An Octanuclear Alkoxy-polyoxomolybdate. The Crystal and Molecular Structure of $[(n\text{-}C_4H_9)_4N]_2[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]$

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Reaction of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ with 2-hydroxymethyl-2-methylpropane-1,3-diol yields $[(C_4H_9)_4N]_2[Mo_8O_{20}(OMe)_4\{MeC(MeO)_3\}_2]$ (**1**), an alkoxypolyoxomolybdate consisting of two tetranuclear $[Mo_4O_{10}(OMe)_2\{MeC(CH_2O)_3\}]^-$ moieties, composed of edge-sharing MoO_6 octahedra, which are connected *via* two corner-sharing interactions through bridging oxo-groups; thermal degradation of (**1**) yields dimethyl ether, formaldehyde, methanol, and water as gaseous products.

Although molybdenum oxides display a remarkable variety of applications as heterogeneous catalysts for organic transformations,[1—3] the intimate details of the chemistry on the molecular level remain exceedingly difficult to elucidate. In view of this lack of structural information for surface-bound intermediates, the co-ordination chemistry of polyoxomolybdates and related polyoxoanion derivatives incorporating organic substrate molecules has received considerable attention in recent years.[4,5] Examples of structurally characterized polyoxomolybdate co-ordination complexes containing organic moieties related to surface intermediates in heterogeneous systems include $[(HCO_2)_2(Mo_8O_{26})]^{6-}$,[6] $[CH_2Mo_4O_{15}H]^{3-}$,[7] $[Mo_4O_8(OCH_2Me)_2\{MeC(CH_2O)_3\}_2]$,[8] $[Mo_8O_{24}(OMe)_4]^{4-}$,[9] and $[Mo_4O_{10}(OCH_3)_6]^{2-}$.[10] Furthermore, chemical systems based on $[Nb_2W_4O_{19}R]^{3-}$ [11] and $[(P_3O_9)MoO_3R]^{2-}$ [12] have been demonstrated to provide solution pathways for incorporating organic substrates into polyoxoanions.

In the course of our investigations of the co-ordination chemistry of organic solvent-soluble polyoxomolybdates,[13] we have noted dramatic influences of reaction conditions and of polyoxoanion precursor on the structures of polyoxomolybdate-ligand complex products. Thus, although the reactions of 2-hydroxymethyl-2-methylpropane-1,3-diol (H_3hmmp) with MoO_3 and its derivatives yield $[MoO_2(Hhmmp)]$,[14] $[Mo_2O_2(OCH_2Me)_2(hmmp)_2]$,[15] and

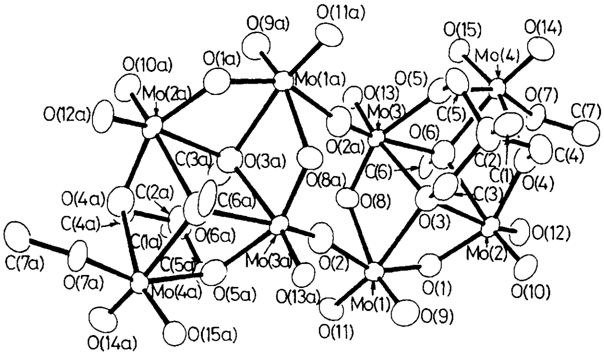

Figure 1. ORTEP view of the structure of $[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$, showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°) Mo–O_t, 1.697(7) average; Mo(1)–O(1), 1.946(7); Mo(2)–O(1), 1.883(6); Mo(1)–O(8), 2.248(6); Mo(3)–O(8), 1.765(6); Mo(2)–O(6), 2.379(7); Mo(3)–O(6), 2.164(7); Mo(4)–O(6), 2.225(7); Mo(1)–O(3), 2.304(6); Mo(2)–O(3), 2.266(6); Mo(3)–O(3), 2.250(6); Mo(1)–O(2), 2.021(6); Mo(3)–O(2a), 1.788(6); Mo(4)–O(7), 1.871(6). O(1)–Mo(1)–O(2), 150.8(3); O(3)–Mo(1)–O(11), 161.3(3); O(8)–Mo(1)–O(9), 159.7(3); O(1)–Mo(2)–O(4), 125.0(2); O(3)–Mo(2)–O(12), 158.2(3); O(6)–Mo(2)–O(10), 160.3(3); O(3)–Mo(3)–O(13), 164.9(3); O(5)–Mo(4)–O(7), 153.4(3); O(4)–Mo(4)–O(15), 161.3(3); O(5)–Mo(4)–O(7), 153.8(3); O(6)–Mo(4)–O(14), 154.8(3).

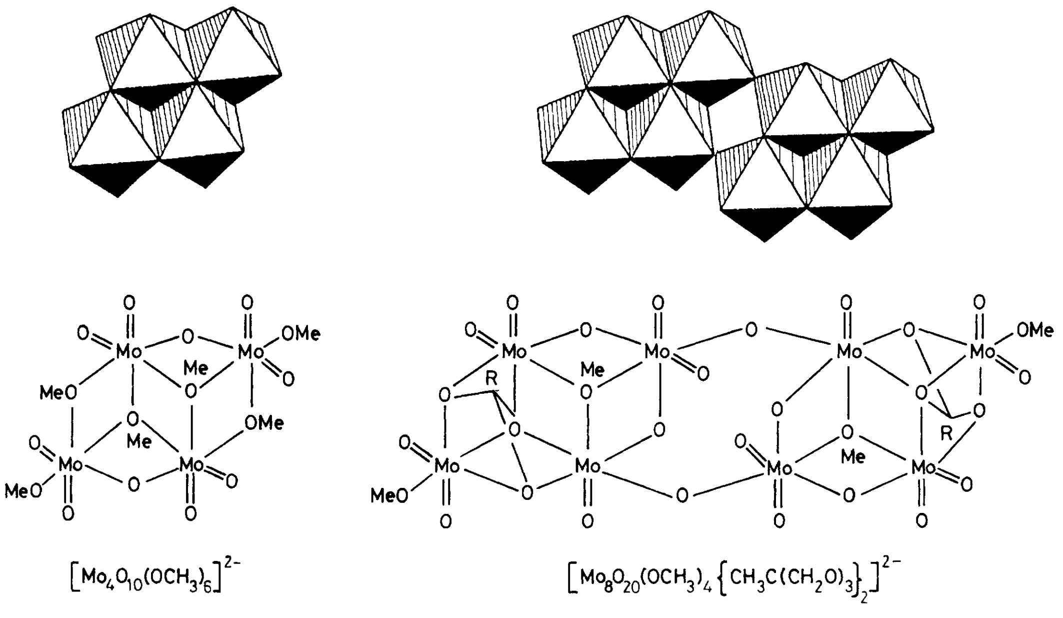

Figure 2. Idealized polyhedral models and schematic representations of the structures of $[Mo_4O_{10}(OMe)_6]^{2-}$ and $[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$, illustrating the construction of the octanuclear unit from corner-sharing tetranuclear cores.

$[Mo_4O_8(OCH_2Me)(hmmp)_2]$,[8] exploitation of the organic-soluble precursors $[(C_4H_9)_4N]_2[Mo_2O_7]$[16] and α-$[(C_4H_9)_4N]_4[Mo_8O_{26}]$[17] produces a novel trinuclear polyoxomolybdate $[Mo_3O_7(hmmp)_2]^{2-}$[18] and the octanuclear species $[(C_4H_9)_4N)]_2[Mo_8O_{20}(OMe)_4(hmmp)_2]$, whose structure we report here.

The reaction of $[(C_4H_9)_4N]_2[Mo_2O_7]$ with (H_3hmmp) (1.34 equiv.) and triethylamine (8.00 equiv.) in methanol followed by removal of solvent and recrystallization from methanol/ether afforded $[(C_4H_9)_4N]Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]$ (**1**) in 30% yield.† *X*-Ray structural analysis of (**1**)‡ revealed the presence of the octanuclear anionic cluster illustrated in Figure 1. The discrete octanuclear molecular anion consists of two tetranuclear $[Mo_4O_{10}(OMe)_2(hmmp)]^{1-}$ moieties related by a centre symmetry located at the midpoint of the O(8)–O(8a) vector and connected by two corner-sharing interactions at O(2) and O(2a), as shown in Figure 2.

The molybdenum centres display the usual pseudo-octahedral $[MoO_6]$ geometry, although the detailed co-ordination about each of the four crystallographically independent molybdenum sites is unique. Two of the alkoxy groups of the (hmmp) ligands are doubly-bridging [O(4) and O(5)], while the third is triply-bridging. The methoxy groups are terminal, to Mo(4) and Mo(4a), and triply-bridging to the Mo(2)–Mo(3)–Mo(4) faces. The oxo groups which connect the tetranuclear $[Mo_4O_{10}(OMe)_2(hmmp)]^-$ units adopt unsymmetrical bridge geometry with Mo(1)–O(2) at 2.021(6) Å and Mo(3)–O(2a) at 1.788(6) Å. Unsymmetrical bridging is even more pronounced at O(8) with Mo(1)–O(8) and Mo(3)–O(8) distances of 2.248(6) and 1.765(6) Å, respectively. Although the Mo(3) site exhibits a single terminal oxo interaction to O(13), the Mo(3)–O(2a) and Mo(3)–O(8) bond lengths are exceedingly short for Mo^{VI}-doubly bridging oxo group distances, which normally average 1.88 to 1.92 Å.[19] This observation suggests that the Mo(3) site adopts the characteristics of a MoO_3 unit with two quasi-terminal oxo groups[20] and co-ordinated to three bridging alkoxy oxygen donors, a structural feature which may be related to the ready isolation of a co-ordinated MoO_3 moiety in $[Mo_3O_7(hmmp)_2]^{2-}$.[18]

The overall geometry of the tetranuclear $[Mo_4O_{10}(OMe)_2(hmmp)]^-$ units from which (**1**) may be constructed is similar to that of the structural prototypes $[Mo_4O_8(OCH_2Me)_2(hmmp)_2]$ and $[Mo_4O_{10}(OMe)_6]^{2-}$ and consists of a compact edge-sharing $[MoO_6]$ polyhedral array, illustrated in Figure 2. Whereas condensation of two $[Mo_4O_{10}(OMe)_6]^{2-}$ units involves either sharing of four edges to yield β-$[Mo_8O_{26}]^{4-}$ or sharing of two edges to give $[Mo_8O_{24}(OMe)_4]^{4-}$,[10] the tetranuclear units of (**1**) adopt a corner-sharing geometry with relatively weak bridging interactions.

As suggested by these weak bridging interactions between the tetranuclear units of (**1**), the cluster dissociates readily under appropriate conditions. Reaction of (**1**) with chloroacetic acid and excess of H_3hmmp yields $[Mo_3O_7(hmmp)_2]^{2-}$ (**2**), a complex incorporating a reactive MoO_3 unit. Treatment of (**2**) with MeI yields $[Mo_3O_6(OMe)(hmmp)_2]^-$ (**3**).[18]

Thermal degradation of (**1**) at 150 °C yields formaldehyde, methanol, dimethyl ether, and water as gaseous products,§ a

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† Satisfactory elemental analyses. i.r. (KBr, cm^{-1}): ν(C–H, methoxy) 2955(m), $\nu_s(Mo–O_t)$ 945(s), $\nu_a(Mo–O_t)$ 905(s), ν(Mo–O–Mo) 765(m).

‡ *Crystal data*: $C_{46}H_{102}N_2O_{30}Mo_8$, monoclinic, space group $P2_1/n$, a = 10.079(3), b = 25.369(4), c = 13.915(4) Å, β = 90.50(1)°, V = 3557.1(11) $Å^3$, Z = 2; D_c = 1.80 g cm^{-3}; μ(Mo-K_α) = 13.79 cm^{-1}; 4270 unique data having $2\theta \leq 45.0°$ were collected on a Nicolet R3m/V diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and coupled θ(crystal)–2θ(counter) scan mode. The structure was solved by direct methods, and structural parameters refined using full-matrix least squares techniques to R = 0.031 and R_w = 0.032 for 2745 reflections having $F_o \geq 6\sigma(F_o)$. These refinement cycles employed anisotropic thermal parameters for all non-hydrogen atoms of the anion. Calculated H atom positions were introduced in the final cycles of refinement, with the C–H bond distances set to 0.96 Å. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The gaseous products are isolated in the ratio methanol : formaldehyde : dimethyl ether : water of 7 : 7 : 1 : 0.5.

process which may involve a cyclic, heterolytic pathway, a mechanism similar to that invoked for heterogeneous oxidation of methanol to formaldehyde over MoO_3 catalyst. We are currently investigating the photochemical degradation of (**1**) and (**3**) and the decomposition reactions of the analogous ethoxy complex $[Mo_8O_{20}(OEt_2)_4(hmmp)_2]^{2-}$.

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