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Developing Remote Metal Binding Sites in Heteropolymolybdates

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Anderson-Type Heteropolymolybdates Containing Tris(alkoxo) Ligands, 2.^[‡] Elaboration of Remote Metal Binding Sites

5 **Bernold Hasenknopf,^[a] Pierre Marcoux,^[a] Jacqueline Vaissermann,^[a] and Pierre Gouzerh*^[a]**

Polyoxometalates / Molybdenum / N ligands {Insert up to 5 keywords.} / {...} / {...}

10 Anderson-type polyoxomolybdates $[\text{MMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ (M = Mn^{III}, Fe^{III}) were prepared and structurally characterized. The trisalkoxo ligands are bound to the central heteroatom by their oxygen atoms. The corresponding compounds with M = Ni^{II} or Zn^{II} are unavailable because of the preference of these cations for the amine function. The pendant amine groups of the manganese-containing derivative were reacted with pyridine-carbaldehydes to give the corresponding imines
15 which provide new mono- and bidentate binding sites for metal cations.

[‡] Part 1: See ref. [Insert reference number], {{or:}} See {insert citation}.

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Introduction

Organic molecules can be grafted onto polyoxometalates (POMs).^[1] This provides an entry in the field of organic/inorganic hybrid compounds which combine the properties of the metal-oxo cluster and the organic component.^[2; 3] Such functionalized POMs have been used in the preparation of polymers,^[4-7] dendrimers^[8] or macroporous materials^[9] by covalently crosslinking the organic groups. The complexation of other metal ions at a remote site of the grafted organic ligand is less common. Maatta et al. prepared a hexamolybdate with a pendant ferrocene group.^[10] In this case, the preformed organometallic complex was attached to the polyoxomolybdate. To the best of our knowledge, no complex formation with a ligand already bound to a polyoxometalate is reported in the literature. On the other hand, there are many examples in the literature where POMs bind other metal ions through their oxo ligands.^[11] In particular, lacunary POMs can be combined with a variety of metal cations, and the resulting complexes have interesting new electrical, optical, magnetic or catalytic properties.^[12-18] Also giant POMs can be generated in this way.^[19]

Thus, our interest focused in the combination of POMs and other metals via organic ligands. This strategy is complementary to the coordination of oxo ligands in order to "bridge the gap between polyoxometalates and classic coordination compounds".^[20] The organic molecules might display other donor atoms than oxygen and may vary their arrangement in the binding site. Therefore, the ligand can be adjusted to the chemical and geometrical preferences of the extra metal centres. Ideally, our approach would permit to select a specific ligand for a chosen metal ion, and to connect it to a chosen POM. The properties of the resulting assembly would be tuned by the individual optimization of the components.

The realization of this concept requires the development of a flexible synthetic strategy. A key role comes to the organic linker between the POM and the remote coordination site. This molecule has to be bifunctional with one side that can merge with a POM, and a reactive group on the other side to build the coordination site. We chose tris(hydroxymethyl)aminomethane ((HOCH₂)₃CNH₂, TRIS) for this purpose. The triol moiety can be incorporated in Anderson,^[21] Lindqvist,^[22-24]

Dawson^[8; 25] or other POMs.^[25-27] The remaining amino group can be used to elaborate the coordination site. We chose first to look at the incorporation of TRIS into Anderson-type polyoxomolybdates.

The Anderson structure $[H_x(M'O_6)_6M_6O_{18}]^{n-}$ ($x = 0-6$, $n = 2-6$) consists of a planar arrangement of six edge-sharing MO_6 ($M = Mo, W$) octahedra around a central heteroatom M' .^[28-30] We have shown recently that two tris(hydroxymethyl)methane residues $RC(CH_2O)_3$ ($R = CH_3, CH_2OH, CH_2NO_2$) can cap both sides of the polyanion.^[21] Two forms were found: in the first one –named δ for its approximate D_3 symmetry– the triol is bound entirely to the heteroatom, while in the second one –named χ for its approximate C_{2v} symmetry– it is capping a tetrahedral cavity. The central heteroatom can be a di- or trivalent transition metal cation, and we have prepared compounds with Mn^{III} , Fe^{III} , Ni^{II} and Zn^{II} and the above mentioned tris(hydroxymethyl)methane derivatives. We present here the results of the reactions with TRIS and the derivatization of the pendant amine group. The protonated form of TRIS has been used as counterion for polyoxometalates.^[31] Also, amide and tertiary amine derivatives have been incorporated into POM frameworks,^[23; 32] but to the best of our knowledge, TRIS itself has not been incorporated into POMs yet. Difficulties with this compound have been linked to its role as a reductant.^[32]

Results and Discussion

Grafting a free amine group on a POM

Treatment of $[N(C_4H_9)_4]_4[\alpha-Mo_8O_{26}]$ with TRIS in the presence of manganese(III) acetate gave $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ **1** which was isolated as orange crystals in 80% yield. The compound was characterized by single crystal X-ray diffraction. Crystal structure data are summarized in Table 1. The overall molecular structure of the anion (Figure 1) is very similar to the analogous compounds reported.^[21] Six edge-sharing MoO_6 octahedra are arranged around a central MnO_6 unit forming the Anderson structure. The two organic moieties cap both sides of the planar

hexagon. The alkoxo ligands are all bound to the Mn^{III} ion, thus the structure corresponds to the δ type. Selected bond lengths and angles are compiled in Table 2. The rigidity of the POM framework prevents the Mn^{III} ion to undergo marked Jahn-Teller distortions. The coordination octahedron is only very slightly elongated.

5 The reaction of [N(C₄H₉)₄]₄[α -Mo₈O₂₆] with TRIS in the presence of iron(III) acetylacetonate gave [N(C₄H₉)₄]₃[FeMo₆O₁₈{(OCH₂)₃CNH₂}₂] **2** which was isolated as yellow crystals in 50% yield. Structural analysis by X-ray diffraction of single crystals (Table 1) revealed the expected δ -type Anderson structure: the Fe^{III} ion in the center of the six edge-sharing MnO₆ octahedra is coordinated to the six alkoxo groups of two TRIS ligands. Selected bond distances and angles are compiled in
10 Table 2.

IR spectra of compounds **1** and **2**, listed in the experimental part, are in agreement with their structures.^[21; 33] It has to be pointed out that they display a single, broad band around 700 cm⁻¹ for the Mo-O-Mo bridges, in accordance with the central arrangement of both TRIS ligands (δ structure). The χ structure would have two bands in this region.^[21]

15 The reactions of nickel(II) acetate or zinc(II) acetate with [N(C₄H₉)₄]₄[α -Mo₈O₂₆] and TRIS did not yield the expected Anderson-type compound. This result is in contrast to other tris(hydroxymethyl)methane derivatives that do form the functionalized Anderson-type POM with a central Ni^{II} or Zn^{II}.^[21] We therefore decided to vary the reaction conditions and to use a different molybdate source. From the reaction of zinc(II) acetate with [N(C₄H₉)₄]₂[Mo₂O₇] in the presence of
20 TRIS, we isolated a compound with the molecular formula [N(C₄H₉)₄]₂[Mo₂Zn₂O₆{(O-CH₂)₂C(NH₂)CH₂OH}₂(CH₃CO₂)₂] **3** in moderate yield (36 %). Structural analysis by single crystal X-ray diffraction (Table 1) revealed the molecular structure. Figure 2 shows a ball-and-stick representation of the anion. It has no internal symmetry. One of the two molybdenum atoms (Mo1) has a distorted octahedral environment, whereas the other one (Mo2) displays distorted
25 tetrahedral coordination. Both molybdenum centres have two terminal oxo ligands. Mo1 is sharing

three bridging alkoxo ligands with zinc, two with Zn1 and one with Zn2. A terminal alkoxo ligand is completing its coordination sphere. Mo2 is sharing one bridging oxo ligand with each zinc. The two zinc atoms also have different environments. Zn1 has a distorted trigonal-bipyramidal environment, whereas Zn2 displays distorted tetrahedral coordination. Each of them is bound to the amine function of a TRIS molecule and to a monodentate acetate ligand, and is connected by a μ -oxo ligands to the Mo2 centre. The μ -alkoxo bridges towards the octahedral molybdenum complete the coordination spheres. Thus, the two TRIS molecules are complexed by two oxygen atoms and the nitrogen, leaving one OH group of each TRIS free.

The compound **3** is not suitable as a building block for hybrid molecular materials. It seems not to be stable in solution, as suggested by ^1H NMR analysis in DMSO. The signals are broad, indicating a dynamic process with several compounds in equilibrium. However, it is important to point out that the amine group is bound to the zinc. Such a coordination mode might explain the impossibility to form the Anderson structure, as it prevents the incorporation of zinc into the molybdenum oxo framework. Based on the well established HSAB concept,^[34] it is not surprising that the soft Zn(II) cation is bound to the nitrogen donor, whereas the hard Mo(VI) centre has more affinity towards the oxygen donors. The same phenomenon is likely to play a role with nickel(II). Indeed, no Anderson-type compound is isolated in the reaction of nickel(II) acetate with $[\text{N}(\text{C}_4\text{H}_9)_4]_4[\alpha\text{-Mo}_8\text{O}_{26}]$ in the presence of TRIS, and only ill-defined mixtures of compounds are obtained.

20 **Elaborating remote binding sites**

The free amine groups on compounds **1** and **2** could serve as ligands for transition metal ions, and we are currently exploring this possibility. Furthermore, they can react with suitable organic substrates to elaborate different binding sites. With this perspective, we chose to form imines by the reaction with aldehydes. Imine formation is known to proceed under mild conditions compatible with the stability of POMs.

The reaction of **1** with 2-pyridinecarbaldehyde affords the compound $[N(C_4H_9)_4]_3-$
 $[MnMo_6O_{18}\{(OCH_2)_3CN=C(2-C_5H_4N)\}_2]$ **4** which was isolated in 77 % yield. The complex was
characterized by single crystal X-ray diffraction. Crystallographic data are compiled in Table 1, and
the molecular structure of the complex anion is represented in Figure 3. The polyoxomolybdate
5 retains the Anderson structure of the parent compound **1**. Bond distances and angles (Table 2) are
very similar in both compounds. The 1,2-diimine function provides a new bidentate chelating site
for transition metal ions on each side of the polyanion.

The reaction of **1** with 4-pyridinecarbaldehyde proceeds in the same manner to give the
corresponding compound $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CN=C(4-C_5H_4N)\}_2]$ **5** in 70 % yield. IR
10 and NMR studies show the similarity of compounds **4** and **5**. Beside the typical vibrational bands
for the Anderson-type core, they present a band for the imine function at 1643 and 1641 cm^{-1}
respectively. In the 1H NMR spectra, all signals are broadened by the presence of the paramagnetic
 Mn^{III} center. The chemical shifts for the pyridine rings are in the normal range between 7 and 9
ppm (for details see Experimental Part), whereas the CH_2O groups are highly deshielded due to the
15 closer proximity to the Mn^{III} center. Nevertheless, they reflect also the imine formation. They are
displayed at 52.5 and 53.9 ppm in compounds **4** and **5** respectively, as compared to 61.1 ppm in the
free amine compound **1**.

Compounds **4** and **5** differ only in the location of the pendant binding sites. Whereas complex **4** has
20 two bidentate binding sites, complex **5** has only monodentate binding sites. This opens the way to
vary the complexation of transition metals with respect to the type of metal ions bound and the
stability of the complex formed. We are currently exploring these possibilities. Our first attempts to
coordinate Cu^{II} or Pd^{II} complexes to the grafted ligands on compounds **4** and **5** gave very insoluble
compounds. As our long term goal is the elaboration of defined structures in solution, we are now
25 modifying the ligand part and the transition metal complex. Our flexible approach which allows the
separate modification of each part is helpful in this respect.

Conclusion

We have shown the possibility to incorporate the TRIS ligand into a heteropolymolybdate. The self-assembly of such a functionalized POM from several metal ions (Mo^{VI} , Mn^{III} , Fe^{III}) and several
5 ligands (oxo, alkoxo) is a highly complex process relying on the molecular recognition of all the components. Their steric and electronic complementarity allows the formation of the expected structure in high yield. The affinity of Zn^{II} and Ni^{II} for nitrogen is incompatible with the preference of Mo^{VI} for oxo and alkoxo ligands, therefore disrupting the formation of the Anderson structure. As a result, mixtures of compounds are present in solutions of molybdate, TRIS and Zn^{II} or Ni^{II} . It
10 was possible to isolate one compound (**3**) of such a mixture in the solid state. This compound is representative for all the fragments which are presumably present in solution: it contains tetra- and hexacoordinated molybdenum with only O donor atoms, and tetra- and pentacoordinated zinc with N and O ligands.

15 The grafted ligands on the POM can be modified by organic reactions.^[35] The elaboration of binding sites presented here is only one aspect of this chemistry, and it is clear that other functions can be introduced in the same way. That is the advantage of this flexible approach where the synthesis of the POM core and the introduction of a specific function are two distinct steps. We are exploring this field by varying separately the POM (molybdates, vanadates, ...) and the function
20 (metal binding, hydrogen bonding, targeting biological substances, ...).

Experimental Section

General Remarks:

($\text{N}(\text{C}_4\text{H}_9)_4$)₄[α - Mo_8O_{26}] was prepared by literature methods.^[36] All other compounds, including
25 solvents, were commercially available as reagent grade and used as received. Elemental analysis

were performed by the "Service de microanalyse", Université Pierre et Marie Curie, Paris, France and by the "Service central d'analyse", CNRS, Vernaison, France.

Spectroscopy

NMR spectra (^1H , ^{13}C) were recorded on a Bruker AC300 spectrometer at 300 MHz and 75.5 MHz
5 respectively. Deuteriated solvent (CD_3CN unless otherwise stated) was used. Chemical shifts δ are expressed in ppm relative to Me_4Si , the downfield direction being positive, with residual solvent peak as standard. ^{13}C NMR was recorded using an INEPT pulsing sequence. Assignment of signals is quoted with respect to numbering within the molecular fragments: *pyr* stands for the pyridine rings, *TBA* stands for the tetrabutylammonium cations.

10 IR spectra were obtained in KBr pellets on a Bio-Rad FTS 165 spectrometer. Relative intensities are given after the wavenumber as vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

X-ray Crystal Structure Determination

A selected single crystal was set up on an automatic diffractometer Mach3 Enraf Nonius. Unit cell
15 dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; for compounds **1**, **2** and **4** (18, 38 and 22 % decay respectively) the data were accordingly scaled. Crystallographic data and other pertinent information are summarized in Table 1. Corrections were made for Lorentz and polarization effects. Secondary extinction corrections
20 were necessary only for compound **2**.

Computations were performed by using the PC version of CRYSTALS.^[37] Atomic form factors for neutral atoms were taken from tabulated values.^[38] Real and imaginary parts of anomalous dispersion were taken into account. The structure was solved by direct methods^[39] and successive Fourier maps. An absorption correction (based on a Psi-scan curve for **1**, using DIFABS^[40] for other
25 compounds) was applied.

For **1** and **2** non-hydrogen atoms were anisotropically refined except for the carbon atoms of the half cation contained in the asymmetric unit which presents some disorder and for the oxygen atoms of the water molecules (compound **1**). Restraints were applied to the carbon-carbon distances in both cations and hydrogen atoms were not introduced. For **3** all non hydrogen atoms were anisotropically refined. Application of restraints to one of the two acetate ligands was necessary. Hydrogen (C-H) atoms were introduced in calculated positions. For **4** because of the few observed reflections only manganese, molybdenum and oxygen atoms were anisotropically refined. Restraints were applied to the carbon-carbon distances of the cations and no hydrogen atoms were introduced. In all cases least square refinements in full matrix were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \sum(|F_o| - |F_c|) / \sum w F_o$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ having values listed in Table 1.

In the last stages of the refinement, each reflection was assigned a weight: $w = w' \{1 - [(|F_o| - |F_c|) / 6\sigma|F_o|]^2\}^2$ with $w' = 1 / \sum_r A_r T_r(X)$ with three coefficients for a Chebyshev series, for which $X = F_c / F_{c(max)}$.

Criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviations being less than 0.2 (except for **2**, due to the restraints applied to the acetate ion, the value is 0.8) and no significant features in the difference Fourier map.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-189392 (**1**), -189393 (**2**), -189394 (**3**) and -189395 (**4**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

25 **Synthesis and characterization**

[N(C₄H₉)₄]₃[MnMo₆O₁₈{(OCH₂)₃CNH₂}₂] (1): A mixture of [N(C₄H₉)₄]₄[α-Mo₈O₂₆] (8.00 g, 3.72 mmol) with Mn(CH₃COO)₃·2H₂O (1.49 g, 5.56 mmol) and (HOCH₂)₃CNH₂ (1.56 g, 12.8 mmol) in 150 mL of acetonitrile was refluxed for 16 h. The orange solution was cooled to room temperature and filtered to remove a very fine black solid. The filtrate was exposed to ether vapors. After 2 h, a white precipitate was filtered off. The orange filtrate was exposed again to ether vapors for several days. Large orange crystals were obtained. They were isolated by filtration, washed with a small amount of acetonitrile and then ether, and dried under vacuum. Yield 7.42 g (80%).

C₅₆H₁₂₄Mo₆MnN₅O₂₄ (1882.21): calcd. C 35.74, H 6.64, Mo 30.58, Mn 2.92, N 3.72; found C 35.73, H 6.72, Mo 29.04, Mn 2.75, N 3.54.

10 IR: ν_{max} = 3290 (ν_{as} NH, w), 2961 (ν CH, s), 2936 (ν CH, s), 2875 (ν CH, s), 1611 (w), 1480 (δ CH, s), 1384 (δ CH, m), 1348 (w), 1256 (w), 1151 (w), 1129 (w), 1108 (ν CO, m), 1040 (ν CO, s), 939 (ν Mo=O, s), 919 (ν Mo=O, s), 902 (ν Mo=O, s), 797 (w), 737 (w), 663 (ν Mo-O-Mo, vs), 563 (m), 520 (w), 461 (m), 413 (m), 368 (s), 321 (m), 282 (w).

¹H NMR ([D₆]DMSO) δ = 0.93 (t, ³J = 7.3 Hz, 36 H, 4-H_{TBA}), 1.31 (sx, ³J = 7.3 Hz, 24 H, 3-H_{TBA}), 1.57 (m, 24 H, 2-H_{TBA}), 3.16 (m, 24 H, 1-H_{TBA}), 61.1 (s, 12 H, CH₂O).

[N(C₄H₉)₄]₃[FeMo₆O₁₈{(OCH₂)₃CNH₂}₂] 2: A mixture of [N(C₄H₉)₄]₄[α-Mo₈O₂₆] (1.08 g, 0.5 mmol) with Fe(acac)₃ (265 mg, 0.75 mmol, acac = acetylacetonate) and (HOCH₂)₃CNH₂ (182 mg, 1.5 mmol) in 20 mL of acetonitrile was refluxed for 16 h. The red suspension was cooled to room temperature, and a yellow-orange solid was removed by filtration. The red filtrate was exposed to ether vapors. After three days, a microcrystalline solid is isolated by filtration. The compound was recrystallized from DMF to obtain analytical pure **2** with 2 molecules of DMF. Yield 615 mg (49%). Crystals suitable for X-ray diffraction were grown by slow ether diffusion into an acetonitrile solution.

$C_{62}H_{138}FeMo_6N_7O_{26}$ (2029.31) calcd. C 36.70, H 6.85, Fe 2.75, Mo 28.37, N 4.83; found C 36.01, H 6.80, Fe 2.17, Mo 28.07, N 4.65.

IR: $\nu(\tilde{)}_{max} = 2961$ (v CH, s), 2935 (v CH, s), 2874 (v CH, s), 1654 (w), 1482 (δ CH, m), 1382 (δ CH, w), 1153 (w), 1129 (w), 1041 (v CO, s), 938 (v Mo=O, vs), 920 (v Mo=O, vs), 902 (v Mo=O, vs), 802 (w), 665 (v Mo-O-Mo, br, vs), 613 (w), 562 (m), 528 (w), 487 (w), 450 (w), 410 (w), 367 (m), 324 (m), 278 (w).

$[N(C_4H_9)_4]_2[Mo_2Zn_2O_6\{(OCH_2)C(NH_2)CH_2OH\}_2(CH_3CO_2)_2]$ **3**: A solution of $[N(C_4H_9)_4]_2[Mo_2O_7]$ (1.58 g, 2 mmol), $Zn(CH_3CO_2)_2$ (878 mg, 4 mmol) and $(HOCH_2)_3CNH_2$ (485 mg, 4 mmol) in 20 mL of acetonitrile was heated to reflux. After 20 min, the mixture became cloudy. After 16 h, the reaction mixture was filtered while hot. The filtrate was cooled to room temperature and exposed to ether vapors. Over a period of two months, colorless crystals formed. They were isolated by filtration and dried under vacuum. Yield 0.91 g (36%).

$C_{44}H_{96}Mo_2N_4O_{16}Zn_2$ (1259.91) calcd. C 41.95, H 7.68, N 4.45; found C 42.05, H 7.69, N 4.60.

IR: $\nu(\tilde{)}_{max} = 2962$ (v CH, s), 2936 (v CH, s), 2876 (v CH, s), 2849 (s, sh), 2875 (w), 1615 (s), 1586 (s, sh), 1486 (δ CH, s), 1460 (δ CH, m), 1418 (m, sh), 1381 (δ CH, s), 1326 (m), 1278 (w), 1153 (m), 1104 (m, sh), 1088 (s, sh), 1075 (s), 1020 (v CO, s), 972 (s), 939 (w, sh), 913 (v Mo=O, vs), 890 (v Mo=O, vs), 847 (v Mo=O, vs), 825 (vs, sh), 792 (m, sh), 739 (w), 671 (m), 662 (m), 615 (w), 561 (w), 525 (m), 449 (w), 421 (w), 336 (w), 330 (w), 292 (w).

1H NMR ($[D_6]DMSO$, 80°C) $\delta = 0.95$ (t, $^3J = 7.0$ Hz, 24 H, 4- H_{TBA}), 1.36 (m, 16 H, 3- H_{TBA}), 1.63 (q, $^3J = 7.5$ Hz, 16 H, 2- H_{TBA}), 1.78 (s, 6 H, CH_3CO_2), 3.22 (m, 16 H, 1- H_{TBA}), 3.5 (br), 4.0 (br), 4.1 (br), 4.2 (br).

^{13}C NMR ($[D_6]DMSO$, 80°C) $\delta = 13.5$ (4- C_{TBA}), 19.2 (3- C_{TBA}), 23.1 (2- C_{TBA}), 23.8 ($\underline{C}H_3COO$), 56.7, 57.5 (1- C_{TBA}), 64.1, 70.8, 78.9, 79.2, 171.5, 176.1.

25

$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CN=C(2-C_5H_4N)\}_2]$ **4**: 2-pyridinecarbaldehyde (330 μ L, 3.5 mmol) and acetic acid (9 μ L, 0.16 mmol) were added to a boiling solution of **1** (3.00 g, 1.59 mmol) in 100 mL of methanol. After 10 min, an orange solid started to precipitate. The mixture was heated to reflux for further 3.5 h. After cooling to room temperature, a methanolic solution of $[N(C_4H_9)_4](OH)$ ($c = 5.09 \cdot 10^{-3}$ M, 34 mL, 0.16 mmol) was added and the orange precipitate was isolated by filtration, washed with methanol and dried under vacuum. Yield 2.54 g (77%).

$C_{68}H_{130}MnMo_6O_{24}N_7$ (2060.40) calcd. C 39.64, H 6.36, N 4.76; found C 39.58, H 6.47, N 4.89.

1H NMR (67°C) $\delta = 0.99$ (br, 36 H, 4- H_{TBA}), 1.41 (br, 24 H, 3- H_{TBA}), 1.65 (br, 24 H, 2- H_{TBA}), 3.14 (br, 24 H, 1- H_{TBA}), 7.20 (s, 2 H, 5- H_{pyr}), 7.88 (s, 4 H, 3- H_{pyr}), 4- H_{pyr}), 8.45 (s, 2 H, pyrCH=N), 8.68 (s, 2 H, 6- H_{pyr}), 54.4 (s, 12 H, CH₂O). ([D₆]DMSO, 80°C) $\delta = 0.93$ (t, $^3J = 7.6$ Hz, 36 H, 4- H_{TBA}), 1.34 (m, $^3J = 7.6$ Hz, 24 H, 3- H_{TBA}), 1.61 (m, 24 H, 2- H_{TBA}), 3.18 (m, 24 H, 1- H_{TBA}), 7.28 (br, 2 H, 5- H_{pyr}), 7.84 (br, 2 H, 4- H_{pyr}), 7.94 (br, 2 H, 3- H_{pyr}), 8.24 (br, 2 H, pyrCH=N), 8.72 (br, 2 H, 6- H_{pyr}), 52.5 (br, 12 H, CH₂O).

^{13}C NMR ([D₆]DMSO, 80°C) $\delta = 12.82$ (4- C_{TBA}), 18.79 (3- C_{TBA}), 22.78 (2- C_{TBA}), 57.71 (1- C_{TBA}), 121.6 (5- C_{pyr}), 125.7 (3- C_{pyr}), 135.8 (4- C_{pyr}), 148.0 (2- C_{pyr}), 151.6 (6- C_{pyr}), 198.0 (pyrCH=N).

IR: ν_{max} = 2961 (v CH, s), 2936 (v CH, s), 2875 (v CH, s), 1643 (C=N, m), 1584 (Ar, w), 1567 (Ar, w), 1482 (δ CH, s), 1469 (δ CH, m), 1381 (δ CH, m), 1345 (w), 1262 (w), 1152 (w), 1095 (w), 1088 (w), 1026 (v CO, s), 992 (w), 941 (v Mo=O, s), 921 (v Mo=O, s), 904 (v Mo=O, s), 803 (w), 782 (w), 664 (v Mo-O-Mo, vs), 592 (w), 562 (m), 463 (m), 410 (m), 366 (s), 321 (m), 260 (m).

$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CN=C(4-C_5H_4N)\}_2]$ **5**: The compound was obtained as an orange solid by the same procedure as for **4**. Compound **5** is more soluble than **4**. Yield 2.23 g (70%).

$C_{68}H_{130}MnMo_6O_{24}N_7$ (2060.40) calcd. C 39.64, H 6.36, N 4.76; found C 39.41, H 6.47, N 4.77.

^1H NMR (67°C) δ = 0.98 (br, 36 H, 4- H_{TBA}), 1.41 (br, 24 H, 3- H_{TBA}), 1.66 (br, 24 H, 2- H_{TBA}), 3.17 (br, 24 H, 1- H_{TBA}), 7.56 (br, 4 H, 3- H_{pyr} , 6- H_{pyr}), 8.41 (br, 2 H, pyrCH=N), 8.68 (br, 4 H, 4- H_{pyr} , 5- H_{pyr}), 53.9 (br, 12 H, CH_2O).

^{13}C NMR ([D6]DMSO) δ = 13.60 (4- C_{TBA}), 19.33 (3- C_{TBA}), 23.07 (2- C_{TBA}), 57.50 (1- C_{TBA}), 123.6
5 (3- C_{pyr} , 6- C_{pyr}), 136.1 (2- C_{pyr}), 149.4 (4- C_{pyr} , 5- C_{pyr}), 197.6 (pyrCH=N), 217.3 (CH_2O).

IR: $\nu(\text{tilde})_{\text{max}}$ = 2961 (v CH, s), 2935 (v CH, s), 2874 (v CH, s), 1641 (C=N, m), 1597 (Ar, m),
1559 (Ar, m), 1480 (δ CH, s), 1467 (δ CH, m), 1408 (m), 1381 (δ CH, m), 1348 (w), 1322 (w), 1232
(w), 1170 (w), 1153 (w), 1094 (w), 1084 (w), 1026 (v CO, s), 940 (v Mo=O, s), 921 (v Mo=O, s),
903 (v Mo=O, s), 818 (w), 803 (w), 736 (w), 664 (v Mo-O-Mo, vs), 563 (m), 521 (w), 465 (m), 410
10 (m), 367 (s), 322 (m).

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((Captions:))

Table 1. Crystal data and structure refinement for compounds **1**, **2**, **3** and **4**.

5 Table 2. Selected bond lengths and angles for the anions in **1**, **2** and **4**.

10 Figure 1. Structure of the anion of **1**: $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$. The TRIS ligands cap both sides of the Anderson structure.

Figure 2. Ball-and-stick representation of the anion of **3**:

$[\text{Mo}_2\text{Zn}_2\text{O}_6\{(\text{OCH}_2)\text{C}(\text{NH}_2)\text{CH}_2\text{OH}\}_2(\text{CH}_3\text{CO}_2)_2]^{2-}$. Note the coordination of the amine groups to zinc.

15

Figure 3. Structure of the anion of **4**: $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CN}=\text{C}(2\text{-C}_5\text{H}_4\text{N})\}_2]^{3-}$. A chelating binding site is displayed at both sides of the Anderson structure.

20 {Insert optional text to be placed underneath the **Graphical Abstract (Table of Contents)**.}

((Tables))

Table 1.

Compound	1	2	3	4
Empirical formula	C ₅₆ H ₁₂₄ MnMo ₆ N ₅ O ₂₆	C ₅₆ H ₁₂₄ FeMo ₆ N ₅ O ₂₄	C ₄₆ H ₉₉ Mo ₂ N ₅ O ₁₆ Zn ₂	C ₆₈ H ₁₃₀ MnMo ₆ N ₇ O ₂₄
Formula mass	1914.2	1883.1	1301.0	2060.4
a[Å]	14.650(4)	25.845(11)	13.690(3)	23.243(4)
b[Å]	24.245(9)	24.518(13)	14.634(4)	14.298(3)
c[Å]	24.453(10)	14.649(12)	18.037(11)	27.595(4)
α[°]	90	90	75.31(4)	90
β[°]	90	101.55(6)	86.11(4)	99.28(1)
γ[°]	90	90	62.69(2)	90
V[Å ³]	8685(5)	9706(9)	3101(2)	9051(3)
Z	4	4	2	4
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	P c m n	C 2/m	P -1	P 21/c
Crystal colour	orange	yellow	none	orange
Linear abs. coef. μ [cm ⁻¹]	10.2	9.9	12.3	9.8
D _{calc} [g·cm ⁻³]	1.46	1.38	1.39	1.51
Radiation	Mo-Kα(0.71069Å)	Mo-Kα(0.71069Å)	Mo-Kα(0.71069Å)	Mo-Kα(0.71069Å)
Scan mode	ω/2θ	ω/2θ	ω/2θ	ω/2θ
Scan range[°]	0.80 + 0.345tan(θ)	0.80 + 0.345tan(θ)	0.80 + 0.345tan(θ)	0.80 + 0.345tan(θ)
θ range[°]	1 - 25	1 - 26	1 - 28	1 - 25
Temperature[K]	221	295	295	295
hkl range	0, 17; 0, 28; 0, 29	0, 31; 0, 30; -18, 17	0, 18; -17, 19; -23,23	0, 27; 0, 16; -32, 32
Nb. of data collected	8355	9343	15540	17021
Nb. of unique data	7813	9132	14920	15879
R _{int}	none	0.03	0.04	0.05
Nb. of data in refinement	2998 (F _o) ² > 3σ(F _o) ²	4048 (F _o) ² > 3σ(F _o) ²	8070 (F _o) ² > 3σ(F _o) ²	4248 (F _o) ² > 2σ(F _o) ²
Absorption correction	Psi-Scan	DIFABS	DIFABS	DIFABS
T _{min} , T _{max}	0.72, 1	0.71, 1	0.93, 1	0.94, 1
Nb. of variables	413	410	650	580
Final R	0.0620	0.0950	0.0458	0.0718
Final R _w	0.0713	0.116	0.0568	0.0791
Goodness of fit	1.04	1.00	1.03	1.10
Extinction coefficient	none	192	none	none
Δρ _{max} [e/ Å ³]	-0.70, +1.13	-0.84, +1.29	-0.56, +0.79	-0.76, +0.97

Table 2.

	1	2	4
Distances			
Mo-O _{terminal}	1.693(10)-1.718(10)	1.650(9)-1.720(14)	1.649(17)-1.703(13)
Mo-O _{bridge}	1.904(9)-1.925(9)	1.892(29)-1.925(11)	1.882(16)-1.952(13)
Mo-O _{alkoxo}	2.341(7)-2.403(7)	2.341(44)-2.360(8)	2.328(17)-2.415(13)
M-O ^[a]	1.943(8)-2.031(12)	1.971(8)-1.991(27)	1.948(16)-1.992(13)
Angles O-M-O^[a]			
same TRIS	92.05(22)-92.88(30)	91.92(31)-92.84(22)	91.92(51)-93.40(50)
opposite TRIS, cis	87.18(32)-88.10(22)	87.16(22)-88.08(31)	86.67(52)-88.02(53)
opposite TRIS, trans	179.42(31)-179.78(49)	180.00(37)	178.99(56)-179.93(51)

^[a] M = Mn (**1**, **4**); Fe (**2**).

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 $(\text{CN}_3\text{H}_6)_3[\text{VIVVV}_5\text{O}_{13}\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}_2] \cdot \text{cntdot} \cdot 4.5\text{H}_2\text{O}$ and trans-
 $(\text{CN}_3\text{H}_6)_2[\text{VV}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}_2] \cdot \text{cntdot} \cdot \text{H}_2\text{O}$
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