FULL PAPER

Developing Remote Metal Binding Sites in Heteropolymolybdates[‡]

Pierre R. Marcoux,[a] Bernold Hasenknopf,*[a] Jacqueline Vaissermann,[a] and Pierre Gouzerh[a]

Anderson-type polyoxomolybdates $[MMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]^{3-}$ (M = Mn^{III}, Fe^{III}) were prepared and structurally characterized. The tris(alkoxo) ligands are bound to the central heteroatom via their oxygen atoms. The corresponding compounds with M = Ni^{II} or Zn^{II} are not accessible since these cations have a preference for the amino functionality.

The pendant amino groups of the manganese-containing derivative react with pyridinecarbaldehydes to give the corresponding imines. This provides new mono- and bidentate binding sites for metal cations.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Organic moieties can be grafted onto polyoxometalates (POMs).[1] This provides an entry into the field of organic/inorganic hybrid compounds which combine the properties of the (oxo)metal cluster with those of the organic component.[2,3] Such functionalized POMs have been used in the preparation of polymers,[4−7] dendrimers,[8] and macroporous materials,[9] by covalently crosslinking the organic groups. Metallo-supramolecular chemistry can be used effectively for the construction of functional assemblies.[10−13] Both complete and lacunary POMs can act as ligands for a variety of metal cations,[14] and the resulting complexes have interesting electrical, optical, magnetic and catalytic properties.[15−21] The extra metal centers occasionally provide the way to the formation of 1-D[22,23] or 2-D[24] POM arrays. However, the complexation of metal ions at remote sites of organic ligands grafted on POMs is less common. Indeed the (ferrocenylimido)hexamolybdate reported by Maatta et al. was obtained by treating a ferrocenyl-substituted imido precursor with hexamolybdate.[25] More recently, Stein and co-workers obtained one-dimensional chains in the solid state by the coordination of Ag^I ions to $[Mo_{12}O_{46}(AsC_6H_4-4-NH_2)_4]^{4-}$.[26] To the best of our knowledge, complex formation in solution involving a ligand already bound to a polyoxometalate has not been reported in the literature.

Thus, our interest focused on the combination of POMs and other metals using organic ligands. This strategy is complementary to that involving the coordination of oxo ligands, in order to "bridge the gap between polyoxometalates and classic coordination compounds".[27] The organic molecules may display donor atoms other than oxygen, and their arrangement around the binding site may differ; thus, they provide the versatility to adjust to the chemical and geometrical preferences of the extra metal centers. Ideally, our approach would permit the selection of 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 implementation of this concept requires the development of a flexible synthetic strategy. A key role is played by 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 develop a coordination site. We chose tris-(hydroxymethyl)aminomethane $[(HOCH_2)_3CNH_2,$ TRIS] for this purpose since tris(alkoxo) moieties can be incorporated in Anderson,[28] Lindqvist,[29−31] Dawson[8,32] and other POMs,[32−34] while the free amino group can be used to create a new coordination site. The incorporation of TRIS into Anderson-type polyoxomolybdates was investigated first.

The Anderson structure $[H_x(M'O_6)M_6O_{18}]^{n-}$ ($x = 0-6$, $n = 2-6$) consists of a planar arrangement of six edge-sharing MO$_6$ (M = Mo, W) octahedra around a central heteroatom M'.[35−37] We have recently shown that two tris-(hydroxymethyl)methane residues RC(CH$_2$O)$_3$ (R = CH$_3$, CH$_2$OH, CH$_2$NO$_2$) can cap both sides of the polyanion.[28] Two forms were found. In the first form − named δ for its approximate D_3 symmetry − the triol caps the central octahedron, while in the second form − named χ for its approximate C_{2v} symmetry − the triol caps 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. Here, we present the results of the reactions with TRIS, and the derivatization of the pendant amino group. The protonated form of TRIS has been used as counterion for polyoxometalates.[38] It has been shown that amide and tertiary amine derivatives can be incorporated into the POM frameworks,[30,39] but to the best of our knowledge, TRIS itself has not been incorporated into the POMs yet. Difficulties with this compound have been linked to its role as a reductant.[39]

Results and Discussion

Grafting a Free Amino Group onto a POM

Treatment of $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ with manganese-(III) acetate in the presence of TRIS gave $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ (**1**) which was isolated as orange crystals in an 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 previously reported.[28] Six edge-sharing MoO_6 octahedra are arranged around a central MnO_6 unit, forming the Anderson structure. The two
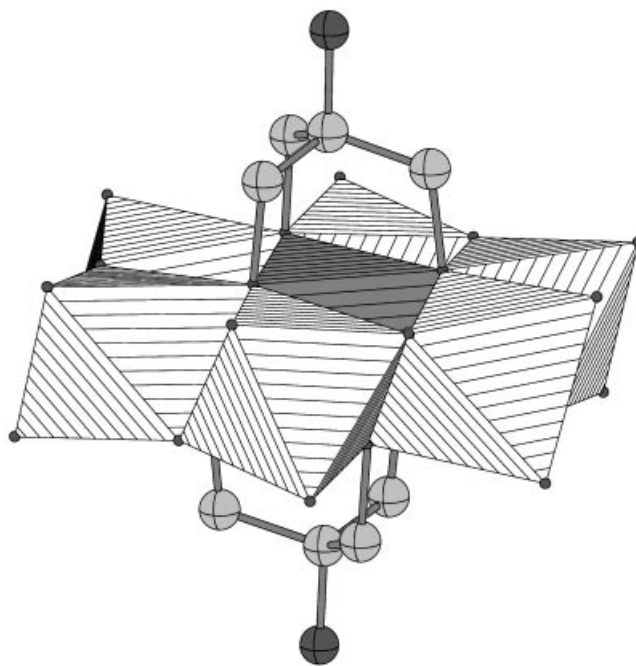

Figure 1. Structure of the anion of **1**: $[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]^{3-}$; the TRIS ligands cap both sides of the Anderson structure

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

Compound	1	2	3	4
Empirical formula	$C_{56}H_{124}MnMo_6N_5O_{26}$	$C_{56}H_{128}FeMo_6N_5O_{24}$	$C_{46}H_{99}Mo_2N_5O_{16}Zn_2$	$C_{68}H_{130}MnMo_6N_7O_{24}$
Formula mass	1914.2	1918.2	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 [Å³]	8685(5)	9706(9)	3101(2)	9051(3)
Z	4	4	2	4
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	$Pcmn$	$C2/m$	$P\bar{1}$	$P2_1/c$
Crystal color	orange	yellow	none	orange
Linear abs. coeff. μ [cm^{-1}]	10.2	9.9	12.3	9.8
$D_{calcd.}$ [g·cm^{-3}]	1.46	1.38	1.39	1.51
Radiation	Mo-K_α (0.71069 Å)	Mo-K_α (0.71069 Å)	Mo-K_α (0.71069 Å)	Mo-K_α (0.71069 Å)
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
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
T [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
No. of data collected	8355	9343	15540	17021
No. of unique data	7813	9132	14920	15879
R_{int}	none	0.03	0.04	0.05
No. of data in refinement	2998 $(F_o)^2 > 3\sigma(F_o)^2$	4048 $(F_o)^2 > 3\sigma(F_o)^2$	8070 $(F_o)^2 > 3\sigma(F_o)^2$	4248 $(F_o)^2 > 2\sigma(F_o)^2$
Absorption correction	ψ-scan	DIFABS	DIFABS	DIFABS
$T_{min.}$, $T_{max.}$	0.72, 1	0.71, 1	0.93, 1	0.94, 1
No. 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
$\Delta\rho_{max}$ [e/Å³]	−0.70, +1.13	−0.84, +1.29	−0.56, +0.79	−0.76, +0.97

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

	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**).

organic moieties cap both sides of the planar hexagon. All the alkoxo ligands are bound to the Mn^{III} ion; thus, the structure corresponds to the δ type. Selected bond lengths and angles are compiled in Table 2. It should be noted that the rigidity of the POM framework prevents the Mn^{III} ion from undergoing marked Jahn$-$Teller distortions: the coordination octahedron is only very slightly elongated.

The reaction of [N(C$_4$H$_9$)$_4$]$_4$[α-Mo$_8$O$_{26}$] with iron(III) acetylacetonate in the presence of TRIS gave [N(C$_4$H$_9$)$_4$]$_3$[FeMo$_6$O$_{18}${(OCH$_2$)$_3$CNH$_2$}$_2$] (**2**) which was isolated as yellow crystals in a 50% yield. Structural analysis by X-ray diffraction of single crystals (Table 1) revealed the expected δ-type Anderson structure. Selected bond lengths and angles are compiled in Table 2.

IR spectra of compounds **1** and **2** (listed in the Exp. Sect.) are in agreement with the crystal structures.[28,40] It has to be pointed out that the IR spectra display a single, broad band at ca. 700 cm^{-1} which is assigned to the Mo$-$O$-$Mo bridges, in accordance with the δ structure. The IR spectra of the χ structure would present two bands in this region.[28]

The reactions of nickel(II) acetate or zinc(II) acetate with [N(C$_4$H$_9$)$_4$]$_4$[α-Mo$_8$O$_{26}$] 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} metal ion.[28] Therefore, we decided to vary the reaction conditions and to use a different source of molybdate. From the reaction of zinc(II) acetate with [N(C$_4$H$_9$)$_4$]$_2$[Mo$_2$O$_7$] in the presence of TRIS, we isolated a compound with the molecular formula [N(C$_4$H$_9$)$_4$]$_2$[Mo$_2$Zn$_2$O$_6${(OCH$_2$)$_2$C(NH$_2$)CH$_2$OH}$_2$(CH$_3$CO$_2$)$_2$] (**3**) in a 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 Mo atom (Mo2) displays distorted tetrahedral coordination. Both molybdenum centers have two terminal oxo ligands. Mo1 shares three bridging alkoxo ligands with the zinc atoms, two with Zn1 and one with Zn2. A terminal alkoxo ligand completes its coordination sphere. Mo2 shares one bridging oxo ligand with each zinc atom. The two zinc atoms also have different environments. Zn1
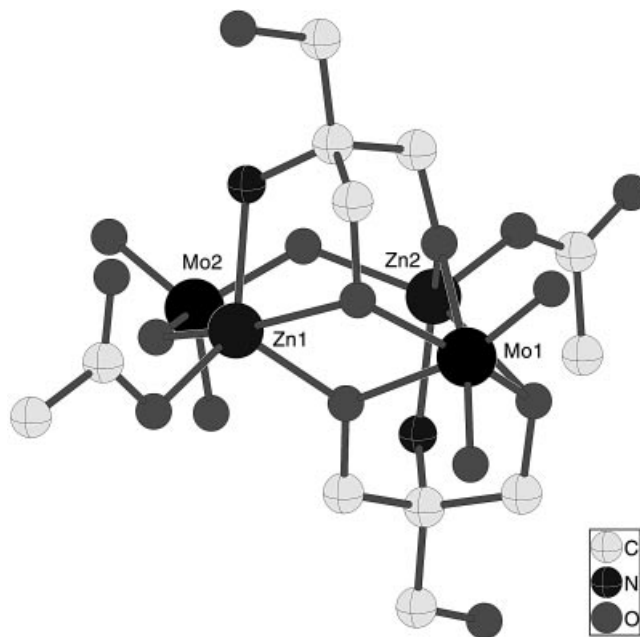

Figure 2. Ball-and-stick representation of the anion of **3**: [Mo$_2$Zn$_2$O$_6${(OCH$_2$)C(NH$_2$)CH$_2$OH}$_2$(CH$_3$CO$_2$)$_2$]$^{2-}$; note the coordination of the amino groups to the zinc atoms

has a distorted trigonal bipyramidal environment, whereas Zn2 displays distorted tetrahedral coordination. Each of the Zn atoms is bound to the amino functional group of a TRIS molecule and to a monodentate acetate ligand, and is connected by a μ-oxo ligand to the Mo2 center. The μ-alkoxo bridges formed with the octahedral molybdenum complete the coordination spheres. Thus, the two TRIS molecules are complexed by two oxygen atoms and a nitrogen atom, leaving one OH group of each TRIS free.

Compound **3** was also analyzed by solution NMR spectroscopy. In addition to the signals arising from the tetrabutylammonium cations and the acetate ligands, the ^{1}H NMR spectrum displays three broad signals of equal intensity which are assigned to the CH$_2$ groups of TRIS. In the ^{13}C NMR spectrum, the TRIS ligands give rise to four signals. This analysis does not exclude the fact that the structure of **3** is maintained in solution, with the overlap of some of the signals of the two TRIS molecules. Yet, it seems more likely

that the spectra correspond to one or more compounds resulting from the fragmentation of **3**. The decomposition of **3** in solution is further supported by the appearance of some weak signals in the ^{13}C NMR spectrum.

Compound **3** is not suitable as a building block for hybrid molecular materials. However, it is important to point out that the amino group is coordinated to the zinc atom. Such a coordination mode may prohibit the formation of the Anderson structure, as it prevents the incorporation of the zinc atom into the (oxo)molybdenum framework. Based on the well-established HSAB concept,[41] it is not surprising that the soft Zn^{II} cation is bound to the nitrogen donor, whereas the hard Mo^{VI} center has a greater affinity towards the oxygen donors. The same factor is likely to play a role with the nickel(II) cation. Indeed, no Anderson-type compound was isolated from the reaction of nickel(II) acetate with $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ in the presence of TRIS, and only ill-defined mixtures of compounds were obtained.

Developing Remote Binding Sites

The free amino groups of 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, thus developing different binding sites. With this perspective, we decided to form imines by reaction with aldehydes. Imine formation is known to proceed under conditions under which the functionalized POMs are stable.

Reaction of **1** with 2-pyridinecarbaldehyde afforded $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CN=C(2\text{-}C_5H_4N)\}_2]$ **(4)** which was isolated in a 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 displayed in Figure 3. The polyoxomolybdate retains the Anderson structure of the parent compound **1**. Bond lengths and angles (Table 2) are very similar in both compounds. The 1,2-diimine functional group provides a new bidentate chelating site for transition metal ions, on each side of the polyanion.

Reaction of **1** with 4-pyridinecarbaldehyde proceeded in the same manner giving the corresponding compound $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CN=C(4\text{-}C_5H_4N)\}_2]$ **(5)**, in a 70% yield. IR and NMR spectroscopic studies show that compounds **4** and **5** are very similar. Beside the typical vibrational bands for the Anderson-type core, the IR spectra present a band for the imine functionality at 1643 and 1641 cm^{-1}, respectively. In the ^{1}H 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 $\delta = 7$ and 9 ppm (for details see Exp. Sect.), whereas the CH$_2$O groups are highly deshielded since they are closer to the Mn^{III} center. Nevertheless, they also reflect imine formation. The signals for the CH$_2$O groups are displayed at $\delta = 52.5$ and 53.9 ppm in compounds **4** and **5**, respectively, relative to $\delta = 61.1$ ppm in the free amino compound **1**.

Compounds **4** and **5** differ only in the nature of the pendant binding sites. Complex **5** only has monodentate bind-
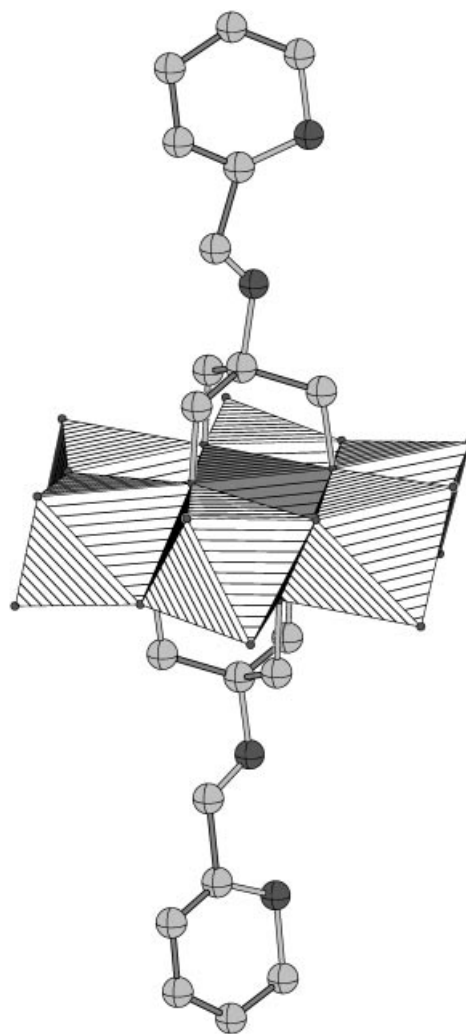

Figure 3. Structure of the anion of **4**: $[MnMo_6O_{18}\{(OCH_2)_3CN=C(2\text{-}C_5H_4N)\}_2]^{3-}$; a chelating binding site is displayed at both sides of the Anderson structure

ing sites, whereas complex **4** has two bidentate binding sites. This opens the way to vary complex formation 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 developing defined structures in solution, we are now modifying the ligand, and the transition metal complex.

Conclusion

We have shown the possibility of incorporating the TRIS ligand into a heteropolymolybdate. The self-assembly of such a functionalized POM arising from several metal ions (Mo^{VI}, Mn^{III}, Fe^{III}) and several ligands (oxo, alkoxo) is a highly complex process which relies on the molecular recognition of all the components. Their steric and electronic properties are complementary, thus allowing for the formation of the expected structure in high yields. The affinity of

Zn^{II} and Ni^{II} metal ions for nitrogen donors the preference of Mo^{VI} for oxo and alkoxo ligands are antagonistic, 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} cations. It was possible to isolate one compound (**3**) of such a mixture in the solid state. This compound contains tetra- and hexacoordinate molybdenum atoms with only O donor atoms, and tetra- and pentacoordinate zinc atoms with N and O ligands.

The grafted ligands on the POM can be modified by organic reactions.[42] The development of the binding sites presented here is only one aspect of this chemistry, and it is clear that other functionalities can be introduced in the same way. The advantage of this flexible approach is that the synthesis of the POM core and the introduction of a specific function are two distinct steps. We are exploring this field by separately modifying the POM (molybdates, vanadates, ...) and the function (metal binding, hydrogen bonding, targeting biological substances, ...).

Experimental Section

General Remarks: [N(C$_4$H$_9$)$_4$]$_4$[α-Mo$_8$O$_{26}$][43] and [N(C$_4$H$_9$)$_4$]$_2$-[Mo$_2$O$_7$][44] were prepared by literature methods. All other chemicals, including solvents, were commercially available as reagent grade and used as received. Elemental analyses 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 (^{1}H, ^{13}C) were recorded with a Bruker AC300 spectrometer at 300 and 75.5 MHz, respectively, at 25 °C unless otherwise stated. Chemical shifts (δ) are expressed in ppm relative to Me$_4$Si, the high frequency direction being positive, with the residual solvent peak as standard. 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. IR spectra were recorded using KBr pellets with a Bio-Rad FTS 165 spectrometer at 4 cm^{-1} resolution. 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: Crystallographic data are summarized in Table 1. Data were recorded at room temperature with an Enraf−Nonius MACH3 diffractometer with graphite-monochromated Mo-K_α radiation. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 automatically centered reflections. Two standard reflections were monitored periodically. Some decay was observed (18, 38 and 22% for compounds **1**, **2** and **4**, respectively) and the data were scaled accordingly. Corrections were made for Lorentz and polarization effects and for absorption (based on Ψ scans for **1** and using DIFABS[45] for other compounds). Secondary extinction corrections were found necessary only for compound **2**. Computations were performed by using the PC version of CRYSTALS.[46] Atomic form factors for neutral atoms were taken from tabulated values.[47] Real and imaginary parts of anomalous dispersion were taken into account. The structures were solved by direct methods[48] and successive Fourier maps. 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 refined anisotropically. 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 refined anisotropically. Restraints were applied to the carbon−carbon distances of the cations and no hydrogen atoms were introduced. In all cases least-squares refinements in full-matrix were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma wF_o$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, 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 $w' = 1/\Sigma_r A_r T_r(X)$ with three coefficients for a Chebyshev series, for which $X = F_c/F_{c(max.)}$. In the final cycles, no parameter changed by more than 0.2σ (except for **2** where the value was 0.8σ due to the restraints applied to the acetate ligand) and the final difference Fourier maps were free of any significant residual density. CCDC-189392 (**1**), -189393 (**2**), -189394 (**3**) and -189395 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis and Characterization

[N(C$_4$H$_9$)$_4$]$_3$[MnMo$_6$O$_{18}${(OCH$_2$)$_3$CNH$_2$}$_2$] (1): A mixture of [N(C$_4$H$_9$)$_4$]$_4$[α-Mo$_8$O$_{26}$] (8.00 g, 3.7 mmol), Mn(CH$_3$COO)$_3$·2H$_2$O (1.49 g, 5.6 mmol) and (HOCH$_2$)$_3$CNH$_2$ (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 vapor. After 2 h, a white precipitate was filtered off. The orange filtrate was again exposed to ether vapor for several days. Large orange crystals were obtained. They were isolated by filtration, washed with a small amount of acetonitrile and ether, and dried under vacuum. The crystal for X-ray analysis contained 2 H$_2$O. Yield: 7.42 g (80%). C$_{56}$H$_{124}$MnMo$_6$N$_5$O$_{24}$ (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. IR: $\tilde{\nu}_{max}$ = 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) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 0.93 (t, ^3J = 7.3 Hz, 36 H, 4-H$_{TBA}$), 1.31 (m, 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, CH$_2$O) ppm.

[N(C$_4$H$_9$)$_4$]$_3$[FeMo$_6$O$_{18}${(OCH$_2$)$_3$CNH$_2$}$_2$] (2): A mixture of [N(C$_4$H$_9$)$_4$]$_4$[α-Mo$_8$O$_{26}$] (1.08 g, 0.5 mmol), [Fe(acac)$_3$] (265 mg, 0.75 mmol, acac = acetylacetonate) and (HOCH$_2$)$_3$CNH$_2$ (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 vapor. After 3 d, a microcrystalline solid was isolated by filtration. The compound was recrystallized from DMF to obtain analytically pure **2** with 2 equiv. 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$_6$N$_7$O$_{26}$

(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: $\tilde{v}_{max}$ = 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) cm^{-1}. The paramagnetic nature of the compound prevents the recording of the NMR spectra.

[N(C$_4$H$_9$)$_4$]$_2$[Mo$_2$Zn$_2$O$_6${(OCH$_2$)C(NH$_2$)CH$_2$OH}$_2$(CH$_3$CO$_2$)$_2$] (3): A solution of [N(C$_4$H$_9$)$_4$]$_2$[Mo$_2$O$_7$] (1.58 g, 2.0 mmol), Zn(CH$_3$CO$_2$)$_2$ (878 mg, 4.0 mmol) and (HOCH$_2$)$_3$CNH$_2$ (485 mg, 4.0 mmol) in 20 mL of acetonitrile was heated under 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 vapor. Colorless crystals formed over a period of 2 months. They were isolated by filtration and dried under vacuum for analysis. Yield: 0.91 g (36%). The crystal used in the X-ray diffraction analysis was found to contain one equiv. of acetonitrile per polyanion. C$_{44}$H$_{96}$Mo$_2$N$_4$O$_{16}$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: $\tilde{v}_{max}$ = 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 (sh), 792 (sh), 739 (w), 671 (m), 662 (m), 615 (w), 561 (w), 525 (m), 449 (w), 421 (w), 336 (w), 330 (w), 292 (w) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 80 °C): δ = 0.95 (t, ^3J = 7.0 Hz, 24 H, 4-H$_{TBA}$), 1.36 (m, 16 H, 3-H$_{TBA}$), 1.63 (m, 16 H, 2-H$_{TBA}$), 1.78 (s, 6 H, CH$_3$CO$_2$), 3.22 (m, 16 H, 1-H$_{TBA}$), 3.4$-$3.6 (br.), 3.9$-$4.05 (br.), 4.1$-$4.25 (br.), (ca. 4 H each) ppm. ^{13}C NMR ([D$_6$]DMSO, 80 °C): δ = 13.5 (C$_{TBA}$-4), 19.2 (C$_{TBA}$-3), 23.1 (C$_{TBA}$-2), 23.8 (CH$_3$COO), 56.7, 57.5 (C$_{TBA}$-1), 64.1, 70.8, 78.9, 176.1 (CH$_3$COO) ppm.

[N(C$_4$H$_9$)$_4$]$_3$[MnMo$_6$O$_{18}${(OCH$_2$)$_3$CN=C(2-C$_5$H$_4$N)}$_2$] (4): 2-Pyridinecarbaldehyde (330 µL, 3.5 mmol) and glacial acetic acid (10 µL, 0.17 mmol) were added to a boiling solution of **1** (3.00 g, 1.6 mmol) in 100 mL of methanol. After 10 min, an orange solid began to precipitate. The mixture was heated under reflux for further 3.5 h. After cooling to room temperature, a methanolic solution of [N(C$_4$H$_9$)$_4$](OH) (c = 5.09·10^{-3} M, 34 mL, 0.17 mmol) was added and the orange precipitate was isolated by filtration, washed with methanol and dried under vacuum. Yield: 2.54 g (77%). Crystals suitable for X-ray diffraction were grown by slow ether diffusion into an acetonitrile solution. C$_{68}$H$_{130}$MnMo$_6$N$_7$O$_{24}$ (2060.40): calcd. C 39.64, H 6.36, N 4.76; found C 39.58, H 6.47, N 4.89. ^{1}H NMR ([D$_6$]DMSO, 80 °C): δ = 0.93 (t, ^3J = 7.6 Hz, 36 H, 4-H$_{TBA}$), 1.34 (m, 24 H, 3-H$_{TBA}$), 1.61 (m, 24 H, 2-H$_{TBA}$), 3.18 (m, 24 H, 1-H$_{TBA}$), 7.28 (2 H, 5-H$_{pyr}$), 7.84 (2 H, 4-H$_{pyr}$), 7.94 (2 H, 3-H$_{pyr}$), 8.24 (2 H, CH=N$_{pyr}$), 8.72 (2 H, 6-H$_{pyr}$), 52.5 (12 H, CH$_2$O) ppm. Heating is necessary for solubilization. The signals corresponding to protons on the anion are broadened due to the presence of Mn^{III}. ^{13}C NMR ([D$_6$]DMSO, 80 °C): δ = 12.82 (C$_{TBA}$-4), 18.79 (C$_{TBA}$-3), 22.78 (C$_{TBA}$-2), 57.71 (C$_{TBA}$-1), 121.6 (C$_{pyr}$-5), 125.7 (C$_{pyr}$-3), 135.8 (C$_{pyr}$-4), 148.0 (C$_{pyr}$-2), 151.6 (C$_{pyr}$-6), 198.0 (CH=N$_{pyr}$) ppm. IR: $\tilde{v}_{max}$ = 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) cm^{-1}.

[N(C$_4$H$_9$)$_4$]$_3$[MnMo$_6$O$_{18}${(OCH$_2$)$_3$CN=C(4-C$_5$H$_4$N)}$_2$] 5: The compound was obtained as an orange solid by the same procedure as for **4**. Compound **5** is more soluble than **4** in polar organic solvents. Yield: 2.23 g (70%). C$_{68}$H$_{130}$MnMo$_6$N$_7$O$_{24}$ (2060.40): calcd. C 39.64, H 6.36, N 4.76; found C 39.41, H 6.47, N 4.77. ^{1}H 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, CH=N$_{pyr}$), 8.68 (br., 4 H, 4-H$_{pyr}$, 5-H$_{pyr}$), 53.9 (br., 12 H, CH$_2$O) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 13.60 (C$_{TBA}$-4), 19.33 (C$_{TBA}$-3), 23.07 (C$_{TBA}$-2), 57.50 (C$_{TBA}$-1), 123.6 (C$_{pyr}$-3, C$_{pyr}$-6), 136.1 (C$_{pyr}$-2), 149.4 (C$_{pyr}$-4, C$_{pyr}$-5), 197.6 (CH=N$_{pyr}$), 217.3 (CH$_2$O) ppm. IR: $\tilde{v}_{max}$ = 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 (m), 367 (s), 322 (m) cm^{-1}.

Acknowledgments

[1] P. Gouzerh, A. Proust, *Chem. Rev.* **1998**, *98*, 77$-$112.
[2] C. Sanchez, G. J. de Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, V. Cabuil, *Chem. Mater.* **2001**, *13*, 3061$-$3083.
[3] C. Hu, Y. Wang, Y. Li, E. Wang, *Chem. J. Internet* **2001**, *3*, 22.
[4] C. R. Mayer, R. Thouvenot, T. Lalot, *Chem. Mater.* **2000**, *12*, 257$-$260.
[5] C. R. Mayer, R. Thouvenot, T. Lalot, *Macromolecules* **2000**, *33*, 4433$-$4437.
[6] A. R. Moore, H. Kwen, A. M. Beatty, E. A. Maatta, *Chem. Commun.* **2000**, 1793$-$1794.
[7] C. G. Hamaker, A. M. Beatty, E. A. Maatta, in *Abstr. Pap. Am. Chem. Soc.* **2001**, vol. 221, pp. INOR-341.
[8] H. Zeng, G. R. Newkome, C. L. Hill, *Angew. Chem. Int. Ed.* **2000**, *39*, 1772$-$1774.
[9] R. C. Schroden, C. F. Blanford, B. J. Melde, B. J. S. Johnson, A. Stein, *Chem. Mater.* **2001**, *13*, 1074$-$1081.
[10] J.-P. Sauvage, *Transition Metals in Supramolecular Chemistry*, John Wiley & Sons, New York, **1999**.
[11] G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483$-$3537.
[12] B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022$-$2043.
[13] B. Hasenknopf, J.-M. Lehn, N. Boumediene, E. Leize, A. Van Dorsselaer, *Angew. Chem. Int. Ed.* **1998**, *37*, 3265$-$3268.
[14] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin, **1983**.
[15] R. Villanneau, A. Proust, F. Robert, P. Gouzerh, *J. Chem. Soc., Dalton Trans.* **1999**, 421$-$426.
[16] M. Sadakane, M. H. Dickman, M. T. Pope, *Angew. Chem. Int. Ed.* **2000**, *39*, 2914$-$2916.
[17] Q.-H. Luo, R. C. Howell, M. Dankova, J. Bartis, C. W. Williams, W. D. Horrocks, Jr., V. G. Young, A. L. Rheingold, L. C. Francesconi, M. R. Antonio, *Inorg. Chem.* **2001**, *40*, 1894$-$1901.
[18] L. Ruhlmann, J. Canny, R. Contant, R. Thouvenot, *Inorg. Chem.* **2002**, *41*, 3811$-$3819.
[19] T. M. Anderson, X. Zhang, K. I. Hardcastle, C. L. Hill, *Inorg. Chem.* **2002**, *41*, 2477$-$2488.
[20] L. Xu, H. Zhang, E. Wang, D. G. Kurth, Z. Li, *J. Mater. Chem.* **2002**, *12*, 654$-$657.
[21] R. Neumann, *Prog. Inorg. Chem.* **1998**, *47*, 317$-$370.
[22] B. Yan, Y. Xu, X. Bu, N. K. Goh, L. S. Chia, G. D. Stucky, *J. Chem. Soc., Dalton Trans.* **2001**, 2009$-$20014.

[23] J. R. Galan-Mascaros, C. Giménez-Saiz, S. Triki, C. J. Gomez-Garcia, E. Coronado, L. Ouahab, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1460−1462.

[24] A. Müller, E. Krickemeyer, S. K. Das, P. Kögerler, S. Sakar, H. Bögge, M. Schmidtmann, S. Sakar, *Angew. Chem. Int. Ed.* **2000**, *39*, 1612−1614.

[25] J. L. Stark, V. G. Young, Jr., E. A. Maatta, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2547−2548.

[26] B. J. S. Johnson, R. C. Schroden, C. Zhu, V. G. Young, Jr., A. Stein, *Inorg. Chem.* **2002**, *41*, 2213−2218.

[27] M. Piepenbrink, M. U. Triller, N. H. J. Gorman, B. Krebs, *Angew. Chem. Int. Ed.* **2002**, *41*, 2523−2525.

[28] B. Hasenknopf, R. Delmont, P. Herson, P. Gouzerh, *Eur. J. Inorg. Chem.* **2002**, 1081−1087.

[29] M. I. Khan, Q. Chen, J. Zubieta, D. P. Goshorn, *Inorg. Chem.* **1992**, *31*, 1556−1558.

[30] Q. Chen, D. P. Goshorn, C. P. Scholes, X. L. Tan, J. Zubieta, *J. Am. Chem. Soc.* **1992**, *114*, 4667−4681.

[31] A. Mueller, J. Meyer, H. Boegge, A. Stammler, A. Botar, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1818−1831.

[32] Y. Hou, C. L. Hill, *J. Am. Chem. Soc.* **1993**, *115*, 11823−11830.

[33] M. I. Khan, Q. Chen, D. P. Goshorn, H. Hope, S. Parkin, J. Zubieta, *J. Am. Chem. Soc.* **1992**, *114*, 3341−3346.

[34] R. Delmont, A. Proust, F. Robert, P. Herson, P. Gouzerh, *C. R. Acad. Sci. Paris, Sér. IIc* **2000**, *3*, 147−155.

[35] M. T. Pope, in *Comprehensive Coordination Chemistry*, vol. 3, 1st ed. (Eds.: S. G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, Oxford, **1987**, pp. 1023−1056.

[36] P. A. Lorenzo-Luis, P. Gili, *Recent Res. Dev. Inorg. Chem.* **2000**, *2*, 185−196.

[37] K. Nomiya, T. Takahashi, T. Shirai, M. Miwa, *Polyhedron* **1987**, *6*, 213−218.

[38] L. Bi, E. Wang, L. Xu, R. Huang, *Inorg. Chim. Acta* **2000**, *305*, 163−171.

[39] Q. Chen, J. Zubieta, *Inorg. Chim. Acta* **1992**, *198−200*, 95−110.

[40] I. L. Botto, A. C. Garcia, H. J. Thomas, *J. Phys. Chem. Solids* **1992**, *53*, 1075−1080.

[41] Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533−3539.

[42] J. F. W. Keana, M. D. Ogan, Y. Lu, M. Beer, J. Varkey, *J. Am. Chem. Soc.* **1986**, *108*, 7957−7963.

[43] N. Hur, W. G. Klemperer, R.-C. Wang, in *Inorg. Synth.*, vol. 27 (Ed.: A. P. Ginsberg), John Wiley & Sons, New York, **1990**, p. 78.

[44] N. H. Hur, W. G. Klemperer, R.-C. Wang, in *Inorg. Synth.*, vol. 27 (Ed.: A. P. Ginsberg), John Wiley & Sons, New York, **1990**, pp. 79−80.

[45] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158−166.

[46] D. J. Watkin, J. R. Carruthers, P. W. Betteridge, *CRYSTALS, An Advanced Crystallographic Computer Program*, Chemical Crystallography Laboratory, Oxford, **1989**.

[47] *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, **1974**, vol. IV.

[48] G. M. Sheldrick, *SHELXS86, Program for Crystal Structure Solution*, University of Göttingen Göttingen, **1986**.