

Hetero-metallic, functionalizable polyoxomolybdate clusters *via* a “top-down” synthetic method

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Two bi-metallic, organophosphonate-stabilised sandwich-type polyoxomolybdate clusters, $[\text{Mo}_6\text{Cu}_4\text{O}_{16}(\text{OH})_2(\text{C}_4\text{H}_9\text{PO}_3)_4(\text{C}_5\text{H}_5\text{N})_2(\text{CH}_3\text{O})_4(\text{H}_2\text{O})]^{2-}$ and $[\text{Mo}_7\text{Cu}_7\text{O}_{19}(\text{OH})(\text{CH}_3\text{O})_7(\text{C}_4\text{H}_9\text{PO}_3)_6(\text{C}_5\text{H}_5\text{N})_2]^{2-}$ are reported. These compounds are accessed *via* the “top-down” *in-situ* disassembly of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ Lindqvist species into reactive oligomers, followed by subsequent reassembly with polynuclear Cu^{II} assemblies to form the reported compounds.

The structural and electronic attributes of polyoxometalates (POMs) and the related transition metal substituted POMs (TMS-POMs) give rise to exiting physicochemical phenomena and applications in diverse areas of science.^{1–4} Recently, significant interest has been directed towards the development of POM-based clusters for the production of renewable fuels through the oxidation of abundant reagents such as biomass or water.^{5–13} In particular, molecular ‘sandwich-type’ TMS-POMs have revealed remarkable catalytic reactivities, and thus synthetic approaches that encapsulate hetero-metals into POM species are highly desirable.^{13–16}

POMs are traditionally synthesised *via* “bottom-up” condensation reactions from a monomeric metal-oxo unit into ever-larger molecular oxo-clusters, up to the extremely large molecules that can be classified as molybdenum blues and browns.^{17–21} Careful control of reaction conditions can yield lacunary POMs,²² which are commonly further assembled into larger TMS-POMs by encapsulating heterometal ions.^{23–26} These approaches have led to a number of rather fascinating mixed-metal systems,^{27,28} but whilst reoccurring structural motifs impart predictability and control, structural diversity is

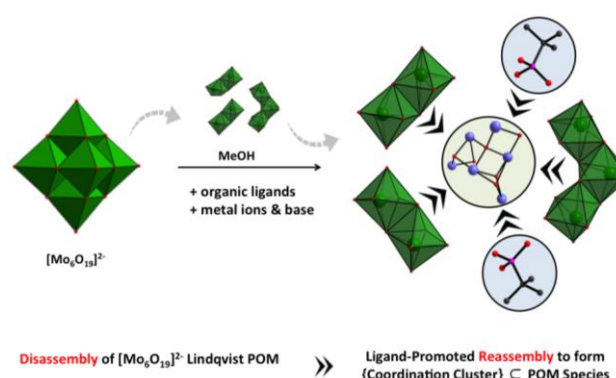


Fig. 1 Schematic representation of the applied “top-down” approach which exploits the disassembly of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ Lindqvist POM into smaller oligomers; the latter re-assemble into mixed-metal clusters upon addition of appropriate heterometal ions and organic ligands.

somewhat limited preferentially leading to entirely inorganic products that require specific functionalization procedure to introduce organic moieties.^{29–31}

A much rarer synthetic alternative is represented by a “top-down” approach.³² While some classic examples of POM transformation are known to proceed *via* a top-down mechanism (e.g. the disassembly of the $[\text{Mo}_8\text{O}_{26}]^{3-}$ species),^{33,34} the method is rarely used as a synthetic tool to generate novel compounds. In this approach, larger oxo-clusters are allowed to disassemble into smaller oligomers in solution.³² These oligomers are in principle highly reactive, and by the addition of suitable ligands or heterometal ions, can be reassembled to produce fundamentally new, mixed-metal TMS-POM species or functionalised POMs. Depending on the nature of the precursor POM, this methodology accesses fundamentally different metal-oxide fragments that are distinctive from the well-established lacunary clusters, allowing greater versatility in TMS-POM structures, even at mild synthetic conditions. Thus, the disassembly-reassembly approach is particularly suited to produce otherwise inaccessible examples of the highly desired ‘sandwich’-type TMS-POMs (Fig. 1).

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Supplementary Information (ESI) available: Full experimental procedures, mass spectrometry details and crystallographic data in CIF format for the structures. See DOI: 10.1039/x0xx00000x

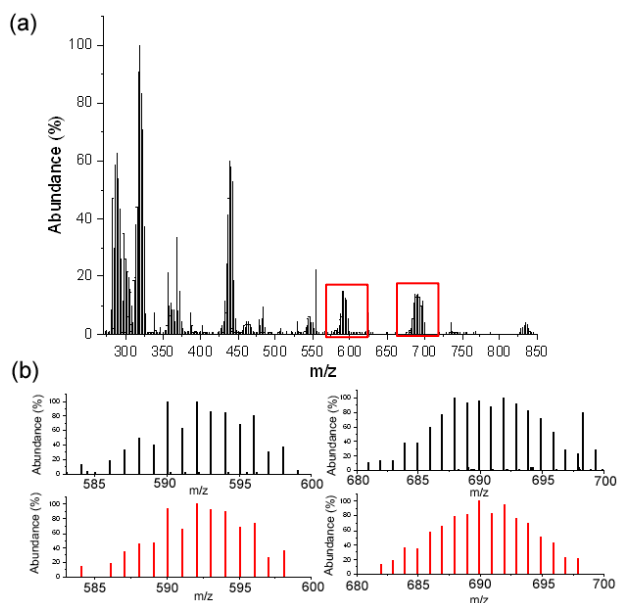


Fig. 2 (a) The negative mode ESI-MS spectrum of $[\text{TBA}]_2[\text{Mo}_6\text{O}_{19}]$ in methanol; (b) expansions of the $[\text{TBA}][\text{Mo}^{\text{V}}_2\text{O}_6(\text{OCH}_3)_2]^-$ and $[\text{TBA}][\text{Mo}^{\text{V}}_3\text{O}_{10}]^-$ signals, with experimental results in black, and simulated spectra in red, respectively.

Here we report two new hybrid $\{\text{Mo}/\text{Cu}\}$ hetero-metallic polyoxomolybdate clusters, which were formed *via* the *in-situ* disassembly of the hexamolybdate Lindqvist POM, $[\text{Mo}_6\text{O}_{19}]^{2-}$. The study is supported by electrospray ionisation (ESI) mass spectrometry, which was used to identify the intermediate di- and trinuclear oligomers, which form *via* the disassembly of the parent POM species in methanol. Reassembly of these oligomers in the presence of Cu^{II} and phosphonate ligands produces $[\text{TBA}]_2[\text{Mo}_6\text{Cu}_4\text{O}_{16}(\text{OH})_2(\text{C}_4\text{H}_9\text{PO}_3)_4(\text{C}_5\text{H}_5\text{N})_2(\text{CH}_3\text{O})_4(\text{H}_2\text{O})] \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) and $[\text{TBA}]_2[\text{Mo}_7\text{Cu}_7\text{O}_{19}(\text{OH})(\text{CH}_3\text{O})_7(\text{C}_4\text{H}_9\text{PO}_3)_6(\text{C}_5\text{H}_5\text{N})_2] \cdot 6\text{CH}_3\text{OH}$ (**2**), whose single crystal X-ray structures are reported.

The outlined disassembly-reassembly technique can be challenging to rationalise, as large numbers of species may be present in solution, many of which can be transient or occur at very low equilibrium concentrations.³⁵ However, mild mass spectrometry techniques such as ESI and MALDI can be invaluable as tools to identify key reaction intermediates in solution.^{36–38} The Lindqvist-structured hexamolybdate POM anion, $[\text{Mo}_6\text{O}_{19}]^{2-}$, is a well studied species and structural synthon in POM chemistry.^{39–44} However, although it is often considered a robust, hydrolytically stable species in solution^{43–45}, equilibration in methanol can be observed between the $[\text{Mo}_6\text{O}_{19}]^{2-}$ cluster and smaller molybdate oligomers. ESI-MS analyses identify various smaller disassembly products, including mono-, di- and trinuclear species such as $[\text{Mo}^{\text{V}}\text{O}_3(\text{OCH}_3)]^-$, $[\text{Mo}^{\text{V}}_2\text{O}_6(\text{OCH}_3)]^-$, $[\text{TBA}][\text{Mo}^{\text{V}}_2\text{O}_6(\text{OCH}_3)_2]^-$ and $[\text{TBA}][\text{Mo}^{\text{V}}_3\text{O}_{10}]^-$ (Fig. 2, ESI).

In a series of cone voltage (CV) variations (ESI), these MS signals are all present at low CV intensities (10 V), and signal intensities generally decrease as the CV increases, indicating these are real species that are present in solution along with their parent cluster, and do not form under experimental conditions inside the spectrometer.^{46–48}

These reactive decomposition oligomers can be reassembled into new architectures by the addition of suitable heterometals and organic ligands. Addition of copper(II) acetate and *tert*-butylphosphonic acid into the $[\text{Mo}_6\text{O}_{19}]^{2-}$ methanol solution results in $[\text{TBA}]_2[\text{Mo}_6\text{Cu}_4\text{O}_{16}(\text{OH})_2(\text{C}_4\text{H}_9\text{PO}_3)_4(\text{C}_5\text{H}_5\text{N})_2(\text{CH}_3\text{O})_4(\text{H}_2\text{O})] \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) and $[\text{TBA}]_2[\text{Mo}_7\text{Cu}_7\text{O}_{19}(\text{OH})(\text{CH}_3\text{O})_7(\text{C}_4\text{H}_9\text{PO}_3)_6(\text{C}_5\text{H}_5\text{N})_2] \cdot 6\text{CH}_3\text{OH}$ (**2**) which crystallise in the monoclinic space groups $P2_1/c$ and $C2/c$, respectively. Both compounds generally form reproducibly in reasonable yields (*ca.* 30–40%) consecutively, separating from the same reaction mixture. Their distinctively different crystal habits and colours (blue plates vs. green blocks, respectively) allow facile manual separation to achieve phase-pure samples.

The *oxo*-cluster species in **1** consists of six molybdenum ions and four copper ions, whereby two trinuclear molybdate moieties formally encapsulate a tetranuclear $\{\text{Cu}_4(\mu_3\text{-OH})_2\}$ subunit that is composed of two fused hydroxo-bridged triangular arrangements (Fig. 3). Each trinuclear Mo moiety contains two bridging *oxo*-ligands and six terminal *oxo*-ligands, resulting in a $\{\text{Mo}_3\text{O}_8\}$ unit in a bend arrangement. The structure is stabilised by four fully deprotonated *tert*-butylphosphonate ligands and four μ -methoxy ligands, all of which bridge between Mo^{VI} and Cu^{II} centres. The encapsulating molybdate moieties thus display distorted edge-

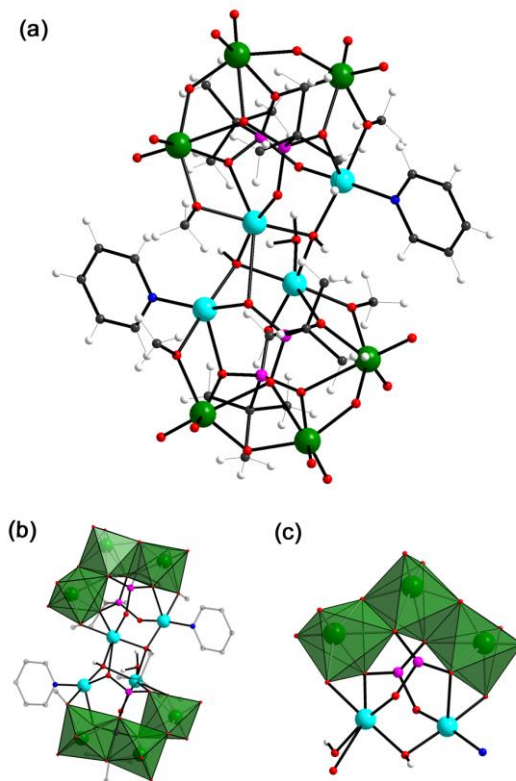


Fig. 3 (a) The structure of the $[\text{Mo}_6\text{Cu}_4\text{O}_{16}(\text{OH})_2(\text{C}_4\text{H}_9\text{PO}_3)_4(\text{C}_5\text{H}_5\text{N})_2(\text{CH}_3\text{O})_4(\text{H}_2\text{O})]^{2-}$ cluster in **1**; (b) Mo-polyhedral representation of $[\text{Mo}_6\text{Cu}_4\text{O}_{16}(\text{OH})_2(\text{C}_4\text{H}_9\text{PO}_3)_4(\text{C}_5\text{H}_5\text{N})_2(\text{CH}_3\text{O})_4(\text{H}_2\text{O})]^{2-}$ (H atoms of the organic ligands removed for clarity); (c) $\{\text{Mo}_3\text{Cu}_2\}$ ring unit in **1**. Colour code: Mo^{VI} green, Cu^{III} light blue, P pink, O red, N blue, C black.

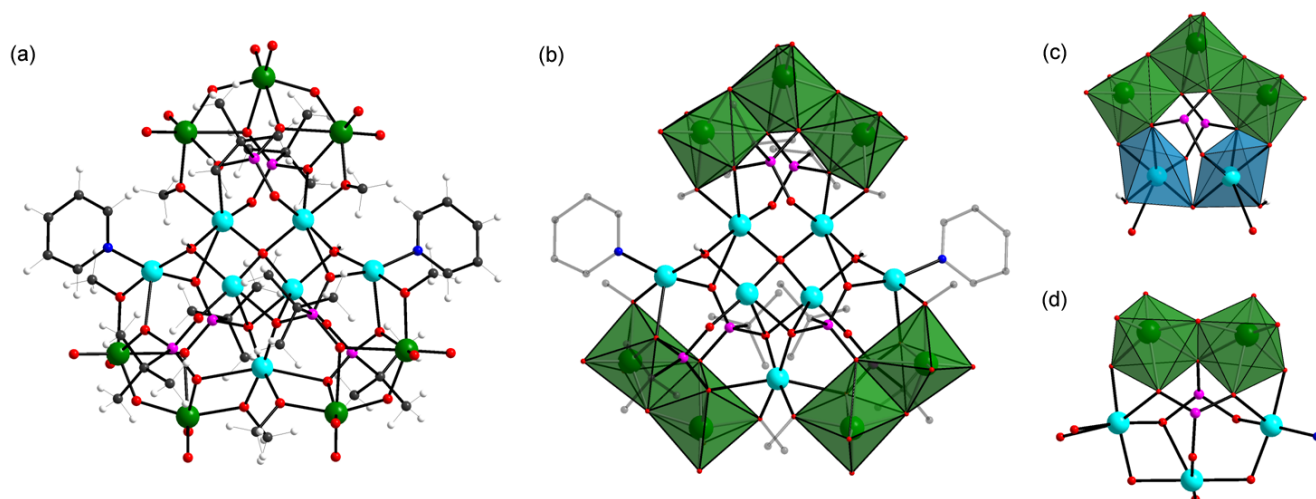


Fig. 4 (a) The structure of the $[\text{Mo}_7\text{Cu}_7\text{O}_{19}(\text{OH})(\text{CH}_3\text{O})_7(\text{C}_4\text{H}_9\text{PO}_3)_6(\text{C}_5\text{H}_5\text{N})_2]^{2-}$ cluster in **2**; (b) Mo-polyhedral representation of $[\text{Mo}_7\text{Cu}_7\text{O}_{19}(\text{OH})(\text{CH}_3\text{O})_7(\text{C}_4\text{H}_9\text{PO}_3)_6(\text{C}_5\text{H}_5\text{N})_2]^{2-}$ (H atoms of the organic ligands removed for clarity) (c) and (d) The $\{\text{Mo}_2\text{Cu}_3\}$ and $\{\text{Mo}_3\text{Cu}_2\}$ ring units in **2**. Color code: Mo^{VI} green, Cu^{III} light blue, P pink, O red, N blue, C black.

sharing $\{\text{MoO}_6\}$ octahedra.

The cluster in **1** may also be envisaged as a dimeric structure of two $\{\text{Mo}_3\text{Cu}_2\}$ ring units that dimerise through the hydroxo bridges. Two fully deprotonated *tert*-butylphosphonate ligands stabilise each ring moiety, binding to each side of the ring cavity in $\eta^1\text{:}\eta^2\text{:}\eta^2\text{:}\mu_5$ binding modes, with the monodentate O-donor coordinating to copper ions. Three of the Cu^{II} ions adopt distorted square pyramidal binding environments, with pyridine N-donors stabilizing the two peripheral Cu^{II} ions. The fourth Cu^{II} ion incorporates an additional water ligand into its coordination sphere, resulting in an octahedral environment. The assigned Mo^{VI} and Cu^{II} oxidation states are consistent with the bond valence sum analysis (BVSA, see ESI).

The crystallization of **1** prevails after the crystallization of **2**, which separates from the mixture within *ca.* one week, possibly influencing the relative ratio of oligomers in the reaction mixture. The cluster in **2** results from the formal encapsulation of a heptanuclear unit by one trinuclear and two dinuclear molybdate units (Fig. 4). As in **1**, the trinuclear unit is a $\{\text{Mo}_3\text{O}_8\}$ moiety, linked to the copper core *via* phosphonate and methoxy ligands. Similarly, the dinuclear unit is a $\{\text{Mo}_2\text{O}_5\}$ unit with one bridging and two terminal *oxo*-ligands, which is connected to the copper core *via* phosphonate and methoxy ligands. The resulting distorted $\{\text{MoO}_6\}$ octahedra share common edges, as in the trinuclear unit. Six fully deprotonated *tert*-butylphosphonate ligands and six methoxy ligands bridge between the Mo and Cu centres.

The Cu^{II} *oxo*/hydroxo-cluster is stabilized a central $\mu_4\text{-O}^{2-}$ bridging *oxo*-ligand and two $\mu_3\text{-O}^-$ donor atoms that derive from hydroxyl/methoxy ligands. As for **1**, the Cu^{II} centres display octahedral geometry and square pyramidal geometries, with two pyridine ligands coordinating to the cluster. The C2 symmetric cluster in **2** can also be considered as a fused structure of three pentanuclear ring moieties, a $\{\text{Mo}_3\text{Cu}_2\}$ ring as observed in **2** and two $\{\text{Mo}_2\text{Cu}_3\}$ rings that share a Cu^{II} ion. Two of the three crystallographically unique phosphonate

adopt $\eta^1\text{:}\eta^2\text{:}\eta^2\text{:}\mu_5$ binding modes, as in **1**. The third organophosphonate displays $\eta^2\text{:}\eta^2\text{:}\eta^3\text{:}\mu_7$ binding behavior, connecting five metal ions in the $\{\text{Mo}_2\text{Cu}_3\}$ ring and two Cu^{II} ions of the two other ring moieties. The observed bond lengths and BVSA (ESI) confirm the assigned Mo^{IV} and Cu^{II} oxidation states.

The phosphonate-capped $\{\text{Mo}_3\text{Cu}_2\}$ and $\{\text{Mo}_2\text{Cu}_3\}$ ring structures bare striking structural similarities to the Strandberg-type $\{\text{Mo}_5\}$ rings which have been comprehensively studied elsewhere.^{51–53} We suggest that phosphonate-templated heterometallic Strandberg-type structures may play a role as intermediate synthetic species.

Investigations of the temperature-dependent magnetic properties agree with the presence of four $S = 1/2$ Cu^{II} centres in **1**. At room temperature, the χT product of *ca.* 1.4 emu K mol⁻¹ (**1**) is in good agreement with the expected value for four paramagnetic Cu^{II} metal ions (1.50 emu K mol⁻¹ is expected with $g = 2.0$). Upon cooling to 2 K, the χT product decreases indicative of predominantly antiferromagnetic interactions between the spin centres. The temperature-dependent magnetic properties of **2** are characterised by rather complex competing ferro- and antiferromagnetic interactions, and a $S \neq 0$ spin ground state. Details of these analyses will be reported elsewhere.

Bands in the infrared spectra of **1** and **2** between 1000–1100 cm⁻¹ can be assigned to the P–O stretching modes of the organophosphonates whilst characteristic Mo=O bands occur at *ca.* 975 cm⁻¹. Both, **1** and **2** undergo thermal degradation in a N_2 atmosphere above *ca.* 180 °C.

In summary, a general synthetic approach to bimetallic, ligand-stabilised polyoxomolybdate clusters using the “top-down” *in-situ* disassembly of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ Lindqvist species is applied. The study is supported by ESI mass spectrometry, which identifies the reactive $\{\text{Mo}_3\}$ and $\{\text{Mo}_2\}$ disassembly products of the parent cluster that can be reassembled upon the addition of Cu^{II} and organophosphonate sources to form

mixed-metal molybdates **1** and **2**. Future studies will investigate the encapsulation of other transition metal ions using this approach and focus on the investigation of the redox-catalytic properties of such systems; further other structurally related polyoxomolybdates and tungstates will be employed in disassembly approaches.

The authors thank the Science Foundation Ireland (SFI; 13/IA/1896), the European Research Council (CoG 2014 – 647719) and the Irish Research Council (Fellowship for C.H.) for the financial support. We acknowledge Dr. Martin Feeney and Dr. Gary Hessman.

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Graphical Abstract