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# Polyoxometalates

Guest Editors: De-Liang Long and Leroy Cronin

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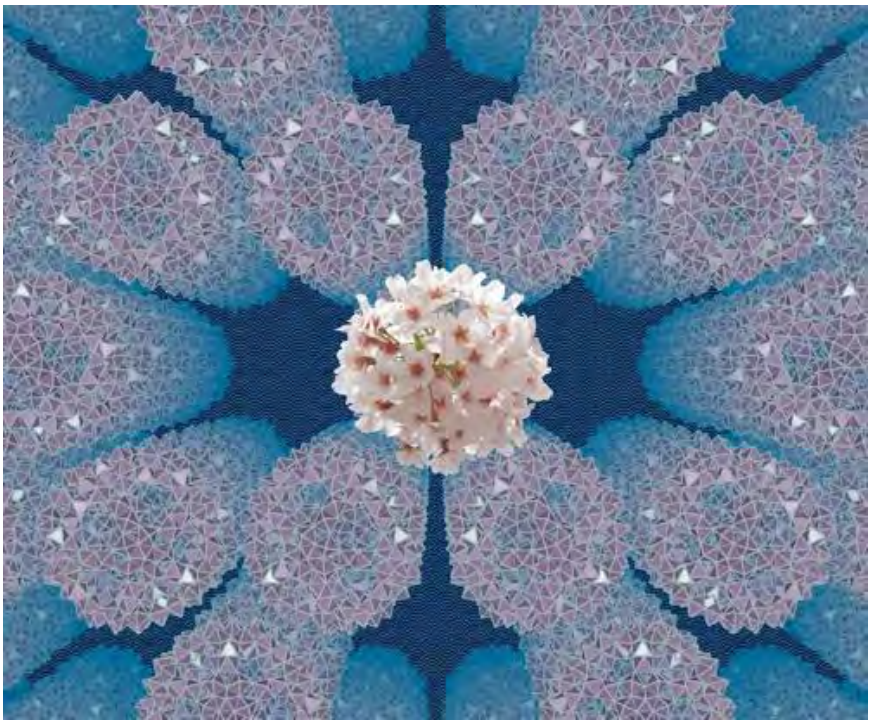

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PAPER

# Mapping the synthesis of low nuclearity polyoxometalates from octamolybdates to Mn-Anderson clusters†

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A comprehensive study of the isomer-independent synthesis of TRIS ($(HOCH_2)_3CNH_2$) Mn-Anderson compounds from $Na_2MoO_4{\cdot}2H_2O$, *via* the corresponding octamolybdate species, is presented. Three octamolybdate salts of $[Mo_8O_{26}]^{4-}$ in the β-isomer form, with tetramethylammonium (TMA), tetraethylammonium (TEA) and tetrapropylammonium (TPA) as the counter cation, were synthesised from the sodium molybdate starting material. Fine white powdery products for the three compounds were obtained, which were fully characterised by elemental analysis, TGA, solution and solid state Raman, IR and ESI-MS, revealing a set ratio of Na and organic cations for each of the three compounds; $(TMA)_2Na_2[Mo_8O_{26}]$ (**1**), $(TEA)_3Na_1[Mo_8O_{26}]$ (**2**) and $(TPA)_2Na_2[Mo_8O_{26}]$ (**3**), and the analyses also confirmed that the three compounds all consisted of the octamolybdate in the β-isomeric form. ESI-MS analyses of **1**, **2** and **3** show similar fragmentation for these β-isomers compared to the previously reported study for the α-isomer ($(TBA)_4[\alpha\text{-}Mo_8O_{26}]$) (**A**) in the synthesis of ($(TBA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$) (**B**), and compounds **1**, **2** and **3** were successfully used to synthesise equivalent TRIS Mn-Anderson compounds: $(TMA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**4**), $(TEA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**5**) and $(TPA)_2Na_1[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**6**), as well as $Na_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**7**). This is the first example where symmetric organically-grafted Mn-Anderson compounds have been synthesised in DMF from anything but the $\{Mo_8O_{26}\}$ α-isomer.

## Introduction

Polyoxometalates (POMs) can be defined as molecular metal oxides formed through condensation reactions of early transition metal–oxygen anions, typically with metals such as W, Mo, V, *etc*., in their highest oxidation state.[1] POMs have great versatility and possible applications range across fields from medicine to catalysis.[2] POM chemistry is a modern science with a long and successful history, for which the number of publications has massively increased over the last 20 years.[3] As early as 1826 it was noted by J. J. Berzelius that the reaction of ammonium molybdate, with an excess of phosphoric acid, leads to the formation of a light yellow precipitate.[4] Following this initial report, several leading scientists investigated these molybdates and related tungsten-based compounds in an attempt to understand the structure and composition of the materials,[3,5] and with crystal structure determination by X-ray diffraction methods, first discovered by M. V. Laue in 1912[6] and pioneered by W. H. Bragg[7] and W. L. Bragg,[8] the unambiguous identification and structural characterisation of the cluster compound was reported by J. F. Keggin in 1933.[9]

The "Anderson structure" was suggested in a letter to Nature by J. S. Anderson in 1937;[10] "*It may readily be seen that six $MoO_6$ octahedra may be so arranged, by sharing corners with each of two neighbouring octahedra, that a hexagonal $Mo_6O_{24}$ annulus is built up. The central cavity of this structure is then the same size and shape as one of the $MoO_6$ octahedra, and can therefore accommodate another cation in the same 6-fold co-ordination*." This structure was later confirmed with Evans' reports of a hexamolybdotellurate, which was finalised in 1974 (see Fig. 1a),[11] and this POM type is now referred to as an Anderson–Evans, or just an Anderson, structure. The W and Mo versions of the Anderson structure, without any organic substituents, may be isolated from aqueous molybdate or tungstate solutions following acidification to within pH 4–5.[12]

It has long been known that organic compounds can be grafted on to POMs,[13] and in 2002 P. Gouzerh *et al.* first reported that two tris(alkoxo) ligands of formula $(HOCH_2)_3CNH_2$, (TRIS), can replace the six hydroxo groups usually found in the Anderson cluster to form symmetrically functionalised Anderson compounds with $Ni^{II}$, $Zn^{II}$, $Fe^{III}$ and $Mn^{III}$ as the central heteroatom (see Fig. 1b).[14] This has been followed up with several publications by Gouzerh and Hasenknopf *et al.* investigating other organic ligands with TRIS moieties that can substitute the TRIS ligand on the Mn-Anderson compounds, in particular, the introduction of pyridine ligands allowing

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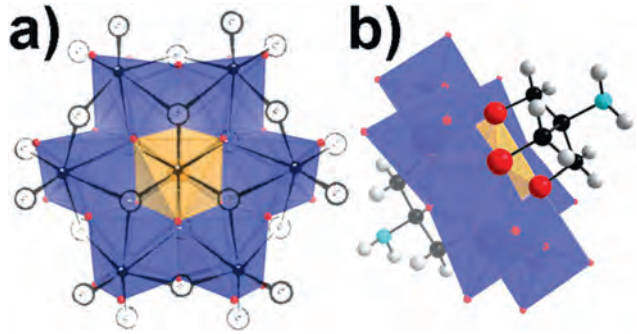



**Fig. 1** (a) Evans' Te–Anderson structure as determined by X-ray analysis, overlaying a more recent crystal structure of a Mn-Anderson compound where the TRIS moieties are omitted for clarity. (b) The structure of TRIS Mn-Anderson. Colour scheme: Mo, blue (polyhedra); O, red; C, black; N, cyan; H, white.


**Fig. 2** A historical time line starting with Scheele and Berzelius's discovery of POMs, with important findings and publications for POMs until Gouzerh *et al.*'s report of a hybrid Mn-Anderson complex, and Cronin *et al.*'s asymmetric discovery.



further coordination to a Ru-porphyrin complex.[15] In 2007 we reported a Mn-Anderson structure symmetrically capped by two pyrene-TRIS ligands, quickly followed by an asymmetrically capped Mn-Anderson, terminated by both $–NH_2$ and $–NO_2$.[16] As well as expanding the library of Mn-Anderson compounds, new techniques have been introduced to investigate the hybrid compounds, for example atomic force microscopy (AFM) has been used to study their self-assembly on surfaces.[16g,17] A time-line of the more significant publications in the development of the Anderson-type structures up until the first report of the asymmetrically functionalised Mn-Anderson structure is presented in Fig. 2.

The published synthetic procedure for hybrid Mn-Anderson compounds starts with the synthesis of tetrabutylammonium (TBA) octamolybdate $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ (**A**), from $Na_2MoO_4\cdot 2H_2O$.[18,19] However, this α-isomer is only one of the eight isomers of octamolybdate that have been isolated, *i.e.*, α-, β-, γ-, δ-, ε-, ζ-, η- and θ-isomers, with the two most common isomers being the α- and β-isomers.[20]

Fuchs and Hartl stated that the $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ can be described as a centrosymmetric anion consisting of a ring made up of six $MoO_6$ octahedra, as the $\{Mo_6\}$ ring in $[TeMo_6O_{24}]$,[11c] linked to one $MoO_4$ tetrahedron above and one below its central

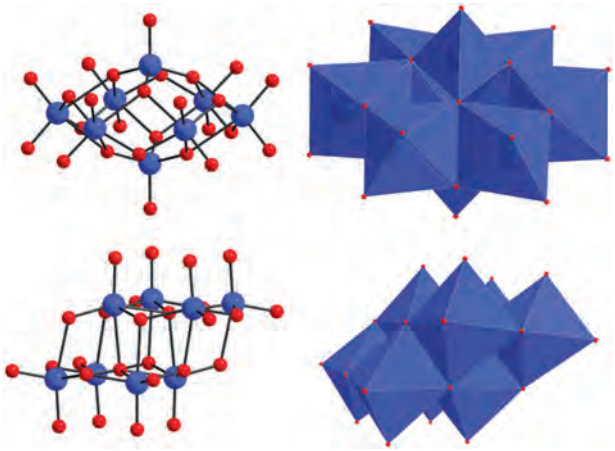


**Fig. 3** A comparison of the two main isomers of $[Mo_8O_{26}]$, with the α-isomer on the top, and the β-isomer below. They are both presented in a ball and stick model on the left, and in a polyhedral model on the right. Colour scheme: Mo, blue (spheres and polyhedra); O, red.

octahedral cavity. This was the first report on structural isomerism in discrete isopolyanions, discussing the similarity of the $(TBA)_4[Mo_8O_{26}]$[18] and the $(NH_4)_4[Mo_8O_{26}]\cdot 4H_2O$,[5i,21] now known as examples of the α- and β-isomers respectively, the major difference being that the β-isomer is made up solely of $MoO_6$ octahedra (see Fig. 3 for a comparison of the α- and β-isomers). Many studies followed this first report attempting to establish the relationship between the different isomeric forms of the octamolybdate salts. It has been established using IR and Raman techniques that $[\beta\text{-}Mo_8O_{26}]^{4-}$ is the predominant octamolybdate isomer in aqueous molybdate solution at pH 2,[20a,22,23] the α-isomer dominates at pH 2.7,[20a] whilst both isomers are present at pH 3–4. The β-isomer was found to be favoured in the presence of small counter ions such as potassium, TMA, TEA and TPA,[24] and crystal structures of TMA β-octamolybdates,[25] along with TEA octamolybdates, as both the α-isomer[26] and β-isomer,[26c] have been reported.

An in-depth mass spectrometry study into the formation of $(TBA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**B**) from $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ (**A**) has been carried out by us where it was observed that the $\{\alpha\text{-}Mo_8O_{26}\}$ fragments into smaller $\{Mo_4O_{13}\}$ units, then further fragments into $\{Mo_2\}$ and $\{Mo_3\}$ units, before it combines with the TRIS base and $Mn^{III}$ to form the full organically grafted Mn-Anderson structure.[27] The most important point is that the $\{Mo_4O_{13}\}$ fragment is a dominant peak envelope in the ESI-MS (Electro Spray Ionisation Mass Spectrometry) of the initial reaction mixture. This strongly indicates that the $\{Mo_8O_{26}\}$ anion instantly fragments into smaller units, and it is these smaller fragments that finally reorganise themselves, producing the TRIS Mn-Anderson compound. Mn-Anderson compounds have been reported with different counter ions, but in all instances this has been achieved *via* cation exchange on the already formed TBA Mn-Anderson compound.[16b,17,28] Hence, all reported hybrid Mn-Anderson compounds are synthesized with TBA as the countercation, and all, with only one exception,[29] use $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ as the starting material. This indicates that the $\{Mo_8O_{26}\}$ unit is very important in the synthesis of hybrid Mn-Anderson compounds.

Synthesising octamolybdate compounds with smaller cations favouring the β-isomer allows us to investigate its reactions with TRIS base and $Mn^{III}$, and the formation of organically grafted Mn-Anderson complexes. This allows a better and more detailed understanding of the self-assembly process of the formation of the Mn-Anderson POM. Moreover, it can give us great insight into how the rearrangement of the $\{Mo_8O_{26}\}$ occurs, and in general of Mn-Anderson POM chemistry.

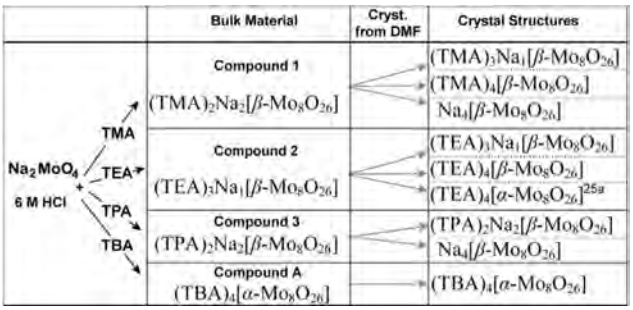
## Results and discussion

### Octamolybdate salts

Compounds **1**, **2** and **3** were successfully precipitated out according to the reported method for synthesising $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$, replacing the TBA·Br salt with TMA·Br, TEA·Br and TPA·Br, respectively. The analysis of the white products confirmed the overall ratio of Na and organic cations for each of the three compounds. However, when the products were re-dissolved and crystallised from DMF, a wealth of Na to organic cation ratios were found for the octamolybdate compounds. The fact that we get so many different crystal structures are not really that surprising when looking at previous publications regarding octamolybdate compounds, and searching for $\{Mo_8O_{26}\}$ in the CDS Crystal Web search engine results in more than 300 hits.

Due to the large amount of crystallographic data obtained for the different octamolybdate compounds presented herein, varying in both cation ratio (organic/Na) and isomer form, the X-ray analyses we have obtained are not suitable for identifying the elemental composition for the overall compound. Instead we have focused on the bulk materials of compounds **1–3**, as given in Scheme 1. To confirm the compositions of the three compounds elemental analyses were employed, giving us the overall formulas of $(TMA)_2Na_2[Mo_8O_{26}]$ (**1**), $(TEA)_3Na_1[Mo_8O_{26}]$ (**2**) and $(TPA)_2Na_2[Mo_8O_{26}]$ (**3**). Details of the results are listed in the experimental section and in the ESI.†

**Crystallography.** Compounds **1–3** were dissolved and crystallised from DMF in an attempt to confirm the isomer configurations for the compounds but, as mentioned previously, the isomer configuration may vary between different states and the isomers seen *via* crystallography may not be the same as in the bulk. Nevertheless, a large amount of crystallographic data was obtained, and an overview of the structures that are presented is given in Scheme 1, with a few examples shown in Fig. 4. For a complete overview of all the crystal structures obtained, see Table 1.




**Scheme 1** An overview of the syntheses of the octamolybdate salts, highlighting multiple crystal structures are obtained from the same bulk material. One additional structure can be obtained if a 1.5 molar excess of TPA·Br is used in the synthesis of compound **3**, highlighted with an * in Table 1.

**Raman spectroscopy.** Previous publications regarding octamolybdate compounds highlight the close relationship between the different isomers, and also discuss in detail the possible transformations of the structure from the product in solution, to that in the solid, and to that seen in single crystal X-ray crystallography.[24] The differences are not huge, but can be the change of the isomer configuration and potentially the ratio of counter cations. Himeno *et al.* reported a Raman spectroscopy study of octamolybdate products in water solutions,[20a] which shows the expected spectra for the various isomers. Due to the large number of possible crystal structures we decided to investigate compounds **1**, **2** and **3** by both solid and solution state Raman spectroscopy to confirm what isomer the compounds exist as when not in the single crystal phase (see Fig. 5).

Looking at the solid state Raman results (Fig. 5a), it can be seen that the three compounds have slightly different spectra, where compound **1** can be clearly assigned as the β-isomer. This is probably because the reference compound we used to help assign the isomers from Himeno's study, $(TMA)_{3.75}Na_{0.25}[Mo_8O_{26}]\cdot H_2O$, is almost identical to compound **1**. The spectrum of compound **3** is not as well defined as compound **1**, but it can still be assigned as the β-isomer. The spectrum of compound **2**, on the other hand, suggests that there might be a mixture of the β- and γ-isomer in the sample. Looking at the solution Raman (see Fig. 5b), where $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ (**A**) has been included for comparison, it is clear that compounds **1**, **2** and **3** all exist in what seems to be the β-isomer, and is different from the one obtained for the α-isomer (**A**).

**IR spectroscopy.** There are also IR studies available which compare the different octamolybdate isomers, where a strong peak at 808 $cm^{-1}$ is expected for the α-isomer, whilst for the β-isomer a strong peak at 717 and a weak peak at 965 $cm^{-1}$ is

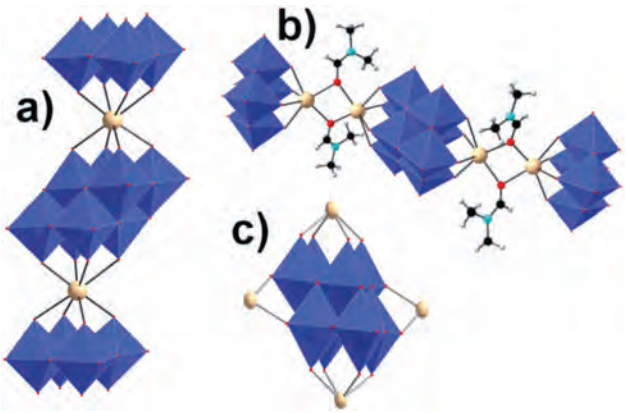



**Fig. 4** Examples of crystal structures obtained for the octamolybdate salts, showing different ways of how Na can coordinate to the terminal oxo ligands, and hence link up the octamolybdate units. Colour scheme: Mo, blue (polyhedra); O, red; C, black; N, cyan; H, white; Na, beige.

**Table 1** Crystallographic data for the octamolybdate salts (TMA compounds are derived from compound **1**, TEA from compound **2** and TPA from compound **3**)

| | $Na_1(TMA)_3[\beta\text{-}Mo_8O_{26}]\cdot 2DMF$ | $(TMA)_4[\beta\text{-}Mo_8O_{26}]\cdot 4DMF$ | $Na_1(TEA)_3[\beta\text{-}Mo_8O_{26}]$ | $(TEA)_4[\beta\text{-}Mo_8O_{26}]\cdot 2DMF$ | $Na_2(TPA)_2[\beta\text{-}Mo_8O_{26}]\cdot 2DMF$ | $(TPA)_4[\alpha\text{-}Mo_8O_{26}]\cdot 1DMF^*$ | $Na_4[\beta\text{-}Mo_8O_{26}]\cdot 6DMF$ |
|---|---|---|---|---|---|---|---|
| Formula | $C_{18}H_{50}Mo_8N_5Na_1O_{28}$ | $C_{28}H_{76}Mo_8N_8O_{30}$ | $C_{24}H_{60}Mo_8N_3Na_1O_{26}$ | $C_{38}H_{94}Mo_8N_6O_{28}$ | $C_{30}H_{70}Mo_8N_4Na_2O_{28}$ | $C_{51}H_{119}Mo_8N_5O_{27}$ | $C_{18}H_{42}Mo_8N_6Na_4O_{32}$ |
| $M_r$ (g mol$^{-1}$) | 1575.14 | 1772.49 | 1597.26 | 1850.71 | 1748.40 | 2002.03 | 1714.06 |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1$ | $P2_1/c$ | $P\bar{1}$ | $Pccn$ | $P2_1/n$ |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic | Orthorhombic | Monoclinic |
| $a$ (Å) | 9.94649(4) | 10.8532(5) | 10.9912(10) | 12.6794(7) | 13.1358(11) | 21.2892(12) | 12.236(2) |
| $b$ (Å) | 20.3666(8) | 25.1978(14) | 22.757(2) | 11.9967(6) | 20.1210(15) | 22.0626(10) | 13.609(2) |
| $c$ (Å) | 11.6803(4) | 11.7908(6) | 18.7179(15) | 20.8920(11) | 23.1313(17) | 16.7364(8) | 14.868(2) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 65.365(3) | 90 | 90 |
| $\beta$ (°) | 93.236(3) | 116.657(3) | 98.239(4) | 95.176(3) | 89.772(4) | 90 | 99.455(7) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 88.935(4) | 90 | 90 |
| $V$ (Å$^3$) | 2248.00(15) | 2881.8(3) | 4633.5(7) | 3164.9(3) | 5556.3(7) | 7861.0(7) | 2442.2(7) |
| $Z$ | 2 | 2 | 4 | 2 | 4 | 4 | 2 |
| $\mu$ (mm$^{-1}$) | 18.591[a] | 1.770 | 2.187 | 1.613 | 1.844 | 1.304 | 2.117 |
| Refl. coll. | 12 277 | 22 348 | 8838 | 42 348 | 75 354 | 32 104 | 18 549 |
| Indep. refl. | 3055 | 5667 | 8838 | 6210 | 21 097 | 7648 | 4691 |
| $R$(int) | 0.0523 | 0.0766 | 0.0000 (twinnabs) | 0.0485 | 0.0305 | 0.0360 | 0.0278 |
| GooF on $F^2$ | 1.102 | 1.003 | 1.080 | 1.050 | 1.108 | 1.059 | 1.063 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0714 | 0.0423 | 0.0778 | 0.0286 | 0.0340 | 0.0276 | 0.0185 |
| w$R_2$ [$I > 2\sigma(I)$] | 0.2541 | 0.0832 | 0.1685 | 0.0687 | 0.0787 | 0.0610 | 0.0424 |
| $R_1$ (all data) | 0.0793 | 0.0795 | 0.1095 | 0.0393 | 0.0407 | 0.0391 | 0.0222 |
| w$R_2$ (all data) | 0.2598 | 0.0982 | 0.1941 | 0.0760 | 0.0825 | 0.0688 | 0.0448 |

[a] Cu-K$_\alpha$ X-ray.

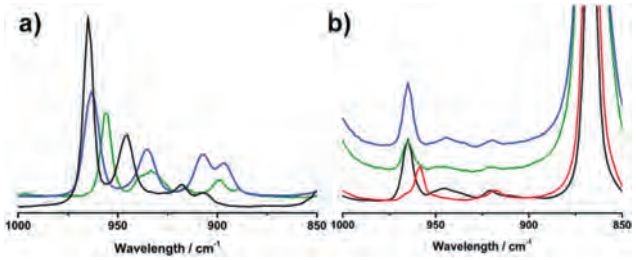



**Fig. 5** (a) Solid state Raman spectra and (b) solution Raman spectra. Compound **1** is shown in blue, **2** in green, **3** in black, and **A** is shown in red. The large peak at about 870 cm$^{-1}$ in (b) belongs to DMF. The solid state Raman of **A** is not included in (a), but has been previously reported by Himeno *et al.*[20a]

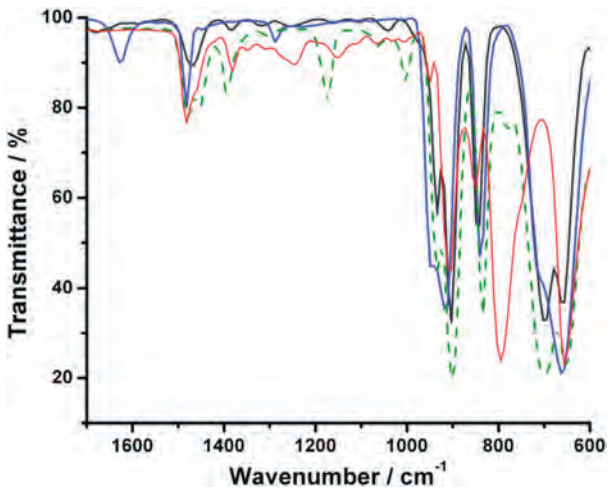



**Fig. 6** IR comparison of **A** (red), **1** (blue), **2** (dashed green) and **3** (black).

expected.[22,24] To further confirm the isomers of compounds **1–3** solid state IR, with an ATR cell, was used and the results are presented in Fig. 6. Discrepancies in the wavenumbers compared to previously presented work are observed, and this is due to the fact the literature values were obtained from standard transmission IR. However, by overlaying the spectra it can be seen that the spectra of the α-isomer (compound **A**) is different from the other three. Compounds **1** and **3** have very similar spectra, again indicating that they exist as the β-isomer in the solid state. The spectrum for compound **2** is slightly different, with unassigned peaks at 1397, 1173 and 1003 cm$^{-1}$, which might be due to the cation. However, focusing on the peaks below 1000 cm$^{-1}$ it seems that compound **2** exists in the same isomer as compounds **1** and **3**, the β-isomer.

**ESI-MS analysis.** For the ESI-MS analyses a small amount of compounds **1–3** were dissolved in DMF, before diluting with MeCN. The resulting ESI-MS spectra are shown in Fig. 7, with the assignments of the most relevant peaks. Although the spectra are of varying quality, there is a clear similarity between them. The most important peak envelopes are the ones that are assigned to the "half cluster" $\{Mo_4O_{13}\}$, which previously has

| Peak Assignment | Observed m/z | Calculated m/z |
|---|---|---|
| $[Mo_4O_{13}Na_1]^{1-}$ | 614.6 | 614.7 |
| $[Mo_4O_{13}(TEA)_1]^{1-}$ | 721.7 | 722.0 |
| $[Mo_4O_{13}(TPA)_1]^{1-}$ | 777.8 | 778.1 |
| $[Mo_6O_{19}(TEA)_1]^{1-}$ | 1009.5 | 1009.9 |
| $[Mo_8O_{26}(TMA)_1Na_2]^{1-}$ | 1304.2 | 1303.6 |
| $[Mo_8O_{26}(TEA)_1Na_2]^{1-}$ | 1359.3 | 1359.7 |
| $[Mo_8O_{26}(TPA)_1Na_2]^{1-}$ | 1416.4 | 1415.8 |

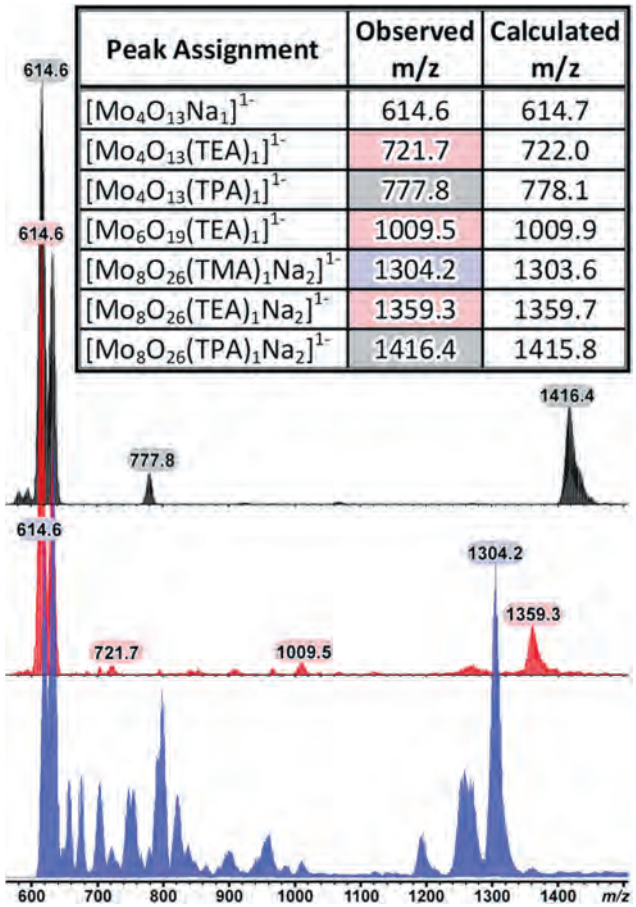



**Fig. 7** ESI-MS spectra obtained for compounds **1** (blue), **2** (red) and **3** (black), where the $[Mo_4O_{13}Na_1]^{1-}$ can be seen in each of the three spectra.

been reported as one of the first steps in the reaction of compound **A** with TRIS base and $Mn^{III}$, forming $(TBA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**B**).[27]

Both $[[Mo_4O_{13}]Na_1]^{1-}$ and $[[Mo_4O_{13}](TXA)_1]^{1-}$, (where X is either P, E or M) can be found, to a varying degree, for the three compounds. It is the presence of those fragments that indicate the strong similarity between the α- and the β-isomers in solution, and which indicates that the β-isomer might also be used as the starting material in the syntheses of TRIS Mn-Anderson compounds.

Peak envelopes assigned to $[[Mo_6O_{19}](TXA)]^{1-}$, a fragment likely corresponding to the Lindqvist anion can also be observed, and the intensity of this peak increases if the solutions are heated before the ESI-MS study.

The presence of the $\{Mo_6O_{19}\}$ can easily be rationalised because the octamolybdate and the Lindqvist anion are strongly linked, and only small experimental steps are needed to convert compound **A** into the yellow-coloured $(TBA)_2[Mo_6O_{19}]$, highlighting how labile the octamolybdate anions are when dissolved, supporting the theory that the different isomers of octamolybdates exist as similar fragments in solution.

**Summary.** Herein, three octamolybdate compounds have been synthesised, and their elemental composition determined in the bulk. The octamolybdate compounds are very labile, and the close relationship between the α- and β-isomers have been reconfirmed by X-ray analysis, and a strong relationship can be seen between the crystallised isomer and the size of the cations employed. The nature of the isomers of the three compounds has also been investigated by both solid state and solution Raman spectroscopy, along with IR spectroscopy, confirming that none of the compounds exist as the α-isomer. Importantly, from ESI-MS analysis of the three compounds it was found that all three compounds speciate and fragment in a similar manner to that observed for the α-isomer during the synthesis of TRIS Mn-Anderson.[27]

### TRIS Mn-Anderson compounds

Following the results for compounds **1–3** above, it can be concluded that compounds **1–3** exist as the β-isomer in both the solid state and in solution (or in the case of compound **2**, at least not as the α-isomer). The ESI-MS analyses of the octamolybdate compounds show similar fragments in solution, independent of the isomer configuration of the starting material, to that observed for compound **A**, and so we set out to synthesise TRIS Mn-Anderson compounds using compounds **1–3** as the starting materials. This would show that $Na_2MoO_4{\cdot}2H_2O$ can be used with a variety of cations and, independent of the isomer configuration of the octamolybdate salt, react with TRIS base and $Mn^{III}$ to form TRIS Mn-Anderson compounds. This would be the first example where a symmetric organically-grafted Mn-Anderson compound has been synthesised from anything other than $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$.

The standard synthesis of $(TBA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**B**) consists of refluxing $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ (**A**) with the TRIS base and $Mn(OAc)_3{\cdot}2H_2O$ in acetronitrile.[14] However, compounds **1–3** have a lower solubility compared to **A**, and the synthesis must be carried out in DMF. Compound **B** was successfully synthesised from **A** in DMF as confirmed by X-ray analysis, before we set out to synthesise TRIS Mn-Anderson compounds from **1–3**. In order to increase the solubility and therefore the reactivity of compounds **1–3**, they were dissolved in DMF at room temperature before the addition of the TRIS base and $Mn(OAc)_3{\cdot}2H_2O$. The reactions were then carried out at 80 °C for about 20 h and the resulting solutions set up for crystallisation at 4 °C. Four compounds of the respective Mn-Anderson compounds were successfully separated within two weeks as crystalline materials, where time resolved crystallisation was used to separate compounds **4** and **7**, as well as compounds **6** and **7**: $(TMA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**4**), $(TEA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**5**) and $(TPA)_2Na_1[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**6**), along with $Na_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (**7**) (see Scheme 2 for an overview of the synthetic route, and the ESI† for further details).

**$^1$H NMR analysis.** Due to the paramagnetic nature of the $Mn^{III}$ central heteroatom, $^1$H NMR analysis can be a very useful tool when analysing organically grafted Mn-Anderson compounds. The 12 protons situated closest to the paramagnetic centre are shifted to 65–60 ppm, and when present it is a strong indicator that the reactions have been successful. A broad peak

| | Compound Number and Formula | |
|---|---|---|
| $Mn(OAc)_3$ + TRIS base (1) | $(TMA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ | (4) |
| (1) | $Na_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ | (7) |
| (2) | $(TEA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ | (5) |
| (3) | $(TPA)_2Na_1[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ | (6) |
| (A) | $Na_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ | (7) |
| | $(TBA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ | (B) |

**Scheme 2** This overview shows that the Mn-Anderson compounds can be made from the β-isomer of the octamolybdate anion. See Table 2 for further details.

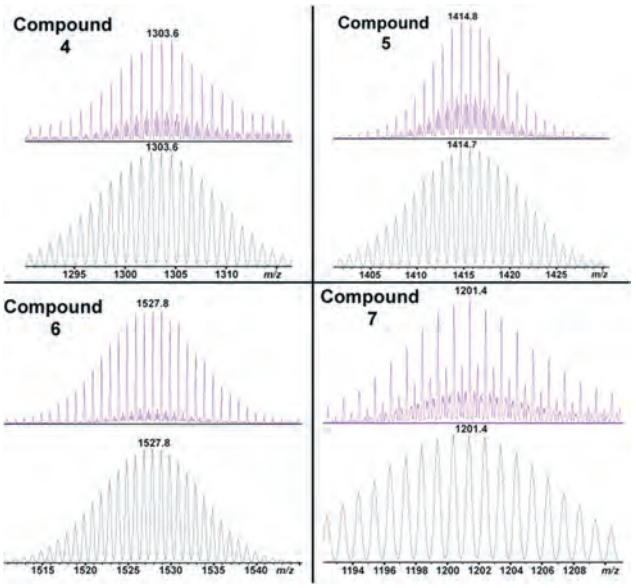



**Fig. 8** An overview of the main peak envelopes observed in ESI-MS for compounds **4**, **5**, **6** and **7**, all in purple (on top), with the corresponding simulated spectra shown in black (below).

can be observed in this region for all four TRIS Mn-Anderson compounds (see ESI† for further details).

**ESI-MS analysis.** The peak envelopes from the ESI-MS spectra obtained for compounds **4**, **5**, **6** and **7** are shown in Fig. 8, with the simulated peaks shown below in black: *m/z* 1303.6 corresponds to $[(TMA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$; *m/z* 1418.8 corresponds to $[(TEA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$; *m/z* 1527.8 corresponds to $[(TPA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$ and *m/z* 1201.4 corresponds to $[(Na)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$. Other fragments of the metal oxide core, as presented by Cronin and co-workers[27] can be found in each of the spectra, all confirming the successful synthesis of the TRIS Mn-Anderson compounds.

**Crystallography.** The structure obtained for compounds **4** and **5** are almost identical to the crystal structure of **A**,[14] with the same TRIS metal oxide unit. Compounds **6** and **7** however, result in TRIS metal oxide units which are coordinated to Na atoms through their terminal oxo ligands. Each unit cell for compound **6** contains one "standard" TRIS Mn-Anderson compound and one TRIS Mn-Anderson coordinated to two Na atoms, which again are coordinating three DMF molecules each (see Fig. 9).

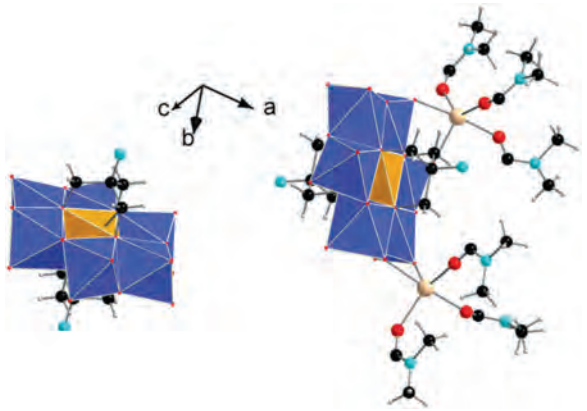



**Fig. 9** In the crystal structure of compound **6**, two types of Mn-Anderson compounds are present. One is the standard TRIS Mn-Anderson, whilst on the right hand side a TRIS Mn-Anderson coordinated to two Na atoms are shown. Colour scheme: Mn, orange (polyhedra); Mo, blue (polyhedra); O, red; C, black; N, cyan; H, white; Na, beige.

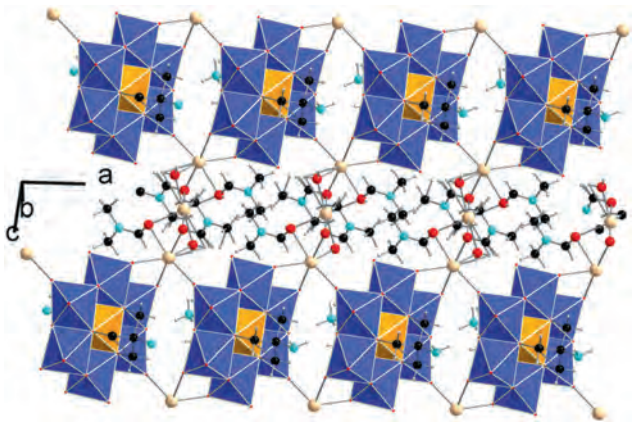



**Fig. 10** The crystal structure of compound **7**. 2D layers packed on top of each other. The DMF molecules are about 4 Å apart in the adjacent layers. Colour scheme is the same as in Fig. 9.

In the crystal structure obtained for compound **7** each TRIS Mn-Anderson unit is coordinated by four Na atoms and each Na atom is again linked into a chain of three Na atoms bridged by DMF molecules. The resulting 2D structure is shown in Fig. 10. This is however, just one of several different phases that compound **7** crystallises in, and an overview of the other structures, along with the crystallographic data for compounds **4–6** with varying solvent content, are listed in Table 2. The first entry in Table 2 is a structure that was only observed once.

**Summary.** All the analytical investigations show that we have successfully synthesised four hybrid Mn-Anderson complexes from the three β-octamolybdate compounds, hence the reactions can be carried out in DMF, and the isomer-configuration of the octamolybdate starting material is irrelevant.

**Table 2** Crystallographic data for the Mn-Anderson compounds **4–7** presented herein

| | $(TMA)_1Na_5(MnMo_6O_{24}C_8N_2H_{16})_2\cdot 14DMF$ (only observed once) | $(TMA)_3(MnMo_6O_{24}C_8N_2H_{16})\cdot 3DMF$ (**4**) | $(TEA)_3(MnMo_6O_{24}C_8N_2H_{16})\cdot 1DMF$ (**5a**) | $(TEA)_3(MnMo_6O_{24}C_8N_2H_{16})\cdot 2DMF$ (**5b**) | $(TPA)_2Na_1(MnMo_6O_{24}C_8N_2H_{16})\cdot 3DMF$ (**6**) | $Na_3(MnMo_6O_{24}C_8N_2H_{16})\cdot 3DMF\cdot 5H_2O$ (**7a**) | $Na_3(MnMo_6O_{24}C_8N_2H_{16})\cdot 4DMF\cdot 4H_2O$ (**7b**) | $Na_3(MnMo_6O_{24}C_8N_2H_{16})\cdot 10DMF$ (**7c**) |
|---|---|---|---|---|---|---|---|---|
| Formula | $C_{62}H_{142}Mn_2Mo_{12}N_{19}Na_5O_{62}$ | $C_{29}H_{73}Mn_1Mo_6N_8O_{27}$ | $C_{35}H_{83}Mn_1Mo_6N_6O_{25}$ | $C_{38}H_{90}MnMo_6N_7O_{26}$ | $C_{41}H_{93}MnMo_6N_7NaO_{27}$ | $C_{17}H_{47}MnMo_6N_5Na_3O_{32}$ | $C_{20}H_{52}MnMo_6N_6Na_3O_{32}$ | $C_{38}H_{86}MnMo_6N_{12}Na_3O_{34}$ |
| $M_r$ (g mol$^{-1}$) | 3522.06 | 1596.53 | 1618.65 | 1691.75 | 1769.79 | 1533.15 | 1588.23 | 1954.74 |
| Space group | $P\bar{1}$ | $C2/c$ | $C2/m$ | $C2/c$ | $Pnma$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Crystal syst. | Triclinic | Monoclinic | Monoclinic | Monoclinic | Orthorhombic | Triclinic | Triclinic | Triclinic |
| $a$ (Å) | 13.393(3) | 29.0498(10) | 15.0770(13) | 24.6971(16) | 52.926(3) | 9.1905(5) | 8.6386(4) | 9.5374(3) |
| $b$ (Å) | 13.860(3) | 9.2853(3) | 23.102(2) | 12.6758(8) | 27.5135(10) | 12.7684(6) | 10.0132(5) | 13.5364(5) |
| $c$ (Å) | 17.702(4) | 24.0873(8) | 15.0791(14) | 18.8241(10) | 9.5169(4) | 12.8684(6) | 14.3392(8) | 28.3397(9) |
| $\alpha$ (°) | 66.991(10) | 90 | 90 | 89 | 90 | 102.444(3) | 109.102(2) | 91.169(2) |
| $\beta$ (°) | 76.601(11) | 102.186(3) | 92.336(5) | 90.641(5) | 90 | 106.754(3) | 92.590(2) | 90.065(2) |
| $\gamma$ (°) | 82.092(11) | 90 | 90 | 90 | 90 | 110.418(3) | 93.587(2) | 109.346(2) |
| $V$ (Å$^3$) | 2938.2(12) | 6350.8(4) | 5247.9(8) | 5892.6(6) | 13 858.3(10) | 1268.31(11) | 1166.91(10) | 3451.3(2) |
| $Z$ | 1 | 4 | 4 | 4 | 8 | 1 | 1 | 2 |
| $\mu$ (mm$^{-1}$) | 1.559 | 11.617[a] | 1.708 | 1.527 | 1.309 | 1.792 | 1.953 | 1.344 |
| Refl. coll. | 32 605 | 15 048 | 19 081 | 23 531 | 33 040 | 18 023 | 16 581 | 50 838 |
| Indep. refl. | 11 175 | 3874 | 5245 | 5603 | 8660 | 4820 | 4556 | 13 543 |
| $R$(int) | 0.0736 | 0.0720 | 0.0293 | 0.0756 | 0.0780 | 0.0469 | 0.0270 | 0.0254 |
| GooF on $F^2$ | 1.017 | 1.053 | 1.032 | 1.054 | 1.031 | 1.018 | 1.034 | 1.037 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0502 | 0.0744 | 0.0456 | 0.0453 | 0.1212 | 0.0570 | 0.0202 | 0.0244 |
| w$R_2$ [$I > 2\sigma(I)$] | 0.1169 | 0.2050 | 0.1279 | 0.0885 | 0.2041 | 0.1543 | 0.0494 | 0.0655 |
| $R_1$ (all data) | 0.0791 | 0.1125 | 0.0605 | 0.0802 | 0.1212 | 0.0775 | 0.0246 | 0.0266 |
| w$R_2$ (all data) | 0.1341 | 0.2425 | 0.1447 | 0.1075 | 0.2237 | 0.1719 | 0.0524 | 0.0670 |

[a] Cu-K$_\alpha$ X-ray. *Note*: A letter added to the compound name in brackets indicates different solvent content.

## Conclusions

The findings presented herein underline the close relationship between the isomers of the octamolybdates, and explain why it took so many years before all the isomers were isolated and characterised. It highlights the small conditional differences that can result in different isomer configurations and cation ratios for the octamolybdate salts. Secondly, it shows that in ESI-MS analysis of both the α- and the β-isomers, the same building blocks, or fragments, are obtained, and that these fragments are vital for the synthesis of the hybrid organic–inorganic TRIS Mn-Anderson complexes. Thirdly, this can help broaden our understanding of POM solution chemistry, and be a tool in the exploration of new and unknown POM clusters, as well as POM complexes with designed properties, making them appropriate for functional devices. Finally, this allows for the direct synthesis of hybrid organic–inorganic Mn-Anderson compounds with novel cations, circumventing the cation exchange reaction step. Indeed, work done by us placing such compounds on surfaces have shown that if one changes the cations on a hybrid Mn-Anderson, then this hugely alters their properties on the surface.[17] The more direct route allows us to incorporate smaller cations that previously have been off limit due to solubility issues. As such, this study gives a unique insight into the speciation and fragmentation of POMs and hybrid POMs, and can possibly be applied to the synthesis of other POMs, as well as in the design and synthesis of functional systems.

## Experimental

### Materials

All reagents and chemicals were supplied by Sigma-Aldrich Chemical Company Ltd and solvents were supplied by Fisher Chemicals, all used without further purification. For details regarding all instrumentation used, see the ESI.†

### Synthesis of TXA $Mo_8O_{26}$ compounds

The syntheses of the $(TXA)_xNa_{4-x}[Mo_8O_{26}]$ were adapted from the literature procedure for $(TBA)_4[Mo_8O_{26}]$.[19] To obtain single crystals of compounds **1–3** for X-ray analysis the precipitates were crystallised from DMF. The synthesis of compound **1** is described here, whilst the synthetic procedure for compounds **2** and **3** are given in the ESI.†

**Synthesis of compound 1 $(TMA)_2Na_2[\beta\text{-}Mo_8O_{26}]$.** $Na_2MoO_4\cdot 2H_2O$ (5.0 g, 20.7 mmol) was dissolved in $H_2O$ (12 mL) before being acidified with 6 M HCl (5.05 mL). The reaction mixture was stirred vigorously for 1–2 min before a solution of TMA·Br (1.6 g, 10.4 mmol) in $H_2O$ (10 mL) was added. The reaction mixture was stirred vigorously for 10 min before the resulting white precipitate was collected. It was successively washed with $H_2O$ (20 mL), EtOH (20 mL), acetone (20 mL) and diethyl ether (20 mL). The compound, $(TMA)_2Na_2[Mo_8O_{26}]$, was obtained as a white powder. **Yield** = 3.18 g, $2.31 \times 10^{-3}$ mol, 88% based on Mo; **EA:** Anal. Calcd for $C_8H_{24}Mo_8N_2Na_2O_{26}$ (1377.77 g $mol^{-1}$): C, 6.97; H, 1.76; N, 2.03; Found: C, 6.88; H, 1.85; N, 1.87; **IR:** 3565 (w, br), 3426 (w, br), 3040 (w, sh), 1268 (m, sh), 1481 (m, sh), 1288 (w, sh), 949 (s, br), 918 (s, br), 841 (s, sh), 664 (vs, br); **Raman:** 971 (s, sh), 943 (m, br), 915 (m, br), 905 (m, br); **ESI-MS:** The peak envelopes at *m/z* 614.16 and 665.7 correspond to $[[Mo_4O_{13}]Na_1]^{1-}$ and $[[Mo_4O_{13}](N(CH_3)_4)]^{1-}$ respectively; **TGA:** The first loss is of 3.94%, with a second loss at about 250 °C of 12.36%. The theoretical value for the loss of the TMA cations is 10.76%.

### Synthesis of TXA Mn-Anderson compounds

The compounds **4–7** were synthesised according to an altered literature procedure for hybrid Mn-Anderson complexes,[14] where the $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ was substituted by compounds **1**, **2** and **3**, respectively obtaining compounds **4**, **5** and **6**, as well as **7**. Due to the low solubility of compounds **1–3**, the reactions were carried out in DMF at 80 °C. The synthesis of compounds **5** and **6** are described in the ESI.†

**Synthesis of compound 4 and 7.** Compound **1** (0.430 g, $0.31 \times 10^{-3}$ mol) was dissolved in 60 mL of DMF at room temperature (30 min). $Mn(OAc)_3\cdot 2H_2O$ (0.127 g, $0.47 \times 10^{-3}$ mol) and TRIS-base (0.131 g, $1.08 \times 10^{-3}$ mol) were added and the resulting solution was heated up to 80 °C for 20 h. During the reaction a brown precipitate was formed, the reaction was then cooled to room temperature and the precipitate removed. The resulting clear orange solution was set up of crystallisation at 4 °C by ether diffusion. This crystallisation led to the formation of crystals and a precipitate. The crystalline material is compound **7**, whilst compound **4** is obtained by re-dissolving the precipitate in DMF and crystallised by ether diffusion at 4 °C.

**Compound 4 $(TMA)_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$. Yield:** 9% based on Mo; **EA:** Anal. Calcd for $C_{20}H_{52}Mn_1Mo_6N_5O_{24}$ (1377.22 g $mol^{-1}$): C, 17.44; H, 3.81; N, 5.09; Found: C, 17.27; H, 2.90; N, 4.57; **IR:** 3497 (w, br), 3433 (w, br), 3356 (w, sh), 3271 (w, br), 3032 (w, sh), 2928 (w, sh), 2862 (w, sh), 1663 (m, sh), 1611 (w, sh), 1787 (m, sh), 1443 (w, sh), 1393 (w, sh), 1306 (w, sh), 1236 (s, sh), 1182 (w, sh), 1125 (m, sh), 1105 (m, sh), 1024 (m, sh), 1001 (m, sh), 986 (m, sh), 937 (s, sh), 916 (s, sh), 901 (s, sh), 648 (vs, sh); **$^1$H NMR ($(CD_3)_2SO$, 400 MHz):** $\delta$ 64.00–58.00 (br, m, $CH_2$, 12H), 3.60 (br, s, $NH_2$, 4H), 3.10 (s, $CH_3$, 36H); **ESI-MS:** The peak envelope at *m/z* 1303.6 corresponds to $[(TMA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$.

**Compound 7 $Na_3[MnMo_6O_{18}(OCH_2)_3CNH_2)_2]$. Yield:** 9% based on Mo; **EA:** Anal. Calcd for $C_8H_{16}Mn_1Mo_6N_2Na_3O_{24}\cdot(DMF)_3$ (1443.04 g $mol^{-1}$): C, 14.15; H, 2.58; N, 4.85; Found: C, 13.68.; H, 2.63; N, 4.36; **IR:** 3484 (w, br), 3441 (w, br), 3356 (w, sh), 3322 (w, br), 2932 (w, br), 1663 (m, sh), 1495 (w, sh), 1441 (w, sh), 1412 (w, sh), 1393 (w, sh), 1308 (w, sh), 1242 (m, br), 1105 (m, sh), 1022 (s, sh), 937 (s, sh), 901 (s, sh), 638 (vs, br); **$^1$H NMR ($(CD_3)_2SO$, 400 MHz):** $\delta$ 64.00–58.00 (br, m, $CH_2$, 12H), 3.60 (br, s, $NH_2$, 4H); **ESI-MS:** The peak envelope at *m/z* 1201.4 corresponds to $[Na_2[MnMo_6O_{18}\text{-}((OCH_2)_3CNH_2)_2]]^{1-}$.

### Crystallographic analyses

Two different types of X-ray diffractometers were used for single crystal structure determination: Bruker Apex II Quasar and

Oxford Diffraction Gemini Ultra. Independent of the type of X-ray diffractometer, corrections for incident and diffracted beam absorption effects were applied utilising analytical numeric absorption correction with a multifaceted crystal model,[30] or using empirical absorption correction.[31] Refinement was carried out with SHELXS-97[32] and SHELXL-97[32] using WinGX[33] *via* a full matrix least-squares on $F^2$ method. All non-hydrogen atoms were refined anisotropically unless otherwise stated. See ESI† for further details.

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