Anderson-Type Heteropolymolybdates Containing Tris(alkoxo) Ligands: Synthesis and Structural Characterization

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Anderson-type molybdopolyanions containing tris(alkoxo) ligands $[MMo_6O_{18}\{(OCH_2)_3CR\}_2]^{3-}$ (M = Mn^{III}, Fe^{III}) and $[H_2MMo_6O_{18}\{(OCH_2)_3CR\}_2]^{2-}$ (M = Ni^{II}, Zn^{II}), (R = CH_3, NO_2, CH_2OH), were prepared by treatment of $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ with tris(hydroxymethyl)methane derivatives in the presence of manganese(III) acetylacetonate, iron(III) acetylacetonate, nickel(II) acetate, or zinc(II) acetate. The complexes were structurally characterized in solution, and also by single-crystal X-ray diffraction in the cases of $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]$, $[N(C_4H_9)_4]_2[H_2NiMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]$, and $[N(C_4H_9)_4]_2[H_2ZnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]$. Two tris(alkoxo) ligands replace the six hydroxo groups usually found in Anderson polyanions of formula $[H_6MMo_6O_{24}]^{n-}$. The complex structures may be divided into two groups: In the first one the tris(alkoxo) ligands are bound entirely to the central heteroatom, while in the second one they cap a tetrahedral cavity.

Introduction

Heteropolymolybdates of the general formula $[H_x(MO_6)Mo_6O_{18}]^{n-}$ ($x = 0-6$, $n = 2-6$) occur with metallic or nonmetallic heteroatoms M.[1,2] Two isomers, α and β, are known; both consist of edge-sharing octahedra.[3,4] The β isomer corresponds to a nonplanar, bent arrangement, as in the structures of $[Mo_7O_{24}]^{6-}$ [5] and $[W_7O_{24}]^{6-}$.[6,7] In the more common α isomer, the so-called Anderson structure, six molybdenum atoms form a planar hexagon around the central heteroatom. Two types of the Anderson structure may be distinguished: the nonprotonated A type, with heteroatoms in high oxidation states, and the hexaprotonated B type, with heteroatoms in low oxidation states.[8] The six nonacidic protons are usually located on the six oxygen atoms bound to the central heteroatom,[9] although a different protonation pattern has been reported in one case.[4]

Several B-type Anderson structures in which the six protons have formally been replaced by two $(As_3O_3)^{3+}$ groups have been reported.[10,11] Analogously, it should be possible to incorporate alkoxo groups in place of the hydroxo groups of the B-type structure, thus formally replacing protons by carbon atoms. The synthesis of Anderson polyanions in alcoholic solvents (methanol or ethanol) has been reported,[12] but no incorporation of the alcohol was found. We therefore decided to investigate the reaction in the presence of tris(hydroxymethyl)methane derivatives $RC(CH_2OH)_3$, because the three alkoxo groups should ideally replace all three hydroxo groups on each side of the Anderson structure. This capping effect should enhance the stability of the complex formed. The residue R could further serve for the introduction of a variety of functionalities.

Results and Discussion

Synthesis

On the basis of our own experience and that of others[12] in polyoxometalate synthesis in organic solvents, and also our previous preparation of $[H_2Mo_8O_{24}\{R(CH_2O)_3\}_2]^{4-}$,[13] we decided to use the same $[\alpha\text{-}Mo_8O_{26}]^{4-}$ precursor and to operate in acetonitrile. The heteroatom should be introduced with a labile ligand, and we chose the acetylacetonate (acac) or acetate (OAc) complexes of Mn^{III}, Fe^{III}, Ni^{II}, and Zn^{II}. Thus, we treated 1 equiv. of $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ with 1.5 equiv. of $M(acac)_3$ (M = Mn^{III}, Fe^{III}) or $M(OAc)_2$ (M = Zn^{II}, Ni^{II}) and 3 equiv. of tris(hydroxymethyl)methane derivatives $RC(CH_2OH)_3$ (R = CH_3, NO_2, CH_2OH) in refluxing acetonitrile. The complexes formed (Table 1) were isolated from the solution as their tetrabutylammonium salts by slow ether vapor diffusion and recrystallization from DMF/ether. While Anderson-type polyoxomolybdates with Mn^{II}, Fe^{III}, Ni^{II}, and Zn^{II} have been reported in the literature,[1,2,12,14,15] compounds **1** appear to be the first with Mn in oxidation state +III.

Crystal Structures

Compounds **1b**, **3c**, and **4a** were characterized by single-crystal X-ray diffraction; crystal structure data are summar-

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Table 1. Compounds prepared

	a, R = CH_3	**b**, R = NO_2	**c**, R = CH_2OH
1, M = Mn^{III}	$[MnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]^{3-}$	$[MnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]^{3-}$	$[MnMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]^{3-}$
2, M = Fe^{III}	$[FeMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]^{3-}$	$[FeMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]^{3-}$	$[FeMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]^{3-}$
3, M = Ni^{II}	$[H_2NiMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]^{2-}$	$[H_2NiMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]^{2-}$	$[H_2NiMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]^{2-}$
4, M = Zn^{II}	$[H_2ZnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]^{2-}$	$[ZnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]^{4-}$	$[H_2ZnMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]^{2-}$

ized in Table 4. The molecular structures of these compounds belong to two groups, described below.

The structure of $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]\cdot 2DMF$ (**1b**·2DMF) is representative of the first group. It consists of three tetrabutylammonium cations, an $[MnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]^{3-}$ anion, and solvent molecules of crystallization. Two views of the anion are presented in Figure 1. The geometry of the polyanion is based on the common Anderson structure, with six MoO_6 octahedral edge-sharing units forming a hexagon around the central MnO_6 octahedron. All metal atoms essentially lie in a common plane, with a maximum deviation of 0.002 Å from the best least-squares plane. Selected bond lengths and angles are compiled in Table 2.

The six triply bridging oxygen atoms surrounding the Mn^{III} center belong to two $RC(CH_2O)_3$ residues. Thus, the organic alkoxide groups effectively replace the six hydroxide groups in B-type Anderson structures. They can be regarded as capping both sides of the planar metal arrangement. The coordination geometry of the central Mn^{III} ion is regular, with a mean Mn−O distance of 1.98(1) Å, and O−Mn−O bond angles of between 86° and 93°. The small distortions observed correspond to a slight compression of the octahedron, bringing the two faces capped by the organic ligands closer together. This distortion might arise from the expected Jahn−Teller effect for Mn^{III}. A similar small Jahn−Teller distortion, resulting in that case in the elongation of the central octahedron, has also been observed in the compound $[H_6CuMo_6O_{24}]^{4-}$.[16,17] The lack of flexibility of the Anderson polyoxometalate apparently prevents larger distortions. Thus, both chemical and crystallographic analysis are consistent with the presence of a Mn^{III} center. Preliminary EPR measurements are also in agreement with this conclusion. This series of compounds therefore represents the first Anderson molybdates with manganese in oxidation state +III. Only the analogous Mn^{II} molybdates have been reported previously.[14,15,18]

The MoO_6 octahedra are distorted, with Mo−O distances that fall into three ranges depending on the type of oxygen atoms bound. The longest distance is that towards the triply bridging alkoxide ligands (average 2.37 Å). The doubly bridging and the terminal oxygen atoms are at distances from the molybdenum atoms of 1.94 Å and 1.71 Å, respectively.

A single-crystal X-ray diffraction study of compound **1a** did not provide enough reflections to refine the structure satisfactorily. However, it was established without any doubt that the overall structure of the polyanion is identical

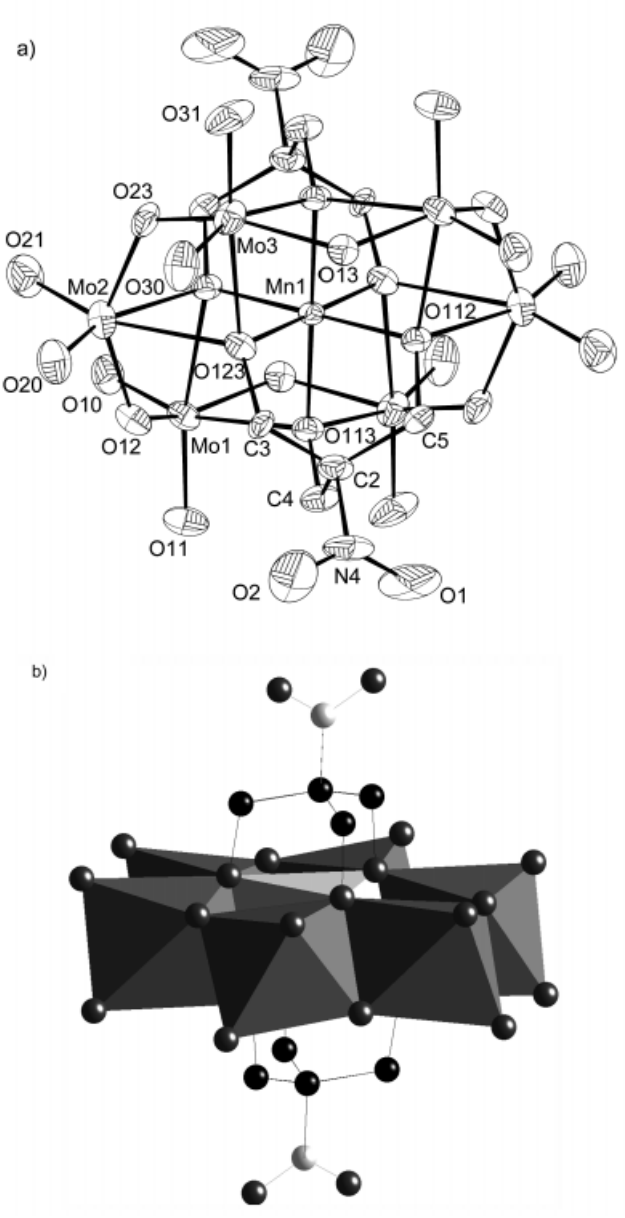

Figure 1. Structure and atom numbering of $[MnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]^{3-}$ (anion of **1b**); (a) thermal ellipsoids, (b) polyhedral representation

to that of **1b**; that is, the $CH_3C(CH_2O)_3$ residues cap the central Mn^{III} ion in the Anderson structure.

The structures of compounds **3c** and **4a** are representative of the second group. They both consist of a heteropolymolybdate − $[H_2MMo_6O_{18}\{(OCH_2)_3CR\}_2]^{2-}$ − that dif-

Table 2. Selected distances [Å] and angles [°] in **1b**, **3c**, and **4a**

1b		**3c**		**4a**	
Mn(1)−O(112)	2.024(7)	Ni(1)−O(112)	2.025(2)	Zn(1)−O(112)	2.030(3)
Mn(1)−O(113)	2.001(7)	Ni(1)−O(113)	2.085(2)	Zn(1)−O(113)	2.133(3)
Mn(1)−O(123)	1.940(7)	Ni(1)−O(123)	2.010(2)	Zn(1)−O(123)	2.041(3)
O(112)−Mn(1)−O(113)	92.1(3)	O(112)−Ni(1)−O(113)	98.5(1)	O(112)−Zn(1)−O(113)	98.7(1)
O(112)′ Mn(1)−O(113)	87.9(3)	O(112)−Ni(1)−O(113)′	81.5(1)	O(112)′ Zn(1)−O(113)	81.3(1)
O(112)−Mn(1)−O(123)	91.7(3)	O(112)−Ni(1)−O(123)	94.7(1)	O(112)−Zn(1)−O(123)	85.9(1)
O(112)′ Mn(1)−O(123)	88.3(3)	O(112)−Ni(1)−O(123)′	85.3(1)	O(112)′ Zn(1)−O(123)	94.1(1)
O(113)−Mn(1)−O(123)	91.8(3)	O(113)−Ni(1)−O(123)	98.2(1)	O(113)−Zn(1)−O(123)	81.8(1)
O(113)′ Mn(1)−O(123)	88.2(3)	O(113)−Ni(1)−O(123)′	81.8(1)	O(113)′ Zn(1)−O(123)	98.2(1)

fers remarkably from **1a** and **1b**. Yet again, the polyanion is based on the Anderson structure, with the heteroatom in the central cavity formed by six MoO_6 units. However, the organic ligands do not cap two faces of the central octahedron, but two tetrahedral cavities as shown in Figures 2 and 3. This causes the loss of the threefold symmetry as displayed in compounds **1a** and **1b**. The bond lengths (Table 2) are similar to those found in **1b**.

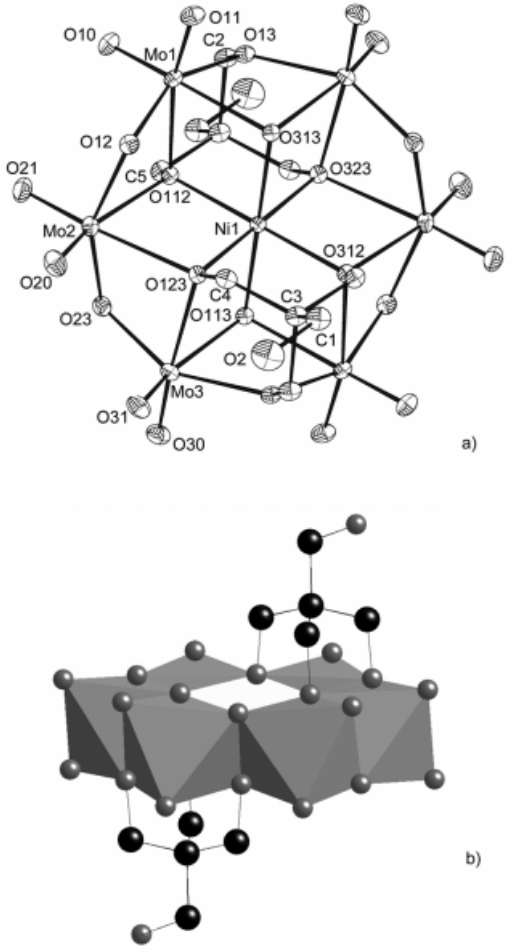

Figure 2. Structure and atom numbering of $[H_2NiMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]^{2-}$ (anion of **3c**); (a) thermal ellipsoids, (b) polyhedral representation

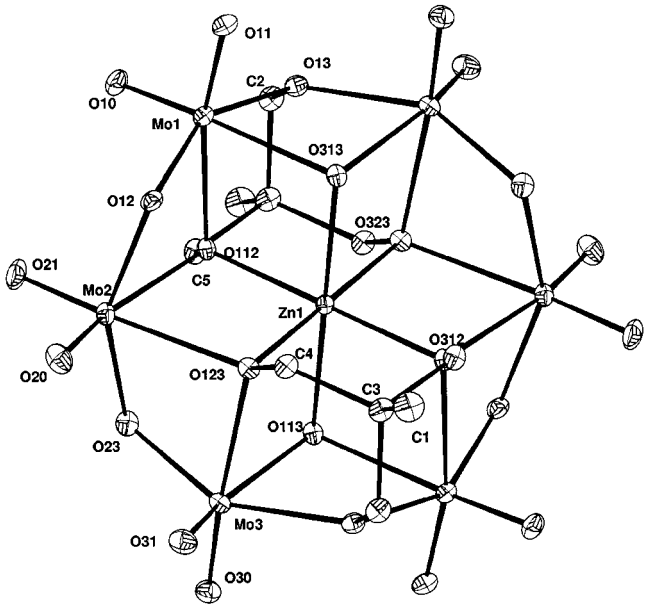

Figure 3. Structure and atom numbering of $[H_2ZnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]^{2-}$ (anion of **4a**), thermal ellipsoids

The crystals contain two $N(C_4H_9)_4$ cations per unit, thus indicating that the polyanions are doubly protonated. The quality of the X-ray diffraction data allowed the hydrogen atoms on the cations, anions, and the DMF molecules to be located. Furthermore, calculations of bond valence sums were performed in order to distinguish between O and OH ligands. It was clearly established that the remaining triply bridging oxygen atoms are protonated and form hydrogen bonds with the DMF oxygen atoms (distance 2.7 Å). The central metal is therefore coordinated to four μ_3-alkoxo and two μ_3-hydroxo ligands. The latter are at a slightly longer distance so that the coordination geometry of the central metal atom is an elongated octahedron.

It should be mentioned that the oxygen atoms bound to carbon atoms in **3c** and **4a** are protonated in the structure of $K_2[H_6\text{-}\alpha\text{-}PtMo_6O_{24}]\cdot 5H_2O$.[4] Thus, just as there are two different protonation patterns for B-type Anderson structures, there are two coordination modes for tris(hydroxymethyl)methane ligands. Below, we refer to the coordination mode in **1a** and **1b** as δ and in **3c** and **4a** as χ.

Table 3. Selected NMR-spectroscopic data

	1a R = CH_3	**1b** R = NO_2	**1c** R = CH_2OH	**4a** R = CH_3	**4b** R = NO_2	**4c** R = CH_2OH
^{1}H NMR CH_2O signals[a]	60.49	61.08	69.07	4.42 (d, 4 H), 4.51 (d, 4 H), 4.59 (s, 4 H)	4.93 (s, 12 H)	4.60 (d, 4 H), 4.65 (d, 4 H), 4.85 (s, 4 H)
^{13}C NMR CH_2O signals[a]				79.6, 89.4	77.6	76.8, 87.1
^{95}Mo NMR [b]				31.6 (2 Mo), 76.6 (4 Mo)	50.7 (6 Mo)	1.9 (2 Mo), 101.8 (4 Mo)

[a] Chemical shifts expressed in ppm relative to Me_4Si. [b] Chemical shifts expressed in ppm relative to aqueous alkaline Na_2MoO_4.

Spectroscopy

In order to assign the structures of the remaining compounds, and to determine their solution structures, we used NMR- and IR-spectroscopic methods.

The diamagnetic nature of compounds **4a**, **4b**, and **4c** allowed them to be investigated by multinuclear NMR. Selected NMR shifts are collected in Table 3; the complete description can be found in the Exp. Sect.

In order to interpret these results, one should discuss the expected pattern based on symmetry considerations [ignoring the atoms comprising R in the $RC(CH_2O)_3$ residues].

The δ form has an idealized D_{3d} symmetry. The methylene hydrogen and carbon atoms are chemically equivalent, as are the six molybdenum atoms. The oxygen atoms can be divided into three groups of terminal and doubly and triply bridging atoms.

The χ form, on the other hand, has a lower symmetry close to C_{2h}. The CH_2O hydrogen atoms can therefore be divided into three groups, and the carbon atoms into two. Furthermore, two types of molybdenum atoms and seven types of oxygen atoms are to be expected.

The ^{1}H and ^{13}C NMR spectra of compound **4b** in acetonitrile, which displayed only singlet signals (Table 3), clearly validated the δ form for the polyanion. Conversely, the spectra of **4a** and **4c** revealed the χ structure. In the latter, the CH_2O hydrogen atoms formed two ABX patterns, appearing as two doublets and one singlet of equal intensities. The corresponding carbon atoms gave rise to two signals of approximate 1:2 intensity. The molybdenum atoms were also observed, as expected, as two signals in a 2:4 ratio. The number of oxygen signals, however, was lower than expected. We found three signals of equal intensity (4 O) at $\delta \approx 900$, attributable to the three different terminal oxygen atoms by comparison with literature findings.[19] Four more signals should arise for the bridging oxygen atoms: four μ_3- and two μ_2-alkoxo, two μ_3-hydroxo and four μ_2-oxo ligands. Only two signals were observed, integrating as four and six oxygen atoms. There is no obvious assignment for these signals, but they are not incompatible with the proposed structure. Indeed, the chemical shifts fitted for bridging oxygen atoms, and hydroxy groups were not observed by ^{17}O NMR in other B-type heteropolymolybdates.[19]

Compound **4a** thus conclusively retains the χ form, as also found in the solid state, in solution. Compound **4c** has the same χ structure, but not compound **4b**, which adopts the δ form instead. This shows that the structure may vary with variation of the substituent R in the tris(hydroxymethyl)methane derivative. It should be mentioned that compound **4b** was obtained in significantly lower yield than **4a** and **4c**, and that it contained the $[\alpha\text{-}Mo_8O_{26}]^{4-}$ starting material as an impurity.

The paramagnetic compounds **1a**−**c**, **2a**−**c**, and **3a**−**c** were also investigated by ^{1}H NMR. In all cases, considerable line broadening was observed for the signals of the tetrabutylammonium cations. Signals for the organic ligand were observed only for compounds **1a**−**c**. They each displayed a broad singlet for the CH_2O groups at $\delta \approx 60$. This was suggestive of the δ structure, in which all CH_2O groups are at the same distance from the paramagnetic Mn^{III} center. In the χ structure, one CH_2O group of each ligand is not bound to the central Mn^{III}, and so these protons should be less deshielded.

In order to determine the structures of the remaining compounds in the series, we analyzed the IR spectra obtained in the solid state in detail. The two forms δ and χ are closely related, and their IR spectra were very similar; Figure 4 shows two representative examples (**1a** and **4a**) with the same tris(alkoxo) ligand. The spectra were typical of Anderson-type compounds,[12,15,20] with vibrational bands between 890 and 950 cm^{-1} for the terminal Mo=O units and between 660 and 710 cm^{-1} for the bridging Mo−O−Mo groups. The O−C bonds gave rise to bands between 1020 and 1120 cm^{-1}. The only difference detectable in the spectra of the compounds with known structures, established by the methods described above, concerned the bands around 700 cm^{-1}. The compounds with δ structure − **1a**, **1b**, and **4b** − each displayed a large and intensive band around 670 cm^{-1}, attributable to the vibration of the bridging Mo−O−Mo oxygen atoms. The reduction of the symmetry on passing to the χ form seemed to cause a splitting of this band. Indeed, **3c** and **4a** each displayed an additional signal of intermediate intensity, at 736 cm^{-1} and 732 cm^{-1}, respectively. On the assumption that an additional signal around 730 cm^{-1} exists in the spectra

of compounds with the χ arrangement, the structures containing the three-valent heteroatoms Mn^{III} and Fe^{III} are all identified as δ.

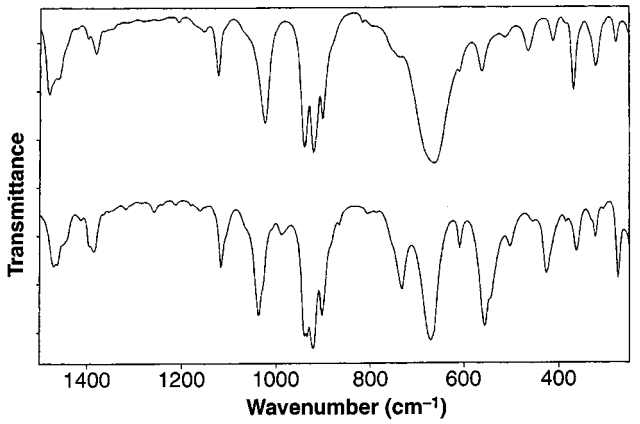

Figure 4. Infrared spectra of $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]$ (**1a**; top trace) and $[N(C_4H_9)_4]_2[H_2ZnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]$ (**4a**; bottom trace); note the splitting of the band around 700 cm^{-1} typical for the χ form

The Ni^{II}-containing compounds **3a** and **3b** each showed a very weak band in this region. This can be interpreted as resulting from a mixture of both form δ and form χ. This assumption was backed up by the elemental analyses of these compounds, which also correlated with mixtures of the two forms.

In summary, we have synthesized and structurally characterized a family of Anderson-type heteropolymolybdates containing tris(hydroxymethyl)methane derivatives. Two types of structures − δ and χ − differing in the site occupied by the alkoxide groups have been identified. In the presence of three-valent heteroatoms Mn^{III} and Fe^{III}, only the δ form occurred. The use of divalent heteroatoms Zn^{II} and Ni^{II} resulted in the formation of either δ or χ structures, or in mixtures of both. The reasons for preference for one or the other form are under investigation.

This work offers the potential to functionalize the heteropolymolybdates further by varying the R group on the $RC(CH_2OH)_3$ triol. If the R group were itself reactive, it should be possible to modify it while attached to the heteropolymolybdate. Thus, different functionalized polyoxometalates should be obtainable from a common precursor. Work in this area is in progress.

Experimental Section

Material: $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ was prepared by literature methods.[21] All other compounds, including solvents, were commercially available as reagent grade and used as received.

Spectroscopy: NMR spectra were recorded with Bruker AC 300 (^1H, ^{13}C) and Bruker AM 500 (^{95}Mo, ^{17}O) spectrometers. Deuterated solvent (CD_3CN unless otherwise stated) was used for ^1H and ^{13}C NMR. Chemical shifts (δ) are expressed in ppm relative to Me_4Si with residual solvent peak as standard. ^{13}C NMR spectra were recorded by use of an INEPT pulsing sequence. ^{17}O and ^{95}Mo NMR spectra were recorded at temperatures between 298 and 343 K at concentrations of 0.02 M in acetonitrile. Chemical shifts (δ) are expressed in ppm relative to water (^{17}O) and external aqueous alkaline Na_2MoO_4 (^{95}Mo). All compounds **4a**−**c** displayed the following signals for $N(C_4H_9)_4$ cations, integrating correctly for the number of cations required by the given formula. ^1H NMR: δ = 0.97 (t, $^3J_{H,H}$ = 7.3 Hz, 12 H, $NCH_2CH_2CH_2CH_3$), 1.38 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 1.61 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 3.10 (m, 8 H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR: δ = 13.8, 20.3, 24.3, 59.1. The signals were broadened in the case of paramagnetic compounds, without significant change in their chemical shifts. IR spectra were obtained on KBr pellets with a Bio-Rad FTS 165 spectrometer. All spectra contained the bands for tetrabutylammonium at 2960, 2874, 1472, and 1382 cm^{-1}. 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. Unit-cell 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; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table 4. Corrections were made for Lorentz and polarization effects. Secondary extinction corrections were necessary. Computations were performed with the PC version of CRYSTALS.[22] Atomic form factors for neutral atoms were taken from tabulated values.[23] Real and imaginary parts of anomalous dispersion were taken into account. The structure was solved by direct methods[24] and successive Fourier maps. An absorption correction based on DIFABS[25] was applied. Non-hydrogen atoms were refined anisotropically. Least-squares refinements in full matrix were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, in which 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 $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ having the values listed in Table 4. 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 $X = F_c/F_c(\text{max.})$. Criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviations being less then 0.2 and no significant features in the difference map. The ellipsoid views of the molecules were obtained with Cameron,[26] polyhedral representations were produced with CrystalMaker.[27] Ellipsoids are shown at the 20% probability level. CCDC-167626 (**1b**), -167627 (**3c**), and -167625 (**4a**) 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 Center, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis

General Method for the Complexes 1−4 a-c: A solution of $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ (1.1 g, 0.5 mmol) and 0.75 mmol of $M(acac)_3$ (M = Mn^{III}, Fe^{III}) or $M(OAc)_2$ (M = Zn^{II}, Ni^{II}) in 20 mL of acetonitrile was heated to reflux overnight (approximately 17 h). On cooling, a very small quantity of an unidentified solid separated and was discarded. On vapor diffusion of ether into the solution over 2 d, a solid crystallized and was filtered off, washed with ether, and air-dried. Recrystallization from DMF/ether gave analytically pure samples.

Table 4. Crystal data and structure refinement for **1b**, **3c**, and **4a**

Compound	**1b**	**3c**	**4a**
Empirical formula	$C_{62}H_{134}N_7MnMo_6O_{30}$	$C_{48}H_{110}Mo_6N_4NiO_{30}$	$C_{48}H_{106}Mo_6N_4O_{26}Zn$
Formula mass	2088.37	1857.76	1796.41
a [Å]	22.550(11)	12.246(2)	12.348(4)
b [Å]	13.593(4)	12.503(5)	12.789(6)
c [Å]	28.776(16)	13.971(3)	13.457(5)
[°]	90	100.02(3)	107.17(3)
β [°]	95.90(1)	105.80(2)	101.80(3)
γ [°]	90	113.81(3)	113.10(3)
V [Å^3]	8774(20)	1782(1)	1739(1)
Z	4	1	1
Crystal system	monoclinic	triclinic	triclinic
Space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
Crystal shape	parallelepiped	parallelepiped	parallelepiped
Crystal color	orange	colorless	colorless
Linear absorption coefficient μ [cm^{-1}]	10.17	13.35	14.42
Density ρ [g·cm^{-3}]	1.58	1.729	1.715
Diffractometer	Philips PW1100	MACH3 Enraf−Nonius	MACH3 Enraf−Nonius
Radiation	Mo-K_α (λ = 0.71069 Å)	Mo-K_α (λ = 0.71069 Å)	Mo-K_α (λ = 0.71069 Å)
Scan type	ω/2θ	ω/2θ	ω/2θ
Scan range [°]	0.8 + 0.345 tgθ	0.8 + 0.345 tgθ	0.8 + 0.345 tgθ
θ limits [°]	1−25	1−25	1−25
Temperature of measurement	room temperature	room temperature	−80 °C
Octants collected	−17, 17;0, 10;0, 17	0, 14;−14, 13; −16, 15	0, 14;−15, 13; −15, 15
No. of data collected	5782	6586	6418
No. of unique data collected	5196	6264	6108
No. of unique data used for refinement	3177 $(F_o)^2 > 3\sigma(F_o)^2$	4951 $(F_o)^2 > 3\sigma(F_o)^2$	4754 $(F_o)^2 > 3\sigma(F_o)^2$
Merging *R*	0.033	0.009	0.032
Decay of standard reflections (%)	< 1	3	7.2
R[a]	0.068	0.037	0.050
Rw[b]	0.070	0.045	0.060
Weighting coefficients[c]	4.34, −0.961, 3.28	6.94, −1.32, 4.85	8.58, −0.086, 6.39
Absorption correction	Difabs (min. 0.88, max. 1. 00)	Difabs (min. 0.74, max. 1. 00)	Difabs (min. 0.62, max. 1. 00)
Secondary extinction coefficient	291.1	97.9	9.64
Goodness of fit	1.093	1.008	1.073
Nb of variables	481	404	385
$\Delta\rho_{min}$ [e/Å^3]	−0.58	−0.55	−1.37
$\Delta\rho_{max}$ [e/Å^3]	0.76	1.44	1.38

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. [c] Weighting scheme of the form $w = w'\{1 - [(||F_o| - |F_c||)/6\sigma|F_o|]^2\}^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients for a Chebyshev series for which $X = F_c/F_c$(max.).

$[MnMo_6O_{18}\{(OCH_2)_3CR\}_2]^{3-}$ Anions of 1a−c: The reaction solutions were orange, with an unknown white solid. The complexes **1a**−**c** were isolated as orange crystals after recrystallization.

$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]$ (1a): Yield 0.91 g (72%). $C_{58}H_{126}MnMo_6N_3O_{24}$·2DMF (2026.42): calcd. C 37.93, H 6.96, Mn 2.71, Mo 28.41, N 3.46; found C 37.90, H 6.95, Mn 2.45, Mo 28.46, N 3.35. IR: $\tilde{\nu}_{max}$ = 1123 m, 1024 s, 939 vs, 919 vs, 900 s, 663 vs. ^{1}H NMR ([D$_6$]DMSO): δ =9.02 (br s, CH_3), 60.49 (br s, CH_2O).

$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]$ (1b): Yield 0.47 g (36%). $C_{56}H_{120}MnMo_6N_5O_{28}$·2DMF (2088.37): calcd. C 35.66, H 6.47, Mn 2.63, Mo 27.56, N 4.69; found C 35.78, H 6.40, Mn 2.48, Mo 26.57, N 4.60. IR: $\tilde{\nu}_{max}$ = 1539 m, 1337 m, 1153 w, 1083 vs, 1056 w, 946 vs, 926 vs, 909 s, 763 sh, 738 sh, 670 vs. ^{1}H NMR: δ = 69.07 (br s, CH_2O).

$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]$ (1c): Yield 0.70 g (55%). $C_{58}H_{126}MnMo_6N_3O_{26}$ (1912.23): calcd. C 36.43, H 6.64, Mn 2.87, Mo 30.1, N 2.2; found C 36.92, H 6.90, Mn 3.06, Mo 28.99, N 2.20. IR: $\tilde{\nu}_{max}$ = 3422 br, 1113 m, 1073 w, 1010 s, 938 vs, 918 vs, 900 s, 665 vs. ^{1}H NMR: δ = 10.01 (br s, CH_2OH), 61.08 (br s, CH_2O).

$[N(C_4H_9)_4]_3[FeMo_6O_{18}\{(OCH_2)_3CR\}_2]$ (2a−c): The reaction solutions were red orange and the unknown solid was orange. The complexes **2a**−**c** were isolated as yellow crystals after recrystallization.

$[N(C_4H_9)_4]_3[FeMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]$ (2a): Yield 0.79 g (63%). $C_{58}H_{126}FeMo_6N_3O_{24}$ (1881.14): calcd. C 37.03, H 6.75, Fe 2.97, Mo 30.6, N 2.23; found C 37.24, H 6.81, Fe 2.93, Mo 30.39, N 2.20. IR: $\tilde{\nu}_{max}$ = 1121 m, 1037 s, 1018 s, 981 w, 938 vs, 919 vs, 902 s, 689 vs.

$[N(C_4H_9)_4]_3[FeMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]$ (2b): Yield 0.45 g (35%). $C_{56}H_{120}FeMo_6N_5O_{28}$·$CH_3CN$ (1984.08): calcd. C 35.11, H 6.25, Fe 2.81, Mo 29.01, N 4.24; found C 35.12, H 6.29, Fe 2.86, Mo 29.31, N 4.33. IR: $\tilde{\nu}_{max}$ = 1538 m, 1337 m, 1169 w, 1083 vs, 946 vs, 927 vs, 909 vs, 812 m, 763 sh, 738 sh, 666 vs.

$[N(C_4H_9)_4]_3[FeMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]$ (2c): Yield 0.86 g (68%). $C_{58}H_{126}FeMo_6N_3O_{26}$ (1913.14): calcd. C 36.41, H 6.64, Fe 2.92, Mo 30.09, N 2.20; found C 35.23, H 6.60, Fe 2.46, Mo 28.09,

N 2.20. IR: $\tilde{\nu}_{max}$ = 3354 br, 1152 w, 1111 m, 1071 w, 1013 m, 936 vs, 917 vs, 903 s, 757 sh, 692 vs.

$[N(C_4H_9)_4]_{4-x}[H_xNiMo_6O_{18}\{(OCH_2)_3CR\}_2]$ (3a−c): The reaction solutions were blue-green, with an unknown white solid. Compounds **3a−c** were isolated as green crystals after recrystallization.

$[N(C_4H_9)_4]_{4-x}[H_xNiMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]$ (3a): Yield 0.84 g (60%). x = 0: $C_{74}H_{162}Mo_6O_{24}N_4Ni$ (2126.47): calcd. C 41.80, H 7.68, Mo 27.07, N 2.63, Ni 2.76; x = 2: $C_{42}H_{92}Mo_6O_{24}N_2Ni$ (1643.54): calcd. C 30.69, H 5.64, Mo 35.02, N 1.70, Ni 3.57; found C 36.63, H 6.91, Mo 27.91, N 3.18, Ni 3.20. IR: $\tilde{\nu}_{max}$ = 1116 m, 1043 s, 1024 m, 988 w, 933 vs, 915 vs, 895 s, 736 sh, 708 sh, 673 vs.

$[N(C_4H_9)_4]_{4-x}[H_xNiMo_6O_{18}\{(OCH_2)_3CCNO_2\}_2]$ (3b): Yield 0.62 g (43%). x = 0: $C_{72}H_{156}Mo_6O_{28}N_6Ni$ (2188.41): calcd. C 39.52, H 7.19, Mo 26.3, N 3.84, Ni 2.68; x = 2: $C_{40}H_{86}Mo_6O_{28}N_4Ni$ (1705.48): calcd. C 28.17, H 5.08, Mo 33.75, N 3.29, Ni 3.44; found C 38.92, H 6.95, Mo 26.81, N 4.01, Ni 2.70. IR: $\tilde{\nu}_{max}$ = 1520 m, 1334 m, 1154 w, 1101 vs, 1030 w, 922 vs, 911 vs, 891 s, 815 m, 744 m, 680 vs.

$[N(C_4H_9)_4]_{4-x}[H_xNiMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]$ (3c): Yield 0.84 g (58%). x = 0: $C_{74}H_{162}Mo_6O_{26}N_4Ni$ (2158.47): calcd. C 41.18, H 7.57, Mo 26.67, N 2.60, Ni 2.72; x = 2: $C_{42}H_{92}Mo_6O_{26}N_2Ni$ (1675.54): calcd. C 30.11, H 5.53, Mo 34.36, N 1.67, Ni 3.50; x = 2: $C_{42}H_{92}Mo_6O_{26}N_2Ni{\cdot}2DMF{\cdot}2H_2O$ (1857.76): calcd. C 30.96, H 7.90, Mo 30.91, N 3.01, Ni 3.15; found C 34.53, H 6.37, Mo 27.93, N 1.97, Ni 3.43. IR: $\tilde{\nu}_{max}$ = 3433 br, 1104 m, 1069 w, 1022 m, 1014 m, 938 vs, 919 vs, 903 s, 736 s, 675 s, 650 m.

$[N(C_4H_9)_4]_{4-x}[H_xZnMo_6O_{18}\{(OCH_2)_3CR\}_2]$ (4a−c): The reaction solutions were colorless, with an unknown white solid. The compounds **4a−c** were isolated as colorless crystals after recrystallization.

$[N(C_4H_9)_4]_2[H_2ZnMo_6O_{18}\{(OCH_2)_3CCH_3\}_2]$ (4a): Yield 0.89 g (81%). $C_{42}H_{92}Mo_6O_{24}N_2Zn{\cdot}2DMF$ (1796.41): calcd. C 32.09, H 5.95, Mo 32.04, N 3.12, Zn 3.64; found C 32.21, H 6.05, Mo 32.06, N 3.32, Zn 3.60. IR: $\tilde{\nu}_{max}$ = 1115 m, 1037 s, 987 w, 939 vs, 933 vs, 921 vs, 904 s, 732 m, 671 vs. ^{1}H NMR: δ = 0.58 (s, 6 H, CH_3), 4.42 (d, 4 H, $^2J_{H,H}$ = 10.8 Hz, CH^aH^bO), 4.51 (d, 4 H, $^2J_{H,H}$ = 10.8 Hz, CH$^aH^b$O), 4.59 (s, 4 H, CH_2O). ^{13}C NMR: δ = 16.8 (CH_3), 79.6 (CH_2O), 89.4 (CH_2O). ^{95}Mo NMR (343 K): δ = 31.6 (2 Mo), 76.6 (4 Mo). ^{17}O NMR (343 K): δ = 322.5 (4 O), 422.5 (6 O), 907.8 (4 O), 914.4 (4 O), 926.2 (4 O).

$[N(C_4H_9)_4]_4[ZnMo_6O_{18}\{(OCH_2)_3CNO_2\}_2]$ (4b): Crude yield 0.50 g (34%, contaminated with $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$). $C_{72}H_{156}Mo_6O_{28}N_6Zn$ (2195.09): calcd. C 39.40, H 7.16, Mo 26.22, N 3.83, Zn 2.98; found C 38.50, H 7.15, Mo 27.45, N 3.81, Zn 2.56. IR: $\tilde{\nu}_{max}$ = 1524 m, 1336 w, 1154 w, 1100 s, 1073 w, 931 vs 911 vs, 890 s, 814 m, 660 vs. ^{1}H NMR: δ = 4.93 (s, 12 H, CH_2O). ^{13}C NMR: δ = 77.6 (CH_2O). ^{95}Mo NMR (343 K): δ = 47.2; (298 K): δ = 50.7.

$[N(C_4H_9)_4]_2[H_2ZnMo_6O_{18}\{(OCH_2)_3CCH_2OH\}_2]$ (4c): Yield 0.56 g (70%). $C_{42}H_{92}Mo_6O_{26}N_2Zn{\cdot}2DMF$ (1828.41): calcd. C 31.53, H 5.84, Mo 31.48, N 3.06, Zn 3.58; found C 30.84, H 5.87, Mo 29.05, N 2.54, Zn 3.63. IR: $\tilde{\nu}_{max}$ = 3457 br, 1106 m, 1069 m, 1035 m, 1017 m, 1004 m, 937 vs, 918 vs, 898 vs, 728 m, 671 vs, 643 sh. ^{1}H NMR: δ = 3.26 (s, 4 H, CH_2OH), 4.60 (d, 4 H, $^2J_{H,H}$ = 10.8 Hz, CH^aH^{b}O), 4.65 (d, 4 H, $^2J_{H,H}$ = 10.6 Hz, CH$^aH^b$O), 4.85 (s, 4 H, CH_2O). ^{13}C NMR: δ = 63.4 (ca. 2 C, CH_2OH), 76.8 (ca. 4 C, CH_2O), 87.1 (ca. 4 C, CH_2O). ^{95}Mo NMR: (323 K): δ = 1.9 (2 Mo), 101.8 (4 Mo).

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