Hydrothermal Synthesis and Crystal and Molecular Structure of a Reduced, Arsenic Rich Heteropolyanion, $Na_4[Mo_4As_6O_{20}(OH)_2]·9H_2O$

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The hydrothermal reaction of $Na_3MoO_4·2H_2O$, Mo metal, MnO_3, $H_5As_3O_{10}$, NaCl and H_2O in the mole ratio 6 : 6 : 6 : 3 : 10 : 166 for 110 h at 180 °C yielded orange crystals of the sodium salt of the arsenic-rich Mo^V–As^{III} polyanion cluster, $Na_4[Mo_4As_6O_{20}(OH)_2]·9H_2O$.

While As–Mo oxygen clusters and polyanions are of interest because of their unusual structural chemistry[1,2] and their importance for catalysis,[3] their chemistry remains relatively unexplored. The As^V-containing clusters are represented by the fully-oxidized and mixed-valence Keggin cores, $[Mo_{12}AsO_{40}]^{3-}$[4] and $[H_nMo^V_nMo_{12-n}O_{40}]^3$ (n = 2 and 4),[1] respectively, and the Dawson polyanion, $[Mo_{18}As_2O_{62}]^{6-}$.[5] Clusters incorporating As^{III} sites have been described for the Mo^V–Mo^{VI} mixed-valence cluster $[H_6As_{10}Mo_{24}O_{90}]^{8-}$[1] and for the $(As_3O_7)^{5-}$-containing Mo^{VI} clusters $[Mo_3As_3O_{15}]^{3-}$ and $[Mo_6CoAs_6O_{30}]^{4-}$.[6] Although the cluster richest in arsenic content described to date corresponded to the composition As/Mo = 1, our experience[7] suggested that reduced polymolybdenum cores could condense with larger numbers of As centres. By exploiting the technique of hydrothermal synthesis under reducing conditions,[8] the unprecedented arsenic rich species with As/Mo = 1.5, $Na_4[Mo_4As_6O_{20}(OH)_2]·9H_2O$ **1**, was isolated.

The reaction of $Na_2MoO_4·2H_2O$, Mo metal, MoO_3, $H_5As_3O_{10}$, NaCl and H_2O in the mole ratio 6 : 6 : 6 : 3 : 10 : 166 for 110 h at 180 °C under autogenous pressure (*ca.* 8 atm) yielded bright orange crystals of **1** in 50% yield.† The IR spectrum of **1** exhibits features at 1092 and 1021 cm^{-1} associated with ν(As–O) and bonds at 947 and 799 cm^{-1} characteristic of ν(Mo=O$_t$) and ν(Mo–O–Mo), respectively.

The structure of the molecular anion of **1**,‡ shown in Fig. 1(*a*), consists of the tetranuclear $\{Mo_4O_{16}\}$ core in which six terminal and two doubly bridging oxygen atoms have been replaced by eight oxygen donors from the two linear triarsenate(III) groups $(HAs_3O_7)^{4-}$. As shown in Fig. 1(*b*), the four MoO_6 octahedra adopt the compact edge-sharing arrangement common to both Mo^{VI} and Mo^V tetranuclear clusters.[9] The presence of reduced Mo^V sites is confirmed by the observation of two pairs of relatively short Mo–Mo distances of 2.720(2) Å. In contrast, the Mo–Mo distances in other examples of the reduced Mo_4-core fall in the range 2.60–2.67 Å. The expansion of the core volume in **1** may reflect the constraints imposed by the two $(HAs_3O_7)^-$ chains which sandwich the central $\{Mo_4O_8\}$ core. Each $(HAs_3O_7)^-$ chain is

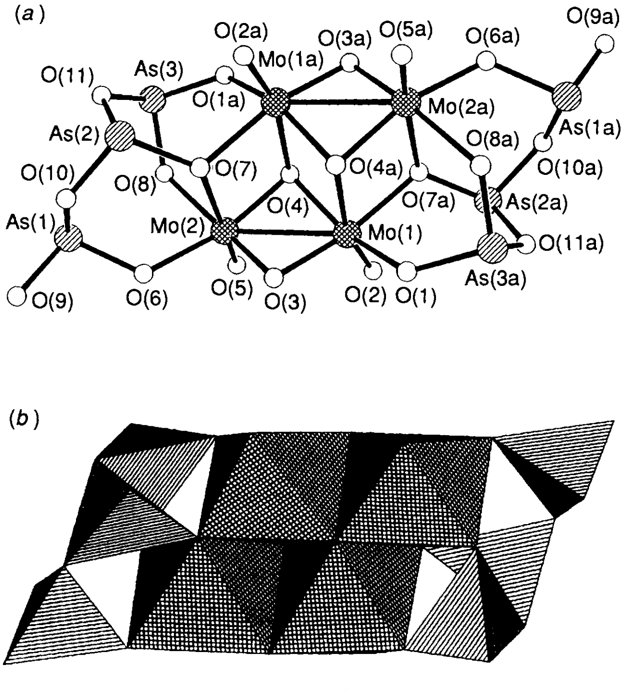

Fig. 1 (*a*) A view of the structure of $[Mo_4As_6O_{20}(OH)_2]^{4-}$, showing the atom-labelling scheme. The molecular anion lies on the crystallographic inversion centre. Selected bond lengths (Å): Mo(1)–Mo(2) 2.770(2), Mo(1)–O(1) 2.13(1), Mo(1)–O(2) 1.70(1), Mo(1)–O(3) 1.89(1); Mo(1)–O(4) 1.99(1), Mo(1)–O(4a) 2.29(1), Mo(1)–O(7a) 2.06(1), Mo(2)–O(3) 2.06(1), Mo(2)–O(4) 1.90(1), Mo(2)–O(5) 1.71(1), Mo(2)–O(6) 2.02(1), Mo(2)–O(7) 2.28(1), Mo(2)–O(8) 2.11(1); As–O range, 1.67(1) to 1.87(1). (*b*) A polyhedral representation of the structure of $[Mo_4As_6O_{20}(OH)_2]^{4-}$. The $\{MoO_6\}$ octahedra are crosshatched; the $\{AsO_3\}$ pyramids are illustrated by polyhedra with parallel lines. The free vertices of the As tetrahedra represent the lone pairs.

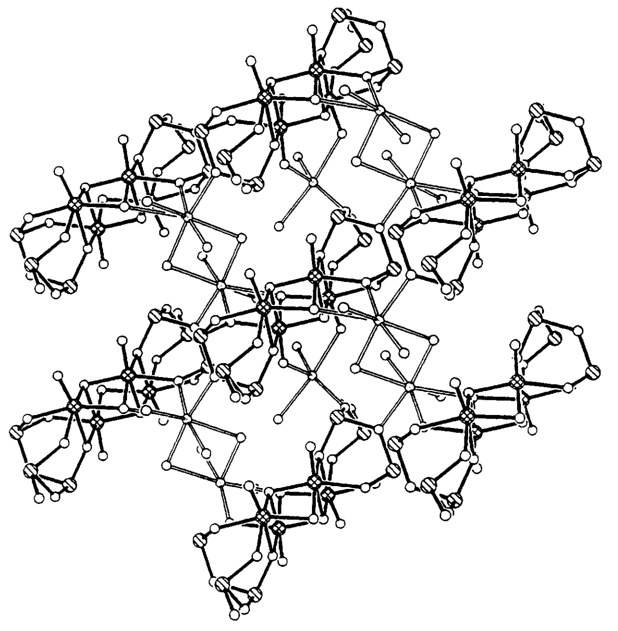

Fig. 2 A view of the Na$^+$ cation environments. Note the $\{Na_2(H_2O)_6\}^{2+}$ units located between four anion clusters. The mononuclear $\{Na(H_2O)_2\}^+$ sites connect two clusters from adjacent anion layers and bond to the pendant OH groups of the $(HAs_3O_7)^-$ ligands.

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† Satisfactory elemental analyses were obtained.

‡ *Crystal data* for $H_2O_{22}Na_4As_6Mo_4·9H_2O$: monoclinic *C*2/*c*, a = 16.858(3), b = 8.488(2), c = 21.753(4) Å, β = 108.12(2)°, V = 2958.3(11) Å^3, Z = 4, D_c = 3.24 g cm^{-3}. Structure solution and refinement based on 2456 reflections with $I_o \geq 3\sigma(I_o)$ converged at a residual of 0.0781. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

constructed from three corner-sharing $\{AsO_3\}$ pyramids. Each chain shares four oxygen atoms with the Mo_4-core. The central arsenic of this unit is bound to two oxygen bridging to the terminal arsenic atoms of the chain and to a third oxygen which bridges two Mo sites. One external arsenic of the chain is bound to two oxygen atoms which bridge two Mo sites, while the other external arsenic coordinates to one oxygen bound to a molybdenum centre and to a pendant OH group. Complex **1** provides a unique example of a coordinated $(HAs_3O_7)^-$ group.

Another unusual features of the structure is the presence of binuclear $\{Na_2(H_2O)_6\}^{2+}$ cations which are located in hydrophilic channels between layers of $[Mo_4As_6O_{20}(OH)_2]^{4-}$ anions and which interact with four anion sites, two from each of two adjacent layers (Fig. 2).

The isolation of **1**, a species exhibiting a reduced Mo^V–As^{III} core, provides yet another example of the power of hydrothermal synthetic techniques in the isolation of reduced polyanion clusters incorporating a variety of organic and inorganic ligands.[9] Furthermore, the isolation of **1** and a variety of mixed valence As^V–As^{III}–Mo^V–Mo^{VI}-oxo clusters, such as $[H_4As_2{}^{III}As^VMo_8{}^VMo_4{}^{VI}O_{40}]^-$[10] and $[H_4As_2{}^{III}As_2{}^VMo_4{}^V$-$Mo_{14}{}^{VI}O_{62}]$,[11] by hydrothermal methods suggests that the cluster chemistry of the As–Mo system may be greatly expanded.

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