x = 20 mg, C) x = 50 mg.

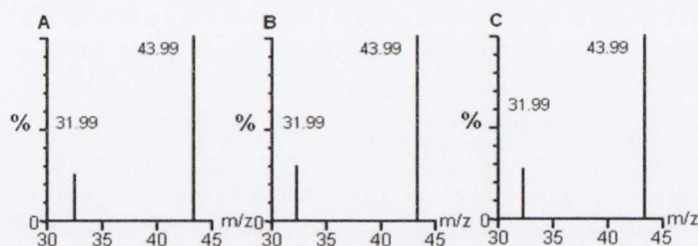


Figure 5.13: GC-MS spectra recorded for the headspace of GC-MS vial following the addition of 0.06 μl of a 33 % (v/v) aqueous H_2SO_4 solution to a system containing 50 mg of: A) **19** dissolved in 1 ml aqueous sodium hydroxide, B) **20** dissolved in 1 ml of an aqueous 0.14 mM diaminobutane solution, C) **22** dissolved in 1 ml 0.1 mM aqueous diaminoheptane solution.

These results prompted us to investigate the timescale for reabsorption of CO_2 using 25 mM solutions of **3** dissolved in 0.15 mM aqueous en solution. The experiments were performed in a gas tight round bottom flask that was sealed with a septum and a layer of parafilm and attached to a retort stand. The headspace samples were obtained by insertion of a gas tight glass syringe through the septum. The sample was relieved of CO_2 through addition of 33% (v/v) aqueous H_2SO_4 acid reducing the pH to 4.0. Following the removal of CO_2 , the system was purged with nitrogen and sealed to prevent contamination with air. An aqueous en solution was added to the system via the septum in order to readjust the pH of the solution to ca. 8.5. 11 cm^3 CO_2 was subsequently added to the system using a gas tight syringe. The GC-MS spectrum of the headspace containing the CO_2 was recorded at ten-minute intervals. The relative intensities of the nitrogen peak at 28.00 m/z and the carbon dioxide peak at 43.99 m/z were used to evaluate any changes in CO_2 concentration in the headspace arising from its absorption into the system. The spectra reveal a gradual absorption of CO_2 with none detectable in the headspace within sixty minutes of its insertion, Figure 5.14. A change in colour of the solution, from ruby-red to green-brown, was initially observed at the interfacial

boundaries within two minutes of introducing CO₂ to the system and within 60 minute the colour of the solution was completely changed to a brown-green colour. An ESI-MS⁺ analysis 24 hours after the observation confirms the reformation of **3** in solution. The experiments were ran in triplicate and ESI-MS⁺ analysis of the solution upon acidification confirmed the presence of **1** and also confirmed the absence of the CO₂ trapping compound **3** from the solutions until the CO₂ was added to the system. The experiment was repeated in the absence of **3** with no observable CO₂ absorption detected.

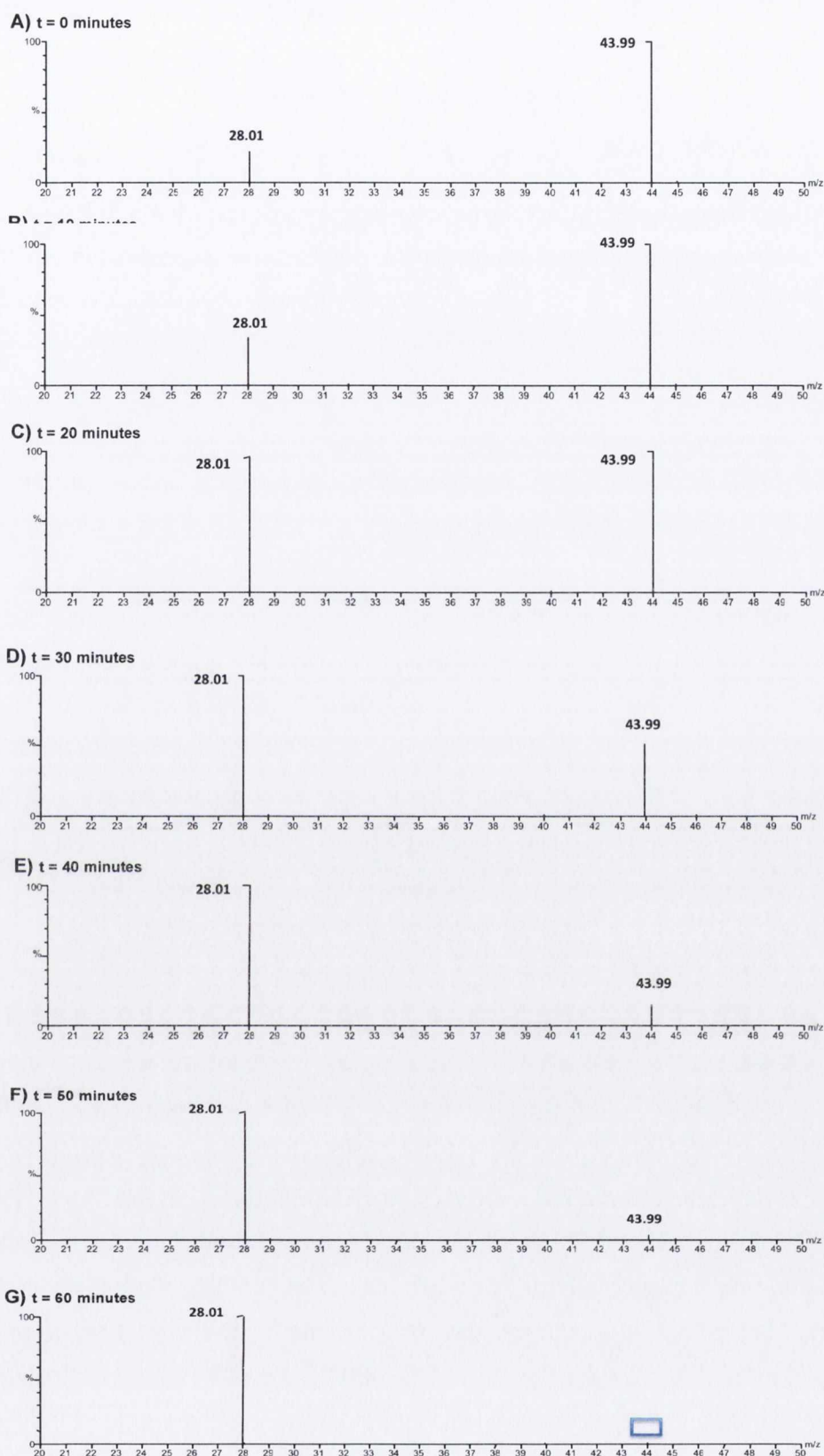


Figure 5.14: GC-MS spectra comparing the relative $\text{N}_2 : \text{CO}_2$ (28.01 m/z : 43.99 m/z) from headspace of 25mM solution of 3 dissolved in 0.15mM aqueous en solution, acidified using 0.12 μl of a 33 % (v/v) aqueous H_2SO_4 solution, to pH 4.0, and the addition of 0.4 μl aqueous en solution to readjust the pH of the system to 8.5.

System analysed under nitrogen post addition of 11 cm³ CO₂ gas. t= time in minutes after the addition of CO₂.

5.4 Electrochemical profiling of 1-3 and 21-25

In these studies cyclic voltammetry (CV) was employed to evaluate the redox activity and establish the formal redox potentials ($E_{1/2}$) of compounds **1-3** and **20-23**. CV also provides information on the stability of the reactive species in the system, the reversibility of the electrochemical processes and the number of electrons involved in the redox process. The experimental apparatus comprised a glassy carbon working electrode, a silver-silver chloride (Ag/AgCl) reference electrode and a platinum wire counter electrode. The working electrode was polished using aqueous pastes of 1.0 micron, 0.3 micron and 0.05 micron micropolish powders. The compounds were prepared in 2 mM concentrations using buffered solutions. 1 ml aliquotes of the solutions were sonicated for ten minutes and degassed using nitrogen prior to analysis. The investigations were undertaken at pH values of 4.5, 7.0 and 8.5. The buffered solutions consisted of 0.1 M Na₂SO₄ and 20 mM CH₃COOH for pH 4.5, 0.1M Na₂SO₄ and 20 mM NaH₂PO₄ for pH 7.0 and the pH 8.5 buffer contained 0.5 M NH₂PO₄ and 0.5 M Na₃PO₄. The compounds' stability in solution was evaluated by repeating the measurements three days after the initial experiment. In each instance the CVs were identical to those recorded of the fresh samples. The redox activities were further investigated using aqueous 0.8 mM H₂SO₄, pH 4.5, deionised water, pH 7.0, and aqueous 1.3 mM NaOH, pH 8.5. The compounds displayed indistinguishably weak quasi-reversible redox coupling.

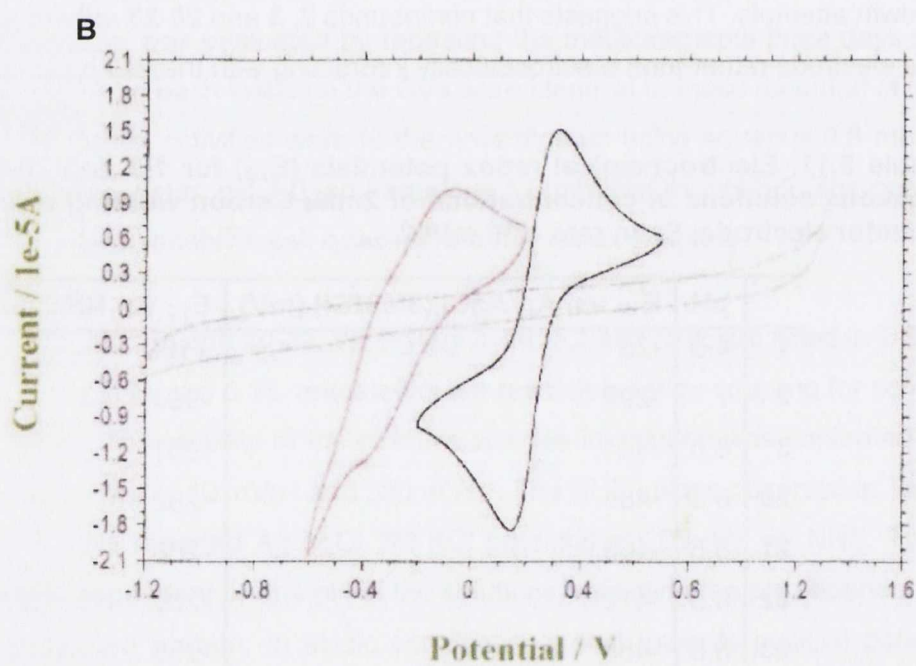
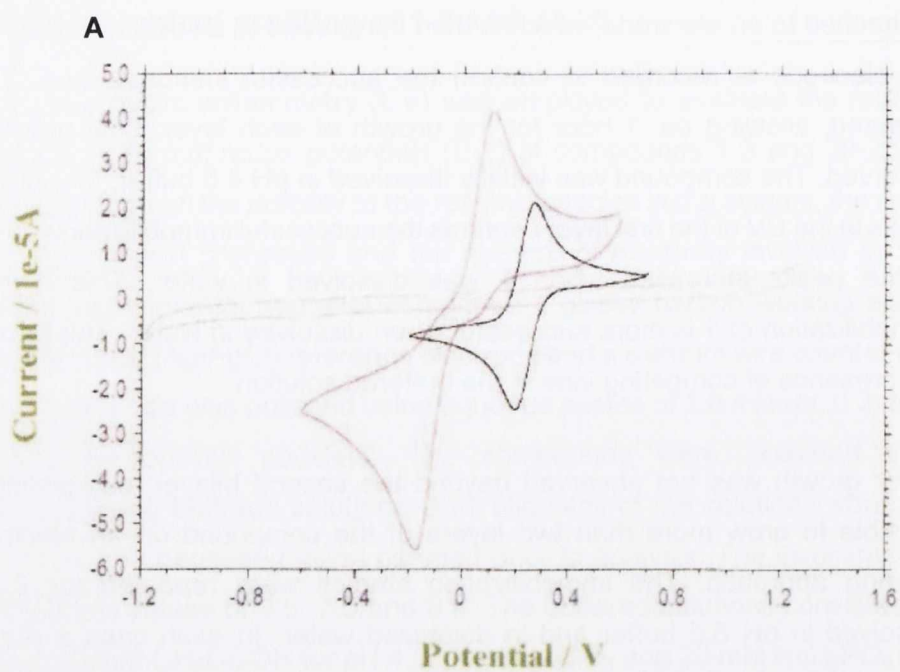
The $E_{1/2}$ values for **1-3** and **20-23**, vs. Ag/AgCl 3M KCl and NHE are listed in Table 5.11. The CV's, seen in Figure 5.15, revealed quasi-reversible redox coupling for compounds **1**, **3** and **20-23**. The stability of the reactive species in solution was confirmed through alternate scan rates of 10 mVs⁻¹ and 350 mVs⁻¹. The NHE values observed in Table 5.11 are based on the reported Ag/AgCl 3M KCl potential of 203 mV vs. NHE. The redox potentials are dependent on the pH of the solutions, reflecting the pH dependent nature of the investigated system. In acidic conditions, a shift towards positive potentials is observed where reduction is less difficult due to the presence of protons. This is highlighted through the difference of ca. 400 mV between the $E_{1/2}$ calculated for **1** and **3**. The pH dependency is further substantiated through observation of the $E_{1/2}$ values for **3** and **21-23**, each displaying comparable values when recorded at pH 8.5. The results from bulk electrochemical analysis were inconclusive.

The immobilization of **1** onto an electrode was also investigated. The polymer PEI was employed as an immobilizing base. In this technique a positively charged base polymer is attached to an electrode, which is then introduced to a solution containing **1**. A CV of the electrode is recorded to confirm the successful immobilization. The process is repeated, allowing ca. 1 hour for the growth of each layer, until growth is no longer observed. The compound was initially dissolved in pH 4.5 buffer. The presence of weak peaks in the CV of the first layer confirms the successful immobilization of **1**. The intensity of the peaks increased when **1** was dissolved in water. This revealed that the immobilization of **1** is more successful when dissolved in water. This is probably due to the presence of competing ions in the buffered solution.

Layer growth was not observed beyond the second bilayer, suggesting that it is not possible to grow more than two layers of the compound on an electrode using this layering approach. The immobilization studies were repeated for **2**, **3** and **20-23** dissolved in pH 8.5 buffer and in deionized water. In each case a reduction peak is observed for the first bilayer however the peak intensities decrease for all subsequent growth attempts. This suggests that compounds **2**, **3** and **20-23** adhere to the surface of the electrode rather than electrostatically interacting with the PEI base layer.

Table 5.11: Electrochemical redox potentials ($E_{1/2}$) for 1-3 and 20-23 in buffered aqueous solutions at concentrations of 2mM. Carbon working electrode, Pt wire counter electrode, Scan rate = 10 mVs⁻¹.

	pH	$E_{1/2}$ vs. Ag/AgCl (3M KCl) (mV)	$E_{1/2}$ vs. NHE (mV)
1	4.5	-23	+180
2	7	-299	-96
3	8.5	-464	-261
20	8.5	-485	-282
21	8.5	-469	-266
22	8.5	-472	-269
23	8.5	-458	-255



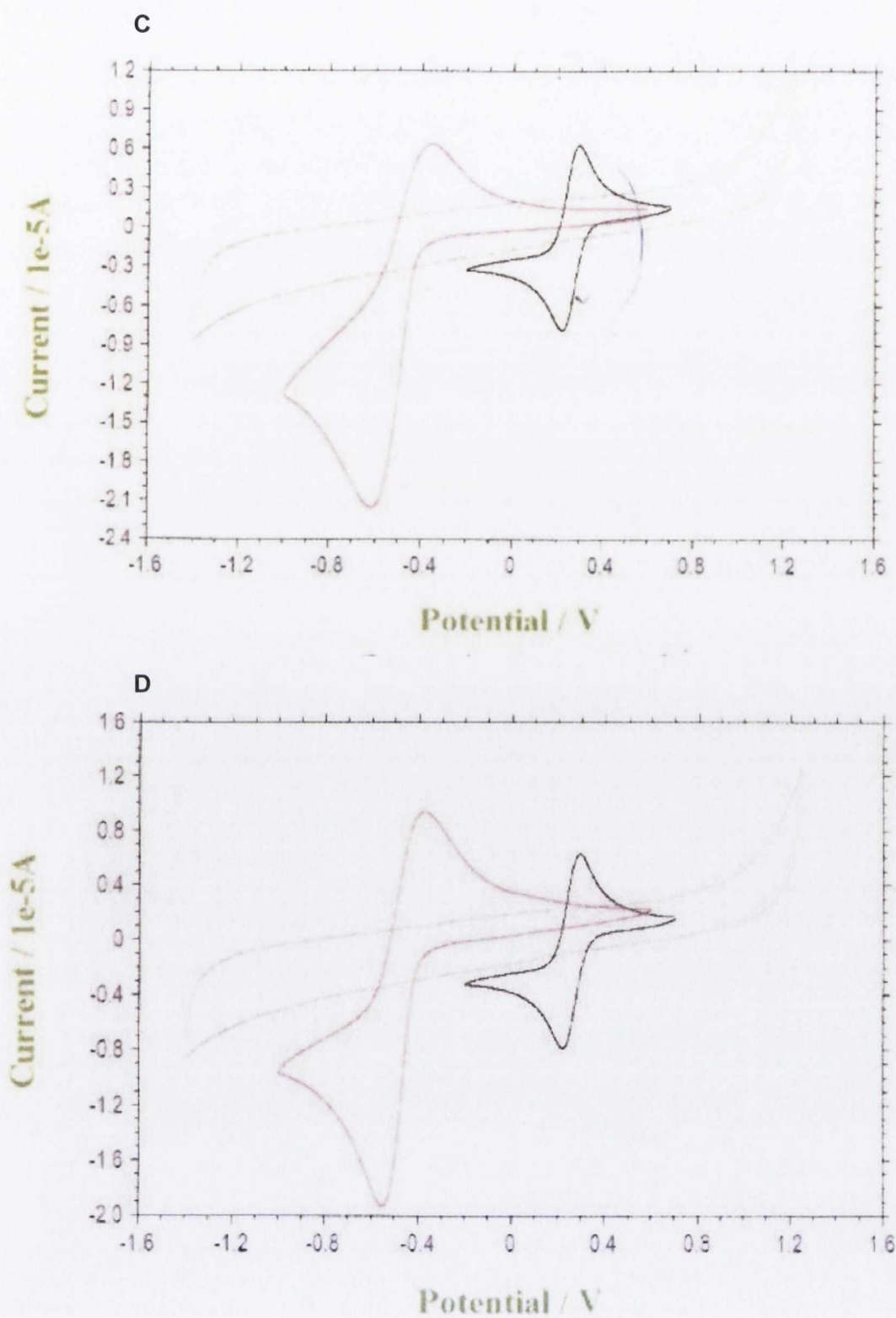


Figure 5.15: CV graphs for buffered 2 mM solutions of A) 1 at pH 4.5 B) 2 at pH 7 C) 3 at pH 8.5 and D) 20 at pH 8.5. CV's compared with a standard 2 mM ferrocyanide recorded under each pH condition. Compounds: red trace, standard: black trace). Carbon working electrode, Pt wire counter electrode, Scan rate = 100 mVs^{-1} .

5.5 Photophysical properties of 1-3 and 20-23 in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$

As mentioned in the introduction, the tetranuclear carbamate and carbonate complexes **3** and **20-23**, which result from the fixation of atmospheric CO_2 , have the potential to act as catalysts in the multi-electron photoreduction of CO_2 .^{123-124, 127} In these investigations the quenching characteristics of **3** and **20-23** were examined using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photosensitiser. The interactions between the excited $[\text{Ru}(\text{bpy})_3]^{2+}$ molecules and these tetranuclear complexes are of particular interest as the efficiency of the electron transfer between an excited photosensitiser and the catalyst is an important factor in the multi-electron photoreduction of CO_2 . The anticipated multi-electron transfer process, using the carbamate complex $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]^-$ in **3** as an example of a transition metal catalyst and $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photosensitiser, can be seen in Figure 5.16.

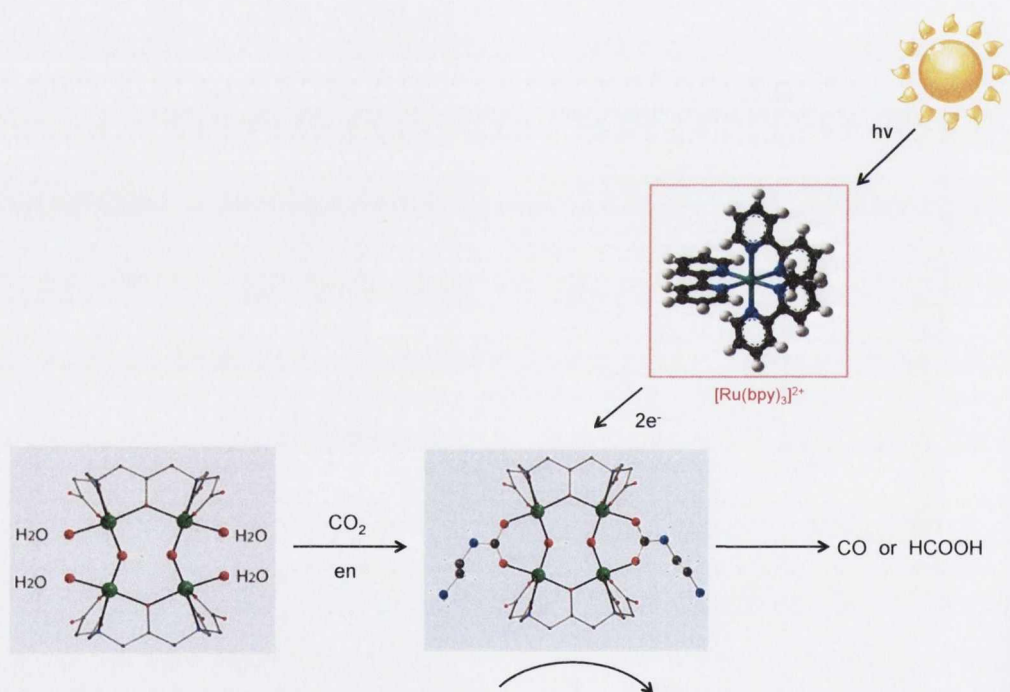


Figure 5.16: The anticipated multi-electron transfer process involved in the photoreduction of CO_2 . The $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitiser, seen in the orange box, is excited by UV light and transfers two electrons to the carbamate complex $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]^-$ in **3**, seen in blue box. **3** uses the $2e^-$ to reduce CO_2 to CO and HCOOH . D = sacrificial donor. en = ethylenediamine. Colour Code: C black, Fe green, N blue, O red.

Initially the emission fluorescence spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ in aqueous solutions were investigated in the presence of variable concentrations of **3**. The compound was prepared according to the literature methods and the crystals were dissolved in pH adjusted deionised water and pure deionised water, respectively.¹²³ The pH of the $[\text{Ru}(\text{bpy})_3]^{2+}$ solutions containing **3** was maintained at 8.5 using aqueous 5×10^{-5} M en solutions. The experiments were evaluated according to the Stern-Volmer approach (Scheme 5.8). An example of fluorescence emission spectra and a Stern-Volmer plot derived from these experiments can be seen in Figure 5.17 and Figure 5.18. In these examples **3** was used as the quencher. A plot of the relative luminescence intensities, against the quencher concentrations resulted in Ksv (Stern-Volmer / equilibrium constant) values of 6358 mol^{-1} and 3698 mol^{-1} for the compounds dissolved in aqueous 5×10^{-5} M en solutions, pH 8.5, and deionised water respectively (blue lines in Figure 5.18).

A single mode of quenching in a fluorescence system is indicated by a Stern-Volmer plot that yields a straight line. The Stern-Volmer plots for the fluorescence quenching in the examined systems displays an upward curvature towards the Y axis that is most prominent in the pH adjusted solutions, (Figure 5.18). This deviation from the straight line indicates that both static and dynamic quenching modes are occurring simultaneously within the system. The former arising from direct interactions between $[\text{Ru}(\text{bpy})_3]^{2+}$ and the $[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]^-$ complex in **3**.

In order to confirm that static and dynamic quenching modes occur simultaneously, within the systems discussed above, it was necessary to perform real time fluorescence lifetime experiments and evaluate them according to the Stern-Volmer approach. Using this approach dynamic quenching is characterised by lifetime intensities that are dependent on the quencher concentration. Static quenching is characterised by lifetime intensities that are independent of the quencher concentrations and yield a straight line for the plot of relative intensities vs concentration. The slopes of the Stern-Volmer plots for **3** have a slight incline with Ksv values of 1001 mol^{-1} and 983 mol^{-1} (green plots in Figure 5.18), which suggests that the lifetime intensities are not entirely independent of the complexes concentration. This observation is characteristic of systems where static and dynamic quenching modes are occurring simultaneously.^{191,192} Considering the Stern-Volmer plot of the lifetime intensities are unaffected by static quenching, one can use the Ksv values to evaluate the bimolecular quenching rate constant (Kq) for the dynamic quenching mode in the systems. According to the Stern-Volmer equation, Scheme 5.8, dividing the Ksv values of 1001 mol^{-1} and 983 mol^{-1} by 3.75 ns, the

reciprocal lifetime (τ_0) for $[\text{Ru}(\text{bpy})_3]^{2+}$, results in bimolecular quenching rate constants of $2.67 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $2.62 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.¹⁹¹

$$\frac{I_0}{I} = 1 + K_Q \tau_0 [Q] = 1 + K_{sv} [Q]$$

Scheme 5.8: Stern-Volmer equation

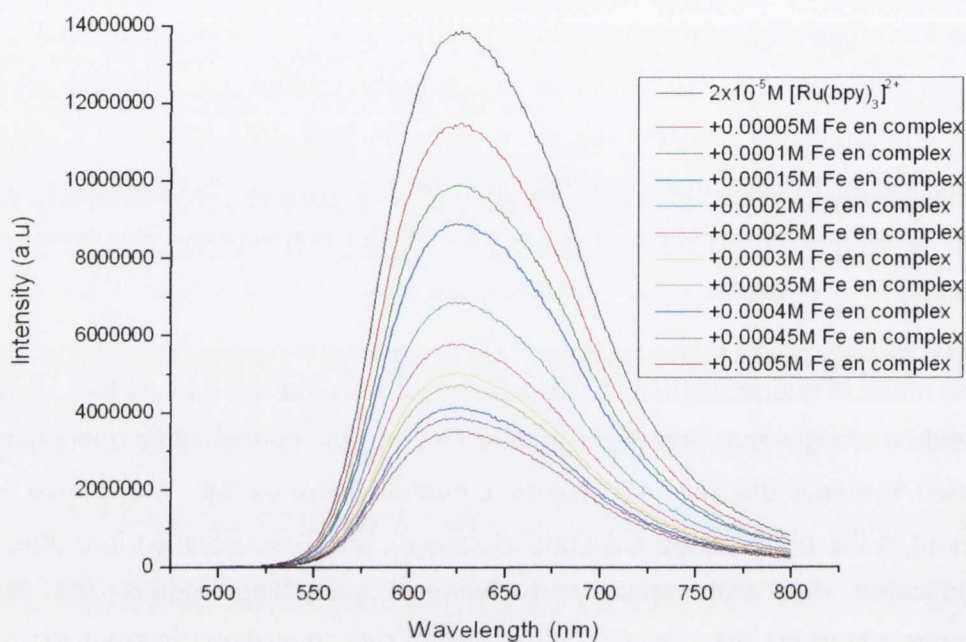


Figure 5.17: The fluorescence emission spectra recorded for $2 \times 10^{-5} \text{ M } [\text{Ru}(\text{bpy})_3]^{2+}$ solutions that contain varied concentrations of 3 dissolved in aqueous $5 \times 10^{-5} \text{ M en}$ solution.

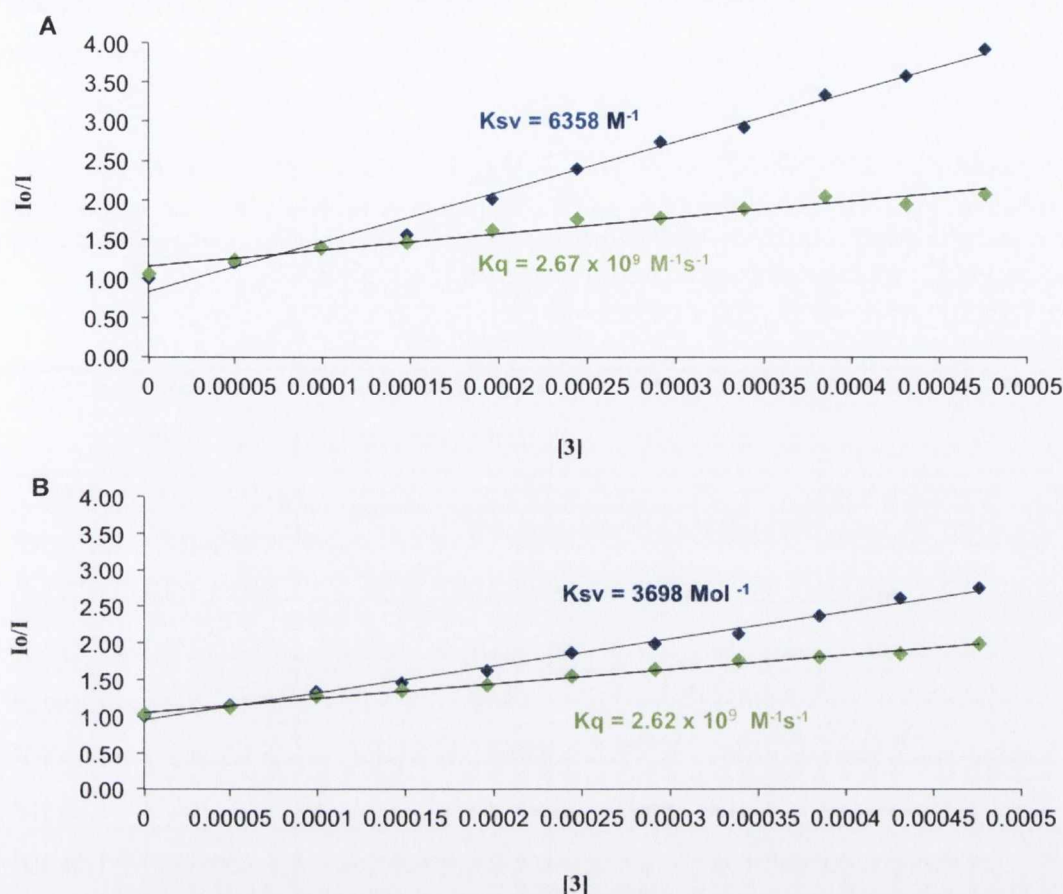


Figure 5.18: The fluorescence (blue markers) and lifetime (green markers) Stern-Volmer plots for $[Ru(bpy)_3]^{2+}$ solutions which contain increasing concentrations of **A**) 3 dissolved in an aqueous 5×10^{-5} M ethylenediamine solution and **B**) 3 dissolved in deionised water.

Stern-Volmer analyses were repeated for systems which contained compounds **20-23** at $\text{pH} = 8.5$ and dissolved in deionised water. The results from these experiments are summarised in Table 5.12. In each case the bimolecular quenching rate constants (K_q) are similar for **20-23** dissolved at $\text{pH} 8.5$ and in pure deionised water, respectively. Whereas the equilibrium constants (K_{sv}) are observably higher when the compounds are dissolved at $\text{pH} 8.5$. This suggests that the ionic strength of the solution affects the static quenching mode of the system whereas under similar conditions the dynamic quenching modes remain constant. Comparison of the K_q values for systems containing **3** and **20-23** dissolved in deionised water suggest that the hexamethylenediamine complex in **22** has the greatest electron scavenging capacity with a K_q value of $3.05 \times 10^9 \pm 2.4 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$. **23** has the lowest quenching capabilities under the explored experimental conditions, $K_q = 1.39 \times 10^9 \pm 1.1 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$. It is worth noting that these values are considerably lower than those of $5.02 \times 10^9 \pm 4 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ and $4.75 \times 10^9 \pm 3.5 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ for the Fe^{III} salts $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. However, since there is no evidence of static quenching in the latter system one could

suggest that complexation of the Fe^{III} ions by *hpdta* in the form of compounds **3** and **20-23**, introduces static quenching into the system at a detriment to their dynamic quenching capabilities.

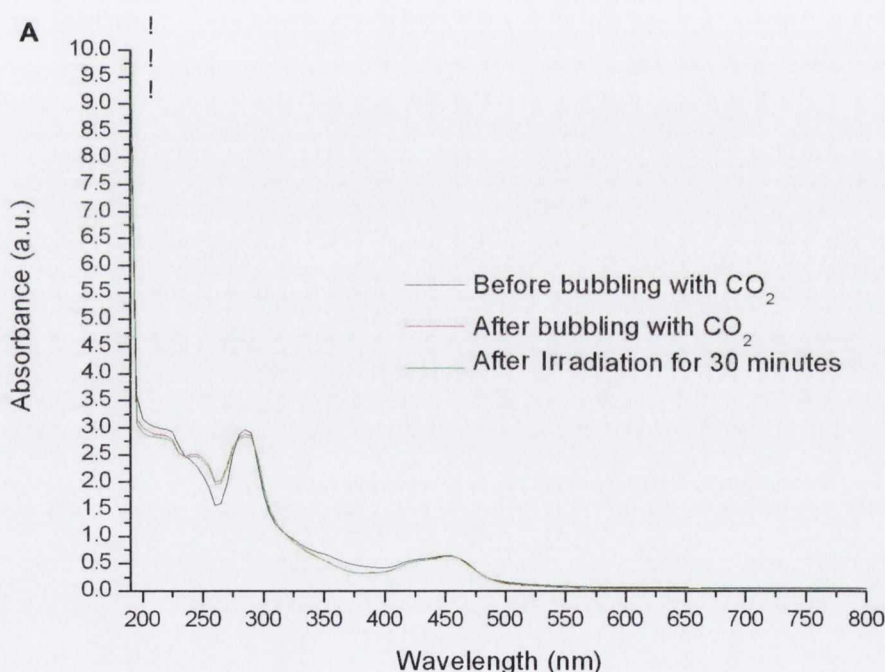
Table 5.12: The equilibrium constants (K_{sv}) and bimolecular quenching rate constants (K_q) for [Ru(bpy)₃]²⁺ solutions that contain the complexes **3 and **20-23** recorded under alkaline and neutral conditions. *pH 8.5**

	K _{sv} equilibrium constant (M ⁻¹)	K _q rate constant (M ⁻¹ s ⁻¹)
Fe(NO ₃) ₃ .9H ₂ O	x	5.02 x10 ⁹ +/- 4x10 ⁸
FeCl ₃ .6H ₂ O	x	4.75 x10 ⁹ +/- 3.5x10 ⁸
3 aq 5x10 ⁻⁵ M en solution*	6358 +/- 508	2.67 x10 ⁹ +/- 2.3x10 ⁸
3 de-ionised water	3698 +/- 295.84	2.62 x10 ⁹ +/- 2.1x10 ⁸
20 aq 3.4x10 ⁻⁵ M DAB solution*	5229 +/- 418.32	2.21 x10 ⁹ +/- 1.6x10 ⁸
20 deionised water	3305 +/- 264.4	2.18 x10 ⁹ +/- 1.7x10 ⁸
21 aq 2.0x10 ⁻⁵ M hyd solution*	6026 +/- 482.08	1.98 x10 ⁹ +/- 1.5x10 ⁸
21 de-ionised water	3674 +/- 293.92	1.93 x10 ⁹ +/- 1.5x10 ⁸
22 aq 2.3x10 ⁻⁵ M hmd solution*	6483 +/- 518.64	2.97 x10 ⁹ +/- 2.4x10 ⁸
22 de-ionised water	4637 +/- 370.96	3.05 x10 ⁹ +/- 2.4x10 ⁸
23 aq 5.5x10 ⁻⁵ M aep solution*	5792 +/- 463.36	1.56 x10 ⁹ +/- 1.3x10 ⁸
23 de-ionised water	3146 +/- 251.68	1.39 x10 ⁹ +/- 1.1x10 ⁸

5.6 Potential applications of tetranuclear Fe^{III} *hpdta* compounds as catalysts in the photochemical reduction of CO₂

The potential applications of tetranuclear Fe^{III} *hpdta* compounds as catalysts in the photochemical reduction of carbon dioxide was assessed using a 300 watt high pressure mercury lamp with an aqueous 0.1 M NaNO₂ solution chemical filter ($\lambda > 400$ nm) and performed in an airtight 5mm quartz cuvette. The effectiveness of the setup was demonstrated using a modified version of the methyl viologen mediated electron relay experiment reported by Kitamura and co-workers.¹⁹³ In this experiment an aqueous solution containing [Ru(bpy)₃]²⁺, methyl viologen (MV) and triethanolamine (TEOA) in a 5:1:60 molar ratio was purged with nitrogen and irradiated for 30 minutes using the above described system. The solution changed from colourless to an intense blue-purple colour. The intense colouration arises from the successful relay of electrons from the

excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ to the MV^{2+} resulting in the accumulation of $\text{MV}^{+\ddagger}$. Comparable results were observed in systems investigated by Kitamura in the absence of carbon dioxide. Reproduction of these results indicated that our system effectively facilitated the photochemical excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ and the subsequent transfer of electrons to a second species in solution. The subsequent addition of equimolar quantities of **20** (**20**: $\text{MV} = 1:1$) into the sealed system resulted in decolourisation of the solution. This indicated that the electrons were being successfully transferred from MV^+ to the Fe^{III} centres in **20**. In subsequent studies 87.5 μM solutions containing equimolar ratios of **20** and $[\text{Ru}(\text{bpy})_3]^{2+}$ dissolved in a 1.5 mM aqueous en solution, pH 8.5, were used in place of the $[\text{Ru}(\text{bpy})_3]^{2+}$ - MV -TEOA mixture. The photoreduction capabilities were investigated in the absence and presence of CO_2 and DMA. Initial UV-Vis spectroscopic analysis of the resultant solutions did not reveal any significant changes in the UV-Vis spectra of the solutions post irradiation for 30 minutes, as observed in Figure 5.19. The spectral changes observed in the absence and presence of DMA post treatment with CO_2 arise from the shift in pH that accompanies dissolution of CO_2 .



[‡] Intense colouration arises due to the reduction of MV^{2+} to MV^+ .

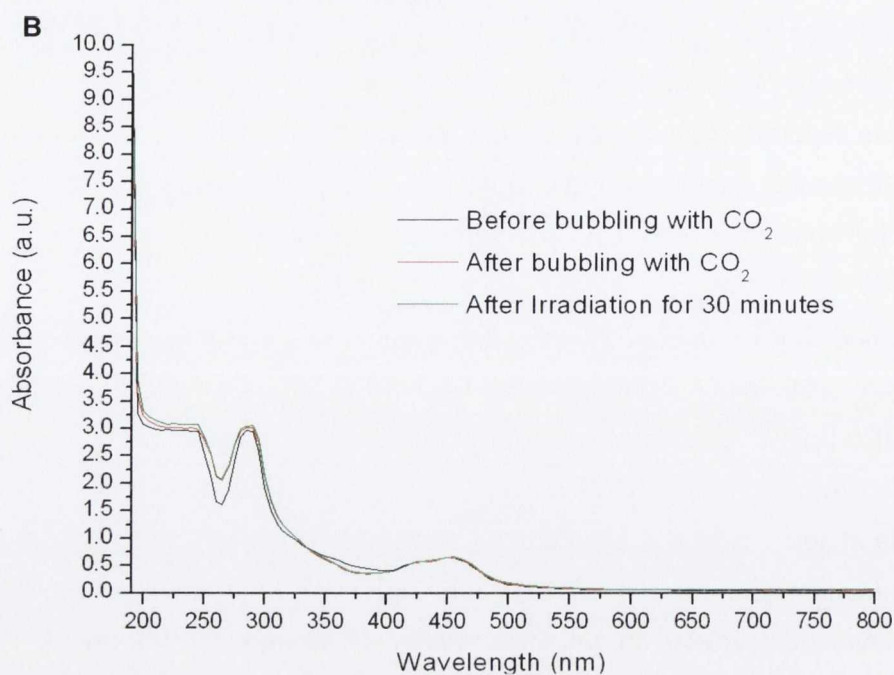


Figure 5.19: UV-Vis spectra of 87.5 μM solutions containing equimolar ratios of 20 : $[\text{Ru}(\text{bpy})_3]^{2+}$ dissolved in aqueous 1.5 mM en solutions, pH 8.5, recorded pre and post-treatment with CO₂ and post irradiation for 30 minutes. A) in the absence of DMA, B) in the presence of DMA. Recorded in a 5 mm quartz cell using a PerkinElmer Lambda 1050 UV/VIS/NIR spectrometer from 800 to 195 nm in 5nm intervals at a scan rate of 923.59 nm /min.

Chapter 6 The counterion mediated formation of supramolecular $\{Al_{15}\}$ coordination assemblies

6.1 Introduction

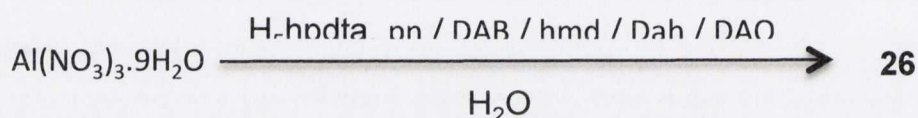
The investigated coordination assemblies are a small class of oxo- and hydroxo- bridged hybrid inorganic materials distinguished by their unprecedented zeolitic packing motifs. The previously reported $\{Al_{15}\}$ clusters in this series, $(pipH_2)(H_3O)[Al_{15}(\mu_3-O)_4(\mu_3-OH)_6(\mu-OH)_{14}(hpdt)_4]\cdot pipz\cdot 41H_2O$ (**25**) and $(EnH_2)(H_3O)[Al_{15}(\mu_3-O)_4(\mu_3-OH)_6(\mu-OH)_{14}(hpdt)_4]\cdot nH_2O$ (**26**), contained exclusively organic counter-ions.⁴ The purpose of these studies was to investigate the counter-ion mediated formation of the $\{Al_{15}\}$ supramolecular coordination assemblies. We were particularly interested in determining if a selection of organic and inorganic counterions could be employed to modify the assemblies packing behaviours and channel dimensions. It was also our aim to examine the compounds' porosities through a successive investigation of their N_2 BET surface areas and gas storage capacities.

6.2 Organic counter ion mediated formation of Al_{15} *hpdt* supramolecular complexes: The inherent stability of $(H_3O)_3[Al_{15}(\mu_3-O)_4(\mu_3-OH)_6(\mu-OH)_{14}(hpdt)_4]\cdot 23H_2O$ (**26**)

A range of organic diamine bases were employed to adjust the pH of the reaction mixtures that led to the formation of the $\{Al_{15}\}$ clusters. Propylenediamine (pn), diaminobutane (DAB), hexamethylenediamine (hmd), diaminoheptane (Dah) and diaminooctane (DAO) were used to investigate the counterion-mediated formation of the compounds under conditions that led to **24** and **25**. The resultant reaction attempts used slightly modified reaction conditions to those reported in the literature.⁴ Aqueous solutions of the polyaminocarboxylic acid ligand, *H₅hpdt* and $Al(NO_3)_3\cdot 9H_2O$ were reacted using a diamino base to adjust the pH to 8.5. White powder precipitated from the reaction mixtures containing hmd, Dah and Dao. Colourless, rectangular shaped, crystals of $(H_3O)_3[Al_{15}(\mu_3-O)_4(\mu_3-OH)_6(\mu-OH)_{14}(hpdt)_4]\cdot 23H_2O$ (**26**) suitable for single-crystal X-ray diffraction experiments were obtained from solutions containing pn and DAB four days post evaporation with dimethylacetamide.

The Al_{15} complex in **26** is shown in Figure 6.1. The $[Al_{15}(\mu_3-O)_4(\mu_3-OH)_6(\mu-OH)_{14}(hpdt)_4]^{3-}$ complex is comparable to that observed in **24** and **25**. The compound

crystallizes in the tetragonal crystal system in the space group $P4_2/ncm$. The packing structure, Figure 6.3a, displays two distinct channels running parallel to the crystallographic c -axis. The refined crystallographic data based on examined single-crystals of **26**, reveal the absence of ammonium counterions in the larger channels. The trivalent negative charge of the $[Al_{15}(\mu_3-O)_4(\mu_3-OH)_6(\mu-OH)_{14}(hpdta)_4]^{3-}$ complex is presumed to be balanced by three hydronium ions. Single-crystal X-ray diffraction experiments coupled with P-XRD experiments, FT-IR, TGA and chemical analyses reveal the influence organic bases exert on the quality and rate of formation of **26**, rather than influencing the nature of the complex. It was concluded that the hydronium-stabilised $[Al_{15}(\mu_3-O)_4(\mu_3-OH)_6(\mu-OH)_{14}(hpdta)_4]^{3-}$ complex forms the inherently stable compound under the applied conditions, Scheme 6.1.



Scheme 6.1: Preparation of 26

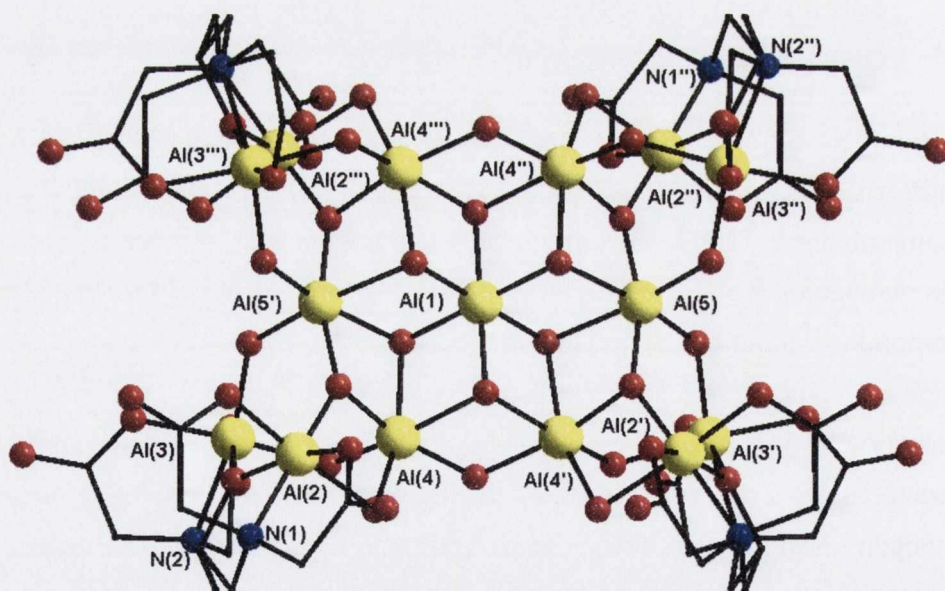


Figure 6.1: The structure of the Al_{15} complex in **26. The hydrogen atoms have been omitted for clarity. Colour Code: Al yellow, C black, N blue, O red.**

6.2.1 Structural characterisation of $(\text{H}_3\text{O})_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 23\text{H}_2\text{O}$ (**26**)

The overall structure consists of an $\{\text{Al}_7(\text{OH})_{12}\}$ core coordinated to four dinuclear units. The $\{\text{Al}_7(\text{OH})_{12}\}$ core can be described as a fragment of the brucite layer structure where the oxygen atoms are hexagonally close packed and six Al^{3+} ions are located in octahedral holes. It is comparable to the minerals barite and gibbsite except in this case the central octahedral site is occupied. The dinuclear units consist of two Al^{3+} ions coordinated by a *hpdta* ligand, three μ -bridging hydroxo ligands and one μ_3 -bridging oxo ligand in an octahedral coordination environment to form the $\{\text{Al}_{15}\}$ cluster illustrated in Figure 6.1. The dinuclear units contain one fully deprotonated organic ligand bound to two Al^{III} centres, Al(2) and Al(3), linked by a μ_2 -bridging alkoxo O atom of the organic ligand. These dinuclear subunits are linked to the $\{\text{Al}_7\}$ core *via* bridging oxo/hydroxo moieties (originating from sixteen deprotonated water molecules) to form the $\{\text{Al}_{15}\}$ complex.

The asymmetric unit contains five Al^{III} ions, Al(1)-Al(5), one fully deprotonated *hpdta* ligand, two μ_3 -bridging hydroxo moieties, O(2) and O(1), four μ -bridging hydroxo moieties, O(3), O(4), O(5) and O(10) and a μ_3 -bridging oxo moiety, O(6), located on the periphery of the $\{\text{Al}_7(\text{OH})_{12}\}^{9+}$ core. The unit also contains six solvent water molecules and a hydronium counter ion. The Al^{III} centres in **26** adopt octahedral coordination environments. The Al(2) and Al(3) ions constitute the dinuclear units which condense and encapsulate the $\{\text{Al}_7\}$ centre to give the $\{\text{Al}_{15}\}$ complex in **26**, Figure 6.1.⁴ The distance between the two Al^{III} centres, Al(2) and Al(3), is *ca.* 3.35 Å with each ion exhibiting comparable coordination environments. More specifically the two are coordinated by N-donor atoms, N(1) and N(2), $\text{O}_{\text{carboxylate}}$ atoms O(7), O(8), O(11) and O(12) and a μ -bridging alkoxo O-donor atom, O(9), of a *hpdta* ligand. The fifth coordination site of Al(2) is occupied by a μ -bridging hydroxo O-donor atom, O(4), and the equatorial plane, as shown in Figure 6.2, is completed by a μ_3 -bridging oxo moiety, O(6). The equatorial plane of Al(3) is completed by μ -bridging hydroxo atoms O(5) and O(10).

The remaining Al^{III} ions Al(1), Al(4) and Al(5) and symmetry generated Al(4'-4''') and Al(5') ions, are located within the central $\{\text{Al}_7(\text{OH})_{12}\}^{9+}$ core. Al(4) is linked to Al(3) via a μ -bridging hydroxo O-donor ligand, O(5) and is linked to Al(2) via the μ -bridging hydroxo ligand, O(4), and a μ_3 -bridging oxo moiety, O(6). The octahedral coordination environments are completed by μ_3 -bridging hydroxo O-donor ligands, O(2) and a symmetry generated O(1''') donor, and an additional μ -bridging hydroxo O-donor ligand,

O(3). The octahedral coordination environment for Al(1) is completed by hydroxo O-donor atoms, O(1) and O(2) and symmetry equivalents, O(1'), O(1''), O(1''') and O(2'). Al(5) is coordinated by O-donor atoms O(1) and symmetry generated O-donor atoms, O(1''), O(6'), O(6''), O(10') and O(10''). The typical distance between two Al^{III} centres bridged by μ_3 -O, μ_3 -OH and μ -OH ligands, e.g. Al(2)-Al(4), Al(4)-Al(1) and Al(3)-Al(4) is *ca.* 2.77 Å, 2.96 Å and 3.27 Å respectively. The average Al^{III}-O_{oxo} and Al^{III}-O_{hydroxo} bond lengths of *ca.* 1.75 Å and 1.87 Å are consistent with those reported for bridging oxo/hydroxo moieties.^{2, 4}

The distorted Al^{III} octahedral coordination environments are illustrated through bond angle examination. The most significant deviations for the ideal 90° angle can be seen for the bond angles O(2)-Al(4)-O(3), O(7)-Al(2)-O(6), O(9)-Al(3)-O(10) and O(10')-Al(5)-O(10'') with values of 75.38(1)°, 101.05(1)°, 102.94(1)° and 99.61(1)°, respectively. Further divergences include the bond angles N(1)-Al(2)-O(7), O(9)-Al(3)-N(2), O(1'')-Al(1)-O(1) and O(6')-Al(5)-O(10') with values of 81.31(1)°, 83.04(1)°, 86.20(1)° and 98.98(1)°, respectively. Minor deviations are observed for the bond angles O(9)-Al(2)-O(4), O(11)-Al(3)-O(9) and O(10')-Al(5)-O(6'') characterised by values of 91.40(1)°, 91.76(1)° and 91.30(1)°, respectively. Non-conformities to the linear modal include the corresponding bond angles O(9)-Al(3)-O(12), O(7)-Al(2)-O(9), O(1)-Al(5)-O(10') and O(8)-Al(2)-O(4) of 161.73(1)°, 164.51(1)°, 167.65(1)° and 175.64(1)°. Other selected bond lengths and angles involving the Al^{III} centres in **26** are summarised in Table 6.1 and Table 6.2.

Table 6.1: Selected bond distances for 26

Atom	Bond	Bond Distance (Å)
Al(1)	Al(1)-O(1)	1.855(7)
	Al(1)-O(1')	1.855(7)
	Al(1)-O(1'')	1.855(7)
	Al(1)-O(1''')	1.855(7)
	Al(1)-O(2)	1.908(12)
	Al(1)-O(2')	1.908(12)
Al(2)	Al(2)-O(6)	1.746(14)
	Al(2)-O(8)	1.885(9)
	Al(2)-O(9)	1.886(17)
	Al(2)-O(7)	1.931(5)
	Al(2)-O(4)	1.954(3)
	Al(2)-N(1)	2.021(23)
Al(3)	Al(3)-O(10)	1.841(32)
	Al(3)-O(5)	1.858(14)
	Al(3)-O(9)	1.893(9)
	Al(3)-O(11)	1.909(24)
	Al(3)-O(12)	1.931(10)
	Al(3)-N(2)	2.111(35)
Al(4)	Al(4)-O(6)	1.833(21)
	Al(4)-O(3)	1.85(4)
	Al(4)-O(4)	1.868(8)
	Al(4)-O(5)	1.875(11)
	Al(4)-O(1''')	2.003(7)
	Al(4)-O(2)	2.001(12)
Al(5)	Al(5)-O(6'')	1.795(27)
	Al(5)-O(6''')	1.795(27)
	Al(5)-O(10'')	1.855(15)
	Al(5)-O(10''')	1.855(15)
	Al(5)-O(1)	2.076(2)
	Al(5)-O(1'')	2.076(2)

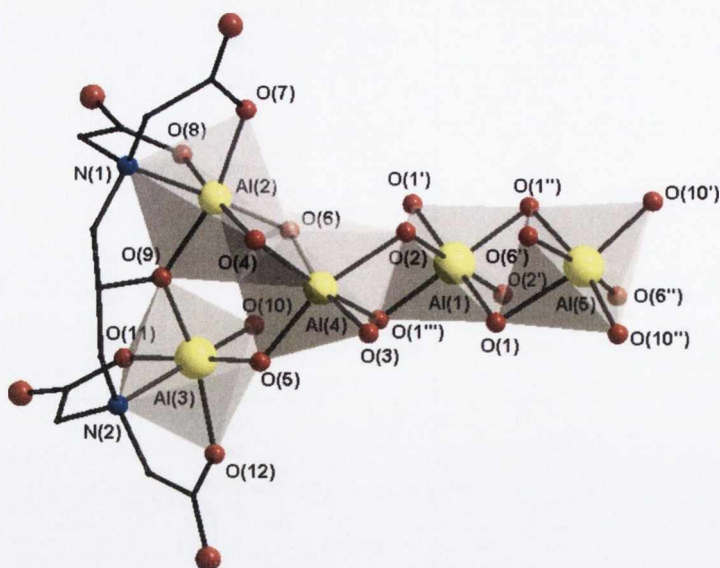


Figure 6.2: Polyhedral representations of the Al^{III} centres in 26. The hydrogen atoms have been omitted for clarity. Colour Code: Al yellow, C black, N blue, O red.

Table 6.2: Selected bond angles for compound 26.

	Bond Angle (°)		Bond Angle (°)
O(1)-Al(1)-O(1'')	86.20(1)	O(12)-Al(3)-O(11)	91.09(1)
O(1)-Al(1)-O(1''')	93.80(1)	O(12)-Al(3)-O(10)	95.20(1)
O(1)-Al(1)-O(1')	180.00(1)	O(12)-Al(3)-O(5)	88.32(1)
O(1)-Al(1)-O(2)	84.13(1)	O(10)-Al(3)-N(2)	167.92(1)
O(1)-Al(1)-O(2')	95.87(1)	O(10)-Al(3)-O(5)	96.81(1)
O(7)-Al(2)-O(4)	90.13(1)	O(10)-Al(3)-O(11)	87.83(1)
O(7)-Al(2)-O(8)	86.98(1)	O(6)-Al(4)-O(4)	81.66(1)
O(7)-Al(2)-N(1)	81.31(1)	O(6)-Al(4)-O(3)	166.75(2)
O(7)-Al(2)-O(9)	164.51(1)	O(6)-Al(4)-O(1''')	79.82(1)
O(9)-Al(2)-N(1)	83.20(1)	O(6)-Al(4)-O(2)	91.39(1)
O(9)-Al(2)-O(4)	91.40(1)	O(6)-Al(4)-O(5)	97.30(1)
O(9)-Al(2)-O(8)	92.25(1)	O(4)-Al(4)-O(1''')	161.47(1)
O(9)-Al(2)-O(6)	94.42(1)	O(4)-Al(4)-O(5)	94.22(1)
O(8)-Al(2)-O(4)	175.64(1)	O(4)-Al(4)-O(2)	102.72(1)
N(1)-Al(2)-O(6)	176.73(1)	O(4)-Al(4)-O(3)	101.63(1)
N(1)-Al(2)-O(8)	86.47(1)	O(2)-Al(4)-O(3)	75.38(1)
N(1)-Al(2)-O(4)	96.33(1)	O(2)-Al(4)-O(5)	161.93(1)
O(8)-Al(2)-O(6)	95.89(1)	O(10')-Al(5)-O(10'')	99.61(1)

O(6)-Al(2)-O(4)	81.46(1)	O(10'')-Al(5)-O(6'')	98.98(1)
O(6)-Al(2)-O(7)	101.05(1)	O(10'')-Al(5)-O(1)	92.59(1)
O(9)-Al(3)-O(12)	161.73(1)	O(10')-Al(5)-O(6'')	91.30(1)
O(9)-Al(3)-O(10)	102.94(1)	O(10'')-Al(5)-O(1'')	167.65(1)
O(9)-Al(3)-O(5)	87.39(1)	O(6')-Al(5)-O(1)	78.72(1)
O(9)-Al(3)-N(2)	83.04(1)	O(6')-Al(5)-O(6'')	164.08(1)
O(9)-Al(3)-O(11)	91.76(1)	O(1'')-Al(5)-O(6')	88.64(1)
O(12)-Al(3)-N(2)	79.55(1)	O(1'')-Al(5)-O(1)	75.28(1)

The packing structure observed for the $\{Al_{15}\}$ units in **26** replicate the zeolite assembly of **24** and **25**. They aggregate to form two distinct channels, with cross sectional diameters of 11 Å and 6 Å, that extend parallel to the crystallographic *c*-axis, Figure 6.3 and Figure 6.4.⁴ The larger pores contain exclusively solvent water molecules and are interlined with hydroxyl groups from the $\{Al_7(OH)_{12}\}^{9+}$ core, protruding non-coordinating oxygen atoms in addition to methylene groups located on neighbouring *hpdta* ligands. The smaller channels contain non-coordinating $O_{\text{carboxylate}}$ atoms of the *hpdta* ligands. The hydronium counter-ions appear to reside in the four corners of a distorted square of the $O_{\text{carboxylate}}$ atoms. This is in contrast to **24** and **25** where the hydronium counterion lies in the centre of the distorted square and is surrounded by a diammonium counterion. The hydronium counterions are presumably disordered over two locations, this is conceivable given the anticipation of prolific dynamic disorder arising from the H-bonds between the counterions and non-coordinated oxygen atoms and the solvent water molecules present in the smaller pores.

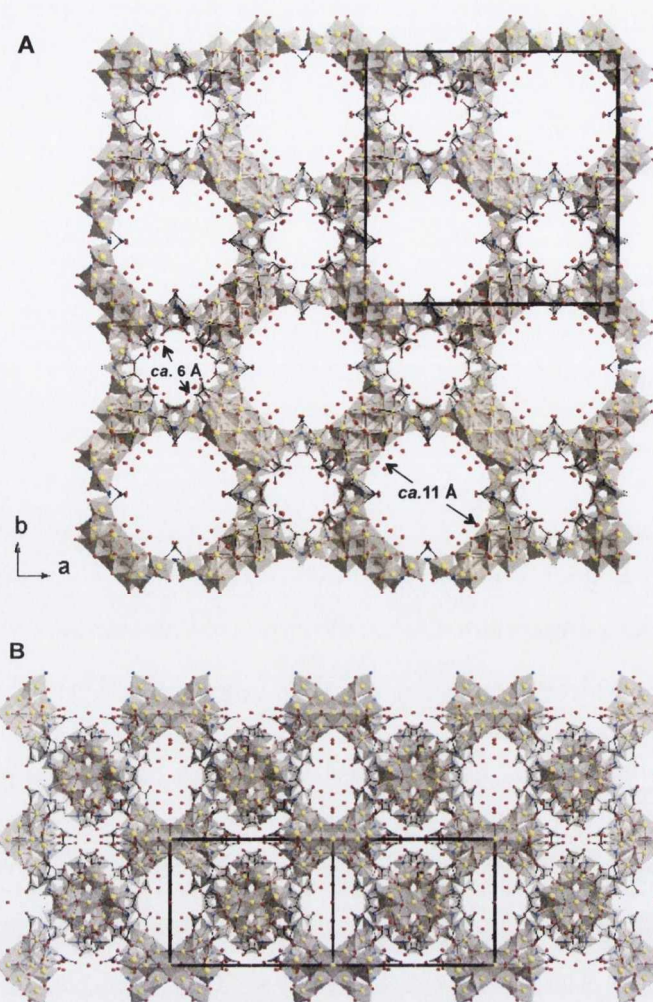


Figure 6.3: Polyhedral representations of Al^{III} centres in 26. A) Viewed along the crystallographic c -axis. B) Exemplifies a projection onto the (110) plane demonstrating the lateral accesses into the smaller channels. The hydrogen atoms have been omitted for clarity. Colour Code: Al yellow, C black, N blue, O red.

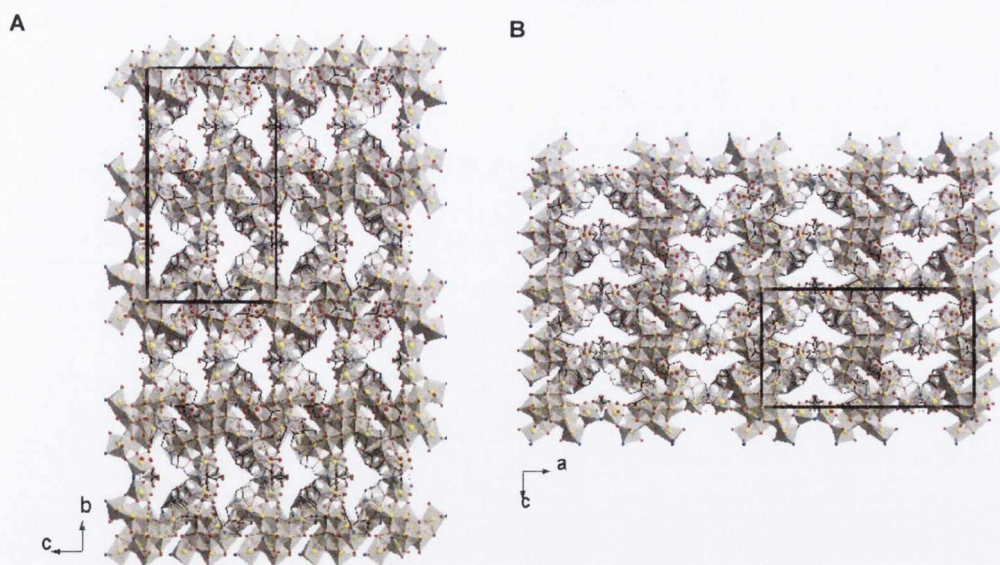


Figure 6.4: Polyhedral representations of the Al^{III} centres in the packing structure of **26**, illustrating the channels extension into the crystallographic c -axis. Viewed along the crystallographic A) a -axis and B) b -axis. The hydrogen atoms have been omitted for clarity. Colour Code: Al yellow, C black, N blue, O red.

The isolation of **26** is important as it demonstrates that hydronium ions can promote the assembly of the $[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4]^{3-}$ clusters. Furthermore it appears that it is not possible to incorporate larger amines, more specifically pn, DAB, hmd, Dah and DAO, into the zeolitic packing motif of **26** under the described experimental conditions.

Examination of the crystallographic data of examined single crystals of **26**, Table 6.3, reveals an R_1 value of 16 %. However, considering the structural similarities between **26**, **24** and **25** and the results from P-XRD analyses, the correctness of the crystallographic model is confirmed. Furthermore, upon application of the SQUEZE routine in the Platon programme to account for the disordered solvent water molecules, the R_1 value can be reduced to 6.8 %.

Table 6.3: Crystal data and structure refinement parameters for 26

Compound	26
Empirical formula	C ₄₄ H ₁₂₇ Al ₁₅ N ₈ O ₈₆
Formula weight	2549.19 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	<i>P</i> 4 ₂ / <i>ncm</i>
Unit cell dimensions	$a = 27.978(6) \text{ Å}$ $\alpha = 90^\circ$. $b = 27.978(6) \text{ Å}$ $\beta = 90^\circ$. $c = 15.522(3) \text{ Å}$ $\gamma = 90^\circ$.
Volume	12150(6) Å ³
Z	5
Density (calculated)	1.070 Mg/m ³
Absorption coefficient	0.189 mm ⁻¹
F(000)	3885
Crystal size	0.2 x 0.08 x 0.18 mm ³
Φ range for data collection	1.029 to 24.990°.
Index ranges	-33 ≤ <i>h</i> ≤ 30, -30 ≤ <i>k</i> ≤ 33, -18 ≤ <i>l</i> ≤ 15
Reflections collected	67152
Independent reflections	5527 [<i>R</i> (int) = 0.2407] on <i>F</i> ²
Completeness to $\theta = 25.08^\circ$	97.2 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	5527 / 0 / 351
Goodness-of-fit on <i>F</i> ²	1.036
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1613, <i>wR</i> 2 = 0.3137
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2108, <i>wR</i> 2 = 0.3305
Largest diff. peak and hole	1.754 and -0.640 e.Å ⁻³

6.2.2 Physicochemical characterisation of 26

FT-IR spectroscopy

The FT-IR spectrum of **26**, Figure 6.5, exhibits the characteristic vibrational bands that are expected for complexes that contain *hpdta* coordinated Al^{III} ions.³⁻⁴ The symmetric and asymmetric -OH stretching of moieties involved in H-bonds occur at *ca.* 3395 cm^{-1} . The unidentate bridging mode of the carboxylate oxygen atoms, O(7), O(8), O(11) and O(12), is characterised by the difference of *ca.* 245 cm^{-1} between the asymmetric carboxylate and symmetric carboxylate stretches, at *ca.* 1630 cm^{-1} and *ca.* 1390 cm^{-1} .¹⁶³ The FT-IR spectrum of **26** was employed as a reference spectrum to identify the precipitates of $\{\text{Al}_{15}\}$ compounds that form under various reaction conditions as microcrystalline products. FT-IR spectral analyses in combination with chemical analyses identified micro-crystalline samples as **26**.

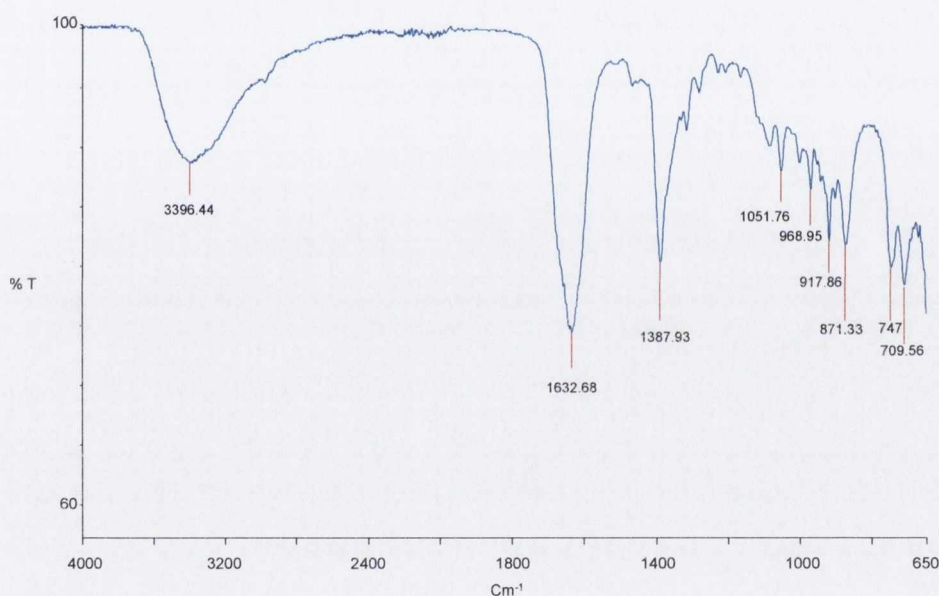


Figure 6.5: FT-IR spectrum of freshly ground microcrystals of **26** recorded using a diffuse reflectance accessory.

Table 6.4: The characteristic FT-IR vibrational bands, and corresponding assignments for 26. ^{136-138, 194}

Wavenumber (cm ⁻¹)	Assignment(s)
3390	O-H ν_s and ν_{as} stretches
1630	ν_{as} COO ⁻
1390	ν_s COO ⁻
915	Out of plane -OH stretch

Elemental Analysis

Elemental analysis was employed to further confirm the chemical formula of **26**, C₄₄H₁₂₇Al₁₅N₈O₈₆. The corresponding theoretical and experimental values, Table 3.27, infer the accuracy of the constitutional assignment and suggest the purity of the sample.

Table 6.5: Theoretical and experimental elemental analysis for 26. Theoretical based on C₄₄H₁₂₇Al₁₅N₈O₈₆.

Element	Theoretical composition (%)	Experimental composition (%)
C	20.73	20.53
Al	15.88	15.95
H	5.02	4.95
N	4.40	4.21

Thermogravimetric analysis

Thermogravimetric analysis was performed to determine the constitutional solvent molecules in **26** and to investigate its thermal stability of the compound. The analysis was carried out in the temperature range between 25 °C and 900 °C, in an air atmosphere. The heating rate was set to 5 °C/minute.

The TGA graph for **26**, Figure 6.6, reveals the loss of 23 water molecules and 3 hydronium ions in the temperature range 25 °C and 110 °C (experimental weight loss: 18.50 %, theoretical weight loss: 18.48 %). A further increase in temperature up to 415 °C gives rise to oxidative organic ligand decomposition with the formation of Al^{III} oxide material (experimental weight loss: 51.61 %, theoretical weight loss: 49.80 %). The final weight of 29.89 % is consistent with the formation of Al₂O₃ oxides (final experimental weight loss: 70.11 %, final theoretical weight loss: 70.00 %). The theoretical mass percentages of the proposed decomposition products were calculated as a percentage of the mass of (H₃O)₃[Al₁₅(μ_3 -O)₄(μ_3 -OH)₆(μ -OH)₁₄(hpdta)₄].23H₂O. These are reported in Table 6.6 and are in agreement with the experimentally observed values.

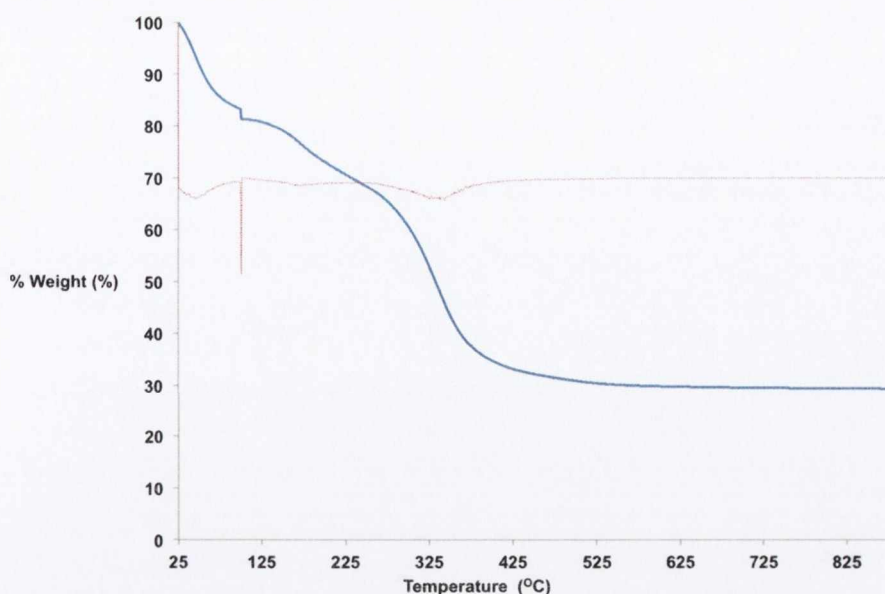


Figure 6.6: TGA curve for **26**. Recorded in an air atmosphere from 25 °C to 900 °C. Heating step was set to 5 °C/minute with an isothermal step at 110 °C for five minutes.

Table 6.6: Results for TGA analyses of **26**, recorded in an air atmosphere from 25 °C to 900 °C. Heating step was set to 5 °C/minute.

Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
$C_{44}H_{127}Al_{15}N_8O_{86}$	100	100	25 (Initial)
$C_{44}H_{72}Al_{15}N_8O_{60}$	81.52	81.50	25 - 110
$7.5 Al_2O_3$	30.00	29.89	110 - 900 (Final)

Powder X-ray Diffraction

Powder X-ray diffraction (P-XRD) experiments were employed to investigate the phase purities for crystalline samples of **26**. Pristine crystals were ground to a powder for the analysis. P-XRD patterns were also recorded for the previously reported compound **25**. Each sample crystalized in the tetragonal space group $P4_2/ncm$. The resultant patterns, seen in green, blue and black in Figure 3.9, match the simulated pattern, seen in red in Figure 3.9. The simulated pattern was generated using crystallographic information file (CIF) for **26**. The corresponding patterns suggest the phase purity of **26** and further establish the accuracy of the refined structural model as determined by the single-crystal X-ray diffraction experiments.

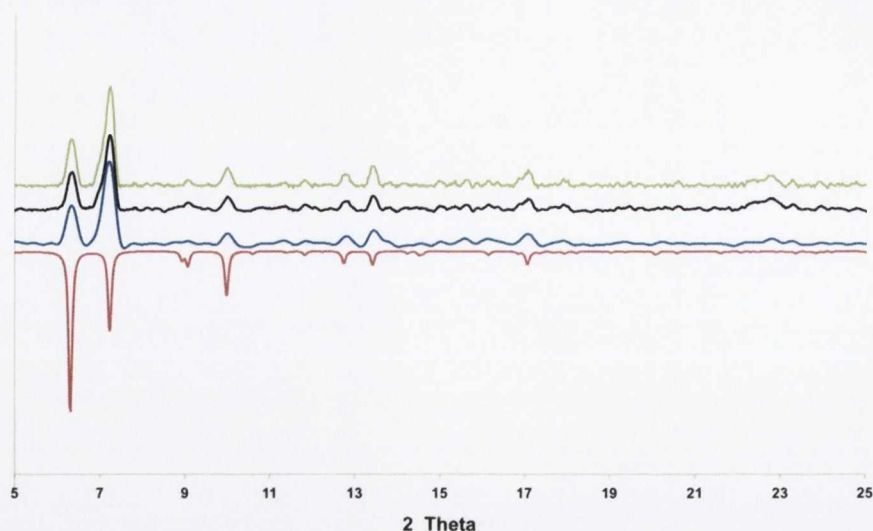


Figure 6.7: P-XRD pattern for crystals of **26** that precipitated from reaction mixtures containing propylenediamine and diamino heptane hydrolysing agents and compound **25** (seen in blue, black and green, respectively). The patterns are compared to a simulated pattern based on the single-crystal X-ray diffraction measurements of **26** (red pattern).

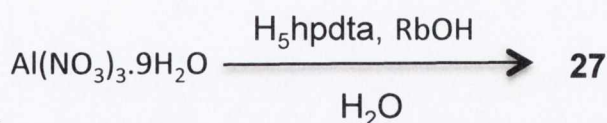
6.3 The inorganic counterion-mediated formation of Al_{15} *hpdt*a complexes

The isolation of **26** demonstrated that diammonium counterions are superfluous to the stabilisation of the zeolite assemblies of $[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4]^{3-}$ complexes. Furthermore the TGA analysis of **26**, **24** and **25** reveal stability limitations. **26** undergoes oxidative decomposition at temperatures above 325 °C whereas **25** and **25** are unstable in temperatures exceeding 400 °C. This motivated us to investigate the inorganic counterion-mediated formation of the supramolecular $\{\text{Al}_{15}\}$ compounds. For this purpose four monovalent ions, Na^+ , K^+ , Rb^+ and Cs^+ , were selected to stabilise the $[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4]^{3-}$ complex. The use of inorganic in place of organic counterions was anticipated to improve the compounds thermal stability and potentially promote their gas sorption capacities.

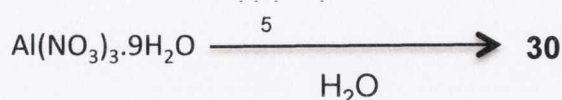
6.3.1 $\text{Rb}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 43\text{H}_2\text{O}$ (**27**), $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 36\text{H}_2\text{O}$ (**28**), $\text{K}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 22\text{H}_2\text{O}$ (**29**) and $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 41\text{H}_2\text{O}$ (**30**)

The $\{\text{Al}_{15}\}$ compounds $\text{Rb}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 43\text{H}_2\text{O}$ (**27**), $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 36\text{H}_2\text{O}$ (**28**), $\text{K}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 22\text{H}_2\text{O}$ (**29**), and $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdt})_4] \cdot 41\text{H}_2\text{O}$ (**30**)

$\text{OH})_{14}(\text{hpdta})_4] \cdot 22\text{H}_2\text{O}$ (**29**) and $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 41\text{H}_2\text{O}$ (**30**) form when the pH of aqueous solutions containing Al^{III} and *hpdta* in a 1 : 4 mole ratio is adjusted to pH 8.5 by drop wise addition of aqueous RbOH , NaOH , KOH and CsOH

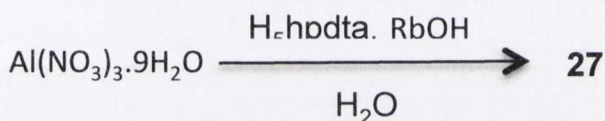


solutions, respectively (

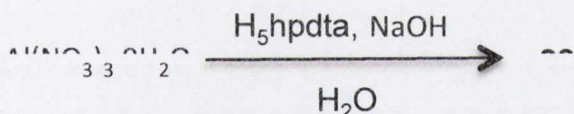


Scheme 6.2 to

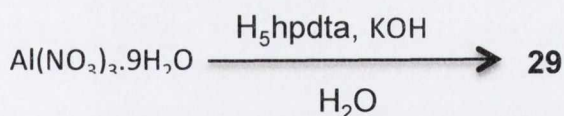
Scheme 6.5). Colourless, plate-like crystals of **27** to **30** suitable for single-crystal X-ray diffraction experiments were obtained by co-evaporation with dimethylacetamide.



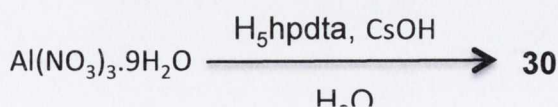
Scheme 6.2: Formation of 27



Scheme 6.3: Formation of 28



Scheme 6.4: Formation of 29



Scheme 6.5: Formation of 30

6.3.2 Structural characterisation of $\text{Rb}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 43\text{H}_2\text{O}$ (27), $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 36\text{H}_2\text{O}$ (28) and $\text{K}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 22\text{H}_2\text{O}$ (29)

Compounds **27** to **29** crystallize in the tetragonal space group $P4_2/ncm$ and are the first examples of the zeotypic $\{\text{Al}_{15}\}$ compounds incorporating alkali metal ions into their structure. Their isolation is important as it demonstrates a synthetic approach that allows for counter-ion variation whilst maintaining the structural integrity of the $[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]^{3-}$ complex.

The Rb^+ , Na^+ and K^+ counterions in **27** to **29** are disordered over several locations and the binding positions are comparable for **27** and **29**, Figure 6.8A. Therefore Rb^+ and K^+ will be denoted 'M' from herein. The Al^{III} coordination environments are analogous to the coordination environments described for **26**. The asymmetric units of **27-29** contain two alkali metal counterions, $\text{M}'(1)$ and $\text{M}'(2)$ or $\text{Na}(1)$ and $\text{Na}(2)$, and five octahedrally coordinated Al^{III} ions, two of which, $\text{Al}(2)$ and $\text{Al}(3)$, are coordinated to a *hpdta* ligand and the remaining three, $\text{Al}(1)$, $\text{Al}(4)$ and $\text{Al}(5)$ are coordinated to bridging oxo/hydroxo moieties derived from deprotonated solvent water molecules. The $\text{Al}^{\text{III}}\text{-O}$ bond lengths range from 1.852(14) Å to 2.062(11) Å and the average $\text{Al}^{\text{III}}\text{-N}$ bond distance is *ca.* 2.091(10) Å. In **27** and **29** two counterions, $\text{M}'(1)$ and symmetry equivalents in Figure 6.8A, bind to the Al_{15} complex via non-coordinating $\text{O}_{\text{carboxylate}}$ atoms, $\text{O}(14)$ and $\text{O}(14''')$ and $\text{O}(14'')$ and $\text{O}(14''')$ located on separate dinuclear Al^{III} units. The average $\text{Rb-O}_{\text{carboxylate}}$ and $\text{K-O}_{\text{carboxylate}}$ bond displays distances of *ca.* 2.96 Å and *ca.* 2.70 Å. In **28** two sodium counterions, $\text{Na}(1)$ and symmetry equivalents in Figure 6.8B, bind to the complex via two μ_3 -bridging hydroxo atoms, $\text{O}(1)$ and symmetry equivalents, with $\text{Na-O}_{\text{hydroxo}}$ bond lengths of *ca.* 2.66 Å. The third counterion in each compound, $\text{M}'(2)$ and $\text{Na}(2)$ in Figure 6.8, does not coordinate to the Al_{15} cluster and resides in the smaller cavities of the compound as observed along the crystallographic *c*-axis, Figure 6.9 and Figure 6.10. The distorted octahedral coordination environments of the ions are completed by disordered constitutional water ligands surrounding the counterions. The remaining atoms within the $[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]^{3-}$ complex are generated through symmetry operations.

The packing structures of **27** to **29** reveal their zeolite type characteristics with large pores of *ca.* 11 Å in diameter and smaller cavities of *ca.* 6 Å that extend parallel to the crystallographic *c*-axis. The larger pores contain exclusively the solvent water molecules

and the smaller cavities contain the inorganic counter ions in addition to solvent water molecules.

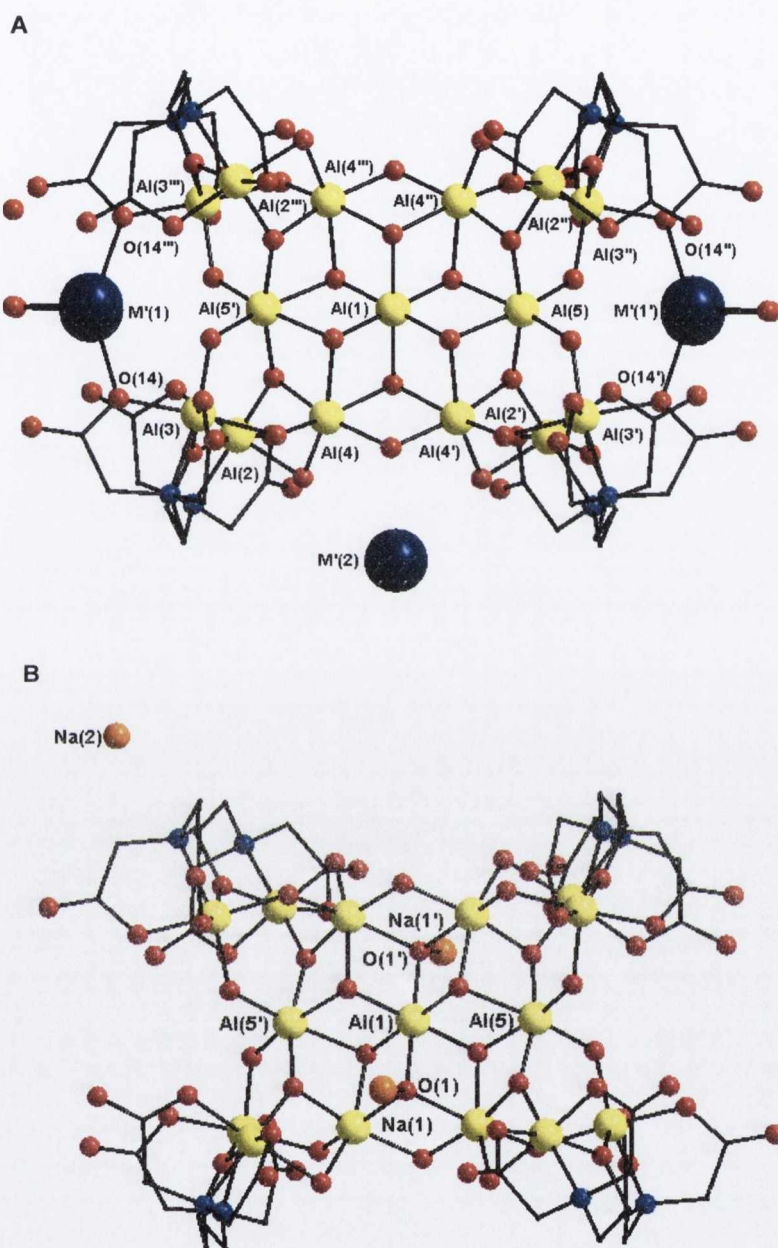


Figure 6.8: The structure of the Al_{15} complex with coordinating counterions in A) 27 and 29, B) 28. The hydrogen atoms and solvent water molecules have been omitted for clarity. Colour Code: Al yellow, C black, N light blue, Na orange, O red, M' dark blue. $\text{M}' = \text{Rb}^+$ or K^+ .

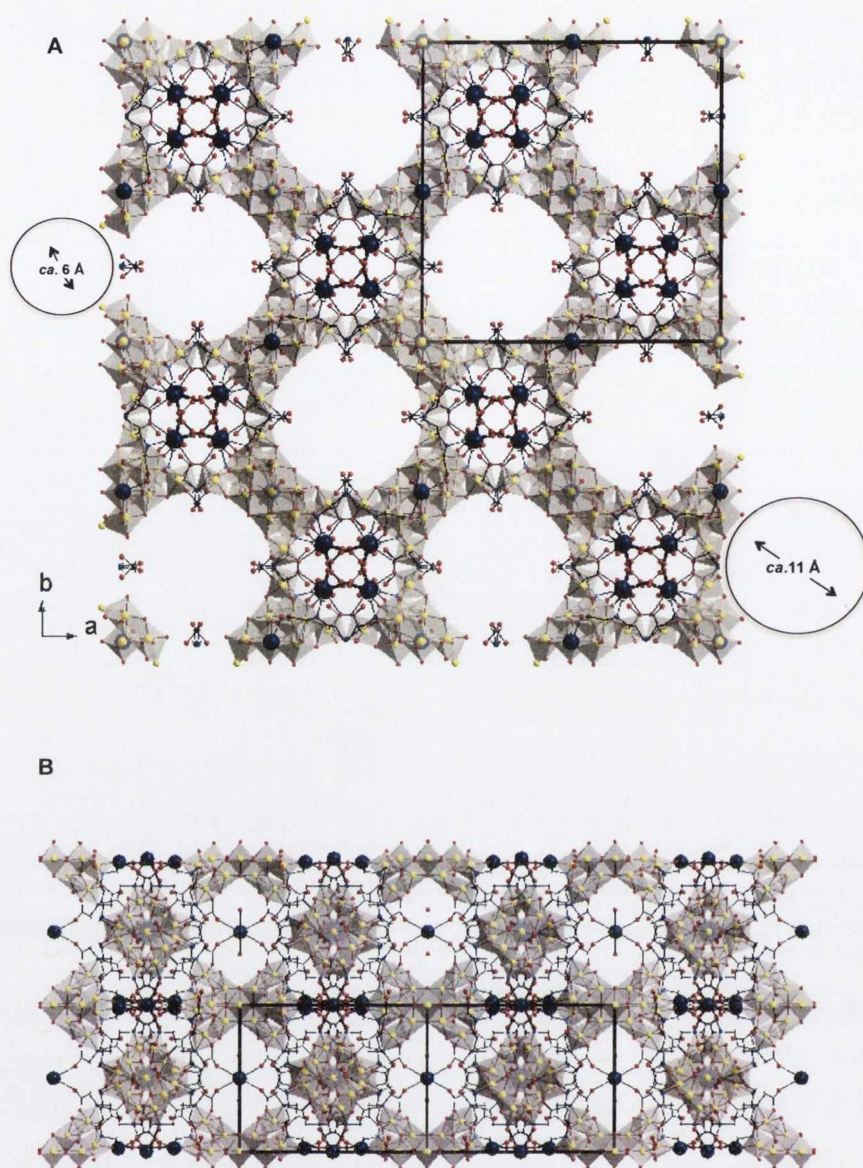


Figure 6.9: Packing structure of 27 and 29. A) Viewed along the crystallographic *c*-axis. B) Exemplifies a projection onto the (110) plane and demonstrates the lateral accesses into the smaller channels. Polyhedral representations of the Al^{III} centres. The hydrogen atoms and solvent water molecules have been omitted for clarity. Colour Code: Al yellow, C black, N light blue, O red, M^I dark blue. M^I = Rb⁺ or K⁺.

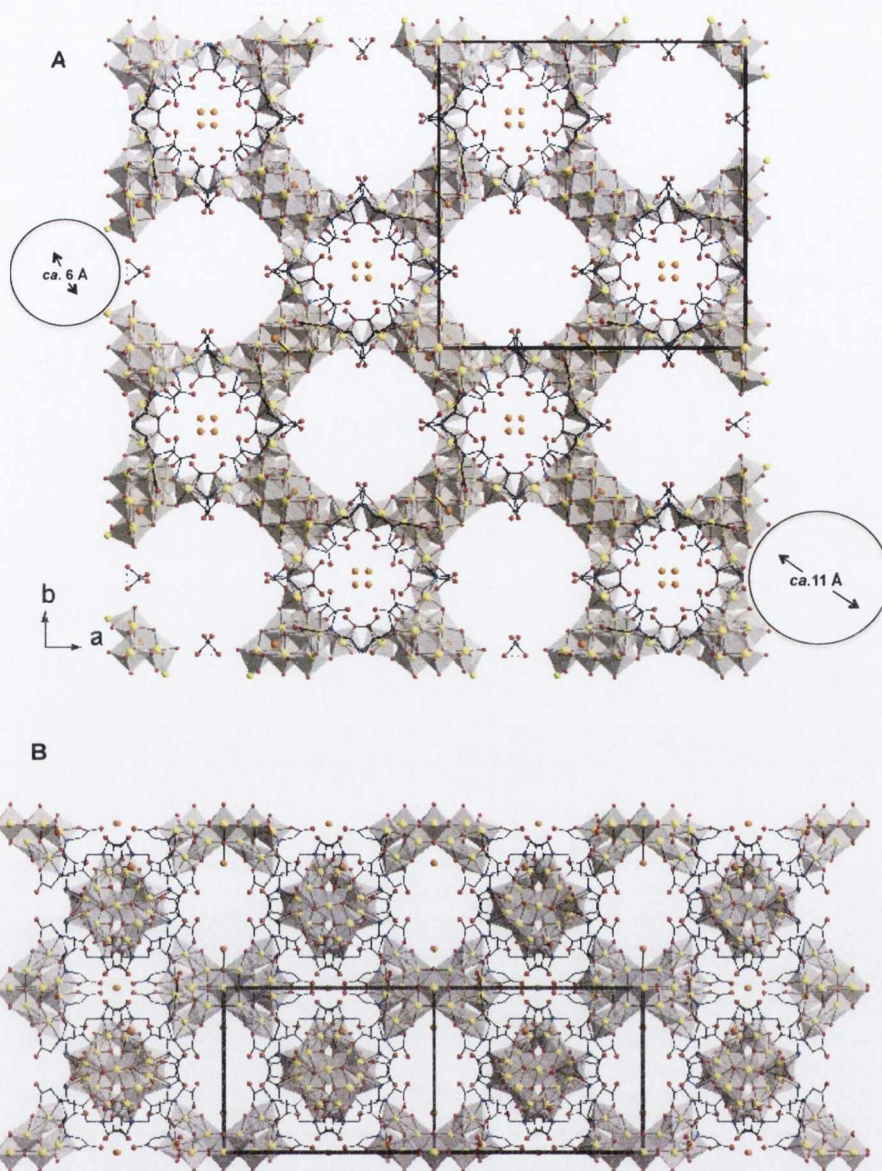


Figure 6.10: Packing structure of 28 viewed along the crystallographic c-axis (A). B) A projection onto the (110) plane demonstrating the lateral accesses into the smaller channels. Polyhedral representations of the Al^{III} centres. The hydrogen atoms and solvent water molecules have been omitted for clarity. Colour Code: Al yellow, C black, N light blue, Na yellow, O red.

The crystallographic data and experimental conditions for examined crystals of **27-29** are detailed in Table 6.7 to Table 6.9, respectively.

Table 6.7: Crystal data and structure refinement parameters for 27

Compound	27
Empirical formula	C ₄₄ H ₁₅₈ Al ₁₅ N ₈ O ₁₀₃ Rb ₃
Formula weight	3108.84 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	<i>P</i> 4 ₂ / <i>n</i> <i>c</i> <i>m</i>
Unit cell dimensions	<i>a</i> = 27.928(19) Å α = 90°. <i>b</i> = 27.928(19) Å β = 90°. <i>c</i> = 15.481(15) Å γ = 90°.
Volume	12075.2(16) Å ³
<i>Z</i>	4
Density (calculated)	1.332 Mg/m ³
Absorption coefficient	1.411 mm ⁻¹
<i>F</i> (000)	4872
Crystal size	0.3 x 0.25 x 0.25 mm ³
Φ range for data collection	1.03 to 25.14°.
Index ranges	-33 ≤ <i>h</i> ≤ 33, -33 ≤ <i>k</i> ≤ 33, -18 ≤ <i>l</i> ≤ 18
Reflections collected	118178
Independent reflections	5574 [<i>R</i> (int) = 0.1120]
Completeness to θ = 25.08°	99.8 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	5574 / 2 / 324
Goodness-of-fit on <i>F</i> ²	1.035
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1007, <i>wR</i> 2 = 0.3055
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1141, <i>wR</i> 2 = 0.3139
Largest diff. peak and hole	2.779 and -2.802 e.Å ⁻³

Table 6.8: Crystal data and structure refinement parameters for 28

Compound	28
Empirical formula	$C_{44}H_{144}Al_{15}N_8Na_3O_{96}$
Formula weight	2795.30 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	$P 4_2/ncm$
Unit cell dimensions	$a = 27.825(2)$ Å $\alpha = 90^\circ$. $b = 27.825(2)$ Å $\beta = 90^\circ$. $c = 15.579(19)$ Å $\gamma = 90^\circ$.
Volume	12062(3) Å ³
Z	4
Density (calculated)	1.171 Mg/m ³
Absorption coefficient	0.213 mm ⁻¹
F(000)	4320
Crystal size	0.25 x 0.10 x 0.05 mm ³
Φ range for data collection	1.035 to 25.36°.
Index ranges	-30 ≤ h ≤ 31, -24 ≤ k ≤ 33, -18 ≤ l ≤ 18
Reflections collected	52245
Independent reflections	5699 [R(int) = 0.1152]
Completeness to $\theta = 25.24^\circ$	100.0 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	5699 / 0 / 304
Goodness-of-fit on F ²	1.091
Final R indices [$I > 2\sigma(I)$]	R1 = 0.1049, wR2 = 0.3148
R indices (all data)	R1 = 0.1521, wR2 = 0.3541
Largest diff. peak and hole	1.724 and -0.569 e.Å ⁻³

Table 6.9: Crystal data and structure refinement parameters for 29

Compound	29
Empirical formula	C ₄₄ H ₁₁₆ Al ₁₅ K ₃ N ₈ O ₈₁
Formula weight	2575.40 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	<i>P</i> 4 ₂ / <i>ncm</i>
Unit cell dimensions	$a = 27.564(4) \text{ Å}$ $\alpha = 90^\circ$ $b = 27.564(4) \text{ Å}$ $\beta = 90^\circ$ $c = 15.407(3) \text{ Å}$ $\gamma = 90^\circ$
Volume	11706(3) Å ³
Z	4
Density (calculated)	1.293 Mg/m ³
Absorption coefficient	0.322 mm ⁻¹
F(000)	4640
Crystal size	0.15 x 0.1 x 0.25 mm ³
Φ range for data collection	1.04 to 25.02°
Index ranges	-32 ≤ h ≤ 32, -32 ≤ k ≤ 32, -13 ≤ l ≤ 18
Reflections collected	60640
Independent reflections	5335 [R(int) = 0.0945]
Completeness to θ= 25.02°	99.8 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	5335 / 0 / 316
Goodness-of-fit on F ²	1.064
Final R indices[I > 2σ(I)]	R1 = 0.0918, wR2 = 0.2456
R indices (all data)	R1 = 0.1150, wR2 = 0.2649
Largest diff. peak and hole	1.795 and -0.612 e.Å ⁻³

6.3.3 Structural characterisation of $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4]\cdot 41\text{H}_2\text{O}$ (**30**)

Compound **30** is the first $\{\text{Al}_{15}\}$ complex that crystalizes in the trigonal crystal system in the space group $R\bar{3}$. The packing structure of **30**, as discussed below, is notably distinct from the packing motifs observed for **26-29**. Thus demonstrating the influence of the nature of the counterion on the supramolecular assembly of $\{\text{Al}_{15}\}$ clusters.

The overall complex can be described as composed of four dinuclear Al^{III} *hpdta* units coordinated to an $\{\text{Al}_7(\text{OH})_{12}\}$ core. The asymmetric units contains eight of the fifteen Al^{III} ions, $\text{Al}(1)\text{-Al}(8)$, two fully deprotonated *hpdta* ligands, two cesium ions, $\text{Cs}(1)$ and $\text{Cs}(2)$, five μ_3 -bridging hydroxo moieties, $\text{O}(13)$, $\text{O}(15)$, $\text{O}(20)$, $\text{O}(6)$ and $\text{O}(16)$, five μ -bridging hydroxo moieties, $\text{O}(7)$, $\text{O}(2)$, $\text{O}(17)$, $\text{O}(18)$ and $\text{O}(19)$ and two μ_3 -bridging oxo moieties, $\text{O}(1)$ and $\text{O}(14)$. In addition, constitutional solvent water molecules surround the Cs^+ counter ions and the cluster entities.

The central Al^{III} ions in **30** adopt a distorted octahedral coordination environment. Within the boehmite like core, the average distance between two μ_3 -oxo bridged Al^{III} centres, e.g. $\text{Al}(2)\text{-Al}(5)$, is ca. 3.34 Å. Distances of ca. 3.36 Å exist between two μ_3 hydroxo bridged Al^{III} centres e.g. $\text{Al}(3)\text{-Al}(5)$. The two, hydroxo μ -bridged, Al^{III} centres are separated by distances of ca. 2.8 Å, e.g. $\text{Al}(2)\text{-Al}(4)$. The two alkoxo-bridged Al^{III} centres in the dinuclear units locate ca. 3.4 Å from each other, e.g. for $\text{Al}(2)\text{-Al}(3)$. The central Al^{III} ions within the dinuclear units, $\text{Al}(2)$, $\text{Al}(3)$, $\text{Al}(7)$ and $\text{Al}(8)$ and symmetry equivalents, are similarly coordinated as in **25-29** with four of the six coordination sites in each case fulfilled by the N- and O-donor atoms of two fully deprotonated *hpdta* ligands and the remaining sites occupied by bridging oxo/hydroxo moieties. For example $\text{Al}(2)$ is coordinated by the N-donor atom $\text{N}(1)$, the $\text{O}_{\text{carboxylate}}$ donor atoms, $\text{O}(4)$ and $\text{O}(5)$ and a methoxy O-donor atom, $\text{O}(3)$, of a fully deprotonated *hpdta* ligand. The coordination sphere of $\text{Al}(2)$ is completed by the μ -bridging and μ_3 -bridging hydroxo moieties, $\text{O}(1)$ and $\text{O}(2)$, respectively. $\text{Al}(2)$ displays an $\text{Al}^{\text{III}}\text{-N}$ bond distance of 2.051(8) Å and $\text{Al}^{\text{III}}\text{-O}$ bond lengths ranging from ca. 1.747(9) Å to ca. 1.933(5) Å. The octahedral coordination spheres of the Al^{III} ions located in the central core, i.e. $\text{Al}(1)$, $\text{Al}(4\text{-}6)$ and symmetry equivalents, are completed by oxygen atoms from bridging oxo and hydroxo moieties. For example $\text{Al}(1)$ is coordinated by μ_3 -bridging hydroxo O-donor atoms, $\text{O}(13)$, $\text{O}(15)$, $\text{O}(20)$ and symmetry equivalents with average $\text{Al}^{\text{III}}\text{-O}_{\text{hydroxo}}$ bond lengths of ca. 1.881(13) Å.

The distorted octahedral coordination environments of the Al^{III} centres are illustrated through bond angle examination. For instance the angles involving the O_{carboxylate} donor atom, O(4), situated on the apical position of Al(2), O(1)-Al(2)-O(4), O(3)-Al(2)-O(4), O(5)-Al(2)-O(4) and N(1)-Al(2)-O(4) of 94.31(11)°, 90.70(12)°, 88.41(14)° and 84.94(13)° deviate from the ideal 90° angle. The bond angles O(4)-Al(2)-O(2), O(26)-Al(7)-O(22), O(1)-Al(4)-O(18') and O(16)-Al(5)-O(13) of 174.74(12)°, 161.43(11)°, 166.34(10)° and 167.94(10)° diverge from the linear modal. Other selected bond lengths and angles involving the Al^{III} centres in **30** are presented in Table 6.10 and Table 6.11.

Table 6.10: Selected bond distances for 30

Atom	Bond	Bond Distance (Å)
Al(1)	Al(1)-O(13)	1.855(3)
	Al(1)-O(13')	1.855(3)
	Al(1)-O(15)	1.867(9)
	Al(1)-O(15')	1.867(9)
	Al(1)-O(20)	1.921(5)
	Al(1)-O(20')	1.921(5)
Al(2)	Al(2)-O(1)	1.747(9)
	Al(2)-O(3)	1.918(2)
	Al(2)-O(5)	1.921(2)
	Al(2)-O(4)	1.928(3)
	Al(2)-O(2)	1.933(5)
	Al(2)-N(1)	2.051(8)
Al(3)	Al(3)-O(6)	1.834(3)
	Al(3)-O(7)	1.897(7)
	Al(3)-O(3)	1.893(1)
	Al(3)-O(8)	1.913(4)
	Al(3)-O(9)	1.926(3)
	Al(3)-N(2)	2.102(1)
Al(4)	Al(4)-O(1)	1.853(4)
	Al(4)-O(7)	1.857(9)
	Al(4)-O(18')	1.869(8)
	Al(4)-O(2)	1.882(4)

	Al(4)-O(13)	1.998(6)
	Al(4)-O(20')	1.994(9)
Al(5)	Al(5)-O(14)	1.787(6)
	Al(5)-O(1)	1.792(1)
	Al(5)-O(16)	1.861(2)
	Al(5)-O(6)	1.877(9)
	Al(5)-O(15)	2.065(1)
	Al(5)-O(13)	2.088(6)
Al(6)	Al(6)-O(14)	1.841(2)
	Al(6)-O(18)	1.854(1)
	Al(6)-O(19)	1.887(1)
	Al(6)-O(17)	1.893(1)
	Al(6)-O(15)	1.985(2)
	Al(6)-O(20)	2.042(1)
Al(7)	Al(7)-O(16)	1.843(5)
	Al(7)-O(17)	1.872(5)
	Al(7)-O(22)	1.896(7)
	Al(7)-O(23)	1.917(7)
	Al(7)-O(26)	1.923(8)
	Al(7)-N(3)	2.135(3)
Al(8)	Al(8)-O(14)	1.752(9)
	Al(8)-O(22)	1.896(4)
	Al(8)-O(25)	1.918(4)
	Al(8)-O(24)	1.913(7)
	Al(8)-O(19)	1.944(8)
	Al(8)-N(4)	2.046(4)

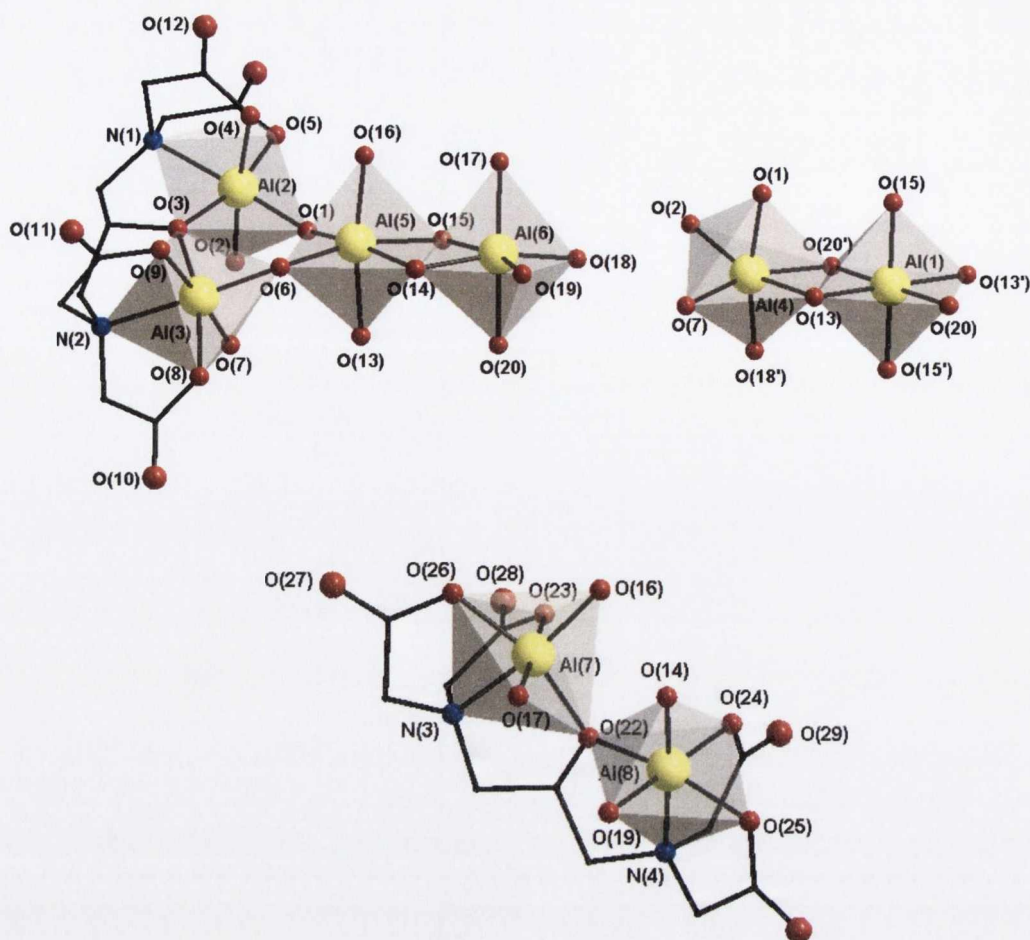


Figure 6.11: Polyhedral representations of the Al^{III} centres in 30. The hydrogen atoms have been omitted for clarity. Colour Code: Al yellow, C black, N blue, O red.

Table 6.11: Selected bond angles for compound 30.

	Bond Angle (°)		Bond Angle (°)
O(13)-Al(1)-O(13')	180.00(10)	O(1)-Al(5)-O(6)	91.32(10)
O(13)-Al(1)-O(15)	93.69(9)	O(16)-Al(5)-O(6)	100.46(10)
O(13')-Al(1)-O(15')	86.31(9)	O(14)-Al(5)-O(15)	78.28(9)
O(13)-Al(1)-O(20')	96.65(8)	O(1)-Al(5)-O(15)	90.93(9)
O(13')-Al(1)-O(20)	83.35(8)	O(16)-Al(5)-O(15)	92.53(9)
O(15)-Al(1)-O(20')	96.91(8)	O(6)-Al(5)-O(15)	166.28(10)
O(15')-Al(1)-O(20)	83.09(8)	O(14)-Al(5)-O(13)	88.57(9)
O(1)-Al(2)-O(3)	95.14(10)	O(1)-Al(5)-O(13)	78.83(9)
O(1)-Al(2)-O(5)	101.53(11)	O(16)-Al(5)-O(13)	167.94(10)

O(3)-Al(2)-O(5)	163.33(12)	O(6)-Al(5)-O(13)	91.50(9)
O(1)-Al(2)-O(4)	94.31(11)	O(15)-Al(5)-O(13)	75.67(8)
O(3)-Al(2)-O(4)	90.70(12)	O(14)-Al(6)-O(18)	166.09(11)
O(5)-Al(2)-O(4)	88.41(14)	O(14)-Al(6)-O(19)	81.19(10)
O(1)-Al(2)-O(2)	81.44(10)	O(18)-Al(6)-O(19)	102.36(10)
O(3)-Al(2)-O(2)	92.75(10)	O(14)-Al(6)-O(17)	96.94(10)
O(5)-Al(2)-O(2)	89.42(13)	O(18)-Al(6)-O(17)	96.17(10)
O(4)-Al(2)-O(2)	174.74(12)	O(19)-Al(6)-O(17)	94.72(10)
O(1)-Al(2)-N(1)	176.28(13)	O(14)-Al(6)-O(15)	79.13(9)
O(3)-Al(2)-N(1)	81.23(12)	O(18)-Al(6)-O(15)	96.59(9)
O(5)-Al(2)-N(1)	82.11(13)	O(19)-Al(6)-O(15)	160.29(10)
O(4)-Al(2)-N(1)	84.94(13)	O(17)-Al(6)-O(15)	88.55(9)
O(6)-Al(3)-O(7)	97.02(10)	O(14)-Al(6)-O(20)	91.48(9)
O(6)-Al(3)-O(3)	100.47(10)	O(18)-Al(6)-O(20)	74.64(9)
O(7)-Al(3)-O(3)	86.72(10)	O(19)-Al(6)-O(20)	102.29(10)
O(6)-Al(3)-O(8)	95.86(10)	O(17)-Al(6)-O(20)	162.00(10)
O(7)-Al(3)-O(8)	88.64(10)	O(15)-Al(6)-O(20)	77.42(8)
O(3)-Al(3)-O(8)	163.45(11)	O(16)-Al(7)-O(17)	94.83(10)
O(6)-Al(3)-O(9)	87.79(10)	O(16)-Al(7)-O(22)	102.86(10)
O(7)-Al(3)-O(9)	175.19(11)	O(17)-Al(7)-O(22)	87.38(10)
O(3)-Al(3)-O(9)	92.45(10)	O(16)-Al(7)-O(23)	87.19(11)
O(8)-Al(3)-O(9)	90.85(10)	O(17)-Al(7)-O(23)	177.62(12)
O(6)-Al(3)-N(2)	168.90(11)	O(22)-Al(7)-O(23)	93.40(10)
O(7)-Al(3)-N(2)	93.20(10)	O(16)-Al(7)-O(26)	95.65(11)
O(3)-Al(3)-N(2)	84.38(10)	O(17)-Al(7)-O(26)	89.71(11)
O(8)-Al(3)-N(2)	80.02(10)	O(22)-Al(7)-O(26)	161.43(11)
O(9)-Al(3)-N(2)	82.00(10)	O(23)-Al(7)-O(26)	88.85(11)
O(1)-Al(4)-O(7)	98.40(10)	O(16)-Al(7)-N(3)	167.14(13)
O(1)-Al(4)-O(18')	166.34(10)	O(17)-Al(7)-N(3)	96.96(12)
O(7)-Al(4)-O(18')	94.88(10)	O(22)-Al(7)-N(3)	82.83(10)
O(1)-Al(4)-O(2)	80.06(10)	O(23)-Al(7)-N(3)	80.91(13)
O(7)-Al(4)-O(2)	94.62(10)	O(26)-Al(7)-N(3)	79.33(11)
O(18')-Al(4)-O(2)	102.14(11)	O(14)-Al(8)-O(22)	94.83(10)

O(1)-Al(4)-O(13)	79.79(9)	O(14)-Al(8)-O(25)	100.18(11)
O(7)-Al(4)-O(13)	87.34(9)	O(22)-Al(8)-O(25)	165.00(10)
O(18')-Al(4)-O(13)	97.68(10)	O(14)-Al(8)-O(24)	95.69(10)
O(2)-Al(4)-O(13)	159.83(11)	O(22)-Al(8)-O(24)	90.17(10)
O(1)-Al(4)-O(20')	91.07(9)	O(25)-Al(8)-O(24)	88.24(10)
O(7)-Al(4)-O(20')	160.76(10)	O(14)-Al(8)-O(19)	81.48(10)
O(18')-Al(4)-O(20')	75.29(9)	O(22)-Al(8)-O(19)	92.60(10)
O(2)-Al(4)-O(20')	103.52(10)	O(25)-Al(8)-O(19)	89.75(10)
O(15)-Al(1)-O(20')	96.91(8)	O(24)-Al(8)-O(19)	176.19(11)
O(1)-Al(2)-O(3)	95.14(10)	O(14)-Al(8)-N(4)	177.26(11)
O(2)-Al(4)-O(20')	103.52(10)	O(22)-Al(8)-N(4)	82.81(10)
O(13)-Al(4)-O(20')	77.86(8)	O(25)-Al(8)-N(4)	82.20(10)
O(14)-Al(5)-O(1)	165.17(11)	O(24)-Al(8)-N(4)	85.71(10)
O(14)-Al(5)-O(16)	91.50(10)	O(19)-Al(8)-N(4)	97.22(10)
O(1)-Al(5)-O(16)	99.19(10)	O(14)-Al(5)-O(13)	88.57(9)
O(14)-Al(5)-O(6)	96.84(10)	O(1)-Al(5)-O(13)	78.83(9)

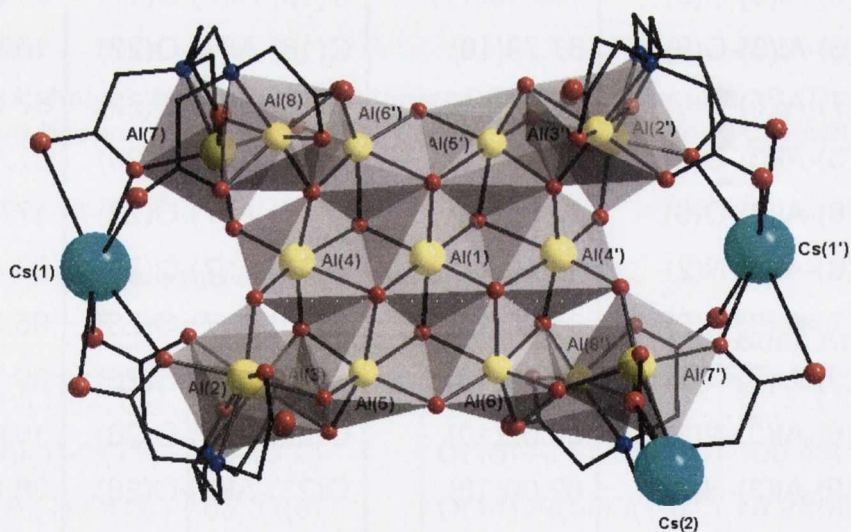


Figure 6.12: The Al_{15} complex in 30 displaying the binding Cs^+ counter-ions. The hydrogen atoms and solvent water molecules have been omitted for clarity. Grey polyhedral representations of the Al^{III} centres in 30. Colour Code: Al yellow, C black, Cs turquoise, N light blue, O red.

The cesium counterions, Cs(1) and Cs(2), coordinate to **30** via the $O_{\text{carboxylate}}$ atoms of the *hpdta* ligands, Figure 6.12, with Cs^I-O bond distances ranging between 2.972(3) Å and 3.652(4) Å. Cs(1) and symmetry equivalents form bonds with two separate dinuclear units within the {Al₁₅} cluster and interconnect single Al₁₅ clusters via $O_{\text{carboxylate}}$ atoms. The Cs(2) counterion and symmetry equivalents coordinate to the oxo-cluster entity via $O_{\text{carboxylate}}$ atoms located on one *hpdta* ligand. The packing structure of **30** is notably distinct from the previously described {Al₁₅} complexes, **24-29**, in that the smaller interconnecting cavities are replaced by larger pores of *ca.* 16 Å in diameter and the compound forms a honeycomb-type of arrangement. The channels contain solvent water molecules and are lined with Cs⁺ counterions, Figure 6.13. The crystallographic data for examined single crystals of **30** are listed in Table 6.12.

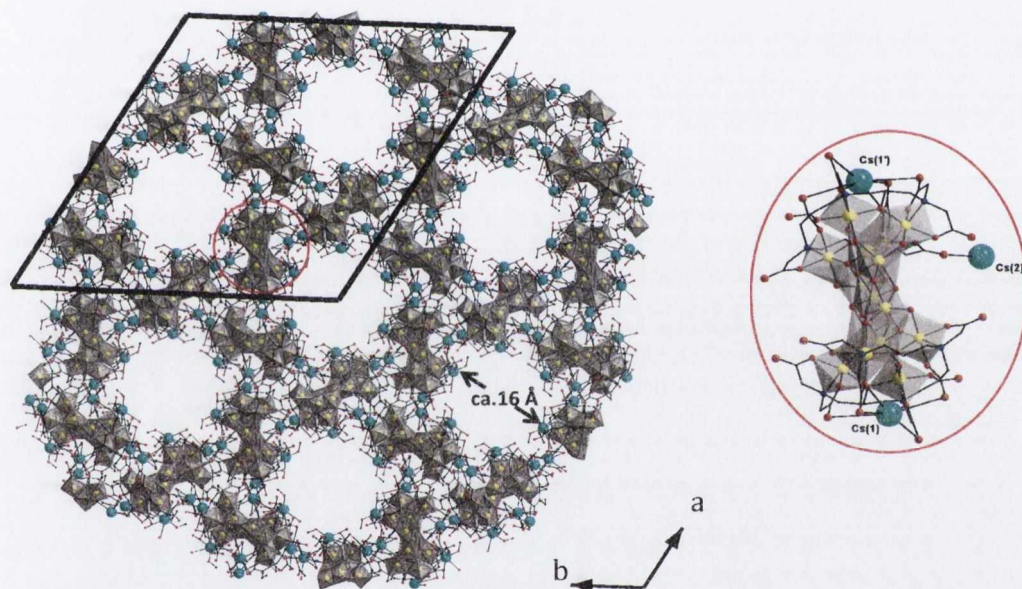


Figure 6.13: The zeotypic packing structure of **30**. Viewed along the crystallographic *c*-axis displaying the pores of *ca.* 16 Å in diameter (A). Red circle highlights a single molecule of **30**. Polyhedral representations of the Al₁₅ centres. The hydrogen atoms and solvent water molecules have been omitted for clarity. Colour Code: Al yellow, C black, Cs turquoise, N blue, O red.

Table 6.12: Crystal data and structure refinement parameters for 30

Compound	30
Empirical formula	C ₄₄ H ₁₅₄ Al ₁₅ CS ₃ N ₈ O ₁₀₀
Formula weight	3199.12 g mol ⁻¹
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	<i>R</i> -3
Unit cell dimensions	a = 47.974(7) Å α = 90°. b = 47.974(7) Å β = 90°. c = 16.270(3) Å γ = 120°.
Volume	32429(9) Å ³
Z	10
Density (calculated)	1.243 Mg/m ³
Absorption coefficient	0.930 mm ⁻¹
F(000)	11988
Crystal size	0.25 x 0.3 x 0.3 mm ³
Φ range for data collection	2.17 to 31.42°.
Index ranges	-64 ≤ h ≤ 66, -68 ≤ k ≤ 68, -23 ≤ l ≤ 21
Reflections collected	81361
Independent reflections	21466 [R(int) = 0.0317]
Completeness to θ = 31.42°	90.0 %
Refinement method	Full-matrix least-squares
Data/restraints/parameters	21466 / 0 / 664
Goodness-of-fit on F ²	1.094
Final R indices[I > 2σ(I)]	R1 = 0.0756, wR2 = 0.2161
R indices (all data)	R1 = 0.0847, wR2 = 0.2260
Largest diff. peak and hole	1.393 and -0.792 e.Å ⁻³

6.3.4 Physicochemical characterisation of 27-30

The physicochemical properties of **27-30** were investigated in support of the crystallographic studies. The analytical techniques of Fourier transform-infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), chemical analysis and powder X-ray diffraction (P-XRD) were employed to analyse bulk samples of **27-30**.

FT-IR

The FT-IR spectra recorded for **27-30** are comparable, Figure 6.14. The broad asymmetric and symmetric -OH stretches are displayed at *ca.* 3410 cm^{-1} , *ca.* 3385 cm^{-1} , *ca.* 3390 cm^{-1} and *ca.* 3395 cm^{-1} in **27-30** respectively. Their resonance is indicative of solvent water molecules engaged in H-bonds. The stretches at *ca.* 1640 cm^{-1} are attributable to the asymmetric COO^- stretches in **27-30** respectively. The stretches between *ca.* 1380 cm^{-1} and 1390 cm^{-1} arise from the symmetric COO^- stretches. The differences between the asymmetric and symmetric stretches, Table 6.14, range between *ca.* 250 cm^{-1} and *ca.* 260 cm^{-1} . The Δv values greater than 200 cm^{-1} reflect the unidentate binding modes observed for the carboxylate moieties in **27-30**.¹⁶³

Table 6.13: The characteristic FT-IR vibrational bands, and corresponding assignments, for compounds 27-30.^{136-138, 194} *res. = respectively.*

Wavenumber (cm^{-1}) compounds 27-30 res.	Assignment(s)
3410, 3385, 3390, 3395.	O-H v_s and v_{as} stretches
1640, 1630, 1640, 1640.	$v_{as}\text{COO}^-$
1380, 1385, 1385, 1390.	$v_s\text{COO}^-$
<i>ca.</i> 920	Out of plane -OH stretch

Table 6.14: The difference in FT-IR stretching frequencies, Δv (cm^{-1}), between the asymmetric and symmetric carboxylate stretches for compounds 27-30.

	<i>ca.</i> ΔE (cm^{-1}) $v_{as}\text{COO}^- - v_s\text{COO}^-$
27	260
28	250
29	255
30	250

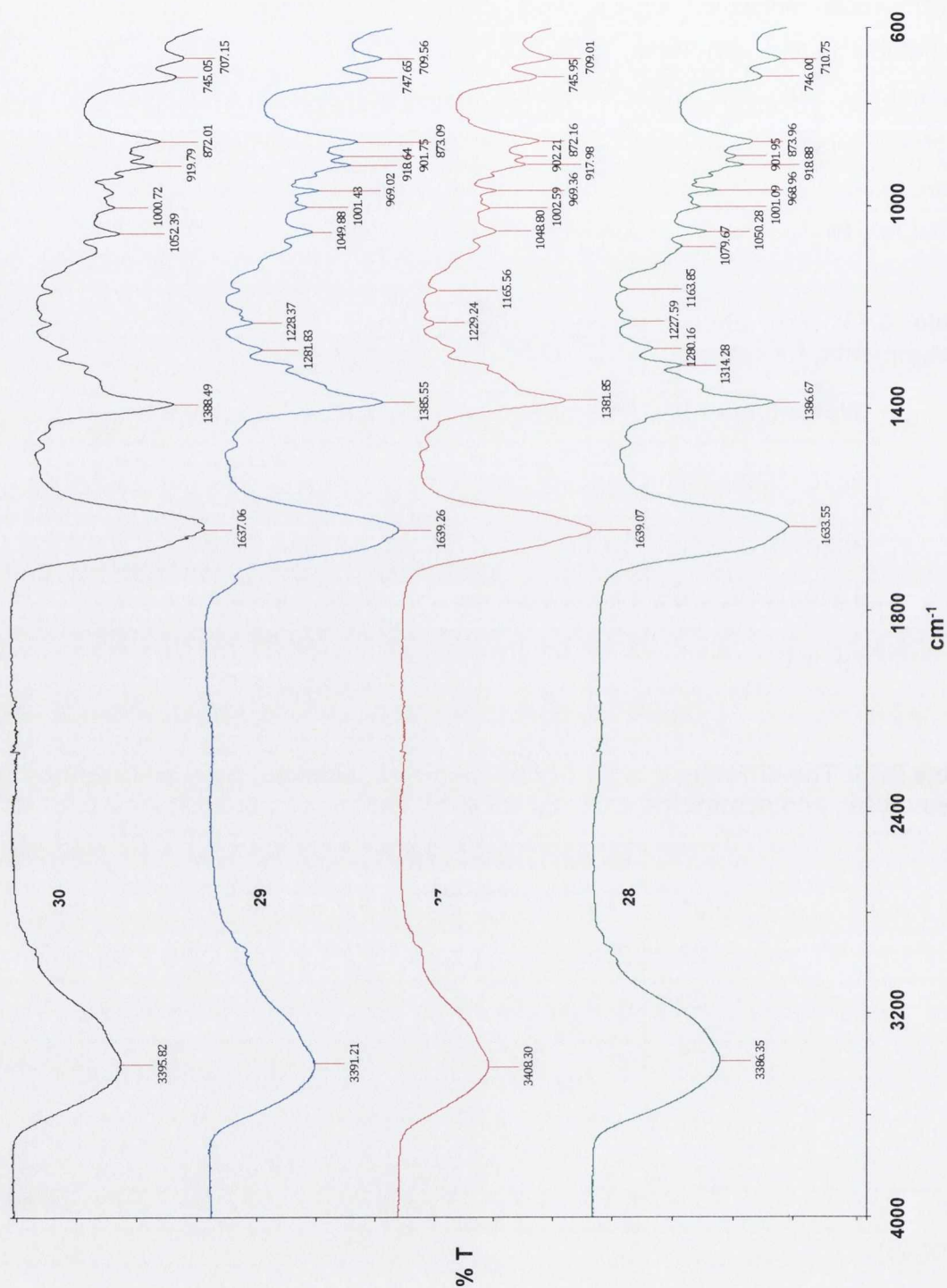


Figure 6.14: FT-IR spectra of freshly ground microcrystals of 27-30 recorded using a diffuse reflectance accessory.

TGA

The solvent content of **27-30** was determined through thermogravimetric (TGA) analysis. The TGA analysis concurrently ascertained the thermal stabilities of the compounds. The experiments were recorded in the temperature range from 25 °C to 900 °C with a heating rate of 1°C/minute and included an isothermal step at 25 °C for fifteen minutes. Isothermal steps were included at 25 °C, 75 °C, 110 °C and 175 °C for **27** and at 75 °C and 110 °C for **28**.

In the temperature range 25 °C to 110 °C the loss of 43 water molecules is observed from **27**, (experimental weight loss: 24.85 %, theoretical weight loss: 24.89 %), the loss of 36 water molecules from **28**, (experimental weight loss: 22.97 %, theoretical weight loss: 23.18 %), 22 from **29**, (experimental weight loss: 15.50 %, theoretical weight loss: 15.38 %) and 41 from **30**, (experimental weight loss: 23.33 %, theoretical weight loss: 23.07 %). An increase in temperature to 900 °C gives rise to oxidative decomposition of the organic ligands and oxide formation. The former occurs in a one step process centred at ca. 380 °C, (experimental weight loss: 47.03 %, theoretical weight loss: 47.11 %), ca. 390 °C, (experimental weight loss: 49.63 %, theoretical weight loss: 49.89 %) and ca. 350 °C, (experimental weight loss: 41.16 %, theoretical weight loss: 41.17 %), in the TGA derivative curves of **28-30** respectively. **27** undergoes oxidative ligand decomposition in a comparable temperature range and results in peaks in the TGA derivative curve centred at ca. 380 °C. Final experimental weight loss for compounds **27-30**: 79.21 %, 70.00 %, 65.13 % and 64.49 %.

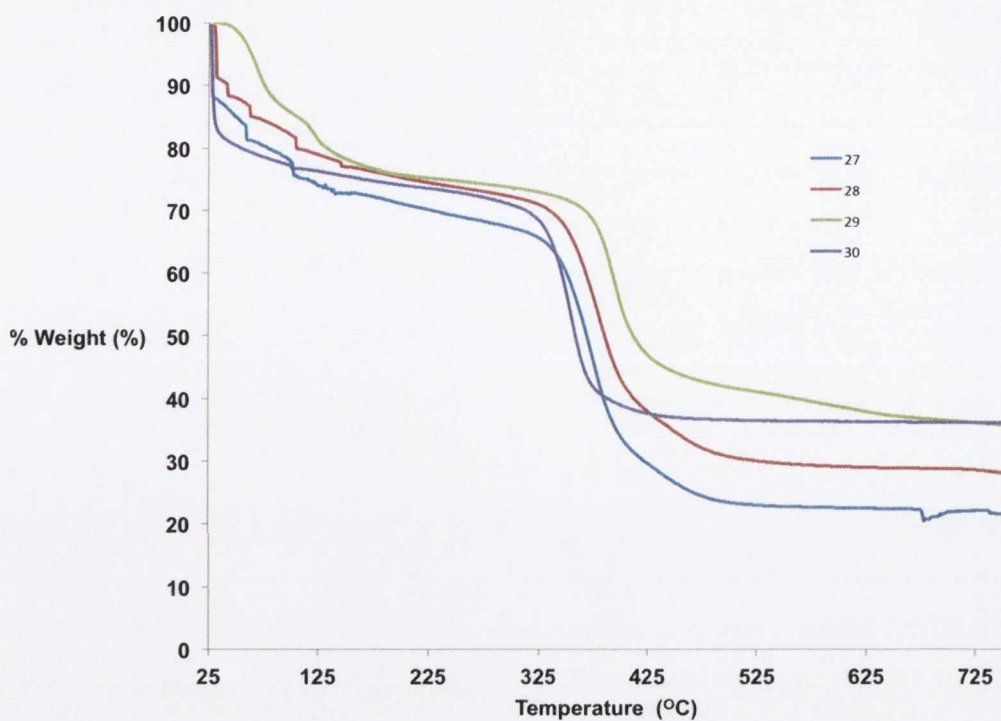


Figure 6.15: TGA curves for 27-30. Recorded in an air atmosphere from 25 °C to 900 °C. The heating rate was set to 1 °C/minute. Isothermal steps were included at 25 °C, 75 °C, 110 °C and 175 °C for 27 and at 75 °C and 110 °C for 28.

Table 6.15: Results for TGA analysis (recorded in an air atmosphere from 25 °C to 900 °C. Linear heating step was set to 1 °C/minute) of 27-30. Isothermal step at 25 °C for fifteen minutes.

	Formula	Theoretical mass (%)	Observed mass (%)	Temperature (°C)
27	C ₄₄ H ₁₅₈ Al ₁₅ N ₈ O ₁₀₃ Rb ₃	100	100	25 (Initial)
	C ₄₄ H ₇₂ Al ₁₅ N ₈ O ₆₀ Rb ₃	75.10	75.15	25 - 110
	7.5Al ₂ O ₃	20.70	20.79	110 – 900 (final)
28	C ₄₄ H ₁₄₄ Al ₁₅ N ₈ Na ₃ O ₉₆	100	100	25 (Initial)
	C ₄₄ H ₇₂ Al ₁₅ N ₈ Na ₃ O ₆₀	76.82	77.03	25 – 110
	7.5Al ₂ O ₃ , 1.5Na ₂ O	29.70	30.00	110 – 900 (final)
29	C ₄₄ H ₁₁₆ Al ₁₅ K ₃ N ₈ O ₈₁	100	100	25 (Initial)
	C ₄₄ H ₇₂ Al ₁₅ K ₃ N ₈ O ₅₉	84.63	84.50	25 – 110
	7.5Al ₂ O ₃ , 1.5K ₂ O	34.73	34.87	110 – 900
30	C ₄₄ H ₁₅₄ Al ₁₅ Cs ₃ N ₈ O ₁₀₀	100	100	25 (initial)
	C ₄₄ H ₇₂ Al ₁₅ Cs ₃ N ₈ O ₅₉	76.93	76.68	25 – 110
	7.5Al ₂ O ₃ , 1.5Cs ₂ O	35.76	35.51	110 - 900

Chemical analysis:

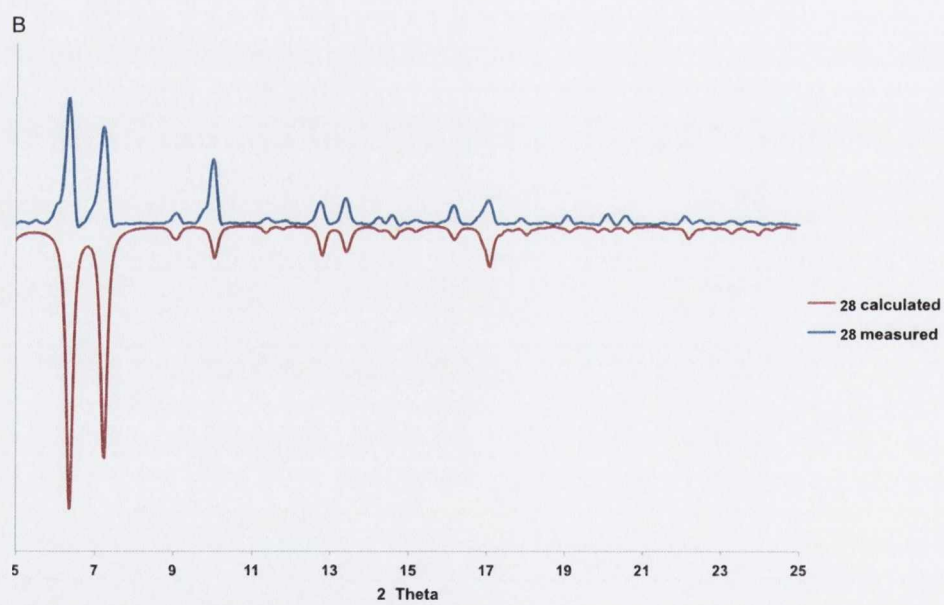
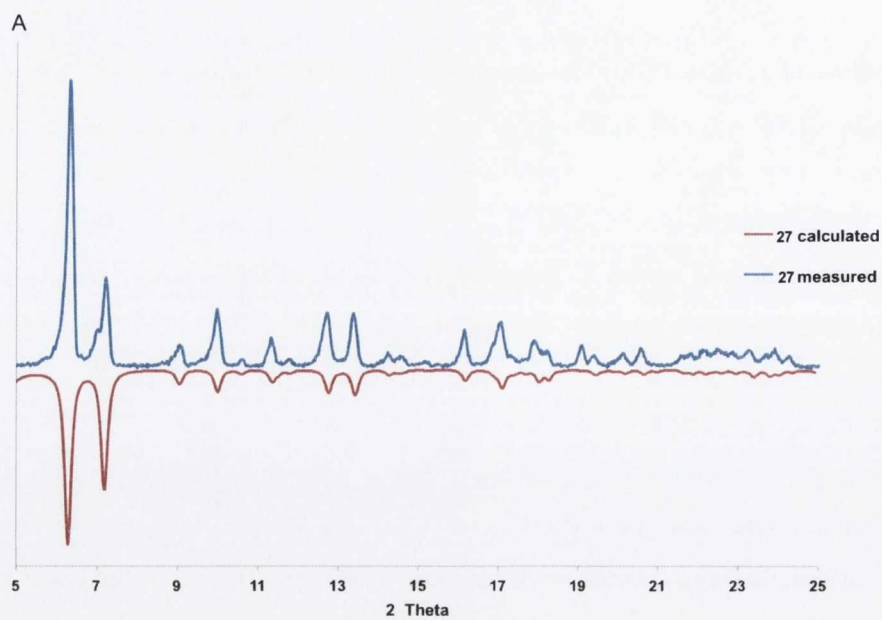
The chemical analysis of **27-30**, Table 6.16, provide further evidence for the chemical formulae of $C_{44}H_{158}Al_{15}N_8O_{103}Rb_3$, $C_{44}H_{144}Al_{15}N_8Na_3O_{96}$, $C_{44}H_{116}Al_{15}K_3N_8O_{81}$ and $C_{44}H_{154}Al_{15}Cs_3N_8O_{100}$, respectively, and further supports the results of the crystallographic and thermogravimetric analyses.

Table 6.16: Theoretical and experimental elemental analysis for 27-30. Theoretical based on $C_{44}H_{158}Al_{15}N_8O_{103}Rb_3$, $C_{44}H_{144}Al_{15}N_8Na_3O_{96}$, $C_{44}H_{116}Al_{15}K_3N_8O_{81}$ and $C_{44}H_{154}Al_{15}Cs_3N_8O_{100}$, respectively.

	Element	Theoretical composition (%)	Experimental composition (%)
27	C	17.00	17.09
	H	5.12	5.04
	Al	13.02	12.98
	N	3.60	3.57
28	C	18.91	18.84
	H	5.19	5.15
	Al	14.48	14.39
	N	4.01	3.97
	Na	2.47	2.45
29	C	20.52	20.47
	H	4.54	4.51
	Al	15.71	15.74
	N	4.35	4.36
30	C	16.52	16.55
	H	4.85	4.79
	Al	12.65	12.71
	N	3.50	3.46

P-XRD

The phase purities of **27-30** and the accuracy of the crystallographic models were further studied using powder X-ray diffraction (P-XRD) experiments. Crystalline samples of **27-30** were ground to a powder for the analysis. The experimental patterns recorded for the samples match the simulated pattern, Figure 6.16, thus suggesting the phase purity of **27-30** and the accuracy of the crystallographic models as determined by the single-crystal X-ray diffraction experiments. The crystallographic information files (CIF) were used to calculate the simulated patterns. It was necessary to record the P-XRD pattern of **30** at 150 K. Powders of **30** were packed into a capillary tube and the experiment was performed on a Bruker APEX2 Duo diffractometer with a constant stream of liquid nitrogen to achieve the temperature of 150 K. The requirement is presumed to arise from the rapid loss of constitutional water molecules at room temperature. Desolvation of **30** at room temperature results in a collapse of the 3D order to give an amorphous powder.



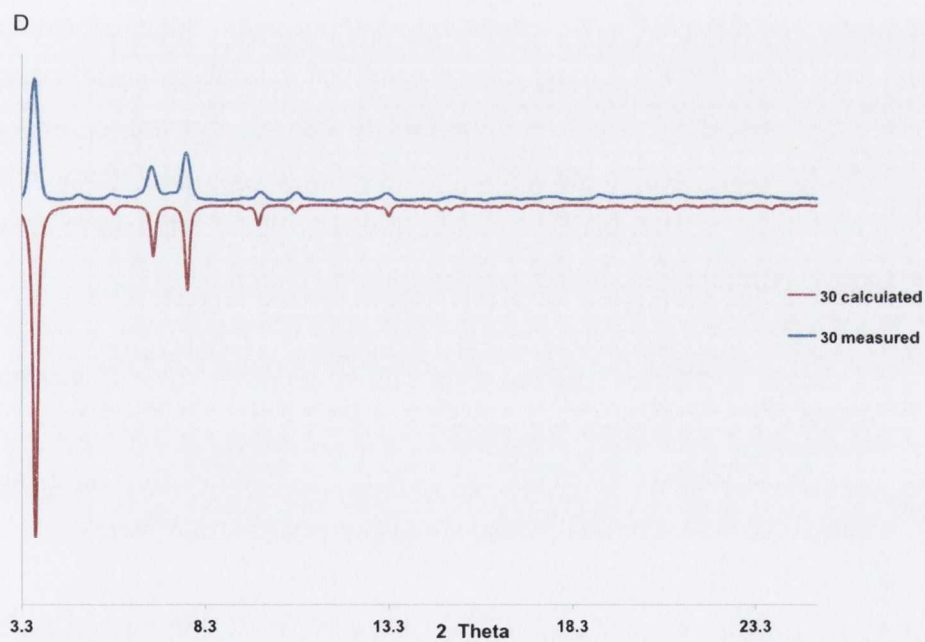
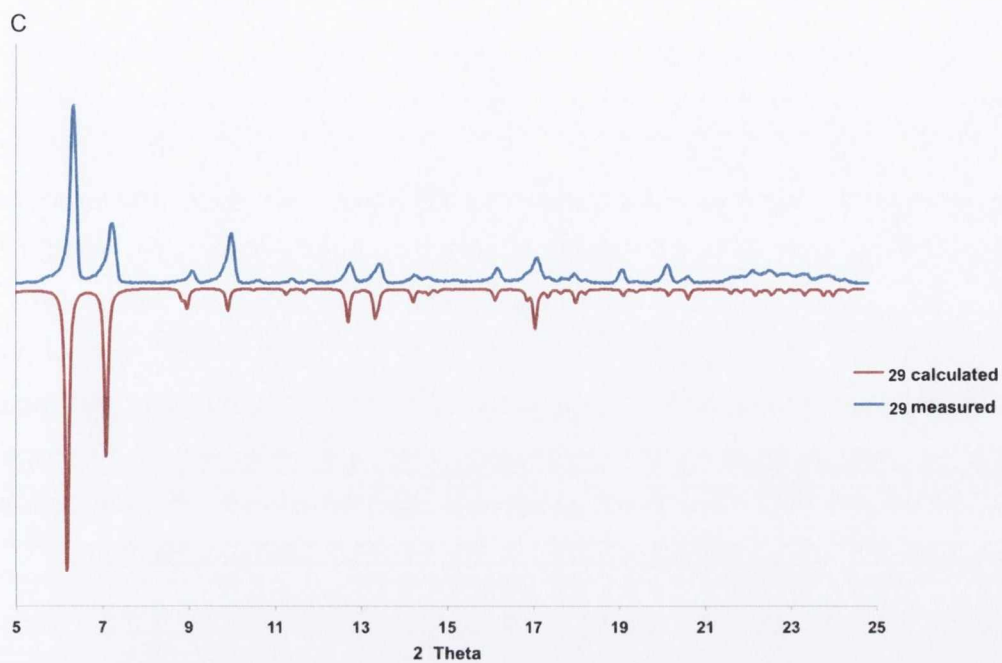


Figure 6.16: P-XRD patterns for crystals of A) 27, B) 28 and C) 29 D) 30 (blue) compared with simulated patterns based on the single-crystal X-ray diffraction experiments (red).

6.4 Surface area determination of compounds 24-30

Given the open framework arrangements in **24-30**, and the fact that Al based network structures are desirable candidates for gas storage applications, it was adventitious to investigate the compound's inherent surface areas and gas storage capabilities. The surface area is an important characteristic of porous materials, especially for applications as gas storage and separation materials. The Brunauer–Emmett–Teller (BET) theory was employed to investigate the surface areas of **24-30**. The studies were further extended to evaluate the H₂ and CO₂ uptakes of the compounds. It was of particular interest to compare the gas storage characteristics of the compounds containing organic counterions with those containing inorganic counter ions, **24-26** and **27-30**, respectively. These investigations are important, as they are the first instance where the gas storage capabilities of these supramolecular {Al₁₅} clusters have been investigated.

6.4.1 Nitrogen adsorption

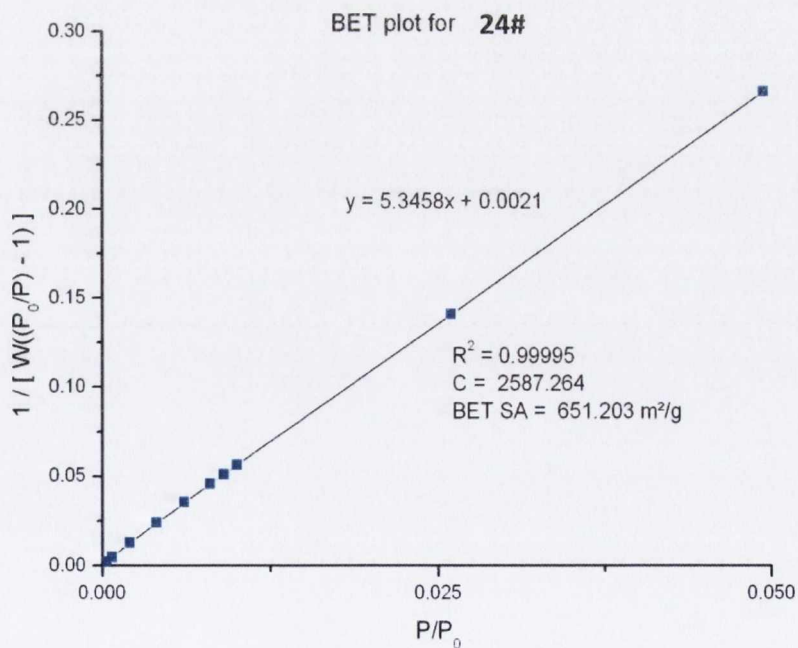
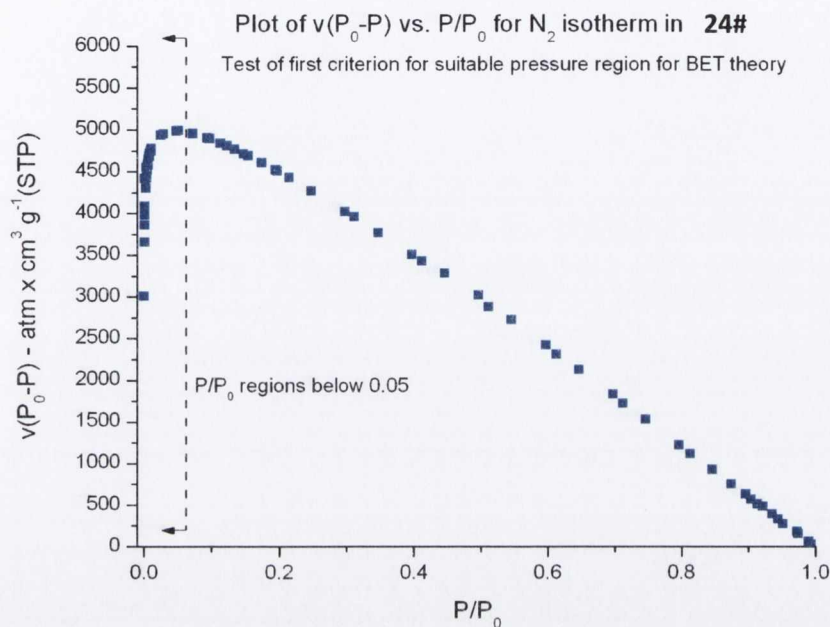
The application of BET theory to nitrogen adsorption isotherms, measured at temperatures of 77 °K, is a widely accepted method to evaluate the surface area of porous samples. The classical "BET" linear range extends over relative pressures of 0.05 to 0.3. However, the linear "BET" range of microporous materials is typically observed at relative pressures less than 0.1. It is important to identify the appropriate pressure regions in order to obtain meaningful values from BET calculations. According to Walton and co-workers the two criteria for successfully applying the BET theory to microporous materials such as compounds **24-30** are as follows: ⁵²

- 3 "The pressure range selected should have values of $V(P_0 - P)$ increasing with P/P_0 ."
- 4 "The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero."

In the case of compounds **24** and **27-29** it was revealed that the linear BET model is applicable in relative pressure regions less than 0.050, 0.029, 0.033, and 0.031 respectively. This lower pressure region was expected to be most relevant as the compounds contain defined channels with cross-sectional diameters of *ca.* 13 Å. This diameter is within the International Union of Pure and Applied Chemistry's (IUPAC) classification of microporous materials which are characterised by cross sectional diameters less than 20 Å.⁵¹ The points selected within the appropriate pressure regions

display positive y intercepts and slope values greater than zero for **24** and **27-29**, Figure 6.17. These results are in line with the criteria suggested by Walton and co-workers.⁵² The experiments were performed using crystalline samples of **24** and **27-29** and were repeated four times for each sample.

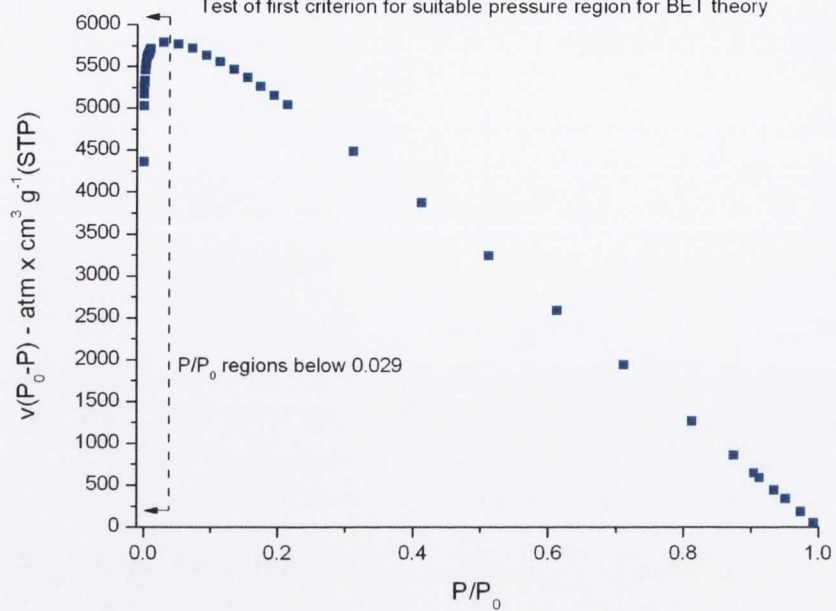
A



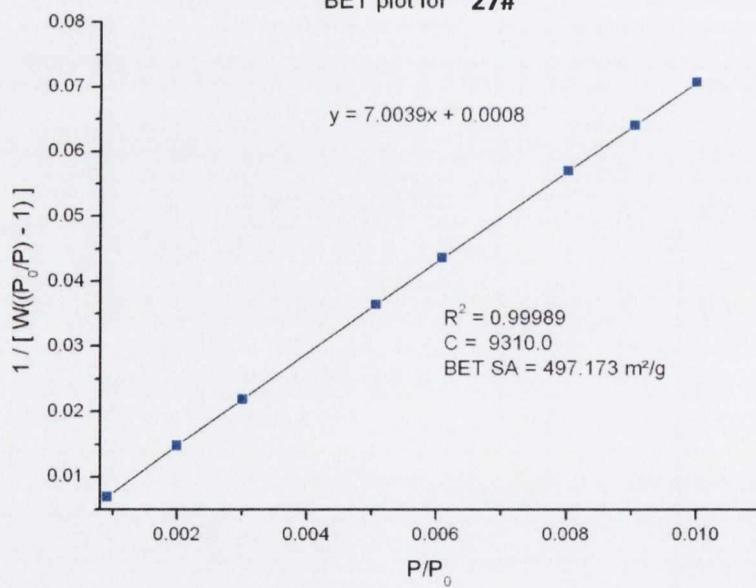
B

Plot of $v(P_0 - P)$ vs. P/P_0 for N_2 isotherm in **27#**

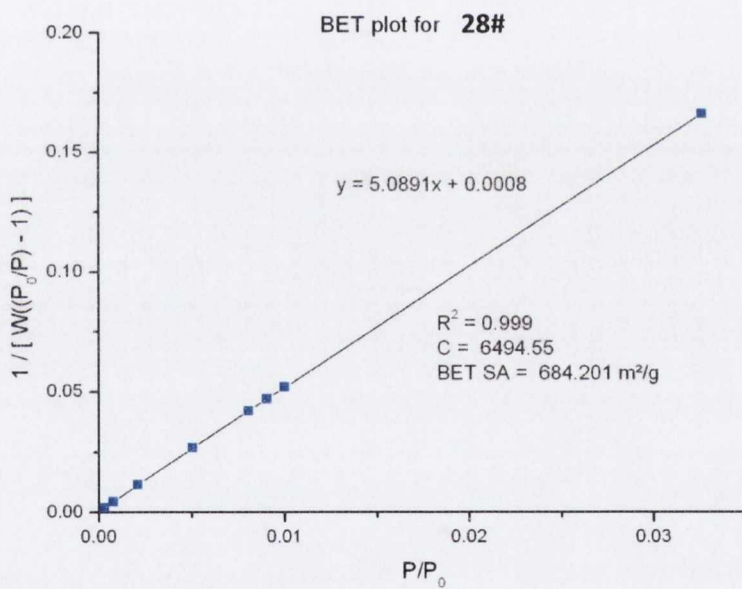
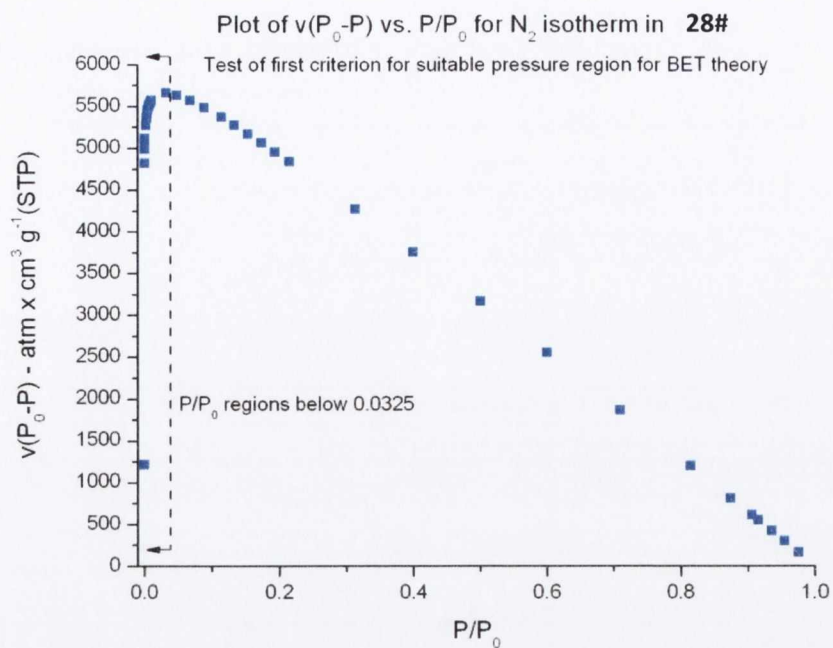
Test of first criterion for suitable pressure region for BET theory



BET plot for **27#**



C



D

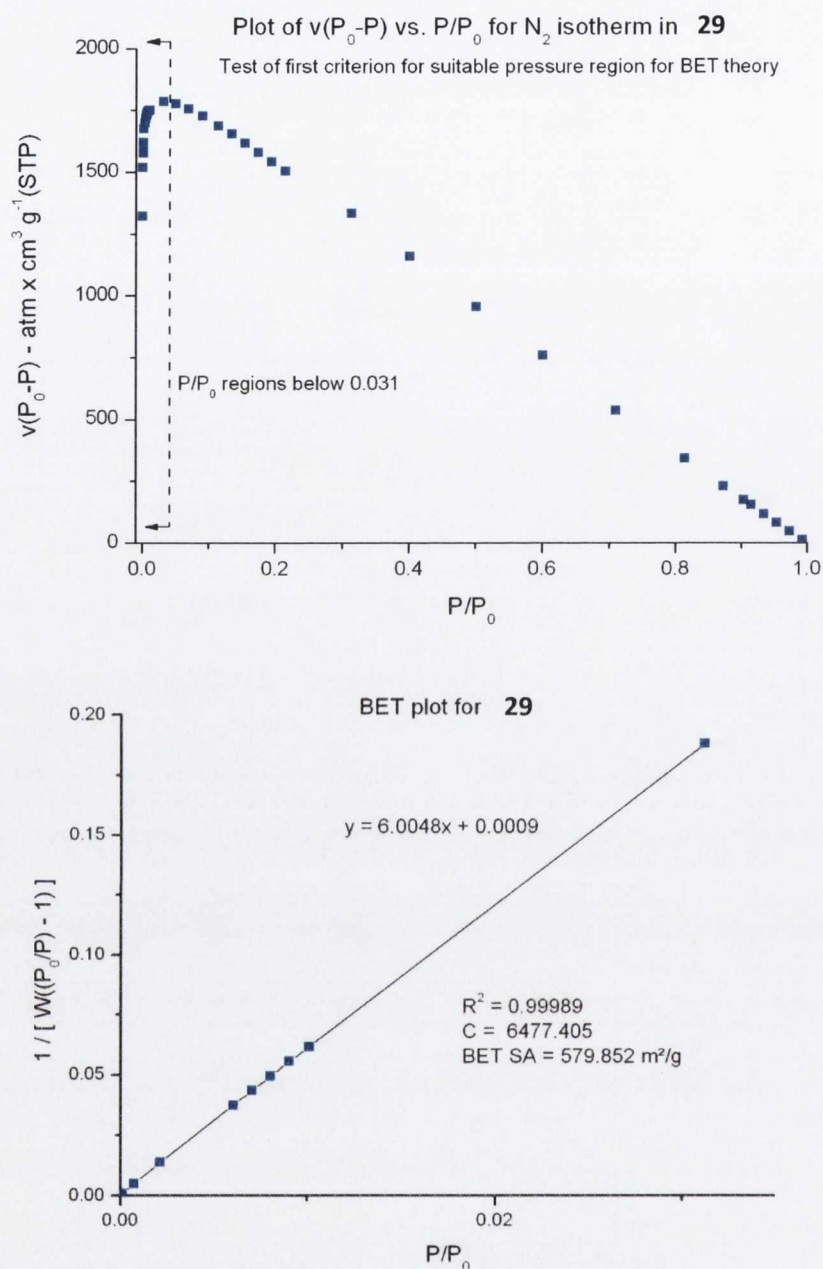


Figure 6.17: A plot of $V(P_0 - P)$ vs. P/P_0 to select a suitable pressure point region for the BET plot and the BET plot showing the positive y intercept and C value greater than 0 for A) compound 25, B) 27, C) 28 and D) 29.

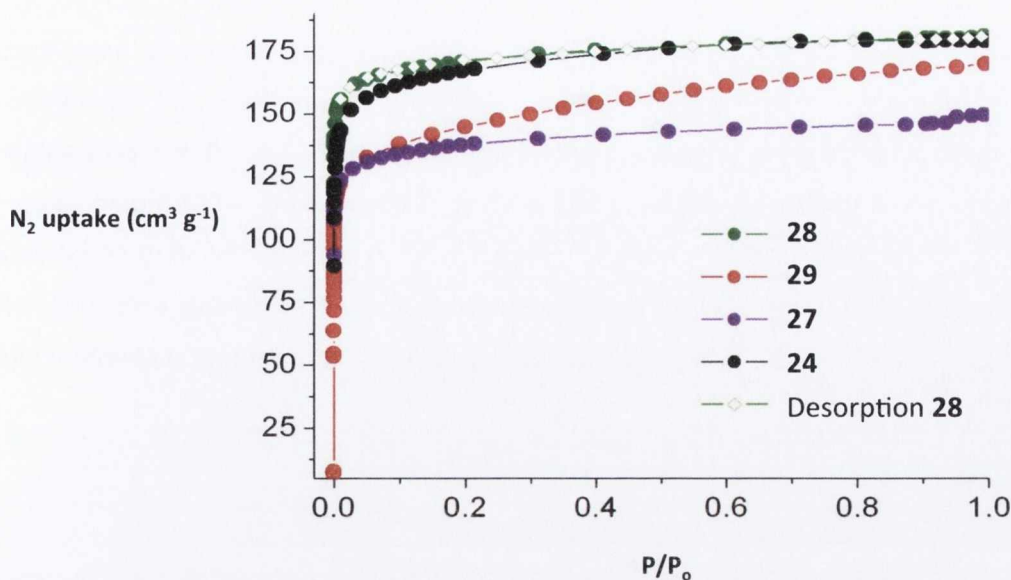


Figure 6.18: Nitrogen adsorption isotherms for **24** and **27-29**. Desorption isotherm for **28** is included to illustrate the continuity of the adsorption-desorption process and informs the reversibility of the process. This ‘overlapping’ adsorption-desorption profile occurs for each of the compounds.

Table 6.17: lists the crystallographic space group, cell parameters and calculated BET surface areas (m^2/g) for compounds **24** and **27-29**.

	Space group	a (Å)	c (Å)	Void Volume ($\text{\AA}^3$)	BET m^2/g
24	$P4_2/ncm$	27.979(3)	15.623(2)	12230	651
27	$P4_2/ncm$	27.825(2)	15.580(2)	12063	538
28	$P4_2/ncm$	27.564(2)	15.407(2)	11706	684
29	$P4_2/ncm$	27.678(2)	15.429(2)	11820	580

Applying BET theory to the nitrogen isotherms for **24** and **27-29**, reveal moderate BET surface areas of $651 \text{ m}^2/\text{g}$, $538 \text{ m}^2/\text{g}$, $684 \text{ m}^2/\text{g}$ and $580 \text{ m}^2/\text{g}$ respectively, Table 6.17. The shapes of the desorption and adsorption curves, Figure 6.18, are characteristic of compounds that contain micropores of less than $20 \text{ \AA}$ in diameter.⁵¹ The desorption and adsorption isotherms coincide. This observation is important as it characterises the reversible nature of the adsorption process and confirms that the compound’s porous, crystalline structure is stable throughout the gas adsorption process. It is conceivable that the relatively higher surface area of $684 \text{ m}^2/\text{g}$ for **28** arises from the location of the Na^+ ions in comparison to location of the Rb^+ and K^+ ions in **27** and **29**. The sizes, the sites and hence the counterion locations appear to effect the accessible void volume of the smaller pores, Figure 6.9B compared with Figure 6.10 B.

Compounds **25**, **26** and **30** did not reveal any porosity post degassing under vacuum at 85 °C for twelve hours. Further investigations revealed that it was not possible to obtain a powder XRD pattern for the degassed samples of **25**, **26** and **30**. It is probable that the zeolite-type structures collapse upon removal of the solvent water molecules from the pores. This is particularly prudent for **30** as it forms a non-crystalline material during the routine P-XRD experiments, as discussed above, and it is necessary to record its P-XRD pattern at 150 K using the Bruker APEX2 Duo diffractometer under a constant stream of nitrogen.

6.4.2 Hydrogen and carbon dioxide uptake

In addition to BET surface area characterisations, H₂ and CO₂ storage capabilities for **24** and **27-29** were evaluated. The H₂ storage capacities of **24** and **27-29** were calculated to be 8.32 mg/g, 7.06 mg/g, 10.59 mg/g and 7.34 mg/g at 1atm. These equate to 0.83 wt%, 0.71 wt%, 1.05 wt% and 0.73 wt%, respectively. The CO₂ sorption studies were undertaken at room temperature as CO₂ is a solid at 77K. In order to stabilise the temperature the sorption cell was submerged in a large water bath. The CO₂ storage capability of **24** and **27-29** at 290 K and 1 atm was found to be 142.57 mg/g, 132.71 mg/g, 207.66 mg/g and 181.19 mg/g, respectively. Equating to 12.48 wt%, 11.72 wt%, 17.20 wt%, and 15.34 wt%. The H₂ and CO₂ adsorption values are similar to those reported for compounds with comparable surface areas in the literature.¹⁹⁵ The H₂ and CO₂ adsorption isotherms for **24** and **27-29** are displayed in Figure 6.19 and Figure 6.20. The H₂ and CO₂ uptake characteristics are summarised in Table 6.18 and Table 6.19.

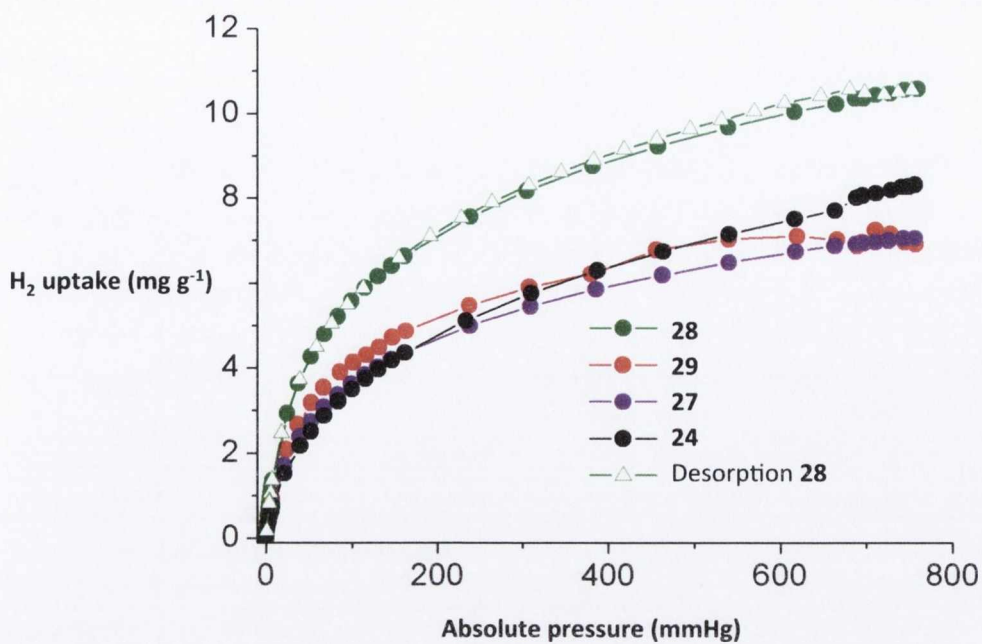


Figure 6.19: Absolute H₂ isotherms for 24 and 27-29 recorded at 77 K.

Table 6.18: Specifies the H₂ uptake capabilities, in mmol/g, mg/g and wt% H₂, of compounds 24 and 27-29

	H ₂ uptake (mmol/g)	H ₂ uptake (mg/g)	wt% (H ₂)
24	4.16	8.32	0.83
27	3.53	7.06	0.71
28	5.29	10.59	1.05
29	3.68	7.34	0.73

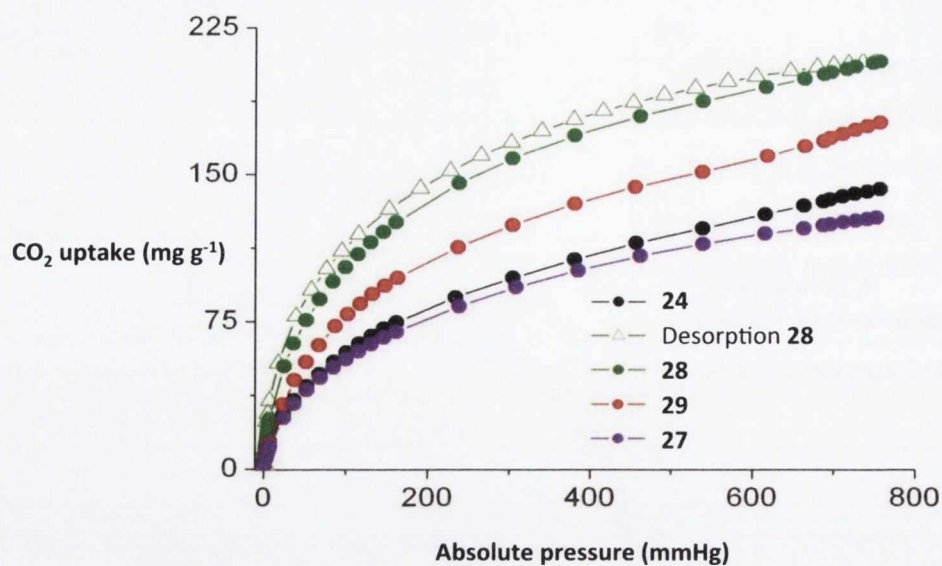


Figure 6.20: Absolute carbon dioxide isotherms for 24 and 27-29 recorded at 290 K.

Table 6.19: Details the carbon dioxide (CO₂) uptake capabilities, in mmol/g, mg/g and wt% CO₂, of compounds 24 and 27-29.

	CO ₂ uptake (mmol/g)	CO ₂ uptake (mg/g)	wt% (CO ₂)
24	3.24	142.57	12.48
27	3.02	132.71	11.72
28	4.71	207.66	17.20
29	4.12	181.19	15.34

Chapter 7 Conclusions

The synthesis, structural and solution characterisation of novel hybrid inorganic-organic materials based on the aqueous hydroxypropane-1,3-diamine-N,N,N',N'-tetraacetic acid (*hpdt*a) ligand have been presented within this thesis. The developed speciation protocols for systems containing the *hpdt*a ligand provide a tool for the identification of potentially catalytic species in solution. This is a fundamental consideration in the search for an appropriate CO₂ reduction system. The research also presents the gas storage capabilities and the fixation, storage and potential activation of carbon dioxide using selected *hpdt*a compounds.

The solution studies were performed under acidic, neutral and basic experimental conditions using compounds **1** and **4-7** as representatives of the Fe^{III} and Al^{III} *hpdt*a systems. The system was characterised using ²⁷Al, ¹³C, ¹H NMR and UV-Vis spectroscopic techniques in combination with ESI-MS. The studies confirmed the stability of the *hpdt*a based compounds in solution and demonstrated their ability to interchange between the aqueous square planar complexes **1** or **5**, the tetrahedral complexes **2** or **6** and the carbamate species **3** or **7** in response to the pH environment.

The complexity of the *hpdt*a/Fe^{III} hydrolytic reaction system was demonstrated through the successful isolation and structural characterisation of a range of novel polynuclear Fe^{III} compounds. These compounds include the dinuclear Fe^{III} compound (NH₃C₃H₆NH₃)_{0.5}K[Fe₂(*hpdt*a)(H₂*hpdt*a)]·4H₂O·NH₂C₃H₆NH₂ (**8**), compound **9** Na₇[{Fe₄(μ-O)(μ-OH)(*hpdt*a)₂(CO₃)(H₂O)₂}{Fe₆(μ-O)(μ-OH)₅(*hpdt*a)₃}]·4H₂O, that contains a hexanuclear and tetranuclear complex linked through {Na-O} bonding and, the trinuclear compound Na[Fe₃(H₂O)₂(μ-O)(C₉H₅N₂O₇)₂]·6H₂O (**10**). An investigation into Ni^{II} and V^{III} *hpdt*a systems yielded the mononuclear Ni^{II} compound EnH₂[Ni(H₁*hpdt*a)]·2H₂O (**11**) and the tetranuclear V^{IV} compound Na₈[V₄(μ-O)₂(*hpdt*a)₂(O)₄]·3H₂O (**12**).

The synthesis of the tetranuclear compound **13** and the three octanuclear compounds **14-16**, show that, the tetranuclear Fe^{III} compounds have the ability to react with the carboxylate functionalised ligands **L3-L6**. Their isolation provides insight into the necessary crystallisation conditions for these compounds and further characterises the coordination of the *hpdt*a ligand. The isolation of octanuclear compounds, **17** and **18**, demonstrate the solution behaviour of the Al^{III} and Mn^{III} metal ions in the aqueous *hpdt*a / 3-(4-carboxy-phenyl) propionic acid reaction system.

A series of novel complexes were prepared from reactions between the aminocarboxylic acid based ligand, *hpdta*, and Fe^{III} in the presence of suitable hydrolysing agents. The applied procedures were adapted from a typical protocol for similar hydrolytic reactions described by Schmitt *et al.*¹²³ Five novel transition metal compounds were successfully derived through aerial CO_2 fixation, the carbonate complex **20** and the carbamate compounds **21-24**. The latter do not decompose upon electrochemical analyses and display redox potentials ranging between -282 and +180 mV vs. NHE depending on the reaction conditions.

The Stern-Volmer approach was successfully utilized to investigate the interactions between $[\text{Ru}(\text{bpy})_3]^{2+}$, a known photosensitiser, and the tetranuclear carbamate complexes **3** and **21-24**. The compounds ability to scavenge electrons from an excited $[\text{Ru}(\text{bpy})_3]^{2+}$ molecule was established, both static and dynamic quenching was demonstrated within each system. The equilibrium constants (K_{sv}) ranged between 3148 and 6483 M^{-1} whilst the dynamic Stern-Volmer quenching resulted in values between 1.39×10^9 and $2.97 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ depending on the reaction conditions. These results indicated that the compounds have a potential to exhibit catalytic behaviour in the photo-catalytic reduction of carbon dioxide. Preliminary investigations of the catalytic behaviour of the carbonate compound **20** in an aqueous DMA reaction mixture in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ and methyl viologen further supports these findings.

Gas-chromatography-mass spectrometry (GC-MS) headspace analyses coupled with electrospray ionisation mass spectrometry (ESI-MS) of the resultant solutions demonstrated an absorption and desorption process which occurs upon consecutive pH adjustments of systems which contain the tetranuclear carbonate compound **20** and carbamate compounds **3** and **21-24**.

Finally, the isolation of **27-31** demonstrated the counter-ion mediated formation of a series of novel $\{\text{Al}_{15}\}$ zeotypic supramolecular assemblies. Their porosity was established through, experimentally determined, N_2 BET surface area analysis and surface areas of between 538 and 651 m^2/g were successfully demonstrated. CO_2 and H_2 adsorption isotherms revealed CO_2 uptakes ranging from *ca.* 132 to 207 mg/g and H_2 storage capacities of between *ca.* 7 and 11 mg/g.

Chapter 8 Experimental

8.1 Materials and Methods

8.1.1 Reagents

All chemicals and solvents were of reagent grade and purchased from Aldrich Chem. Co. Ltd., Fluka Chemica-Biochemica (U.K.) or local solvent suppliers, and used without further purification. Water was deionised before use.

8.1.2 Glassware preparation

Prior to use, all glassware was washed with deionised water, acetone, and dichloromethane (DCM) and was heated in an oven at 70°C for no less than 4 hours. Glass syringes, needles, and magnetic stirrer bars were treated similarly

8.1.3 Single Crystal X-ray Diffraction

X-ray analyses for crystals described in this report were performed by Dr. Tom McCabe, Dr. Lei Zhang, Dr. Brendan Twamley or I 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. The 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 SMART and SAINT-PLUS software.^{196,197} The structures were solved using direct methods with the SHELXTL 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.¹⁹⁸ Space group determination, structure solution and refinement were obtained using the Crystalstructure ver.3.8 and the Bruker SHELXTL software.¹⁹⁹ Datasets collected on the Bruker APEX2 Duo were processed and the structures solved using Bruker APEX v2011.8-0 software.²⁰⁰ Crystal

structure images were produced, using refined data sets, with the Diamond 2[®] software package.²⁰¹

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. Water hydrogen atoms or H atoms involved in hydrogen bonding, were located from difference maps and their positions refined with O-H distance restraints (DFIX) and isotropic thermal parameters fixed at 1.2 times that of the adjoining oxygen atom.

8.1.4 Infrared Spectroscopy

Infrared spectroscopy was recorded on a PerkinElmer Spectrum One FT-IR spectrometer using either a universal ATR sampling accessory or a diffuse reflectance sampling accessory. Data was collected and processed using Spectrum v5.0.1 (2002 PerkinElmer Instrument LLC) software. The scan rate was 4 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: s, strong; m, medium; w, weak; sh, shoulder and br, broad.

8.1.5 Thermogravimetric Analysis

Thermogravimetric analysis was carried out using a Perkin Elmer Pyris 1 TGA. The measurements, unless stated, were recorded in air using a platinum crucible (ca. 5 mg sample; heating rate of 1 °C; range 25-900 °C). The instrument was calibrated to Fe and Ni standards in air atmosphere.

8.1.6 Elemental Analysis

Elemental analysis was performed by the analytical laboratory, UCD Belfield using an Exeter Analytical CE 440.

8.1.7 Mass Spectrometry

GC mass spectra were collected by Dr. Martin Feeney, using a GC-MS (Gas Chromatography – Mass Spectrometry, LCT Premier) instrument supplied by Waters Corp. The Samples were introduced into the MS via a split mode injection port (2:1) set at 200°C, using an agilent 10µl gas tight syringe. The carrier gas was helium with a flow rate of 60 Lh⁻¹ and the column diameters were 30m x 0.250mm x 0.25µm. The isothermal temperature was set at 26°C. The retention window value for each scan was set between 0 and 60 minutes, m/z range set between 30 and 600, scan time at 0.9 sec and inter-scan delay set at 0.1 sec.

Electrospray ionization (ESI) mass spectra were collected by Dr. Martin Feeney, using a TOF-MS (Time-of-Flight – Mass Spectrometer, LCT Premier) instrument supplied by Waters Corp. An injection of a standard sodium formate ($\text{Na}[\text{CHO}_2\text{Na}]_n$, 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 110°C and 200°C , respectively. The ion polarity for all MS scans were recorded in negative mode with voltage of the capillary tip set between 2.0-3 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. All data, including simulated isotope patterns and molecular weight calculations, were processed using Masslynx v 4.0 (Waters Corp.) data analysis software.²⁰²

8.1.8 Fluorescence emission spectroscopy

Fluorescence spectra were recorded in the range 500-850 nm with an excitation wavelength of 450 nm, 2 nm grating and scan number = 14 on a Fluorolog Horiba Jobin Yvon spectrophotometer at room temperature using quartz cells of 1 cm path length, unless otherwise stated.

8.1.9 Lifetime emission spectroscopy

Lifetime fluorescence spectra were recorded using a Horiba Jobin Yvon Single Photon Counting Controller. The spectra were recorded in TSCP reverse mode using a 458 nm LED as the excitation source. The emission was recorded at 600 nm with a Coaxil delay of 40 ns, a TAC range of 2 microseconds, the peak pre-set was 10000 counts and the repetition rate was 1000 KHz. The polished quartz cell had a path length of 1cm, unless stated. All of the data was recorded and processed using the fluorohub data station operating programme and DAS6 data analysis software.

4.1.10 Nuclear magnetic resonance spectroscopy

^1H NMR spectra were recorded on a Bruker DPX 400 machine operating at 400.13 MHz by either Dr. John O'Brien or Dr. Manuel Rüther. Samples were carried out in deuterated solvents and are listed for each spectrum. Standard abbreviations for spectra: s, singlet; d, doublet; t, triplet; qt quartet; q, quaternary; m, multiplet; br broad, J, coupling constant.

8.1.10 X-ray powder diffraction

X-ray powder diffraction was performed using a Siemens D500 diffractometer or a Bruker APEX2 Duo diffractometer with $\text{Cu-K}\alpha_1$ radiation with a wavelength of $\lambda = 1.54056 \text{ \AA}$. Samples were analysed in 2θ range from 5° to 25° . The measurements, unless stated, were carried out at room temperature.

8.1.11 Ultraviolet-visible spectroscopy

UV-Vis spectra were recorded on a PerkinElmer Lambda 1050 UV/VIS/NIR spectrometer from 800 to 195 nm in 5nm intervals at a scan rate of 923.59 nm / min, using, unless stated, a quartz cell of 1cm path length.

8.1.12 Gas absorption measurements

N_2 , H_2 and CO_2 adsorption measurements were recorded on an Autosorb-IQ (Quantachrome) volumetric analyser. Sample were outgassed to 10^{-6} torr and at temperatures specific for each sample. The dead volume was estimated using helium, under the assumption that it is not absorbed at any of the studied temperatures. Measurements undertaken at 77 K were performed in a liquid N_2 bath. Room temperature measurements were conducted in a water bath. To provide optimal accuracy and precision in determining the p/p_0 the saturation pressure was measured throughout the experiments by means of a dedicated saturation pressure transducer. Ultra-high grade N_2 , H_2 , CO_2 and He (99.99 % purity) were used throughout the experiments. The non-ideality of gases were obtained from the second virial coefficient at experimental temperature.²⁰³ The surface area of the relevant samples was determined from the N_2 isotherms.

8.1.13 Electrochemistry

The electrochemical experiments were performed by Dr Tim Mc Cormac's research group in Dundalk Institute of Technology.

8.2 Synthesis of metal complexes from chapter 3

$\text{NH}_4[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4]\cdot 12.5\text{H}_2\text{O}$ (**1a**), $(\text{pipH}_2)_{1.5}[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})_3(\text{hpdta})_2]\cdot 6\text{H}_2\text{O}$ (**2a**), $(\text{enH})[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_2\text{H}_4\text{NH}_3)_2]\cdot 6.5\text{H}_2\text{O}$ (**3**), $\text{Na}_2[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{CO}_3)_2]\cdot \text{ca.}20\text{H}_2\text{O}$ (**4**) and $(\text{enH}_2)[\text{Al}_4(\mu\text{-OH})_4(\text{hpdta})_2]\cdot 7.5\text{H}_2\text{O}$ (**6**) were prepared according to literature methods.^{1, 2, 3}

8.2.1 $(\text{enH})[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4]\cdot n\text{H}_2\text{O}$ (**1b**)

0.081g (0.25 mmol) *hpdta* was dissolved in 3ml distilled water by drop wise addition of 75 μl of concentrated ethylenediamine. 0.202g (0.5mmol) $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was added to the reaction mixture followed by 30 μl concentrated ethylenediamine to adjust the pH to 4.5. Co-evaporation with 2.5ml dimethylacetamide led to the formation of red-orange crystals of **1b** after 4 days. The compound was dried for 24 hours at 120°C. Yield = 65% based on $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$. Chemical analysis for $(\text{enH})[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{H}_2\text{O})_4]$, **1b** with the loss of solvent water molecules. Calculated: C% 28.15, H% 4.33, N% 8.21, Fe% 21.81. Found: C% 28.29, H% 4.46, N% 8.34, Fe% 21.74. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3423 cm^{-1} (s, br); 3198 (sh); 1637 cm^{-1} (vs.); 1384 cm^{-1} (vs.); 919 cm^{-1} (m); 742 cm^{-1} (m); 606 cm^{-1} (m).

8.2.2 $(\text{enH}_2)_{1.5}[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})_3(\text{hpdta})_2]\cdot n\text{H}_2\text{O}$ (**2b**)

0.081g (0.25 mmol) *hpdta* was dissolved in 10ml distilled water by drop wise addition of 80 μl of concentrated ethylenediamine. 0.202g (0.5mmol) $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was added to the reaction mixture followed by 60 μl concentrated ethylenediamine to adjust the pH to 7.2. Co-evaporation with 5ml dimethylacetamide led to the formation of red-brown crystals of **2b** after 2 days. The compound was dried for 12 hours at 120°C. Yield = 67% based on $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$. Chemical analysis for $(\text{enH}_2)_{1.5}[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})_3(\text{hpdta})_2]$, **2b** with the loss of solvent water molecules. Calculated: C% 29.50, H% 4.36, N% 9.63, Fe% 21.94. Found: C% 29.41, H% 4.28, N% 9.55, Fe% 21.88. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3443 cm^{-1} (s, br); 1629 cm^{-1} (vs.); 1377 cm^{-1} (vs.); 910 cm^{-1} (m); 738 cm^{-1} (m); 612 cm^{-1} (m).

8.2.3 (enH)[Al₄(μ-O)(μ-OH)(hpdta)₂(H₂O)₄] $\cdot$ nH₂O (**5**)

0.081 g (0.25 mmol) *hpdta* was dissolved in 5ml distilled water by drop wise addition of 65μl of concentrated ethylenediamine. 0.188g (0.5mmol) Al(NO₃)₃·9H₂O was added to the reaction mixture followed by 45μl concentrated ethylenediamine to adjust the pH to 4.2. Co-evaporation with 2 ml dimethylacetamide led to the formation of white powders of **5** after 12 hours. The powder was dried for 24 hours at 120°C. Yield = 63% based on Al(NO₃)₃·9H₂O. Chemical analysis for (enH)[Al₄(μ-O)(μ-OH)(hpdta)₂(H₂O)₄], **5** with the loss of solvent water molecules. Calculated: C% 31.73, H% 4.88, N% 9.25. Found: C% 31.69, H% 4.96, N% 9.34. FT-IR (diffuse reflectance) $\nu_{\max}$ cm⁻¹: 3398 cm⁻¹ (s, br) 1588 cm⁻¹ (vs.); 1362 cm⁻¹ (vs.); 910 cm⁻¹ (m); 738 cm⁻¹ (m); 620 cm⁻¹ (m).

8.2.4 (enH)[Al₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₂H₄NH₃)₂] $\cdot$ nH₂O (**7**)

0.081 g (0.25 mmol) *hpdta* was dissolved in 15 ml distilled water by drop wise addition of 65μl of concentrated ethylenediamine. 0.188g (0.5mmol) Al(NO₃)₃·9H₂O was added to the reaction mixture followed by 67 μl concentrated ethylenediamine to adjust the pH to 8.5. Co-evaporation with 5ml dimethylacetamide led to the formation of white powders of **5** within 4 days. Yield = 48% based on Al(NO₃)₃·9H₂O. Elemental analysis, calculated for (enH)[Al₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₂H₄NH₃)₂], **7** with the loss of solvent water molecules: Calculated: C% 34.49, H% 5.02, N% 13.41. Found: C% 34.67, H% 5.11, N% 13.49%. IR data: 3387 cm⁻¹ (s, br); 1630 cm⁻¹ (vs.); 1540 cm⁻¹ (s); 1522 cm⁻¹ (ms); 1378 cm⁻¹ (vs.); 910 cm⁻¹ (m); 835 cm⁻¹ (m).

8.2.5 (NH₃C₃H₆NH₃)_{0.5}K[Fe₂(hpdta)(H₂hpdta)] $\cdot$ 4H₂O $\cdot$ NH₂C₃H₆NH₂ (**8**)

0.081g (0.25mmol) H₅hpdta was dissolved in 5ml of distilled water by addition of 0.5ml of a propylenediamine/potassium hydroxide solution (50:1 v:v). 0.135g (0.5mmol) FeCl₃·6H₂O was added to the reaction mixture followed by 0.77ml propylenediamine/potassium hydroxide solution (50:1 v:v) to adjust the pH to 8. The reaction vessel was sealed for 3 weeks followed by the addition of 2.5ml dimethylacetamide. Light green crystals of **2** formed from the unsealed vessel 4 days after the addition of dimethylacetamide. The compound was dried for 24 hours at 120°C. Yield = 54% based on FeCl₃·6H₂O. Chemical analysis for (NH₃C₃H₆NH₃)_{0.5}K[Fe₂(hpdta)(H₂hpdta)] $\cdot$ 4H₂O $\cdot$ NH₂C₃H₆NH₂ Calculated: C% 26.16, H%

4.97, N% 11.24, Fe% 12.80. K% 4.48. Found: C% 26.21, H% 5.01, N% 11.18, Fe% 12.73, K% 4.39. FT-IR (diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3372.39(s, br), 2931 (s), 1586 (vs), 1359 (s), 1306 (s), 1168 (m), 1114 (s), 1052 (m), 912 (s), 770 (m).

8.2.6 $\text{Na}_7\{[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdt})_2(\text{CO}_3)(\text{H}_2\text{O})_2]\{\text{Fe}_6(\mu\text{-O})(\mu\text{-OH})_5(\text{hpdt})_3\}\}\cdot 4\text{H}_2\text{O}$ (**9**)

0.081g (0.25mmol) H_5hpdt was dissolved in 10ml of deionised water by addition of 0.5ml sodium hydroxide solution (2M). 0.135g (0.5mmol) $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ was added to the reaction mixture followed by 0.15ml sodium hydroxide solution (0.1M) to adjust the pH to 7. Co-evaporation with 5 ml dimethylacetamide led to the formation of Dark red crystals of **9** after 2 weeks. The product co-crystallises with oxides and crystals of **9** were manually extracted from the reaction vessel. The compound was dried for 24 hours at 120°C . Yield = 22% based on $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$.

8.2.7 $\text{Na}[\text{Fe}_3(\text{H}_2\text{O})_2(\mu\text{-O})(\text{C}_9\text{H}_5\text{N}_2\text{O}_7)_2]\cdot 6\text{H}_2\text{O}$ (**10**)

0.081g (0.25mmol) H_5hpdt was dissolved in 10ml of distilled water by addition of 0.5ml sodium hydroxide solution (2M). 0.135g (0.5mmol) $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ was added to the reaction mixture and the pH was adjusted to 7.1 by the slow addition of 1ml (0.1M) sodium hydroxide solution. The solution was covered and left to stand for 24 hours followed by the addition of 0.081g (0.125mmol) of hemin ($\text{C}_{34}\text{ClFeH}_{32}\text{N}_4\text{O}_4$) and 2.5 ml of dimethylacetamide. The solution was refluxed for five days. Cubic red crystals of **10** formed 4 weeks after the refluxing process. The compound was dried for 24 hours at 120°C . Yield = 62% based on $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. Chemical analysis for $\text{Na}[\text{Fe}_3(\text{H}_2\text{O})_2(\mu\text{-O})(\text{C}_9\text{H}_5\text{N}_2\text{O}_7)_2]\cdot 6\text{H}_2\text{O}$ Calculated: C% 24.89, H% 4.41, N% 6.45, Fe% 19.28. Found: C% 25.01, H% 4.41, N% 6.62, Fe% 19.33. FT-IR (diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3342 (s, br), 2970 (vs), 2931 (m), 1614 (m), 1466 (m), 1378 (s), 1306 (m), 1159 (m), 1128 (s), 960 (vs), 816 (s).

8.2.8 $\text{enH}_2[\text{Ni}(\text{H}_1\text{hpdt})]\cdot 2\text{H}_2\text{O}$ (**11**)

0.081g (0.25mmol) H_5hpdt was dissolved in 15ml of distilled water by addition of 40 μl of concentrated ethylenediamine. 0.145g (0.5mmol) $\text{Ni}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ was added to the reaction mixture followed by 65 μl concentrated ethylenediamine to adjust the pH to 8.5. Light purple, plate like, crystals of **11** formed 5 days after the addition of dimethylacetamide. The compound was dried for 24 hours at 120°C . Yield = 81% based on $\text{Ni}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$. Chemical analysis for $\text{enH}_2[\text{Ni}(\text{H}_1\text{hpdt})]\cdot 2\text{H}_2\text{O}$ Calculated: C% 27.48,

H% 6.00, N% 12.82, Ni% 13.43. Found: C% 27.78, H% 5.91, N% 12.66, Ni% 13.12. FT-IR (diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3382 (s), 2926 (s), 1598 (vs), 1396 (s), 1316 (s), 1133 (m), 1067 (m), 922 (m), 912 (w), 727 (m).

8.2.9 $\text{Na}_8[\text{V}_4(\mu\text{-O})_2(\text{hpdta})_2(\text{O})_4]\cdot 3\text{H}_2\text{O}$ (**12**)

0.162g (0.5mmol) H_5hpdta was dissolved in 6ml of degassed distilled water, under a nitrogen atmosphere, by addition of 0.08g of sodium hydroxide. 0.157g (1mmol) VCl_3 was added to the reaction mixture followed by 3ml methanol and 0.02g of sodium hydroxide to adjust the pH to 4.3. Blue-silver, square shaped, crystals of **12** were obtained fifteen days after exposure to the atmosphere and co-evaporation with dimethylacetamide. Yield = 73% based on VCl_3 . Chemical analysis for $[\text{V}_4(\mu\text{-O})_2(\text{hpdta})_2(\text{O})_4](\text{Cl})_2\cdot 3\text{H}_2\text{O}$ Calculated: C% 17.61, H% 2.53, N% 5.87. Found: C% 17.88, H% 2.45, N% 5.93. FT-IR (diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3333 (s, br), 2923 (s), 1634 (vs), 1609 (vs), 1373 (s), 1319 (m), 1340 (m), 1268 (m), 944 (m), 913 (s).

8.3 Synthesis of metal complexes from chapter 4

8.3.1 $\text{Na}_3[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2\}\{(\text{OCC}_6\text{H}_5)\}_2]\cdot 12\text{H}_2\text{O}\cdot \text{DMF}$ (**13**)

0.162g (0.5mmol) H_5hpdta was dissolved in 5ml of a, degassed, distilled water/methanol solution (1:1 v/v) by addition of 0.07g sodium hydroxide. The reaction was performed under a nitrogen atmosphere. 0.270g (1mmol) $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ was added to the reaction mixture and the pH was adjusted to 7 by addition of 0.01g sodium hydroxide. 0.061g (0.5mmol) of benzoic acid was dissolved in 1ml of a, degassed, distilled water/methanol solution (1:1 v/v) by addition of 0.07g sodium hydroxide and was added to the reaction mixture followed by 5 ml dimethylformamide. Brown, reflective, plate like, crystals of **13** formed after 7 days. The compound was dried for 24 hours at 120°C . Yield = 58% based on $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. Chemical analysis for $\text{Na}_3[\{\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2\}\{(\text{OCC}_6\text{H}_5)\}_2]\cdot 12\text{H}_2\text{O}\cdot \text{DMF}$ Calculated: C% 31.41, H% 4.60, N% 4.70, Na% 4.62, Fe% 14.98. Found: C% 31.43, H% 4.62, N% 4.68, Na% 4.59, Fe% 14.95. FT-IR (diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3340 (s, br), 2925 (m), 1635 (s), 1590 (m), 1435 (m), 1385 (s), 1320 (m), 1110 (w), 910 (m).

8.3.2 $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2\{(\text{OOC}\text{C}_6\text{H}_4\text{COO})\}_2]\cdot 43\text{H}_2\text{O}$ (**14**)

The synthetic procedure for **13** was repeated in 18 ml of a, degassed, distilled water/methanol solution (5:1 v/v) and using 0.040g (0.25mmol) terephthalic acid rather than benzoic acid. Green-red, rectangular, crystals of **14** formed after 4 days. The compound was dried for 24 hours at 120°C. Yield = 66% based on $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. Chemical analysis for $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2\{(\text{OOC}\text{C}_6\text{H}_4\text{COO})\}_2]\cdot 43\text{H}_2\text{O}$ Calculated: C% 29.37, H% 4.60, N% 4.70, Na% 4.62, Fe% 14.98. Found: C% 29.32, H% 3.17, N% 5.54, Na% 7.46, Fe% 18.24. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3390 (s, br), 2932 (m), 1605 (s), 1540 (m), 1435 (m), 1370 (s), 1320 (m), 1113 (w), 910 (m).

8.3.3 $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2\text{hpdta}\}_2\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})\}_2]\cdot 35\text{H}_2\text{O}$ (**15**)

The synthetic procedure for **13** was repeated in 12 ml of a, degassed, distilled water/methanol solution (3:1 v/v) and using 0.030g (0.125mmol) 4,4'-biphenyl-dicarboxylic acid in place of benzoic acid. Dimethylformamide was used in place of dimethylacetamide as a co-solvent. Dark green-brown, rectangular, crystals of **15** formed after 10 days. The compound was dried for 24 hours at 120°C. Yield = 72% based on $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. Chemical analysis for $\text{Na}_8[\{\text{Fe}_4(\mu\text{-O})_2\text{hpdta}\}_2\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})\}_2]\cdot 35\text{H}_2\text{O}$ Calculated: C% 27.83, H% 4.51, N% 3.61, Na% 5.92, Fe% 14.38. Found: C% 27.85, H% 4.47, N% 3.56, Na% 5.95, Fe% 14.36. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3385 (s, br), 2925 (m), 1605 (s), 1540 (m), 1370 (s), 1320 (m), 1100 (w), 910 (m).

8.3.4 $\text{Na}_5(\text{H}_3\text{O})[\{\text{Fe}_4(\mu\text{-O})_2\text{hpdta}\}_2\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})\}_2]\cdot 15\text{H}_2\text{O}\cdot \text{DMA}\cdot \text{ligand}$ (**15a**)

0.081g (0.25mmol) H_5hpdta was dissolved in 7.4ml of distilled water by addition of 0.6ml sodium hydroxide solution (2M). 0.135g (0.5mmol) $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ was added to the reaction mixture and the pH was adjusted to 7 by the slow addition of 1ml (0.1M) sodium hydroxide solution. 0.030g (0.125mmol) 4,4-biphenyl-dicarboxylic acid was dissolved in 1ml of 0.1M sodium hydroxide solution and added to the reaction mixture followed by 5 ml dimethylacetamide. Light green, square, crystals of **15a**, formed after six days. The compound was dried for 24 hours at 120°C. Yield = 49% based on $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3347 (s, br), 2958 (s), 2929 (s), 1599 (vs), 1550 (s), 1327 (vs), 1052 (m), 1001 (s), 913(s), 830 (m).

8.3.5 $\text{Na}_{10}[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\text{Cl}_2\cdot 26\text{H}_2\text{O}$ (**16**)

The synthetic procedure for **13** was repeated in 7.4 ml of distilled water and using 0.024g (0.125mmol) 3-(4-carboxy-phenyl)propionic acid in place of benzoic acid. Light green, square, crystals of **16** formed after 10 days. The compound was dried for 24 hours at 120°C. Yield = 62% based on $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. Chemical analysis for $\text{Na}_{10}[\{\text{Fe}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\text{Cl}_2\cdot 26\text{H}_2\text{O}$ Calculated: C% 25.92, H% 4.11, N% 3.78, Na% 7.75, Fe% 15.06. Found: C% 26.01, H% 4.16, N% 3.83, Na% 7.69, Fe% 15.10. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3335 (s, br), 2923 (m), 1605 (s), 1570 (m), 1395 (s), 1340 (m), 1106 (w), 910 (m).

8.3.6 $\text{Na}_8[\{\text{Al}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\cdot 39\text{H}_2\text{O}$ (**17**)

The synthetic procedure for **16** was repeated in 10 ml of distilled water and using 0.081g (0.25mmol) *hpdta* and using 0.120g (0.5mmol) $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ in place of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. **17** precipitated as a white powder immediately following the addition of DMA. The powder was dried for 24 hours at 120°C. Yield = 59% based on $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$. Chemical analysis for $\text{Na}_8[\{\text{Al}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\cdot 39\text{H}_2\text{O}$ Calculated: C% 26.95, H% 5.19, N% 3.93, Na% 6.45. Found: C% 26.93, H% 5.21, N% 4.02, Na% 6.44. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3380 (s, br), 2927 (m), 1603 (s), 1422 (m), 1383 (s), 1326 (m), 1110 (w), 913 (m).

8.3.7 $\text{Na}_8[\{\text{Mn}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\cdot 25\text{H}_2\text{O}$ (**18**)

The synthetic procedure for **16** was repeated in 10 ml of distilled water and using 0.081g (0.25mmol) *hpdta* and using 0.10g (0.5mmol) $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ in place of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. **18** precipitated as a dark brown powder after 48 hours. The powder was dried for 24 hours at 120°C. Yield = 63% based on $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$. Chemical analysis for $\text{Na}_8[\{\text{Mn}_4(\mu\text{-O})_2(\text{hpdta})_2\}_2(\text{OOC}\text{C}_8\text{H}_8\text{COO})_2]\cdot 25\text{H}_2\text{O}$ Calculated: C% 27.22, H% 4.25, N% 3.97, Na% 6.51. Found: C% 27.85, H% 4.27, N% 3.96, Na% 6.49. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3381 (s, br), 2929 (m), 1612 (s), 1429 (m), 1383 (s), 1326 (m), 1108 (w), 913 (m).

8.4 Synthesis of metal complexes from chapter 5

8.4.1 $\{\text{Na}\}_5[\text{Fe}^{\text{III}}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{CO}_3)_2]\cdot 15\text{H}_2\text{O}$ (**19**)

0.081g (0.25mmol) H_5hpdta was dissolved in 6ml of deionised water by addition of 0.5ml sodium hydroxide solution (2M). 0.202g (0.5mmol) $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was added to the

reaction mixture followed by 0.25ml sodium hydroxide solution (0.1M) to adjust the pH to 8.5. Co-evaporation with 2.5 ml dimethylacetamide led to the formation of green crystals of **19** after 4 days. The compound was dried for 24 hours at 120°C. Yield = 55% based on $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $\{\text{Na}\}_5[\text{Fe}^{\text{III}}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{CO}_3)_2] \cdot 15\text{H}_2\text{O}$ Calculated: C% 20.65, H% 4.12, N% 4.01, Fe% 16.00 Na% 8.23. Found: C% 20.59, H% 4.15, N% 3.98, Fe% 16.08, Na% 8.29. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3376 (s, br), 2927 (s), 2925 (s), 1608 (vs), 1481 (br, m), 1324 (s), 1165 (m), 1055 (m), 1003 (m), 915 (s), 853 (w).

8.4.2 $(\text{NH}_2\text{C}_4\text{H}_8\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_4\text{H}_8\text{NH}_3)_2] \cdot 10\text{H}_2\text{O}$ (**20**)

The synthetic procedure for **19** was repeated using 1,4-diaminobutane, rather than (2M) sodium hydroxide solution, to adjust the pH to 8.5. **4** precipitated as a green powder within four days. The compound was dried for 24 hours at 120°C. Yield = 50% based on $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $(\text{NH}_2\text{C}_4\text{H}_8\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_4\text{H}_8\text{NH}_3)_2] \cdot 10\text{H}_2\text{O}$ Calculated: C% 30.35, H% 5.94, N% 9.83, Fe% 15.68. Found: C% 30.33, H% 5.88, N% 9.70, Fe% 15.64. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3327 (s, br), 2927 (s), 2890 (s), 1614 (s), 1557 (s), 1510 (s), 1366 (s), 1240 (s), 1219 (s), 999 (s), 914(s), 863 (s), 652 (m).

8.4.3 $(\text{NH}_2\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHNNH}_3)_2] \cdot 9\text{H}_2\text{O}$ (**21**)

The synthetic procedure for **19** was repeated using hydrazine, rather than (2M) sodium hydroxide solution, to adjust the pH to 8.5. Green powders of **21** formed within four days. The compound was dried for 24 hours at 120°C. Yield = 45% based on $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $(\text{NH}_2\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHNNH}_3)_2] \cdot 9\text{H}_2\text{O}$ Calculated: C% 23.28, H% 4.72, N% 11.31, Fe% 18.04. Found: C% 23.16, H% 4.64, N% 11.25, Fe% 18.06. FT-IR (diffuse reflectance) ν_{max} cm^{-1} : 3329 (s, br), 2934 (s), 2890 (s), 1622 (s), 1556 (s), 1507 (s), 1366 (s), 1240 (s), 1219 (s), 997 (s), 911(s), 863 (s), 652 (m).

8.4.4 $(\text{NH}_2\text{C}_6\text{H}_{12}\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_6\text{H}_{12}\text{NH}_3)_2] \cdot 9\text{H}_2\text{O}$ (**22**)

The synthetic procedure for **22** was repeated using hexamethylenediamine, rather than (2M) sodium hydroxide solution, to adjust the pH to 8.5. Green powders of **22** formed within four days. The compound was dried for 24 hours at 120°C. Yield = 45% based on $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $(\text{NH}_2\text{C}_6\text{H}_{12}\text{NH}_3)[\text{Fe}_4(\mu\text{-O})(\mu\text{-OH})(\text{hpdta})_2(\text{O}_2\text{CNHC}_6\text{H}_{12}\text{NH}_3)_2] \cdot 9\text{H}_2\text{O}$ Calculated: C% 33.84, H% 6.36, N% 9.40, Fe% 14.99. Found: C% 33.77, H% 6.29, N% 9.36, Fe% 15.04. FT-IR (diffuse reflectance) ν_{max}

cm⁻¹: 3365 (s, br), 2931 (s), 2919 (s), 1616 (vs), 1559 (s), 1500 (s), 1367 (vs), 1311 (s), 1162 (m), 1089 (m), 911(s), 863 (br), 663 (s).

8.4.5 (NHC₂H₄NC₄H₈NH₃)[Fe₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₂H₄NC₄H₈NH₂)₂].8H₂O (23)

The synthetic procedure for **19** was repeated using 1-(2-aminoethyl) piperazine, rather than (2M) sodium hydroxide solution, to adjust the pH to 8.5. Green powders of **23** formed within four days. The compound was dried for 24 hours at 120°C. Yield = 50% based on Fe(NO₃)₃·9H₂O. Chemical analysis for (NHC₂H₄NC₄H₈NH₃)[Fe₄(μ-O)(μ-OH)(hpdta)₂(O₂CNHC₂H₄NC₄H₈NH₂)₂].8H₂O Calculated: C% 33.37, H% 5.93, N% 12.05, Fe% 14.78. Found: C% 33.34, H% 5.90, N% 12.08, Fe% 14.73. FT-IR (diffuse reflectance) ν_{max} cm⁻¹: 3376 (s, br), 2935 (s), 2919 (s), 1623 (s), 1504 (s), 1439 (m), 1369 (vs), 1297 (s), 998 (s), 911 (s), 666 (vs).

8.5 Synthesis of metal complexes from chapter 6

(pipH₂)(H₃O)[Al₁₅(μ₃-O)₄(μ₃-OH)₆(μ-OH)₁₄(hpdta)₄].pipz·41H₂O (24) and (EnH₂)(H₃O)[Al₁₅(μ₃-O)₄(μ₃-OH)₆(μ-OH)₁₄(hpdta)₄].nH₂O (25) were prepared according to literature methods.⁴

8.5.1 (H₃O)₃[Al₁₅(μ₃-O)₄(μ₃-OH)₆(μ-OH)₁₄(hpdta)₄].23H₂O (26)

0.162g (0.5mmol) H₅hpdta was dissolved in a 6ml deionised water by addition of 120μl concentrated propylenediamine. 0.750g (2mmol) Al(NO₃)₃·9H₂O was dissolved in 15ml deionised water and added to the stirring hpdta solution. A further 120μl concentrated propylenediamine was slowly added to adjust the pH to ca. pH 8.5. Co-evaporation with dimethylacetamide formed colourless, rectangular shaped crystals of **26** within 4 days.

Yield = 62% based on Al(NO₃)₃·9H₂O. Chemical analysis for {(H₃O)₃[Al₁₅(μ₃-O)₄(μ₃-OH)₆(μ-OH)₁₄(hpdta)₄].23H₂O} Calculated: C% 20.73, H% 5.02, N% 4.40, Al% 15.88. Found: C% 20.53, H% 4.95, N% 4.21, Al% 15.95. FT-IR (diffuse reflectance) ν_{max} cm⁻¹: 3396 (s, br), 2944 (s), 1632 (vs), 1481 (br, m), 1387 (s), 1165 (m), 917 (s), 871 (w).

8.5.2 Rb₃[Al₁₅(μ₃-O)₄(μ₃-OH)₆(μ-OH)₁₄(hpdta)₄].43H₂O (27)

The synthetic procedure for **26** was repeated in 200ml deionised water using RbOH (1M) to adjust the pH to ca. pH 8.5. Colourless, rectangular, plates of **27** formed within 4 days.

Yield = 58% based on $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $\text{Rb}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 43\text{H}_2\text{O}$ Calculated: C% 17.00, H% 5.12, N% 3.60, Al% 13.02. Found: C% 17.09, H% 5.04, N% 3.57, Al% 12.98. FT-IR (diffuse reflectance) $\nu_{\text{max}} \text{ cm}^{-1}$: 3408 (s, br), 2931 (s), 1639 (vs), 1381 (s), 918 (s), 873 (w).

8.5.3 $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 36\text{H}_2\text{O}$ (28)

The synthetic procedure for **26** was repeated in 24ml deionised water using NaOH (2M) to adjust the pH to *ca.* pH 8.5. Colourless, rectangular, plates of **28** formed within 4 days. Yield = 61% based on $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $\text{Na}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 36\text{H}_2\text{O}$ Calculated: C% 18.91, H% 5.19, N% 4.01, Al% 14.48, Na% 2.47. Found: C% 18.84, H% 5.15, N% 3.97, Al% 14.39, Na% 2.45. FT-IR (diffuse reflectance) $\nu_{\text{max}} \text{ cm}^{-1}$: 3386 (s, br), 2931 (s), 1633 (vs), 1386 (s), 918 (s), 873 (w).

8.5.4 $\text{K}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 22\text{H}_2\text{O}$ (29)

The synthetic procedure for **26** was repeated in 20ml deionised water using KOH (2M) to adjust the pH to *ca.* pH 8.5. Colourless, rectangular, plates of **29** formed within 4 days. Yield = 58% based on $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $\text{K}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 22\text{H}_2\text{O}$ Calculated: C% 20.52, H% 4.35, N% 4.01, Al% 15.71. Found: C% 20.47, H% 4.51, N% 4.36, Al% 15.74. FT-IR (diffuse reflectance) $\nu_{\text{max}} \text{ cm}^{-1}$: 3391 (s, br), 2931 (s), 1639 (vs), 1385 (s), 918 (s), 873 (w).

8.5.5 $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 41\text{H}_2\text{O}$ (30)

The synthetic procedure for **26** was repeated in 34ml deionised water using CsOH (1M) to adjust the pH to *ca.* pH 8.5. Colourless, rectangular, plates of **30** formed within 4 days. Yield = 66% based on $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Chemical analysis for $\text{Cs}_3[\text{Al}_{15}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{14}(\text{hpdta})_4] \cdot 41\text{H}_2\text{O}$ Calculated: C% 16.52, H% 4.85, N% 3.50, Al% 12.65. Found: C% 16.55, H% 4.79, N% 3.46, Al% 12.71. FT-IR (diffuse reflectance) $\nu_{\text{max}} \text{ cm}^{-1}$: 3395 (s, br), 2931 (s), 1637 (vs), 1388 (s), 918 (s), 873 (w).

8.6 Preparation of samples for ^{27}Al , ^{13}C and ^1H , ESI-MS $^-$ and UV-Vis solution studies:

8.6.1 Reaction mixtures

0.32g (1mmol) *hpdt*a was dissolved in 400ml deionised water by addition of 8 μL concentrated ethylenediamine. 0.81g (2mmol) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or 0.48g (2mmol) $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was added followed by the successive addition of ca. 3 μL , ca. 4 μL and ca. 4 μL concentrated ethylenediamine to adjust the successive pH values to ca. pH 4.0, ca. pH 7.0 and ca. pH 10 respectively.

8.6.2 Metal complexes dissolved in solution

12.5 μmoles of compounds **1** and **5** were dissolved in 10ml aqueous $8 \times 10^{-4}\text{M}$ sulphuric acid solutions (pH 4). Final concentration of solutions = 1.2mM.

12.5 μmoles **2** and **6** were dissolved in 10ml deionised water. Final concentration of solutions = 1.2mM.

12.5 μmoles **3** and **7** were dissolved in 10ml solutions of an aqueous $2 \times 10^{-4}\text{M}$ ethylenediamine solution (pH 8.5). Final concentration of solutions = 1.2mM.

12.5 μmoles **1**, **3**, **5** and **7** were dissolved in 10ml deionised water. Final concentration of solutions = 1.2mM.

1.5ml samples were removed from the reaction mixtures at each pH value and from the metal complexes dissolved in solution for spectroscopic analysis. Prior to analysis 0.5ml deuterated water was added to the solutions for the NMR studies and the samples for UV-Vis spectroscopic studies were diluted, using deionised water, by a factor of 10.

8.7 The capture and release of CO_2

8.7.1 **3 and 19-23 dissolved in an aqueous $2 \times 10^{-4}\text{M}$ ethylenediamine solution**

Five identical solutions were prepared and treated as described below. At each step a solution was sent for ESI-MS $^-$ analysis.

Release of CO₂ through addition of an acid

0.01mmoles of metal complex was dissolved in 100µl of an aqueous 2x10⁻⁴M ethylenediamine solution and added to a GC-MS vial followed by 50µl of an aqueous 1x10⁻³M sulphuric acid solution. The vial was sealed with a septum and covered with parafilm. Headspace analysis was performed after 2 and 24 hours.

Absorption of CO₂ through addition of ethylenediamine

After 24 hours 10µl of ethylenediamine was added to the vial through the septum, using a gas tight micro syringe. Headspace analysis was performed after 10 and 20 minutes.

Rerelease of CO₂ through addition of an acid

After 20 minutes 50µl of an aqueous 1x10⁻³ M sulphuric acid solution was added to the vial through the septum, using a gas tight micro syringe. After 24 hours the headspace analysis was performed.

Reabsorption of CO₂ through addition of ethylenediamine

After 24 hours a second 10µl of ethylenediamine was added to the vial through the septum, using a gas tight micro syringe. Headspace analysis was performed after 10 and 20 minutes.

8.7.2 3 and 19-23 as solids

The procedures as described above were repeated using 0.01mmol of metal complexes **3** and **19-23**.

8.7.3 Control experiments

The experiments described above were repeated using 0.01mmol of **2** in place of the CO₂ trapping compounds **3** and **19-23**.

The experiments were also repeated in the absence of a metal compound using 100µl of deionised water and 100µl of the aqueous 2x10⁻⁴M ethylenediamine solution.

Aqueous 2x10⁻⁴M ethylenediamine solutions containing 0.0025mmoles, 0.005mmoles and 0.01mmoles of the CO₂ trapping compounds **3** and **19-23** were acidified by addition of 50µl of an aqueous 1x10⁻³ M sulphuric acid solution in order to convey the underlying roles of **3** and **19-23** in the examined process. GC-MS headspace analysis was performed after 24 hours.

8.8 Preparation of solutions for fluorescence and lifetime titration

1ml $[\text{Ru}(\text{bpy})_3]^{2+}$ ($2 \times 10^{-2} \text{mM}$) was added to a 5mm^3 quartz cuvette. The solution was titrated with $50 \mu\text{l}$ of a metal complex stock solution ($1 \times 10^{-2} \text{M}$) in $5 \mu\text{l}$ aliquots. Fluorescence and lifetime spectra were recorded for metal concentrations of 0mM , $5 \times 10^{-2} \text{mM}$, $1 \times 10^{-1} \text{mM}$, $1.5 \times 10^{-1} \text{mM}$, $2 \times 10^{-1} \text{mM}$, $2.5 \times 10^{-1} \text{mM}$, $3 \times 10^{-1} \text{mM}$, $3.5 \times 10^{-1} \text{mM}$, $4 \times 10^{-1} \text{mM}$, $4.5 \times 10^{-1} \text{mM}$ and $5 \times 10^{-1} \text{mM}$.

The experiment was repeated for metal complex = **2**, **3** and **19-23**.

8.9 Methyl viologen experiments

Sample preparation:

0.51g MV^{2+} (0.2mmoles), $24 \mu\text{L}$ of a 0.025M stock solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ ($5.9 \times 10^{-1} \mu\text{moles}$) and 8ml (5.34mmoles) triethanolamine were added to a 10ml volumetric flask and made up to the meniscus using deionised water.

Experimental procedure:

The previously reported Methyl viologen experiment was slightly modified by the use of N_2 in place of CO_2 .¹⁹³ 3ml of the sample was bubbled with N_2 at a flow rate of 2ml/minute and irradiated for 30minutes . The solution was subsequently transferred into a 5ml test tube and stirred continuously. $200 \mu\text{moles}$ of **19** was added to the solution in $50 \mu\text{molar}$ intervals. Colour changes were observed.

8.10 Preparation of stock solutions for CO_2 reduction experiments

0.0158g ($125 \mu\text{moles}$) of **3** was dissolved in a 0.5ml of an aqueous $2 \times 10^{-4} \text{M}$ ethylenediamine solution ($\text{pH } 8.5$). 0.5ml ($125 \mu\text{moles}$) of $[\text{Ru}(\text{bpy})_3]^{2+}$ stock solution (0.025M) was added followed by 101ml of an aqueous $2 \times 10^{-4} \text{M}$ ethylenediamine solution ($\text{pH } 8.5$) final concentration = $122 \mu\text{M}$.

8.10.1 Experiment 1: Measured using 1cm square quartz cuvette – in the absence of dimethylacetamide (DMA) and CO_2 .

2.5ml of the $122 \mu\text{M}$ stock solution and 1ml deionised water was added to a 1cm square quartz cuvette (final concentration = $87.5 \mu\text{M}$). The quartz cuvette was sealed with a septum. The sample was irradiated for 30minutes . The sample was re-irradiated for 30minutes and the UV-Vis absorption spectrum was re-recorded.

8.10.2 Experiment 2: Measured using 1cm square quartz cuvette – in the presence of dimethylacetamide (DMA) and CO₂.

2.5ml of the 122 μ M stock solution and 1ml DMA was added to the 1cm square quartz cuvette (final concentration = 87.5 μ M). The quartz cuvette was sealed with a septum. The sample was bubbled with CO₂ at a flow rate of 2 ml/minute for 25 minutes through a needle inserted into the septum). The sample was irradiated for 30 minutes. UV-Vs absorption spectra were recorded after irradiation. The experiment was repeated using 5mm square and 2mm rectangular quartz cuvettes.

8.10.3 Experiment 3: Measured using 5mm square quartz cuvette – in the absence of dimethylacetamide (DMA) and the presence CO₂.

2.5ml of the 122 μ M stock solution and 1ml deionised water was added to a 10 ml test tube (final concentration of = 87.5 μ M). The test tube was sealed with a septum and the sample was bubbled with CO₂ at a flow rate of 2 ml/minute for 25 minutes through a needle inserted into the septum. 1ml of the sample was added to the 5mm square quartz cuvette that was subsequently sealed with a septum. The sample was irradiated for 30 minutes. The experiment was repeated using a 2mm rectangular quartz cuvette.

References

1. W. Schmitt, P. A. Jordan, R. K. Henderson, G. R. Moore, C. E. Anson, A. K. Powell, *Coordination Chemistry reviews*, 2002, **228** (2), 115-126.
2. W. Schmitt, C. E. Anson, R. Sessoli, M. van Veen, A. K. Powell, *Journal Of Inorganic Biochemistry*, 2002, **91** (1), 173-189.
3. W. Schmitt, *Hydrolyse von Eisen (III)- und aluminium(III)salzen in aminocarbonsäure-stabilisierten, protischen reaktionssystemen*, Universität Karlsruhe (Germany), 2002.
4. W. Schmitt, E. Baissa, A. Mandel, C. E. Anson, A. K. Powell, *Angewandte Chemie International Edition*, 2001, **40**, 5.
5. G. M. J. Schmidt, *Pure and Applied Chemistry*, 1971, **27**, 647-678.
6. S. Maginn, *Journal of Applied Crystallography*, 1991, **24** (3), 265.
7. I. P. Parkin, *Applied Organometallic Chemistry*, 2001, **15** (3), 236-236.
8. G. R. Desiraju, *Angewandte Chemie International Edition*, 1995, **34**, 2311.
9. E. Weber, Y. Aoyama, *Design of Organic Solids*, Springer, 1998.
10. J.-M. Lehn, *Angew. Chem. Int. Ed.*, 1990, **29**, 1304-1319.
11. R. R. Sinden, *DNA Structure and Function*, Academic Press, 1994.
12. W.H. Casey, B.L. Phillips, G. Furrer, *Reviews in Mineralogy and Geochemistry*, 2001, **44**, 167.
13. W. H. Casey, M. M. Olmstead, B. L. Phillips, *Inorganic Chemistry*, 2005, **44**, 4888.
14. L. Allouche, C. Gérardin, T. Loiseau, G. Férey, F. Taulelle, *Angewandte Chemie International Edition*, 2000, **39**, 511.
15. Y. Izumi, K. Urabe, M. Onaka, *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*, Kodansha Ltd., Tokyo 1992, pp 100-105.
16. <http://www.usetute.com.au/zeolites.html>, Accessed 22/05/2014.
17. A. W. Chester, E. G. Derouane, *Zeolite Characterization and Catalysis: A Tutorial*, Springer, 2009.
18. C. Baerlocher, L. B. Mc Cusker, D. H. Olson, *Atlas of Zeolite Framework Types*, Elsevier Science, 2007.
19. S. Bhatia, *Zeolite Catalysts: Principles and Applications*, Taylor & Francis, 1989.
20. T. Duan, T. Nakano, Y. Nozue, *e-Journal of Surface Science and Nanotechnology*, 2007, **5**, 6-11, Accessed 03/04/2013.
21. G. Férey, *Chemistry of Materials*, 2001, **13**, 3084.
22. J. V. Smith, *Chemical Reviews*, 1988, **88**, 149.
23. J. B. Parise, *Inorganic Chemistry*, 1985, **24**, 4312.
24. S. M. Kuznicki, U.S. Patent 4 853 202, 1989.
25. C. Sanchez, F. Ribot, T. Lalot, C. R. Mayer, V. Cabuil, *Chemistry of Materials*, 2001, **13**, 3061-3083.
26. D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Accounts of Chemical Research*, 2005, **38**, 273.
27. K. Byrappa, M. Yoshimura, *Handbook of Hydrothermal Technology*, Elsevier Science, 2008.
28. P. M. Forster, A. R. Burbank, C. Livage, G. Férey, A. K. Cheetham, *Chemical Communications*, 2004, 368.
29. P. M. Forster, N. Stock, A. K. Cheetham, *Angewandte Chemie International Edition*, 2005, **44**, 7608.
30. S. Bauer, T. Bein, N. Stock, *Inorganic Chemistry*, 2005, **44** (16), 5882-5889.
31. F. Feigl, *Journal of the Brazilian Chemical Society*, 1944, **3**.
32. J. H. Rayner, H. M. Powell, *Journal of the Chemical Society*, 1952, 319.
33. L. R. MacGillivray, *Metal-Organic Frameworks: Design and Application*, Wiley, 2010.
34. A. Thirumurugan, M. B. Avinash, C. N. Rao, *Dalton Transactions*, 2006, 221.
35. H. Li, M. Eddaoudi, M. O'Keefe, O. M. Yaghi, *Nature*, 1999, **402**, 276.

36. A. Thirumurugan, C. N. R. Rao, *Journal of Materials Chemistry*, 2005, **15**, 3852.
37. P. M. Forster, A. K. Cheetham, *Angewandte Chemie International Edition*, 2002, **41**, 457.
38. R. Vaidhyanathan, S. Natarajan, C. N. Rao, *Dalton Transactions*, 2003, 1459.
39. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature*, 2003, **423** (6941), 705-714.
40. M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Accounts of Chemical Research*, 2001, **34** (4), 319-330.
41. H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim, O. M. Yaghi, *Science*, 2010, **329** (5990), 424-428.
42. N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science*, 2003, **300** (5622), 1127-1129.
43. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science*, 2002, **295** (5554), 469-72.
44. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science*, 2002, **295**, 583.
45. H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim, O. M. Yaghi, *Science*, 2010, **329**, 425.
46. J. R. Li, R. J. Kuppler, H. C. Zhou, *Chemical Society Reviews*, 2009, **38** (5), 1477-1504.
47. M. Dierendonck, S. De Koker, C. Cuvelier, J. Grooten, C. Vervaet, J. P. Remon, B. G. De Geest, *Angewandte Chemie International Edition*, 2010, **49** (46), 8620-8624.
48. Z. Wang, G. Chen, K. L. Ding, *Chemical Reviews*, 2009, **109** (2), 322-359.
49. K. M. Fromm, *Coordination Chemistry Reviews*, 2008, **252** (8-9), 856-885.
50. D. P. Broom, *International Journal of Hydrogen Energy*, 2007, **32** (18), 4871-4888.
51. J. Rouquerol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pernicone, J. D. Ramsay, K. S. Sing, K. K. Unger, *Pure and Applied Chemistry*, 1994, **66**, 1739-1758.
52. K. S. Walton, R. Q. Snurr, *Journal of the American Chemical Society*, 2007, **129** (27), 8552-8556.
53. H. Furukawa, M. A. Miller, O. M. Yaghi, *Journal of Materials Chemistry*, 2007, **17** (30), 3197-3204.
54. M. Kondo, T. Yoshitomi, H. Matsuzaka, S. Kitagawa, K. Seki, *Angewandte Chemie International Edition*, 1997, **36** (16), 1725-1727.
55. M. P. Suh, H. J. Park, T. K. Prasad, D. W. Lim, *Chemical Reviews*, 2011, **112** (2), 782-835.
56. D. Zhao, D. Yuan, H. C. Zhou, *Energy and Environmental Science*, 2008, **1**, 222.
57. H. Frost, T. Duren, R. Q. Snurr, *The Journal of Physical Chemistry B*, 2006, **110** (19), 9565-70.
58. H. Frost, R. Q. Snurr, *The Journal of Physical Chemistry C*, 2007, **111** (50), 18794-18803.
59. *Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles*; US Department of Energy: 2009/09//, 2009.
60. M. Hirscher, K. Hirose, *Handbook of Hydrogen Storage: New Materials for Future Energy Storage*, Wiley, 2010.
61. H. L. Jiang, T. A. Makal, H. C. Zhou, *Coordination Chemistry reviews*, 2013, **257** (15-16), 2232-2249.
62. S. S. Chui, S. M. Lo, J. P. Charmant, A. G. Orpen, I. D. Williams, *Science*, 1999, **283** (5405), 1148-1150.
63. V. K. Peterson, Y. Liu, C. M. Brown, C. J. Kepert, *Journal of the American Chemical Society*, 2006, **128** (49), 15578-15579.
64. Y. Liu, C. M. Brown, D. A. Neumann, V. K. Peterson, C. J. Kepert, *Journal of Alloys and Compounds*, 2007, **446-447**, 385-388.

65. P. Bénard, R. Chahine, *Scripta Materialia*, 2007, **56** (10), 803-808.
66. S. Ma, J. Eckert, P. M. Forster, J. W. Yoon, Y. K. Hwang, J. S. Chang, C. D. Collier, J. B. Parise, H. C. Zhou, *Journal of the American Chemical Society*, 2008, **130** (47), 15896-15902.
67. H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keefe, J. Kim, O. M. Yaghi, *Science*, 2010, **329**, 424.
68. <http://co2now.org/>, Accessed 13/01/2011, 2011.
69. http://www.ipcc.ch/publications_and_data/publications_and_data_reports.shtml, Accessed 02/12/2010, 2010.
70. A.H. Tinnemans, T.P. Koster, D. Thewissen, A. Mackor, *Recueil des Travaux Chimiques des Pays-Bas Journal of the Royal Netherlands Chemical Society*, 1984, **103**, 288.
71. T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature*, 1979, **277** (5698), 637-638.
72. O. Ishitani, C. Inoue, Y. Suzuki, T. Ibusuki, *Journal of Photochemistry and Photobiology A: Chemistry*, 1993, **72** (3), 269-271.
73. H. Ishida, T. Terada, K. Tanaka, T. Tanaka, *Inorganic Chemistry*, 1990, **29**, 905-911.
74. K. R. Thampi, J. Kiwi, M. Gratzel, *Nature*, 1987, **327** (6122), 506-508.
75. H. Fujiwara, H. Hosokawa, K. Murakoshi, Y. Wada, S. Yanagida, T. Okada, H. Kobayashi, *The Journal of Physical Chemistry B*, 1997, **101** (41), 8270-8278.
76. T. Ogata, S. Yanagida, B. S. Brunschwig, E. Fujita, *Journal of the American Chemical Society*, 1995, **117**, 6708-6716.
77. E. Fujita, *Coordination Chemistry Reviews*, 1999, **185-186**, 373-384.
78. J. Grodkowski, T. Dhanasekaran, P. Neta, P. Hambright, B. S. Brunschwig, K. Shinozaki, E. Fujita, *Journal of Physical Chemistry A*, 2000, **104**, 11332-11339.
79. K. Ikeue, H. Yamashita, M. Anpo, T. Takewaki, *The Journal of Physical Chemistry B*, 2001, **105** (35), 8350-8355.
80. J. H. Jeoung, H. Dobbek, *Science*, 2007, **318** (5855), 1461-1464.
81. Q. Chen, Y. Qian, *Chemical Communications*, 2001, **15**, 1402-1403.
82. M. M. Taqui-Khan, J. Bhatt, *Bulletin of the Chemical Society of Japan*, 1990, **63**, 2393-2396.
83. S. Matsuoka, K. Yamamoto, T. Ogata, M. Kusaba, N. Nakashima, E. Fujita, S. Yanagida, *Journal of the American Chemical Society*, 1993, **115**, 601-609.
84. T. Ogata, Y. Yamamoto, Y. Wada, K. Murakoshi, M. Kusaba, N. Nakashima, A. Ishida, S. Takamuku, S. Yanagida, *Journal of Physical Chemistry*, 1995, **99**, 11916-11922.
85. J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R. D. Srivastava, *International Journal of Greenhouse Gas Control*, 2008, **2** (1), 9-20.
86. R. R. Willis, A. I. Benin, R. Q. Snurr, A. O. Yazaydin, "Nanotechnology for Carbon Dioxide Capture" in "Nanotechnology for the Energy Challenge", Wiley, 2010.
87. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, *Chemical Reviews*, 2011, **112** (2), 724-781.
88. C. A. Scholes, K. H. Smith, S. E. Kentish, G. W. Stevens, *International Journal of Greenhouse Gas Control*, 2010, **4** (5), 739-755.
89. O. Shekhah, J. Liu, R. A. Fischer, C. Woll, *Chemical Society Reviews*, 2011, **40** (2), 1081-1106.
90. J. R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H. K. Jeong, P. B. Balbuena, H. C. Zhou, *Coordination Chemistry reviews*, 2011, **255** (15-16), 1791-1823.
91. Y. Yoo, H. K. Jeong, *Chemical Communications*, 2008, **21**, 2441-2443.
92. D. Zacher, O. Shekhah, C. Woll, R. A. Fischer, *Chemical Society Reviews*, 2009, **38** (5), 1418-1429.
93. S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, *Journal of the American Chemical Society*, 2008, **130** (33), 10870-10871.
94. N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keefe, O. M. Yaghi, *Journal of the American Chemical Society*, 2005, **127**, 1504.

95. J. L. C. Rowsell, O. M. Yaghi, *Journal of the American Chemical Society*, 2006, **128** (4), 1304-1315.
96. W. Zhou, H. Wu, T. Yildirim, *Journal of the American Chemical Society*, 2008, **130** (46), 15268-15269.
97. D. Britt, H. Furukawa, B. Wang, T. G. Glover, O. M. Yaghi, *Proceedings of the National Academy of Sciences U.S.A.*, 2009, **106**, 20637.
98. P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. J. Zaworotko, *Nature*, 2013, **495** (7439), 80-84.
99. A. R. Millward, O. M. Yaghi, *Journal of the American Chemical Society*, 2005, **127** (51), 17998-17999.
100. K. T. Chue, J. N. Kim, Y. J. Yoo, S. H. Cho, R. T. Yang, *Industrial & Engineering Chemistry Research*, 1995, **34** (2), 591-598.
101. [http://www.molecularsieve.org/Zeolite Molecular Sieve.htm](http://www.molecularsieve.org/Zeolite_Molecular_Sieve.htm), Accessed 01/07/2014, 2014.
102. [http://www.buyactivatedcharcoal.com/what is activated charcoal](http://www.buyactivatedcharcoal.com/what_is_activated_charcoal), Accessed 03/07/2014, 2014.
103. D. Walther, M. Ruben, S. Rau, *Coordination Chemistry reviews*, 1999, **182**, 67-100.
104. A. J. Morris, G. J. Meyer, E. Fujita, *Accounts of Chemical Research*, 2009, **42** (12), 1983-1994.
105. E. Fujita, *Coordination Chemistry reviews*, 1999, **185-186**, 373-384.
106. X. Wang, P. He, Y. Fang, *Journal of Luminescence*, 2010, **130**, 1481-1484.
107. B. O'Regan, M. Gratzel, *Nature*, 1991, **353**, 737.
108. L. Hammarstrom, S. Styring, *Philosophical Transactions of the Royal Society*, 2008, **363**, 1283-1291.
109. L. Sun, M. K. Raymond, A. Magnuson, D. LeGourrierec, M. Tamm, M. Abrahamsson, P. H. Kenez, J. Martensson, G. Stenhagen, L. Hammarstrom, S. Styring, B. Akermarck, *Journal of Inorganic Biochemistry*, 2000, **78**, 15-22.
110. S. Lima, R. Leandro Bonifacio, G. C. Azzellini, N. Coichev, *Talanta*, 2002, **56**, 547-556.
111. J. M. Lehn, R. Ziessel, *Journal of Organometallic Chemistry*, 1990, **382**, 157-73.
112. J. M. Lehn, R. Ziessel, *Proc. Natl. Acad. Sci. U. S. A.*, 1982, **79**, 701-704.
113. C. A. Craig, L. O. Spreer, J. W. Otvos, M. Calvin, *Journal of Physical Chemistry*, 1990, **94**, 7957-7960.
114. J. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos, M. Calvin, *Dalton Transactions*, 1987, 2105-2109.
115. B. Gholamkhash, H. Mametsuka, K. Koike, T. Tanabe, M. Furue, O. Ishitani, *Inorganic Chemistry*, 2005, **44**, 2326-2336.
116. M.D. Doherty, D.C. Grills, E. Fujita, *Inorganic Chemistry*, 2009, **48**, 1796.
117. H. Takeda, K. Koike, H. Inoue, O. Ishitani, *Journal of the American Chemical Society*, 2008, **130**, 2023.
118. M. D. Doherty, D. C. Grills, J. T. Muckerman, D. E. Polyansky, E. Fujita, *Coordination Chemistry reviews*, 2010, **254**, 2472-2482.
119. B. Gholamkhash, H. Mametsuka, K. Koike, T. Tanabe, M. Furue, O. Ishitani, *Inorganic chemistry*, 2005, **44** (7), 2326-2336.
120. Z. Y. Bian, K. Sumi, M. Furue, S. Sato, K. Koike, O. Ishitani, *Inorganic Chemistry*, 2008, **47** (23), 10801-10803.
121. G. Anderegg, F. Arnaud-Neu, R. Delgado, J. Felcman, K. Popov, *Pure and Applied Chemistry*, 2005, **77**, 1445-1495.
122. H. Wullens, B. Tinant, J.-P. Declercq, M. Devillers, *Inorganica Chimica Acta*, 2003, (343), 7.
123. W. Schmitt, C. E. Anson, R. Sessoli, M. van Veen, A. K. Powell, *Journal of Inorganic Biochemistry*, 2002, **91**, 173-189.

124. W. Schmitt, C. E. Anson, B. Pilawa, A. K. Powell, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2443-2457.
125. S. B. Mukkamala, R. Clerac, C. E. Anson, A. K. Powell, *Polyhedron.*, 2006, **25**, 8.
126. S. M. Gorun, R. T. Stibrany, A. Lillo, *Inorganic Chemistry*, 1998, **37**, 2.
127. W. Schmitt, P. A. Jordan, R. K. Henderson, G. R. Moore, C. E. Anson, A. K. Powell, *Coordination Chemistry Reviews*, 2002, **228**, 115-126.
128. J. Frohlich, S. Berger, *Synlett*, 2005, **16**, 2522.
129. C. I. Onet, L. Zhang, R. Clérac, J. B. Jean-Denis, M. Feeney, T. McCabe, W. Schmitt, *Inorganic chemistry*, 2010, **50** (2), 604-613.
130. C. F. Geraldès, M. C. Alpoim, M. P. Marques, A. D. Sherry, M. Singh, *Inorganic chemistry*, 1985, **24**, 3876.
131. M. K. Johnson, D. B. Powell, R. D. Cannon, *Spectrochimica Acta Part A*, 1981, **37** (11), 11.
132. C. K. Huang, P. F. Kerr, *The American Mineralogist*, 1960, **45** (March-April), 311-324.
133. A. Barth, *Progress in Biophysics and Molecular Biology*, 2000, **74**, 141-173.
134. W. Schmitt, C. E. Anson, R. Sessoli, M. van Veen, A. K. Powell, *Journal of Inorganic Biochemistry*, 2002, **91**, 173-189.
135. W. Schmitt, C. E. Anson, B. Pilawa, A. K. Powell, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2443-2457.
136. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A*. 6th ed., Wiley, 2009.
137. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B*. 6 ed., Wiley; New Jersey, 2009.
138. G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Wiley, 2004.
139. I. McKeogh, J. P. Hill, E. S. Collins, T. McCabe, A. K. Powell, W. Schmitt, *New Journal Chemistry*, 2007, **31**, 1882-1886.
140. G. L. Spina. *Synthesis, Structural Studies and Physicochemical Properties of Hybrid Inorganic-Organic Materials: Novel Materials based on Iminodiacetic Acid Substituted Aromatic Ligands*, University of Dublin, Dublin, 2011.
141. T. Engel, *Quantum Chemistry and Spectroscopy*, prentice hall, 2013.
142. M. J. Genge, A. P. Jones, G. D. Price, *Geochimica et Cosmochimica Acta*, 1995, **59** (5), 927-937.
143. J. W. Akitt, *Progress in Nuclear Magnetic Resonance Spectroscopy*, 1989, **21** (1), 1-149.
144. D. Coucouvanis, *Inorganic Syntheses*, Wiley, 2004.
145. P. A. Jordan, N. J. Clayden, S. L. Heath, G. R. Moore, A. K. Powell, A. Tapparo, *Coordination Chemistry reviews*, 1996, **149**, 281-309.
146. *NMR of newly accessible nuclei- Chemically and biochemically important elements* Vol. 2, Academic Press inc.; London, 1983.
147. G.L. Gaines Jr., *Journal of Organic Chemistry*, 1985, 410.
148. M. Shamma, D. M. Hindenlang, *Carbon-13 nmr shift assignments of amines and alkaloids*, Plenum Press, 1979.
149. P. Y. Bruice, *Organic chemistry*, Prentice Hall, 1998.
150. <http://www.chem.wisc.edu/areas/reich/handouts/nmr-c13/cdata.htm>, Accessed 12/01/2012, 2012.
151. http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi, Accessed 14/01/2012, 2012.
152. G. Tircso, A. Benyei, E. Brucher, A. Kis, R. Kiraly, *Inorganic Chemistry*, 2006, **45** (13), 4951-4962.
153. R. Song, F. Li, L. Li, *Magnetic Resonance in Chemistry*, 1992, **30**, 4.
154. J. L. Sudmeier, C. N. Reilley, *Analytical Chemistry*, 1964, **36**, 1698.
155. J. L. Sudmeier, C. N. Reilley, *Analytical Chemistry*, 1964, **36**, 1707.

156. P. N. Sirotkova, E. Dvořáková, I. Valášková, J. Majer, *Chemical papers*, 1984, **5** (39), 9.
157. <http://triton.igfr.csic.es/guide/eNMR/eNMRsolv/wg.html>, Bruker, Accessed 05/01/2014, 2014.
158. E. A. Ebsworth, D. W. Rankin, S. Cradock, *Structural methods in inorganic chemistry* 2nd ed., Blackwell Scientific, 1991.
159. G. McLendon, R. J. Motekaitis, A. E. Martell, *Inorganic Chemistry*, 1976, **15** (9), 2306-2308.
160. A. F. Panasci, C. A. Ohlin, S. J. Harley, W. H. Casey, *Inorganic Chemistry*, 2012, **51** (12), 6731-6738.
161. G. Tircso, A. Benyei, E. Brucher, A. Kis, R. Kiraly, *Inorganic Chemistry*, 2006, **45** (13), 4951-4962.
162. K. S. Murray, *Coordination Chemistry reviews*, 1974, **12** (1), 133.
163. G.B. Deacon, R.J. Phillips, *Coordination Chemistry reviews*, 1980, **33** (3), 23.
164. J. Sanders-Loehr, W. D. Wheeler, A. K. Shiemke, B. A. Averill, T. M. Loehr, *Journal of the American Chemical Society*, 1989, **111** (21), 9.
165. A. Khatib, F. Aqra, D. Deamer, A. Oliver, *Letters in Inorganic Chemistry*, 2009, **2009**, 1-5.
166. J. A. Davies, *Synthetic Coordination Chemistry: Principles and Practice*, World Scientific, 1996.
167. M. Clugston, R. Flemming, *Advanced Chemistry*, OUP Oxford, 2000.
168. N. G. Connelly, W. E. Geiger, *Chemical Reviews*, 1996, **96** (2), 877-910.
169. W. Schmitt, C. E. Anson, B. Pilawa, A. K. Powell, *Zeitschrift für anorganische und allgemeine Chemie*, 2002, **628** (11), 2443-2457.
170. J. C. Robles, Y. Matsuzaka, S. Inomata, M. Shimoi, W. Mori, H. Ogino, *Inorganic Chemistry*, 1993, **32** (1), 13-17.
171. K. Kanamori, K. Yamamoto, K. Okamoto, *Chemistry Letters*, 1993, **7**, 1253-4.
172. G. R. Pacigová, J. Tatiarsky, M. Sivák, *Dalton Transactions*, 2008, **2**, 9.
173. C. Calvo, D. Manolescu, *Acta Crystallographica Part B*, 1973, **29**, 1743.
174. E. S. Larrea, J. L. Mesa, J. Pizarro, D. Fernandez, F. Rodriguez, T. Rojo, M. I. Arriortua, *Dalton Transactions*, 2012, **41** (46), 14170-14179.
175. D. E. Hamilton, *Inorganic Chemistry*, 1991, **30** (7), 11.
176. W. Schmitt, C. E. Anson, W. Wernsdorfer, A. K. Powell, *Chemical Communications*, 2005, 2098-2100.
177. J. E. Bond, J. M. Dakka, S. M. Gorun, G. W. Schriver, R. T. Stibrany, T. H. Vanderspurt, G. H. Via, B. Zhang, *Catalytic production of aryl alkyl hydroperoxides by polynuclear transition metal aggregates*. EP0891368 A1, 1999.
178. H. Wullens, N. Bodart, M. Devillers, *Journal of Solid State Chemistry*, 2002, **167**, 14.
179. T. Tanase, Y. Yamada, K. Tanaka, T. Miyazu, M. Kato, K. Lee, Y. Sugihara, W. Mori, A. Ichimura, I. Kinoshita, Y. Yamamoto, M. Haga, Y. Sasaki, S. Yano, *Inorganic Chemistry*, 1996, **35**, 6230-6239.
180. D. L. Jameson, C. L. Xie, D. N. Hendrickson, J. A. Potenza, H. J. Schugar, *Journal of the American Chemical Society*, 1987, **109** (3), 740-746.
181. K. Håkansson, M. Carlsson, L. A. Svensson, A. Liljas, *Journal of Molecular Biology*, 1992, **227** (4), 1192-1204.
182. A. E. Eriksson, A. Liljas, *Proteins: Structure, Function, and Bioinformatics*, 1993, **16** (1), 28-42.
183. J. E. Coleman, *Annual Review of Biochemistry*, 1992, **61**, 897-946.
184. S. J. Archibald, A. M. Harris, P. H. Walton, *Journal of Inorganic Biochemistry*, 1999, **74** (1-4), 67-67.
185. S. Caglar, I. E. Aydemir, M. Cankaya, M. Kuzucu, E. Temel, O. Buyukgungor, *Journal of Coordination Chemistry*, 2014, Ahead of Print.
186. R. D. Brown, S. H. Koenig, *Inorganica Chimica Acta*, 1984, **91** (3), 183-7.

187. W. A. Eger, M. Presselt, B. O. Jahn, M. Schmitt, J. Popp, E. Anders, *Inorganic Chemistry*, 2011, **50** (8), 3223-3233.
188. J. B. Lambert, *Introduction to organic spectroscopy*, Macmillan; New York, 1987.
189. <http://orgchem.colorado.edu/Spectroscopy/irtutor/aminesir.html>, Accessed 06/03/2014, 2014.
190. W. Schmitt, A. O'Toole, *Sequestration and release of carbon dioxide using tetranuclear complexes*. WO2013072906A2, 2013.
191. J. R. Lakowicz, *Principles of fluorescence spectroscopy* 3rd ed., Springer, 2006.
192. M. E. B. Santiago, C. Declet-Flores, A. n. Diaz, M. M. Velez, M. Z. Bosques, Y. Sanakis, J. L. Colon, *Langmuir*, 2007, **23**, 7810-7817.
193. N. Kitamura, S. Tazuke, *Chemistry Letters*, 1983, **12** (7), 1109-1112.
194. B. J. Saikia, *Journal of Modern Physics*, 2010, **01** (04), 206-210.
195. K. Koike, S. Naito, S. Sato, Y. Tamaki, O. Ishitani, *Journal of Photochemistry and Photobiology A: Chemistry*, 2009, **207**, 109-114.
196. Bruker SMART, Version 5.629, 1997-2003, Bruker-Axs Inc.
197. Bruker Saint-Plus, Version 6.22, 1997-2003, Bruker-Axs Inc.
198. Rigaku Americas Corporation, Crystalclear-SM 1.4.0 software, 9009 New Trails Drive, The Woodlands, TX 77381, United States.
199. G. M. Sheldrick, Version 5.1, 1999, Bruker Axs-Inc.
200. Software Reference Manual, version 5.625; Bruker Analytical X-Ray Systems Inc.: Madison, WI, 2001.
201. K. Brandenburg, H. Putz, M. Berndt, *Crystal Impact*, Kreuzherrenstr; Germany, 2011.
202. Masslynx, version 4.0, 2002, Waters Corp.
203. J. H. Dymond, E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*, Clarendon Press; Oxford, 1980.

Appendix

Appendix

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1.0 Pictorial representations of $\text{Na}_5\cdot\text{H}_3\text{O}\{[\text{Fe}_4(\mu\text{-O})_2\text{hpda})_2]_2\{(\text{OOC}\text{C}_{12}\text{H}_{16}\text{COO})\}_2\}\cdot 15\text{H}_2\text{O}\cdot\text{DMA}\cdot\text{ligand (15a)}$

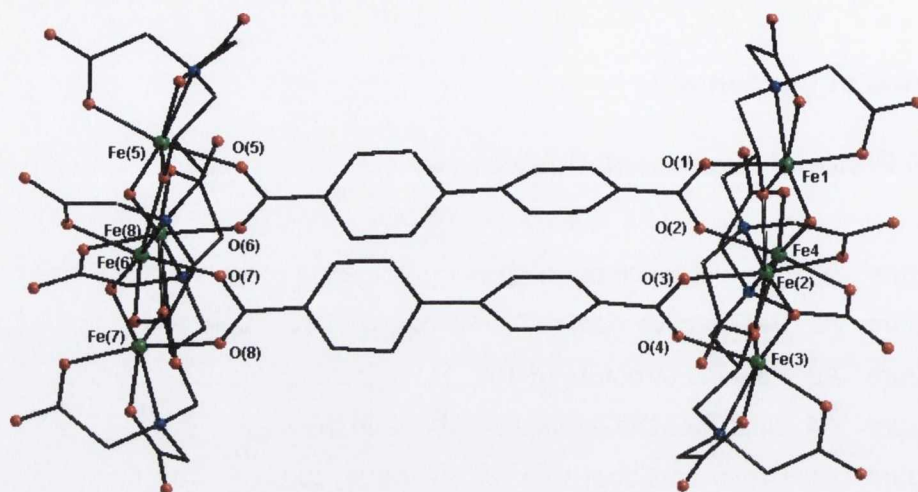


Figure A1: The octanuclear complex contained in the asymmetric unit of 15a. Hydrogen atoms and constitutional ligands have been omitted for clarity. Colour code: C black, Fe green, N blue, O red.

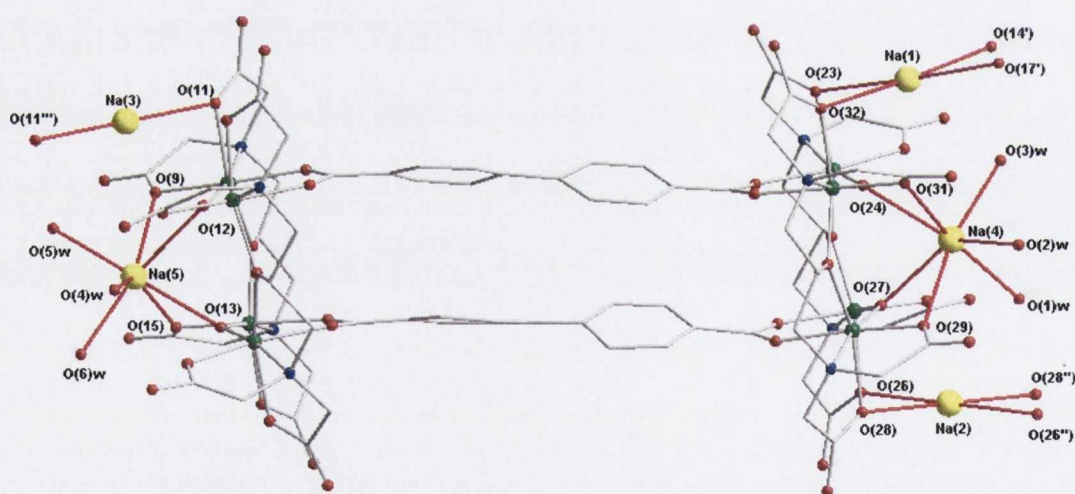


Figure A2: Perspective view of $\text{Na}^+\text{-O}$ bonds in 15a. The hydrogen atoms, H_3O^+ counter ions and constitutional water molecules have been omitted for clarity. Colour code: C light grey, Fe green, N blue, Na yellow, O red.

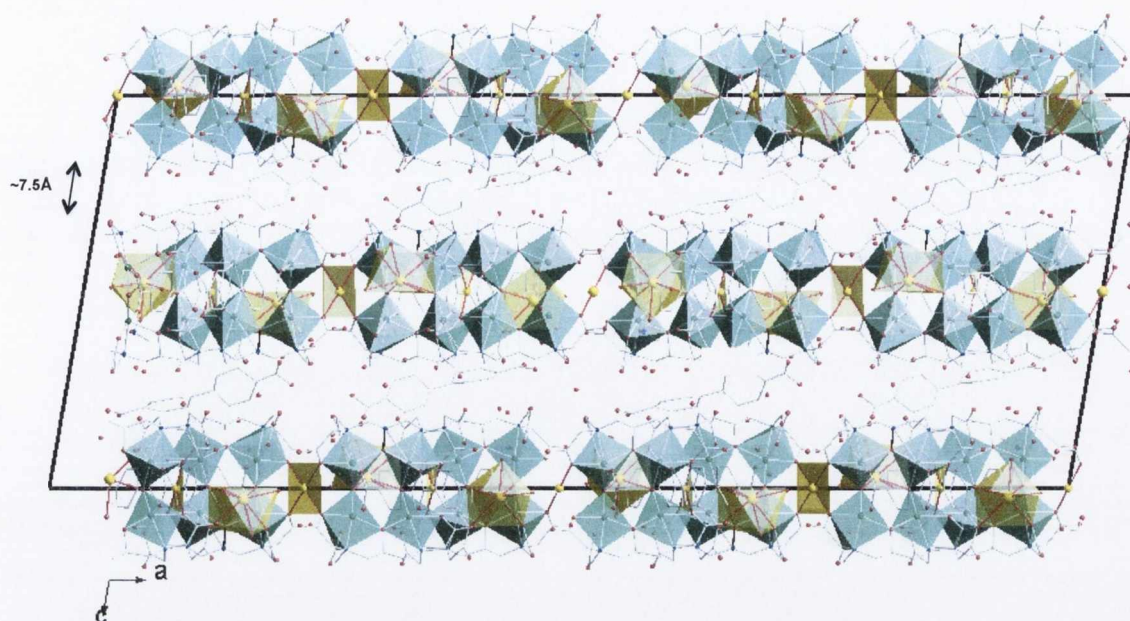


Figure A3: Packing structure of 15a. Viewed along the crystallographic *b*-axis. The hydrogen atoms have been omitted for clarity. Colour code: C light grey, Fe green, N blue, Na yellow, O red.

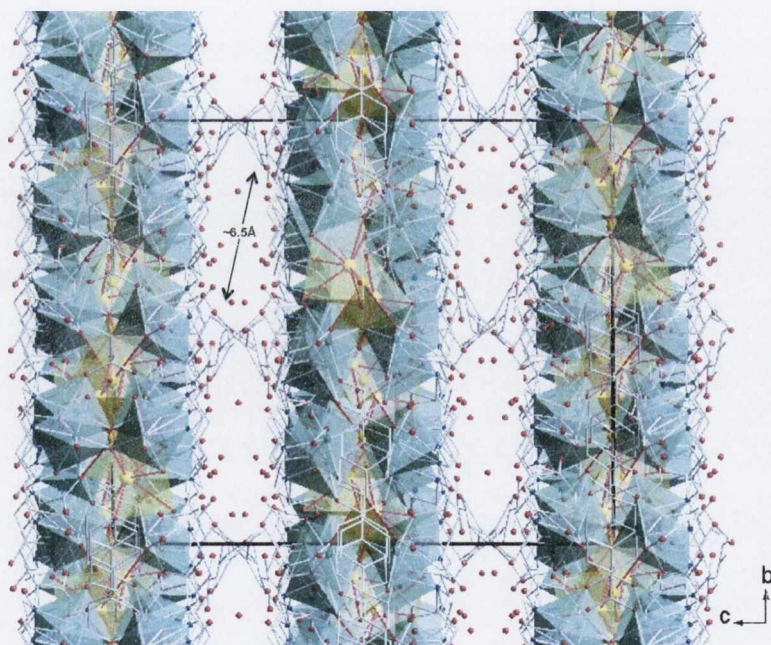


Figure A4: Illustrates the expansion of 15a in the *bc*-plane. The hydrogen atoms have been omitted for clarity. Colour code: C light grey, Fe green, N blue, Na yellow, O red.

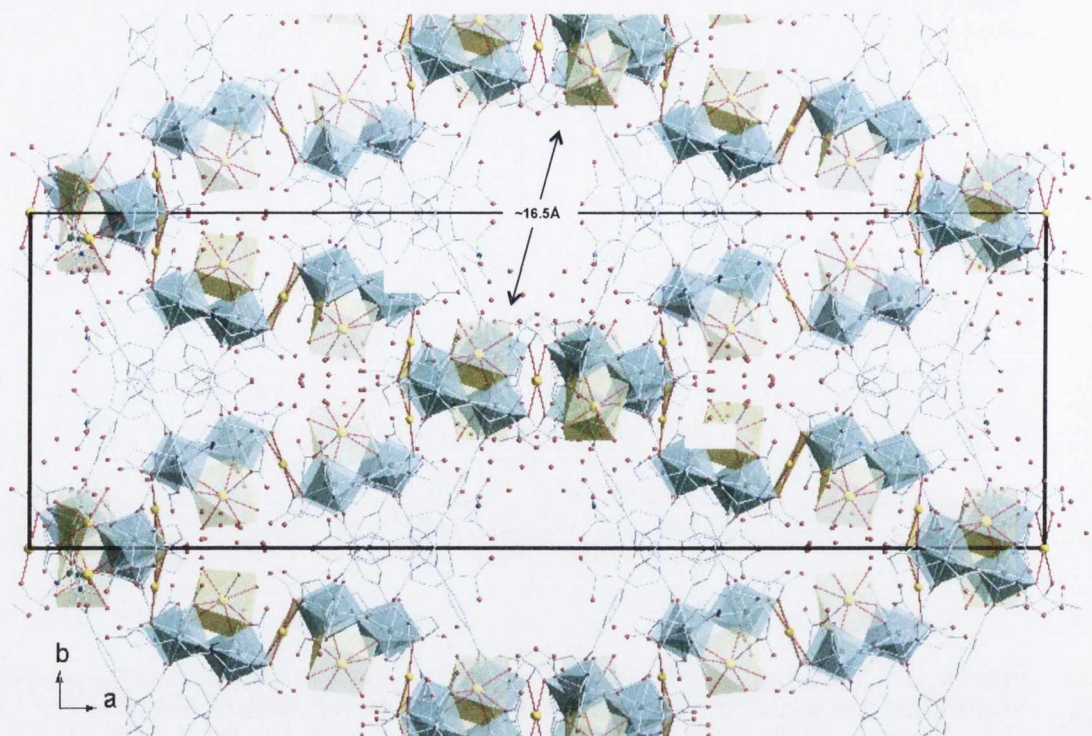


Figure A5: Cross sectional view of the honeycomb motif in the packing structure of 15a, viewed along the crystallographic *c*-axis. The hydrogen atoms have been omitted for clarity. Colour code: C light grey, Fe green, N blue, Na yellow, O red.

