Merging Organometallic Chemistry with Polyoxometalate Chemistry

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Dedicated to Professor Achim Müller on the occasion of his 60th birthday

Abstract: A series of polyoxomolybdate-incorporated organometallic complexes has been obtained by reaction of $[MBr(CO)_5]$ or solvated $\{M(CO)_3\}^+$ ions (M = Mn or Br) with $(nBu_4N)_2[Mo_2O_7]$ in methanol, sometimes in the presence of triols of the type $RC(CH_2OH)_3$ (R = Me or CH_2OH). Their molecular structures are related to those of previously described polyoxoalkoxomolybdates through the formal replacement of *fac*-$\{MoO_2(OR)\}^+$ units by topologically equivalent *fac*-$\{M(CO)_3\}^+$ units. Representative pairs of structurally related clusters include $[Mo_2O_6(OMe)_4\{Re(CO)_3\}_2]^{2-}$ and $[Mo_4O_{10}(OMe)_6]^{2-}$, $[Mo_2O_4\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}]^-$ and $[Mo_3O_6(OMe)\{MeC(CH_2O)_3\}_2]^-$, $[Mo_2O_4\{HOCH_2C(CH_2O)_3\}_2\{Mn(CO)_3\}_2]$ and $[Mo_4O_8(OEt)_2\{MeC(CH_2O)_3\}_2]$, $[Mo_6O_{16}(OMe)_2\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}_2]^{2-}$ and $[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$. Although the frameworks of the majority of derivatives are based on tetranuclear units which display the common rhomb-like structure, the alternative cubane-type arrangement is observed in $[Mo_2O_5(OMe)_5\{M(CO)_3\}_2]^-$.

Keywords: manganese · molybdenum · organometallic oxides · polyoxometalates · rhenium

Introduction

Organometallic derivatives of polyoxometalates now form a full class of compounds.[1] Klemperer,[2a], Knoth,[3] and Finke[4a] have pioneered this field which has expanded steadily since then, mainly due to contributions from the groups of Klemperer[2] and Finke,[4] and also those of Isobe[5] and Siedle.[6] The conceptual difference between organometallic compounds *supported on* and *incorporated into* a polyoxometalate has been emphasized by Finke.[4a] A third group of compounds is composed of the organometallic cation salts of polyoxometalates.[5d, 6, 7] Polyoxometalate-supported organometallic complexes provide discrete analogues of solid-oxide-supported organometallic complexes.[2, 4] In a general way, organometallic derivatives of polyoxometalates are of interest as potential polyoxometalate-based catalysts or precatalysts. Representative examples include the synthesis of C_{n+1} carboxylic acids from C_n olefins by sequential one-pot hydroxylation and oxidation steps using $[(Ph_3P)_2Rh(CO)]_4[SiW_{12}O_{40}]$ as a bifunctional catalyst,[6a] oxidation and reduction catalytic reactions of cyclohexene with $[(1,5\text{-cod})IrP_2W_{15}Nb_3O_{62}]^{8-}$ (cod = 1,5-cyclooctadiene),[8] and selective oxidation of propene to acetone with vanadate-supported rhodium catalysts.[9] Although polyoxometalate-based organometallic compounds are merely a class of organometallic oxides,[10] they have been generally reviewed separately due to their rather specific structures. However as new structural types are being discovered, the distinction between classical organometallic oxides and polyoxometalate-based organometallic compounds is expected to vanish progressively.

Our entrance in this field stemmed from the study of the reactions of $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$[11] with $[\{Cp^*RhCl(\mu\text{-}Cl)\}_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) and $[MBr(CO)_5]$ (M = Mn or Re). The structurally related complexes $[Mo_5O_{13}(OMe)_4(NO)\{Cp^*Rh(H_2O)\}]^-$[12] and $[Mo_5O_{13}(OMe)_4(NO)\{M(CO)_3(H_2O)\}]^{2-}$[13] have been isolated and characterized as tetrabutylammonium salts. In addition, it was found that $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ eventually dissociates into smaller fragments that subsequently combine with organometallic fragments to give novel aggregates. These observations led us to investigate the reactivity of $[MBr(CO)_5]$ with simple polyoxomolybdates such as $(nBu_4N)_2[Mo_2O_7]$. As trisalkoxo ligands of the type $\{RC(CH_2O)_3\}^{3-}$ are known to stabilize trinuclear complexes that may further aggregate to form higher nuclearity clusters,[14, 15] some reactions were carried out in the presence of variable amounts of $RC(CH_2OH)_3$. In this way we have obtained a number of clusters with different nuclearities. Their molecular structures have been determined by single-crystal X-ray diffraction and compared to those of their parent polyoxo(alkoxo)molybdates. Structural relationships reveal some electronic connections between low-valent and high-valent complex fragments.

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Results and Discussion

Syntheses: Discrete integrated organometallic oxides, that is compounds where the organometallic component is incorporated in the polyoxometal framework, have been obtained in several ways, including the incorporation of an organometallic moiety into a lacunary polyoxometalate,[2a] the oxidation of carbonyl dimers [$\{Cp^*M(CO)_2\}_2$] (M = W[16a] or Mo[16b]) and various aggregation processes triggered by protons and/or Lewis acids in aqueous or non-aqueous media.[2, 5, 17] The latter strategy has been used throughout this work.

Under nitrogen and in the dark, the reaction of $(n\mathrm{Bu}_4\mathrm{N})_2$-[$Mo_2O_7$] with an equimolar amount of [$MnBr(CO)_5$] in MeOH yields a crystalline product mostly composed of green cubic crystals of **1a** with a minor amount of red octahedral crystals of **2**. When the reaction is carried out in non-deoxygenated MeOH, **3** is obtained together with **1a**. [$Re(CO)_3(MeCN)_3$](BF_4) also reacts with $(n\mathrm{Bu}_4\mathrm{N})_2$[$Mo_2O_7$] in MeOH to give several compounds, of which **1b** and **4** have been isolated.

$(n\mathrm{Bu}_4\mathrm{N})[\mathrm{Mo_2O_5(OMe)_5\{M(CO)_3\}_2}]$ **1a**: M = Mn, **1b**: M = Re

$[\mathrm{Mo_2O_4(OMe)_6\{Mn(CO)_3\}_2}]$ **2**

$(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{Mn(H_2O)_2\{Mo_5O_{16}(OMe)_2Mn(CO)_3\}_2}]$ **3**

$(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo_2O_6(OMe)_4\{Re(CO)_3\}_2}]$ **4**

Reaction of $(n\mathrm{Bu}_4\mathrm{N})_2$[$Mo_2O_7$] with [$MnBr(CO)_5$] in MeOH has been further investigated in the presence of $RC(CH_2OH)_3$ (R = Me, CH_2OH). The compounds **5**, **6a, b**, and **7** have been obtained in this way.

$(n\mathrm{Bu}_4\mathrm{N})[\mathrm{Mo_2O_4\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}}]$ **5**

$[\mathrm{Mo_2O_4\{RC(CH_2O)_3\}_2\{Mn(CO)_3\}_2}]$ **6a**: R = Me; **6b**: R = CH_2OH

$(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo_6O_{16}(OMe)_2\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}_2}]$ **7**

This paper deals with compounds **1**, **2**, **4**, **5**, **6**, and **7**. The anion of **3** contains two $\{Mo_5O_{16}(OMe)_2\}^{4-}$ moieties structurally related to $\{Mo_5O_{13}(OMe)_4(NO)\}^{3-}$,[12] each bound to a $\{Mn(CO)_3\}^+$ unit by three contiguous donor groups (the two methoxo groups and one equatorial bridging oxo ligand) and to a Mn^{2+} center by two axial terminal oxygen atoms. An improved synthesis and the detailed structure of **3** will be reported elsewhere.

Oxomethoxo clusters: Compounds **1a** and **1b** are isostructural. The clusters $[\mathrm{Mo_2O_5(OMe)_5\{M(CO)_3\}_2}]^-$ display a tetrahedral arrangement of the metal atoms (Figure 1). They formally derive from the clusters [$\{M(CO)_3(\mu\text{-}OH)\}_4$] (M = Mn,[18a] Re[18b]) by substitution of two $\{MoO_2(OMe)\}^+$ units for $\{Mn(CO)_3\}^+$ units, one μ_3-oxo ligand for one μ_3-hydroxo ligand, and μ_3-methoxo ligands for the three remaining μ_3-hydroxo ligands. The environments of the two molybdenum atoms in **1** are similar and consist of three oxo ligands—two terminal and one triply bridging—and three methoxo ligands—one terminal and two triply bridging. Accordingly, the Mo–O distances lie into four distinct ranges, 1.66 to 1.73 Å for Mo=O_t, 1.97 to 2.01 Å for Mo–(μ_3-O), 1.87 to 1.91 Å for Mo–OMe, and 2.26 to 2.38 Å for Mo–(μ_3-OMe) (Table 1). Given that the Mo–(μ_3-O) and Mo–OMe distances are not very different, the molybdenum atoms practically display the typical two short/two intermediate/two long Mo–O bond pattern usually observed in polyoxomolybdates.[19] On the other hand, the environments of the two heterometal centers (M = Mn or Re) are different, although each of them displays MO_3C_3 coordination: one is ligated to three carbonyl ligands and three triply bridging methoxo ligands, while the other is ligated to three carbonyl ligands, two triply bridging methoxo ligands, and one triply bridging oxo ligand. This difference does not translate into significant variations within M–C or M–O distances. However, as expected, the M–C distances are longer in **1b** (av Re–C 1.87 Å) than in **1a** (av Mn–C 1.79 Å). In the crystal, the anions $[\mathrm{Mo_2O_5(OMe)_5\{M(CO)_3\}_2}]^-$ possess an approximate symmetry plane which passes through the M centers, the triply bridging oxo ligand, and one triply bridging methoxo ligand. The ^1H and ^{13}C NMR spectrum of **1a** in CD_3COCD_3 shows that the C_s symmetry of the anion is retained in solution. At least these data indicate that only one form of **1a** is present in CD_3COCD_3. However it is noteworthy that the methoxo signals could not be observed in CD_3OD, which could be indicative of exchange between the complex and the solvent.

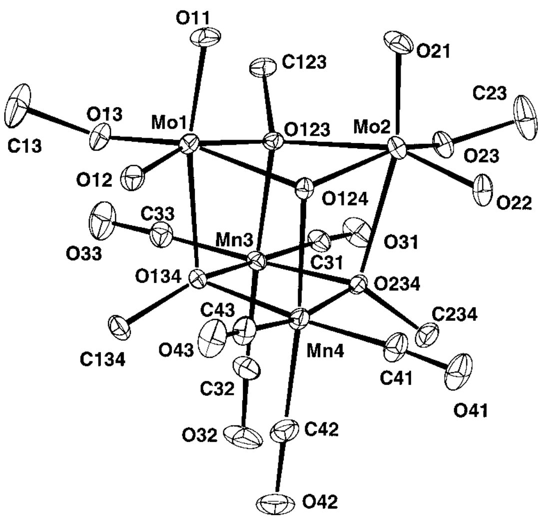

Figure 1. Structure of the anion of **1a**.[44c] Thermal ellipsoids are shown at the 12% probability level.

Unlike **1**, and despite the close connection between the compositions of these clusters, **2** and the anion of **4** adopt the rhomb-like structure based on four edge-sharing octahedra common to many tetramolybdates.[20] The cluster $[\mathrm{Mo_2O_6(OMe)_4\{Re(CO)_3\}_2}]^{2-}$ (anion of **4**, Figure 2) formally derives from $[\mathrm{Mo_4O_{10}(OMe)_6}]^{2-}$ (anion of **8**) [19] by substitution of *fac*-$\{Re(CO)_3\}^+$ units for two *fac*-$\{MoO_2(OR)\}^+$ units.

$(\mathrm{PPh_3Me})_2[\mathrm{Mo_4O_{10}(OMe)_6}]$ **8**

The anions $[\mathrm{Mo_2O_6(OMe)_4\{Re(CO)_3\}_2}]^{2-}$ in **4** (Figure 2) are located at crystallographic inversion centers. The unique

Table 1. Selected bond lengths [Å] in **1a**, **1b**, **2**, **4**, **5**, **6b**, and **7**.

1a							
Mo1–O11	1.692(3)	Mo1–O12	1.691(3)	Mo1–O13	1.903(3)	Mo1–O123	2.285(3)
Mo1–O124	1.978(3)	Mo1–O134	2.285(3)	Mo2–O21	1.681(4)	Mo2–O22	1.694(3)
Mo2–O23	1.908(3)	Mo2–O123	2.257(3)	Mo2–O124	1.969(3)	Mo2–O234	2.329(3)
Mn3–C31	1.793(5)	Mn3–C32	1.777(5)	Mn3–C33	1.802(6)	Mn3–O123	2.049(3)
Mn3–O134	2.054(3)	Mn3–O234	2.042(3)	Mn4–C41	1.781(6)	Mn4–C42	1.787(6)
Mn4–C43	1.796(6)	Mn4–O124	2.047(3)	Mn4–O134	2.044(3)	Mn4–O234	2.037(3)
O13–C13	1.376(7)	O23–C23	1.381(7)	C31–O31	1.145(6)	C32–O32	1.155(6)
C33–O33	1.144(6)	C41–O41	1.157(6)	C42–O42	1.162(7)	C43–O43	1.149(6)
O123–C123	1.453(5)	O134–C134	1.441(5)	O234–C234	1.427(6)		
1b							
Mo1–O11	1.68(2)	Mo1–O12	1.69(2)	Mo1–O13	1.87(1)	Mo1–O123	2.29(1)
Mo1–O124	2.01(1)	Mo1–O134	2.38(1)	Mo2–O21	1.73(2)	Mo2–O22	1.66(2)
Mo2–O23	1.89(2)	Mo2–O123	2.34(1)	Mo2–O124	2.00(1)	Mo2–O234	2.32(1)
Re3–C31	1.84(3)	Re3–C32	1.86(3)	Re3–C33	1.91(2)	Re3–O123	2.16(1)
Re3–O134	2.17(1)	Re3–O234	2.17(1)	Re4–C41	1.91(3)	Re4–C42	1.81(3)
Re4–C43	1.91(3)	Re4–O124	2.10(1)	Re4–O134	2.16(1)	Re4–O234	2.15(1)
O13–C13	1.43(3)	O23–C23	1.41(3)	O31–C31	1.20(3)	O32–C32	1.17(3)
O33–C33	1.16(3)	O41–C41	1.15(3)	O42–C42	1.21(3)	O43–C43	1.15(3)
O123–C123	1.49(2)	O134–C134	1.48(2)	O234–C234	1.52(3)		
2							
Mo1–O112	2.252(5)	Mo1–O112′	2.260(5)	Mo1–O120	1.990(5)	Mo1–O12	1.972(5)
Mo1–O111	1.693(5)	Mo1–O11	1.690(5)	Mn2–O112	2.069(5)	Mn2–O120′	2.043(5)
Mn2–O12	2.046(5)	Mn2–C23	1.81(1)	Mn2–C22	1.76(1)	Mn2–C21	1.79(1)
O112–C112	1.477(9)	O120–C120	1.444(9)	O12–C12	1.45(1)	O22–C22	1.16(1)
O23–C23	1.13(1)	O21–C21	1.14(1)				
4							
Re1–O12	2.154(8)	Re1–O21	2.101(9)	Re1–O104	2.110(9)	Re1–C101	1.88(2)
Re1–C102	1.88(2)	Re1–C103	1.81(2)	Mo2–O1	1.705(9)	Mo2–O2	1.704(9)
Mo2–O12	2.247(8)	Mo2–O12′	2.392(8)	Mo2′–O21	1.810(8)	Mo2–O104	2.087(8)
O12–C120	1.47(1)	O101–C101	1.17(2)	O102–C102	1.17(2)	O103–C103	1.19(2)
O104–C104	1.44(2)						
5							
Mo1–O123	2.27(1)	Mo1–O12	2.19(1)	Mo1–O31	2.11(1)	Mo1–O13	1.91(1)
Mo1–O10	1.68(1)	Mo1–O11	1.69(1)	Mo2–O123	2.25(1)	Mo2–O12	2.15(1)
Mo2–O23	2.06(1)	Mo2–O22	1.88(1)	Mo2–O20	1.69(1)	Mo2–O21	1.71(2)
Mn3–O123	2.03(1)	Mn3–O23	2.05(1)	Mn3–O31	2.03(1)	Mn3–C61	1.77(2)
Mn3–C60	1.79(2)	Mn3–C62	1.84(2)	O123–C1	1.44(2)	O12–C2	1.44(2)
O23–C3	1.45(2)	O31–C4	1.37(2)	O22–C5	1.41(2)	O13–C6	1.39(2)
O61–C61	1.18(2)	O60–C60	1.12(2)	O62–C62	1.14(2)	C1–C10	1.57(3)
C2–C9	1.52(3)	C3–C9	1.56(3)	C4–C9	1.59(3)	C5–C10	1.58(3)
C6–C10	1.53(3)	C7–C10	1.57(3)	C8–C9	1.58(3)		
6b							
Mo1–O11	1.967(7)	Mo1–O12′	1.972(7)	Mo1–O15	2.260(6)	Mo1–O15′	2.247(6)
Mo1–O41	1.680(7)	Mo1–O42	1.669(7)	Mn1–O11	2.053(7)	Mn1–O12	2.055(7)
Mn1–O15	2.073(6)	Mn1–C1	1.83(1)	Mn1–C2	1.78(1)	Mn1–C3	1.79(1)
O1–C1	1.11(1)	O2–C2	1.15(1)	O3–C3	1.16(1)	O11–C11	1.45(1)
O12–C12	1.46(1)	O15–C13′	1.45(1)	C10–C11	1.52(1)	C10–C12	1.54(1)
C10–C13	1.56(1)	C10–C14	1.50(1)	C14–O141	1.39(2)	C14–O142	1.20(3)
7							
Mo1–O10	1.799(6)	Mo1–O11	1.684(6)	Mo1–O12	1.766(5)	Mo1–O14	2.039(5)
Mo1–O123	2.305(6)	Mo1–O134	2.201(6)	Mo2–O10′	1.996(6)	Mo2–O12	2.215(6)
Mo2–O21	1.701(6)	Mo2–O22	1.706(6)	Mo2–O23	1.930(6)	Mo2–O123	2.298(5)
Mo3–O23	1.902(6)	Mo3–O31	1.699(7)	Mo3–O32	1.699(7)	Mo3–O34	2.014(6)
Mo3–O123	2.269(5)	Mo3–O134	2.301(6)	Mn1–O14	2.017(5)	Mn1–O34	2.042(7)
Mn1–O134	2.049(6)	Mn1–C41	1.80(1)	Mn1–C42	1.80(1)	Mn1–C43	1.80(1)
O14–C5	1.43(1)	O34–C4	1.43(1)	O41–C41	1.12(1)	O42–C42	1.14(1)
O43–C43	1.14(1)	O123–C2	1.45(1)	O134–C134	1.45(1)	C1–C3	1.56(1)
C2–C3	1.53(1)	C3–C4	1.54(1)	C3–C5	1.52(1)		

molybdenum atom displays the typical two short/two intermediate/two long Mo–O bond pattern. The structural parameters of the $\{Re(CO)_3\}^+$ unit in **4** are similar to those for **1b**. A noteworthy feature of **4**, also observed in **8**, is the marked dissymmetry in the $Mo_2(\mu_3\text{-}OMe)$ bridges. The centrosymmetrical complex **2** (Figure 3) only differs from $[Mo_2O_6(OMe)_4\{Re(CO)_3\}_2]^{2-}$ in the substitution of Mn for Re and that of methoxo ligands for two doubly bridging oxo ligands. Again the molybdenum atom displays the typical two short/two intermediate/two long Mo–O bond pattern. However, the $Mo_2(\mu_3\text{-}OMe)$ bridges are nearly symmetrical in **2**. The structural parameters of the $\{Mn(CO)_3\}^+$ unit in **2** are

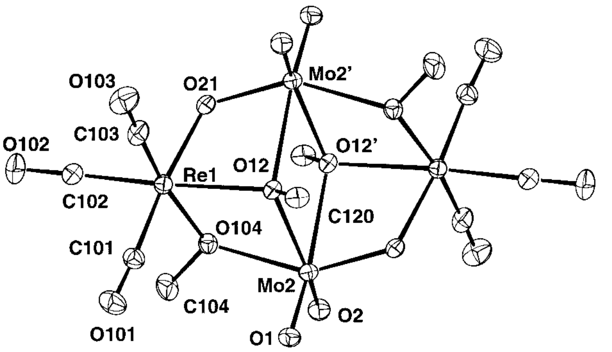

Figure 2. Structure of the anion of **4**.[44c] Thermal ellipsoids are shown at the 12 % probability level.

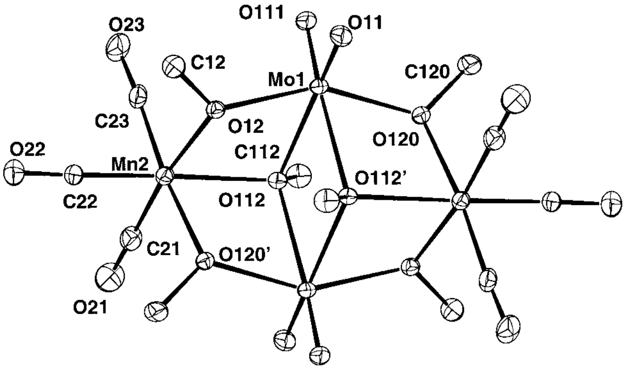

Figure 3. Structure of **2**.[44c] Thermal ellipsoids are shown at the 12 % probability level.

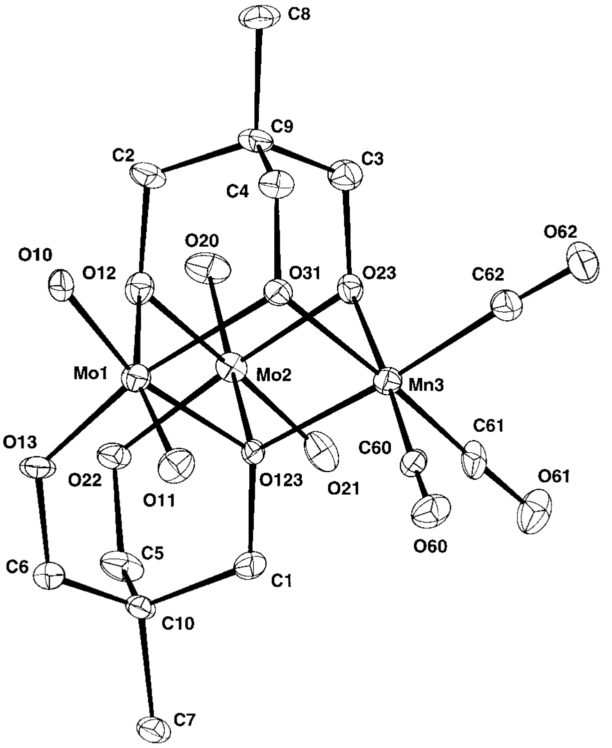

Figure 4. Structure of the anion of **5**.[44c] Thermal ellipsoids are shown at the 12 % probability level.

similar to those for **1a**. Given the compositions of **2** and **4**, the formation of $[Mo_2O_4(OMe)_6\{Re(CO)_3\}_2]$ and $[Mo_2O_6(OMe)_4\{Mn(CO)_3\}_2]^{2-}$ might be anticipated although these complexes have not be isolated so far.

Oxotrisalkoxo clusters: The discrete trinuclear anion $[Mo_2O_4\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}]^-$ in **5** is shown in Figure 4. Its formation provides a further illustration of the efficacy of trisalkoxo ligands in stabilizing trinuclear clusters.[14, 15] The structure of this cluster is related to that of $[Mo_3O_6(OMe)\{MeC(CH_2O)_3\}_2]^-$ (anion of **9**)[14] through the substitution of a *fac*-$\{Mn(CO)_3\}^+$ unit for a *fac*-$\{MoO_2(OMe)\}^+$ unit. Alternatively, this species can be viewed as deriving from $[Mo_2O_4\{MeC(CH_2O)_3\}_2]^{2-}$ (anion of **10**)[14b] by grafting a $\{Mn(CO)_3\}^+$ unit. The Mo–O distances in **5** get into four ranges, 1.68 to 1.71 Å for terminal oxo ligands, 1.88 to 1.91 Å for terminal alkoxo groups, 2.06 to 2.19 Å for doubly bridging alkoxo groups, and 2.25 to 2.27 Å for triply bridging alkoxo groups. The equivalency of the trisalkoxo ligands in the dinuclear precursor, where they display the μ-κ^1O:κ^1O:κ^2O coordination mode is lost in $[Mo_2O_4\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}]^-$ where one ligand displays the μ-κ^2O:κ^2O:κ^2O coordination mode while the second displays the μ-κ^1O:κ^1O:κ^3O mode. The equivalency is restored on coordination of a second $\{Mn(CO)_3\}^+$ unit, which leads to **6a**. The inequivalence of the trisalkoxo ligands in **5** is clearly apparent in the ^{1}H and ^{13}C NMR spectrum of **5** in CD_3CN. NMR data indicate C_s symmetry for the anion as far as the trisalkoxo ligands are concerned. However the carbonyl ligands appear equivalent, which could be indicative of some fluxionality.

$(nBu_4N)[Mo_3O_6(OMe)\{MeC(CH_2O)_3\}_2]$ **9**

$(nBu_4N)_2[Mo_2O_4\{MeC(CH_2O)_3\}_2]$ **10**

Both clusters **6a** and **6b** have been prepared, but only **6b** is sufficiently soluble for recrystallization and characterization in solution. Crystals with the composition **6b**·2THF were obtained from THF and were analyzed by X-ray diffraction. The clusters are located at crystallographic inversion centers (Figure 5). Their structure is similar to that of **11**[21] and other

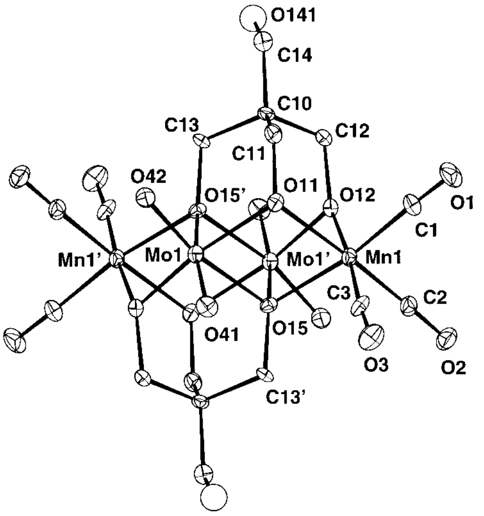

Figure 5. Structure of **6b**.[44c] Thermal ellipsoids are shown at the 20 % probability level.

tetranuclear oxotrisalkoxo complexes of molybdenum and vanadium, all of which display a rhomb-like structure. In **6b**, as in **11**,[21] $[V_4O_4(OMe)_6\{MeC(CH_2O)_3\}_2]$,[22] and

$[Mo_4O_8(OEt)_2\{MeC(CH_2O)_3\}_2]$ **11**

$[V_2Mo_2O_8(OMe)_2\{HOCH_2C(CH_2O)_3\}_2]^{2-}$,[23] the trisalkoxo ligands cap opposite tetrahedral cavities of the oxometal framework and thus display the μ_4-κ^2:κ^2:κ^3 coordination mode. This is the usual situation although the ligand may also cap a metal octahedron, for example in $[M_4O_{10}\{MeC(CH_2O)_3\}_2]^{2-}$ (M = Mo or W).[24] The ^{1}H NMR spectrum of **6b** in CD_3COCD_3 is consistent with the C_s symmetry of the solid-state molecular structure.

In **7**, the anions $[Mo_6O_{16}(OMe)_2\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}_2]^{2-}$ (Figure 6) are located at crystallographic inversion centers. The two equivalent halves of the anions are connected by two nearly linear Mo-O-Mo bridges with an angle of 162.5(10)°. The full anion is related to $[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$ (anion of **12**)[25] through the formal replacement of the *fac*-$\{MoO_2(OMe)\}^+$ units by *fac*-$\{Mn(CO)_3\}^+$ units. Both the anions of **7** and **12** are formally related to the hypothetical cluster $[Mo_8O_{30}]^{12-}$ which can be derived from the β-$[Mo_8O_{26}]^{4-}$ ion by shearing of the Mo_4 subunits parallel to one another.[1, 19] The anion of **7** may also be viewed as the product of the condensation of two rhombic anions $[Mo_3O_9(OMe)\{MeC(CH_2O)_3\}\{Mn(CO)_3\}]^{3-}$ by the sharing of two corners. The discrete tetranuclear subunit is not expected to be fairly stable because the environment of Mo2 does not fulfill the Lipscomb restriction.[26] Dimerization prevents violation of this rule. However the Mo1-O10-Mo2′ bridge and especially the Mo1-O12-Mo2 bridge are clearly dissymmetrical so that the geometrical parameters of the Mo1-O10-O11-O12 unit (Mo1–O10 1.81(1), Mo1–O11 1.70(2), Mo1–O12 1.73(1) Å) are reminiscent of those of a unit containing three *terminal* oxo ligands. A similar feature is noticeable in **12**.[25] The structural parameters for the $\{Mn(CO)_3\}^+$ unit are similar to those for **1a**, **2**, **5**, and **6b**.

$(nBu_4N)_2[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]$ **12**

Molecular topology: Clusters **1**, **2**, **4**, **5**, **6**, and **7** are properly viewed as integrated complexes. However clusters **5** and **6** can alternatively be viewed as adducts based on the dinuclear complexes $[Mo_2O_4\{RC(CH_2O)_3\}_2]^{2-}$ which have been reported for R = NO_2.[14a] Thus, clusters **5** and **6** may be considered as integrated complexes as well as polyoxomolybdate-supported organometallic complexes.

Clusters **1** provide the first examples of discrete monocubane-type polyoxometalate derivatives. The cubane-type geometry is the alternative to the rhombic geometry for compact complexes based on four edge-sharing octahedra.[20c] The cubane-type core is relatively rare in polyoxometalate structural chemistry although it is quite common for cyclopentadienyl oxide clusters of Groups 5 and 6.[10] Cubane-type $\{Mo_4(\mu_3\text{-}O)_4\}^{n+}$ cores may also be found in multiple cubane-type organometallic oxide clusters,[5] and in extended solids.[27] Additionally, the hydrated lithium tungstate $7Li_2WO_4 \cdot 4H_2O$ is presumed to contain tetrahedral $[LiW_4O_{16}]^{7-}$ ions[28] and a polyoxoanion-supported organometallic compound composed of a cubane-type $[W_4O_{16}]^{8-}$ unit capped by six {Ir(1,5-cod)}$^+$ groups has been reported.[4c] Neither the discrete tetrahedral species $[Mo_4O_{12}(\mu_3\text{-}O)_4]^{8-}$ nor the rhomb-like species $[Mo_4O_{10}(\mu\text{-}O)_4(\mu_3\text{-}O)_2]^{8-}$ are known, presumably in part because of the high charge density in these species, and also because the environments of the four molydenum atoms in the former, and those of two molybdenum atoms in the latter, would violate the Lipscomb rule. Derivatization by the replacement of a terminal oxo ligand by an alkoxo ligand or by replacement of a *fac*-$\{MoO_3\}$ group by an equivalent group, for example *fac*-$\{M(CO)_3\}^+$, prevents violation of the Lipscomb rule and could lead to the stabilization of both the cubane and the rhombic structures. The stabilization of the

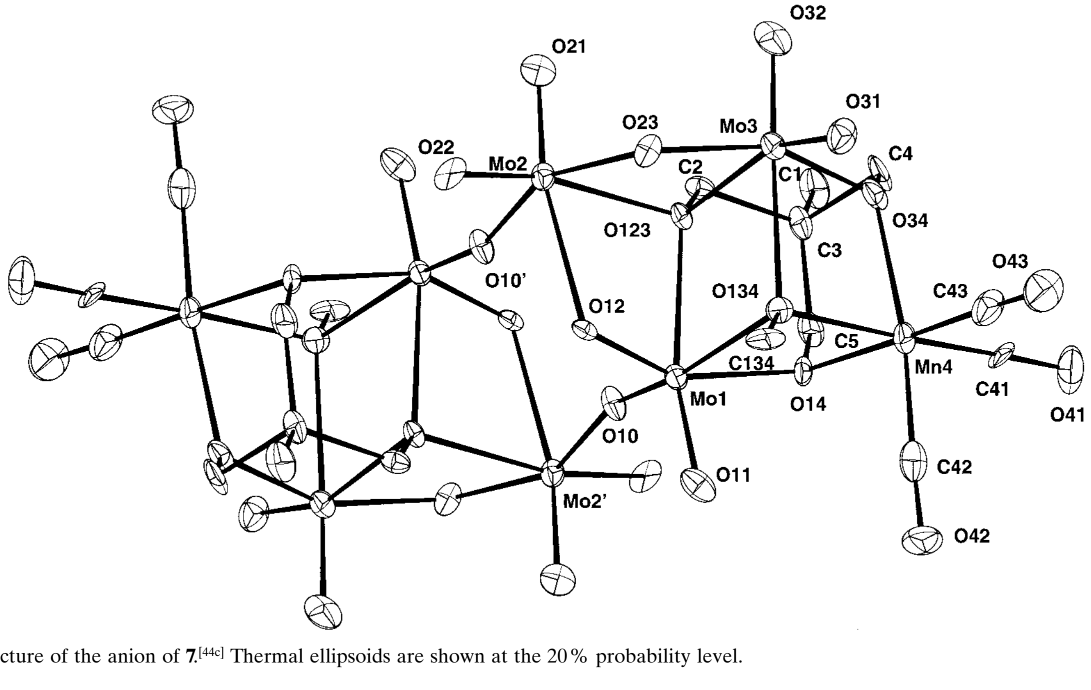

Figure 6. Structure of the anion of **7**.[44c] Thermal ellipsoids are shown at the 20% probability level.

clusters **1**, **2**, **4**–**7** can be explained in this way. However, it is not yet clear why **1a** was obtained in higher yields than **2**, while the rhomb-like compound **4** was obtained much more easily than the cubane-type cluster **1b**. Structural effects due to chelating ligands also need to be considered. For instance, the incorporation of trisalkoxo ligands probably favours the rhomb-like arrangement over the tetrahedral one in view of the tendency of these ligands to cap tetrahedral cavities in the polyoxometalate framework. Further work is needed to consider the question of structural preferences from all angles.

Electronic connections: As already pointed out, the molecular structures of clusters **2**, **5**, **6**, and **7** are related to those of $[Mo_4O_{10}(OMe)_6]^{2-}$, $[Mo_3O_6(OMe)\{MeC(CH_2O)_3\}_2]^-$, $[Mo_4O_8(OEt)_2\{MeC(CH_2O)_3\}_2]$, and $[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$, respectively, through the formal substitution of *fac*-$\{Mn(CO)_3\}^+$ units for *fac*-$\{MoO_2(OR)\}^+$ units (R = Me or Et). Further pairs of structurally related clusters can be found in the literature. For example, the framework of the cluster $[Mo_6O_{20}(OMe)_2(RhCp^*)_2]^{2-}$, obtained by the reaction of $(nBu_4N)_2[Mo_2O_7]$ with $[\{Cp^*RhCl(\mu\text{-}Cl)\}_2]$ in MeOH has been connected with that of the γ-$[Mo_8O_{26}]^{4-}$ ion.[5] However comparison with the $[Mo_8O_{24}(OMe)_4]^{4-}$ ion[29] is also appropriate, so that $[Mo_6O_{20}(OMe)_2(RhCp^*)_2]^{2-}$ can be formally derived from $[Mo_8O_{24}(OMe)_4]^{4-}$ by substitution of $\{RhCp^*\}^{2+}$ units for two *fac*-$\{MoO_2(OMe)\}^+$ units. Similarly, the species $[Mo_3O_8(OMe)_5(RhCp^*)]^-$, a key intermediate in the formation of $[Mo_6O_{20}(OMe)_2(RhCp^*)_2]^{2-}$,[30] can be derived from $[Mo_4O_{10}(OMe)_6]^{2-}$ by replacement of one *fac*-$\{MoO_2(OMe)\}^+$ unit by one $\{RhCp^*\}^{2+}$ unit. As another example, the similarity between the polyoxometalate-supported species $[\{(OC)_3Mn\}\{Mo_5O_{18}(TiCp)\}]^{2-}$ and $[(MoO_2Cl)\{Mo_5O_{18}(TiCp)\}]^{2-}$ (Cp = η^5-C_5H_5) shows some connection between the fragments $\{Mn(CO)_3\}^+$ and *fac*-$\{MoO_2Cl\}^+$.[31] A further example is provided by the cluster $[Mo_2O_6(OMe)_4[Ru(\eta^6\text{-}(p\text{-cymene})_2]$ which can be formally derived from $[Mo_4O_{10}(OMe)_6]^{2-}$ by replacement of two *fac*-$\{MoO_2(OR')\}^+$ units by $\{Ru(\eta^6\text{-}(p\text{-cymene})\}^{2+}$ units.[32a] Altogether these examples are indicative of an analogy between the fragments d^0-*fac*-$\{MoO_2X\}$ (X = O, OR, Cl) and d^6-*fac*-$\{ML_3\}$ (M = Mn, Re, Ru, Rh), where the charge have been omitted for convenience. It is worth to point out that it has been shown that $\{Re(CO)_3\}$ and $\{ReO_3\}$ are isolobal.[33] Thus $\{Re(CO)_3\}^+$ and $\{WO_3\}$ should also be isolobal. Electronic connections are not restricted to conical d^0 and d^6 fragments. For instance, there are several pairs of structurally related clusters where $\{MoO\}^{4+}$ units are replaced by $\{Mo(NO)\}^{3+}$ units, *e.g.* $[Mo_6O_{19}]^{2-}$,[34] and $[Mo_6O_{18}(NO)]^{3-}$,[35] $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$,[36] and $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$,[37] $[Mo_{154}O_{462}(H_2O)_{70}H_x]^{y-}$,[38] and $[Mo_{154}O_{420}(NO)_{14}(OH)_{28}(H_2O)_{70}]^{(25\pm5)-}$.[39] The isolobal analogy between the fragments d^0-$\{MoO\}^{4+}$ and d^4-$\{Mo(NO)\}^{3+}$ clearly emerge from the qualitative molecular orbital schemes of these fragments.[40]

Conclusion

The results reported here are noteworthy for several reasons. These clusters provide the first examples of polyoxometalates incorporating $\{Mn(CO)_3\}^+$ and $\{Re(CO)_3\}^+$ units. In addition, they provide a family of organometallic complexes whose structures led to the recognition of topological equivalent organometallic and oxo(alkoxo)metal units. Clusters **1** represent the first observation of discrete mono-cubane-type polyoxometalate derivatives, the alternative to the rhombic structure for compact complexes based on four edge-sharing octahedra. The latter might not be as favoured as often assumed, at least when the derivatization of the parent $\{M_4O_{16}\}^{8-}$ core prevents violation of the Lipscomb rule. The structural versatility within the field of polyoxometalate derivatives incorporating d^6-$\{ML_3\}$ units is further illustrated by the cluster $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$ obtained from $[\{(p\text{-cymene})RuCl_2\}_2]$ and sodium molybdate in aqueous solution.[32b]

The reactivity of these novel clusters is currently under investigation. This work will be extended to assess the generality of the synthetic approach described here and to extend the concept of topological equivalent units.

Experimental Section

Materials: $(nBu_4N)_2[Mo_2O_7]$,[41] $[MnBr(CO)_5]$,[42a] and $[ReBr(CO)_5]$,[42b] were prepared as described in the literature. $[Re(CO)_3(MeCN)_3][BF_4]$ was prepared according the the procedure reported for the perchlorate salt,[42c] using $AgBF_4$ instead of $NaClO_4$. 1,1,1-Tris(hydroxymethyl)ethane, pentaerythrytol, and tetrabutylammonium hydroxyde in methanol were obtained from commercial sources and used as received. Extra dry methanol was obtained by the standard method.[43]

Methods: IR spectra were recorded from KBr pellets on a Bio-Rad FT 165 spectrometer. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AC 300 spectrometer. Electronic absorption spectra were recorded with a Shimadzu UV-2101PC spectrometer. Elemental analyses were performed either by the Analytical Service of University Pierre and Marie Curie or by that of the CNRS (Vernaison, France).

Preparations of $(nBu_4N)[Mo_2O_5(OMe)_5\{Mn(CO)_3\}_2]$ (1a) and $[Mo_2O_4(OMe)_6\{Mn(CO)_3\}_2]$ (2): A mixture of $(nBu_4N)_2[Mo_2O_7]$ (0.4 g, 0.5 mmol) and $[MnBr(CO)_5]$ (0.27 g, 1 mmol) in MeOH (5 mL) was refluxed under N_2 for 3 h. The resulting dark green solution was allowed to stand at −30 °C for one week. The green crystalline precipitate proved to be a mixture of large green cubic crystals of **1a** (major product) and a few small red octahedral crystals of **2** (minor product) which were separated mechanically. **1a:** Yield 0.25 g (53 %); IR (KBr): $\tilde{\nu}$ = 2037 (s), 2025 (s), 1925 (br), 1910 (br) (ν(CO)), 1060 (sh), 1045 (m), 1018 (m) (ν(O-CH_3)), 940 (s), 920 (s), 900 cm^{-1} (s) (ν(Mo=O_t)); ^1H NMR (300.13 MHz, CD_3COCD_3, 22 °C, TMS): δ = 4.38 (s, 6H; OCH_3), 4.40 (s, 3H; OCH_3) 4.54 (s, 6H; OCH_3); ^{13}C NMR (75.47 MHz, CD_3COCD_3, 22 °C, TMS): δ = 64.2 (s, 2C; OCH_3), 68.6 (s, 1C; OCH_3), 69.7 (s, 2C; OCH_3), 220.3 (s, 2C; CO), 221.5 (s, 2C; CO), 223.1 (s, 1C; CO), 223.9 (s, 1C; CO); UV/Vis (MeOH): λ_{max} (ε) = 390 nm (2330); $C_{27}H_{51}Mn_2Mo_2NO_{16}$ (947.5): calcd C 34.23, H 5.43, Mn 11.60, Mo 20.25, N 1.48; found: C 34.19, H 5.38, Mn 11.36, Mo 20.45, N 1.52. **2**: IR (KBr): $\tilde{\nu}$ = 2042 (s), 1940 (sh), 1925 (br) (ν(CO)), 1017 (s), 977 (s) (ν(O-CH_3)), 942 (s), 920 cm^{-1} (s) (ν(Mo=O_t)).

Preparation of $(nBu_4N)[Mo_2O_5(OMe)_5\{Re(CO)_3\}_2]$ (1b): $(nBu_4N)_2[Mo_2O_7]$ (0.4 g, 0.5 mmol) and $[Re(CO)_3(MeCN)_3][BF_4]$ (0.24 g, 0.5 mmol) were dissolved in MeOH (10 mL) and the solution was refluxed under N_2 for 18 h. The resulting light yellow solution was evaporated to dryness under a N_2 flux at room temperature, the crude product was redissolved in MeOH (2 mL) and the solution was allowed to stand at −30 °C. The light yellow microcrystalline precipitate of **1b** was filtered off after three days. Yield 0.05 mg (8 %); IR (KBr): $\tilde{\nu}$ = 2032 (s), 2020 (s), 1890 (br) (ν(CO)), 1045 (s), 1000 (s) (ν(O-CH_3)), 940 (s), 920 (s), 900 cm^{-1} (s) (ν(Mo=O_t)); $C_{27}H_{51}Mo_2NO_{16}Re_2$ (1210): calcd: C 26.80, H 4.25, Mo 15.86, N 1.16; found: C 27.36, H 4.29, Mo 16.03, N 1.31. A few crystals of **1b** suitable for a crystal structure determination were obtained as follows: a mixture of

$[\mathrm{ReBr(CO)_5}]$ (0.2 g, 0.5 mmol) and $\mathrm{AgNO_3}$ (0.085 g, 0.5 mmol) in MeOH (10 mL) was stirred for 2 h. After filtration, $(n\mathrm{Bu_4N})_2[\mathrm{Mo_2O_7}]$ (0.2 g, 0.25 mmol) was added to the filtrate and the reaction mixture was refluxed for 24 h. After filtration, the filtrate was cooled to −30 °C whereupon a few pale yellow crystals of **1b** deposited overnight.

Preparation of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_2O_6(OMe)_4\{Re(CO)_3\}_2}]$ (4): $(n\mathrm{Bu_4N})_2[\mathrm{Mo_2O_7}]$ (0.24 g, 0.31 mmol) and $[\mathrm{Re(CO)_3(MeCN)_3}][\mathrm{BF_4}]$ (0.296 g, 0.62 mmol) were dissolved in MeOH (10 mL). One equivalent of $(n\mathrm{Bu_4N})\mathrm{OH}$ (0.62 mL of a 1M solution in MeOH) per equivalent Re was added and the mixture was stirred under $\mathrm{N_2}$ for 18 h at room temperature. The light yellow solution was then evaporated to dryness under a $\mathrm{N_2}$ flux. The crude solid was redissolved in MeOH (3 mL) and the solution was allowed to stand at 20 °C. Crystallization was apparent after a few hours and large pale yellow crystals of **4** were collected after a week. Yield 0.22 g (50 %); IR (KBr) $\tilde{\nu} = 1995$ (s), 1860 (br) (ν(CO)), 1045 (sh), 1022 (m) ($\nu(\mathrm{O\text{-}CH_3})$), 917 (s), 892 (s) ($\nu(\mathrm{Mo{=}O_t})$), 780 $\mathrm{cm^{-1}}$ (s) ν(MoOMo)); ^{1}H NMR (300.13 MHz, $\mathrm{CD_3COCD_3}$, 22 °C, TMS): $\delta = 4.30$ (s; $\mathrm{OCH_3}$); $\mathrm{C_{42}H_{84}Mo_2N_2O_{16}Re_2}$ (1437.4): calcd: C 35.1, H 5.89, N 1.95; found: C 36.27, H 6.29, N 2.21.

Preparations of $(n\mathrm{Bu_4N})[\mathrm{Mo_2O_4\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}}]$ (5) and $[\mathrm{Mo_2O_4\{RC(CH_2O)_3\}_2\{Mn(CO)_3\}_2}]$ (R = Me, 6a; R = $\mathrm{CH_2OH}$, 6b): A solution of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_2O_7}]$ (0.79 g, 1 mmol), $[\mathrm{MnBr(CO)_5}]$ (0.27 g, 1 mmol), and $\mathrm{MeC(CH_2OH)_3}$ (0.12 g, 1 mmol) was heated in MeOH (15 mL) for 6 h. A yellow solid (**6a**) began to deposit after 15 min. After separation of **6a** (0.095 g), the filtrate was concentrated and layered with diethyl ether. Dark yellow crystals of compound **5** (0.1 g) were obtained within two days. Doubling the amounts of $\mathrm{MeC(CH_2OH)_3}$ and of $[\mathrm{MnBr(CO)_5}]$ led to the precipitation of **6a** in 70 % yield. Compound **6b** was similarly obtained in 55 % yield from pentaerythritol. Its recrystallization from THF gave yellow-orange crystals of **6b**·2THF. **5:** IR (KBr): $\tilde{\nu} = 2031$ (s), 1928 (s), 1905 (s) $\mathrm{cm^{-1}}$ (ν(CO)), 1122 (m), 1046 (s), 1002 (w) $\mathrm{cm^{-1}}$ ($\nu(\mathrm{O\text{-}CH_3})$), 925 (s), 902 (s) $\mathrm{cm^{-1}}$ (ν(Mo=O)); ^{1}H NMR (300.13 MHz, $\mathrm{CD_3COCD_3}$, 22 °C, TMS): $\delta = 4.69$ (s, 2H; $\mathrm{OCH_2}$), 4.62 (s, 2H; $\mathrm{OCH_2}$), 4.55 (d, ^2J(H,H) = 9 Hz, 2H; $\mathrm{OCH_2}$), 4.26 (d, ^2J(H,H) = 9 Hz, 2H; $\mathrm{OCH_2}$), 4.16 (d, ^2J(H,H) = 9 Hz, 2H; $\mathrm{OCH_2}$), 4.10 (d, ^2J(H,H) = 9 Hz, 2H; $\mathrm{OCH_2}$), 0.72 (s, 3H; $\mathrm{CH_3}$), 0.47 (s, 3H; $\mathrm{CH_3}$); ^{13}C NMR (75.47 MHz, $\mathrm{CD_3COCD_3}$, 22 °C, TMS) $\delta = 222$ (s, 3C; CO), 88.2 (s, 2C; $\mathrm{OCH_2}$), 87.4 (s, 2C; $\mathrm{OCH_2}$), 83.3 (s, 1C; $\mathrm{OCH_2}$), 81.1, (s, 1C; $\mathrm{OCH_2}$); 41.9 (s, 1C; $C\mathrm{(CHO)_3}$), 36.5 (s, 1C; $C\mathrm{(CH_2O)_3}$), 16.9 (s, 1C; $\mathrm{CH_3}$), 16.5 (s, 1C; $\mathrm{CH_3}$); UV/Vis (MeOH) λ_{max} (ε) 390 nm (1310). $\mathrm{C_{29}H_{54}MnMo_2NO_{13}}$ (871.6): calcd C 39.97, H 6.25, N 1.61; found: C 39.95, H 6.35, N 1.55; **6a**: IR (KBr): $\tilde{\nu} = 2047$, 1943 (br) $\mathrm{cm^{-1}}$ (ν(CO)). $\mathrm{C_{16}H_{18}Mn_2Mo_2O_{16}}$ (768.1): calcd: C 25.02, H 2.36; found: C 24.93, H 2.39; **6b**: IR (KBr): $\tilde{\nu} = 2048$ (s), 1954 (s), 1931 (s) $\mathrm{cm^{-1}}$ (ν(CO)); UV/Vis (THF) λ_{max} (ε) = 393 nm (2680). ^{1}H NMR (300.13 MHz, $\mathrm{CD_3COCD_3}$, 22 °C, TMS) $\delta = 5.27$ (s, 4H; $\mathrm{OCH_2}$), 4.94 (d, 4H; $\mathrm{OCH_2}$) 4.89 (d, 4H; $\mathrm{OCH_2}$), 3.68 (s, 4H; $\mathrm{C}H_2\mathrm{OH}$); $\mathrm{C_{16}H_{18}Mn_2Mo_2O_{18}}$ (800.1): calcd: C 24.02, H 2.27; found: C 24.52, H 2.39.

Preparation of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6O_{16}(OMe)_2\{MeC(CH_2O)_3\}_2\{Mn(CO)_3\}_2}]$ (7): $(n\mathrm{Bu_4N})_2[\mathrm{Mo_2O_7}]$ (0.79 g, 1 mmol) and $\mathrm{MeC(CH_2OH)_3}$ (0.24 g, 2 mmol) and $[\mathrm{MnBr(CO)_5}]$ (0.54 g, 2 mmol) were stirred in MeOH (15 mL) at room temperature until all solids were dissolved (about two hours). The mixture turned red while CO evolved. The clear red solution was cooled in an ice bath and then was allowed to warm slowly to room temperature. Orange needles of compound **7** deposited upon standing within one day. Yield 0.38 g (60 % yield, based on Mo); IR (KBr): $\tilde{\nu} = 2034$ (s), 1930 (br), 1925 (sh) $\mathrm{cm^{-1}}$ (ν(CO)); UV/Vis (MeOH): λ_{max} (ε) = 395 nm (2790); ^{1}H NMR (300.13 MHz, $\mathrm{CD_3CN}$, 22 °C, TMS) $\delta = 4.66$ (dd, ^2J(H,H) = 10.5 Hz, ^4J(H,H) = 2.4 Hz, 2H; $\mathrm{OCH_2}$), 4.57 (dd, ^2J(H,H) = 10.6 Hz, ^4J(H,H) = 1.4 Hz, 2H; $\mathrm{OCH_2}$), 4.44 (dd, ^2J(H,H) = 11.7 Hz, ^4J(H,H) = 1.5 Hz, 2H; $\mathrm{OCH_2}$), 4.41 (dd, ^2J(H,H) = 10.6 Hz, ^4J(H,H) = 1.9 Hz, 2H; $\mathrm{OCH_2}$), 4.39 (s, 6H, $\mathrm{OCH_3}$), 4.38 (dd, ^2J(H,H) = 10.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; $\mathrm{OCH_2}$), 4.10 (dd, ^2J(H,H) = 11.9 Hz, ^4J(H,H) = 2.4 Hz, 2H; $\mathrm{OCH_2}$), 0.51 (s, 6H; $\mathrm{CH_3}$); ^{13}C NMR (75.47 MHz, $\mathrm{CD_3CN}$, 22 °C, TMS): $\delta = 222.3$ (s, 4C; CO), 207.4 (s, 2C; CO), 89.4 (s, 2C; $\mathrm{OCH_2}$), 84.7 (s, 2C; $\mathrm{OCH_2}$), 80.2 (s, 2C; $\mathrm{OCH_2}$), 40.8 (s, 2C; $C\mathrm{(CH_2O)_3}$), 16.8 (s, 2C; $\mathrm{CH_3}$); $\mathrm{C_{50}H_{96}Mn_2Mo_6N_2O_{30}}$ (1890.8): calcd: C 31.76, H 5.12, N 1.48; found: C 31.37, H 5.11, N 1.49.

Crystal structure analyses: Crystal structure data are summarized in Table 1. Data were recorded at room temperature on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71069$ Å). Crystals were mounted on glass fibers and sealed with an epoxy cement except for **6b**·2THF which was put in a Lindemann glass tube. Lattice parameters and the orientation matrix were obtained from a least-squares fit of 25 atomatically centered reflections in the range 15–15.2° for **1a**, 12–12.5° for **1b**, 13–13.4° for **2**, 14–14.5° for **4** and **6b**·2THF, 14–14.3° for **5** and **7**. References were periodically monitored for intensity and orientation control. No decay was observed except for the crystal of **7** which had decayed by about 23 %. Intensities were corrected for Lorentz and polarization effects and for absorption (empirical). Only those with $I \geq 3\sigma(I)$ were retained for calculations. Data processing was performed using the program CRYSTALS.[44a] The structures were solved by direct methods[44b] and subsequent electron density maps. All atoms were refined anisotropically. Hydrogen atoms were not included in the refinements. The asymmetric unit of **4** contains the '$\mathrm{MoO_3(OMe)_2\{Re(CO)_3\}^-}$' half-anion and one $n\mathrm{Bu_4N^+}$ ion. The asymmetric unit of **6b** contains the '$\mathrm{MoO_2\text{-}\{HOCH_2C(CH_2O)_3\}\{Mn(CO)_3\}}$' half-cluster and one THF molecule. The pendant OH group of the cluster and the molecule of THF were found to be disordered. The asymmetric unit of **7** contains the '$\mathrm{Mo_3O_8(OMe)\{MeC(CH_2O)_3\}\{Mn(CO)_3\}^-}$' half-anion and one $n\mathrm{Bu_4N^+}$ ion. Neutral-atom scattering factors were used, with anomalous dispersion correction applied. Final residuals are given in Table 2.[45] Despite rather large standard deviations due to the poor quality of crystals, the composition and the molecular structure of the cluster anion in **5** are unequivocal. Molecular structures were drawn with the program CAMERON.[44c]

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Table 2. Crystal structure data for compounds **1a**, **1b**, **2**, **4**, **5**, **6b**, and **7**.

	1a	**1b**	**2**	**4**	**5**	**6b**·2THF	**7**
formula	$C_{27}H_{51}Mn_2Mo_2N_1O_{16}$	$C_{27}H_{51}Mo_2N_1O_{16}Re_2$	$C_{12}H_{18}Mn_2Mo_2O_{16}$	$C_{42}H_{84}Mo_2N_2O_{16}Re_2$	$C_{29}H_{54}Mn_1Mo_2N_1O_{13}$	$C_{24}H_{34}Mn_2Mo_2O_{20}$	$C_{50}H_{96}Mn_2Mo_6N_2O_{30}$
M_r [g mol^{-1}]	947.43	1210.00	720.02	1437.44	871.57	944.28	1890.83
color	yellow	white	red	white	yellow	yellow	orange
crystal system	triclinic	triclinic	orthorhombic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\,cab$	$P\bar{1}$	$P2_1cn$	$C2/c$	$P2_1/n$
T [K]	ambient	ambient	ambient	ambient	ambient	ambient	ambient
a [Å]	11.770(3)	11.755(2)	11.505(7)	11.055(3)	12.720(4)	26.88464)	12.391(3)
b [Å]	12.911(3)	13.141(2)	12.598(7)	11.224(3)	14.708(4)	11.258(3)	22.163(4)
c [Å]	13.854(4)	13.496(2)	16.212(4)	12.223(3)	20.084(2)	12.312(4)	15.862(3)
α [°]	90.18(3)	92.59(1)	90	67.58(2)	90	90	90
β [°]	107.43(3)	93.90(1)	90	85.06(2)	90	115.68(3)	112.43(2)
γ [°]	95.69(2)	94.16(1)	90	80.77(2)	90	90	90
V [Å^3]	1997(1)	2071.9(4)	2350(2)	1384.4(5)	3757(2)	3359(2)	4026(2)
Z	2	2	4	1	4	4	2
ρ_{calcd} [g cm^{-3}]	1.575	1.94	2.035	1.725	1.541	1.85	1.559
μ [cm^{-1}]	12.53	65.41	20.96	49.123	10.1	14.97	12.407
$2\theta_{max}$ [°]	50	50	50	50	50	50	50
refl. measured	7318	7642	2372	5135	3452	6560	7642
unique refl. (R_{int})	6996 (0.013)	7254 (0.017)	-	4858 (0.024)	-	2965 (0.02)	7075 (0.04)
observed ($I > 3\sigma(I)$)	5735	4670	1405	3732	2281	1426	3775
refined parameters	435	434	146	290	331	203	407
R[a]	0.036	0.061	0.037	0.048	0.060	0.052	0.054
Rw[b]	0.039	0.071	0.041	0.052	0.065	0.059	0.063
$\Delta\rho$(max/ min) [e Å^{-3}]	0.52/ – 0.56	2.34/ – 3.0	0.5/ – 0.29	1.29/ – 0.85	2.98/ – 2	0.84/ – 0.54	1.01/ – 0.73

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ ($w = 1$ except for compounds **6b**·2THF and **7**: $w = w'[1 - ((||F_o| - |F_c||)/(6\sigma(F_o))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ for which X is F_c/F_c (max) with three coefficients for a Chebyshev Series: 12.4, 5.6, and 10.8 for **6b**·2THF and 7.07, –1.39 and 5.33 for **7**).

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[45] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101142 (**1a**, **4**, **5** and **7**), CCDC-138191 (**1b**), CCDC-138190 (**2**), and CCDC-138189 (**6a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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