Synthesis and ^{17}O Nuclear Magnetic Resonance Spectroscopic Structure Determination of $[(PhAs)_4Mo_{12}O_{46}]^{4-}$

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Summary The $[(PhAs)_4Mo_{12}O_{46}]^{4-}$ anion, a novel organoarsonomolybdate, has been synthesized and shown by ^{17}O n.m.r. spectroscopy to be isostructural with $[H_4As_4Mo_{12}O_{50}]^{4-}$.

We recently reported[1] the solution structures of $[As_2Mo_6O_{26}]^{6-}$ (**1**) and $[(PhAs)_2Mo_6O_{24}]^{4-}$ (**2**), the first members of a new structural class of polyoxomolybdates.[2] When an aqueous solution of (**1**) is acidified to pH $<$ 1, a new species $[H_4As_4Mo_{12}O_{50}]^{4-}$ (**3**) is formed.[3,4] Both anions (**1**) and (**3**) contain tripod arsenate ligands which have only three of the four arsenate oxygens bonded to molybdenum. Since (**1**) and (**2**) are isostructural, acidification of (**2**) in aqueous solution should yield a new species $[(PhAs)_4Mo_{12}O_{46}]^{4-}$ (**4**), related to (**3**) by replacement of $HOAsO_3^{2-}$ sub-units with $PhAsO_3^{2-}$ [see Figure (a)]. We report here the synthesis and structure of this new phenylarsonate complex.[5]

Acidification of phenylarsonic acid and sodium molybdate (1:3 molar ratio) with HCl to pH 1 in hot, aqueous solution followed by addition of $[Bu^n_4N]Br$ yields (**4**) as the $[Bu^n_4N]^+$ salt. The ^{17}O n.m.r. spectrum of this compound,

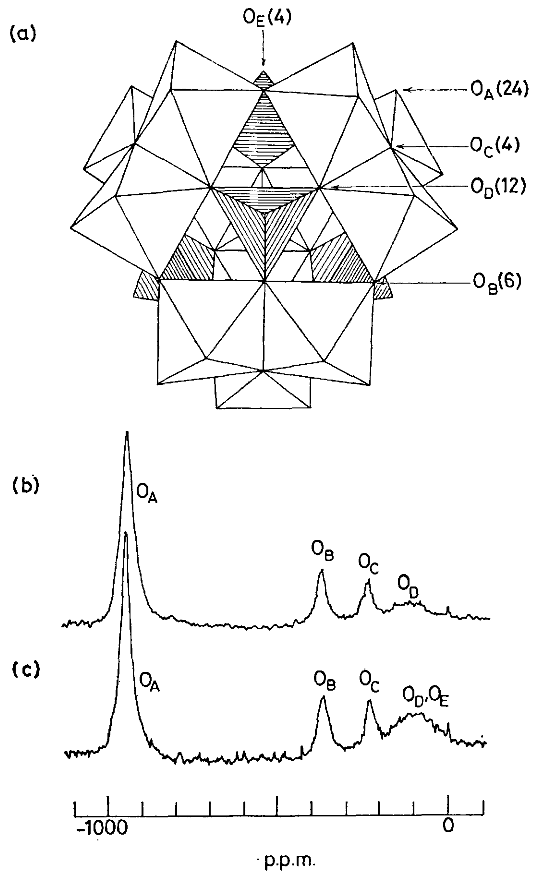

FIGURE. Polyhedral model of the tetrahedral $[H_4As_4Mo_{12}O_{50}]^{4-}$ anion is shown in (a), where octahedra represent co-ordination polyhedra about Mo atoms and tetrahedra represent co-ordination polyhedra about As atoms. One oxygen from each set of symmetry equivalent oxygens is labelled, and the number of oxygens in each set is enclosed in parentheses. ^{17}O Fourier transform n.m.r. spectra of $[Bu^n_4N]_4[(PhAs)_4Mo_{12}O_{46}]$ (4), at 94 °C, and $[Bu^n_4N]_4[H_4As_4Mo_{12}O_{50}]$ (3), at 80 °C, enriched to about 25 at. % ^{17}O, in MeCN are shown in (b) and (c), respectively. On the scale shown, pure water at 30 °C is assigned a chemical shift of 0 p.p.m., and negative numbers indicate downfield shifts.

dissolved in MeCN, is shown in Figure (b). The spectrum is consistent with the structure shown in Figure (a) where O_E sites are occupied by phenyl groups.[6] Since the O_A resonance is shifted unusually far downfield for a *cis* dioxo terminal oxygen,[6] we prepared a $[Bu^n_4N]^+$ salt of (3) in order to measure ^{17}O chemical shifts for the parent compound of known structure. Its ^{17}O n.m.r. spectrum, shown in Figure (c), is almost identical to the spectrum of (4), confirming the structural assignment of (4). As was observed for (1),[1] the resonances for nonequivalent oxygens bonded to arsenic in (3) are too broad to be resolved, even at elevated temperatures.

Although the dimeric 1 : 3 arsenomolybdates (1) and (2) as well as the tetrameric species (3) and (4) all possess only *cis* dioxo terminal oxygens and no monoxo terminal oxygens, their chemical and spectroscopic properties differ significantly. In contrast to (1) and (2), both (3) and (4) are easily reduced[7] and are stable in strongly acidic solutions ($pH < 0$). Also, the ^{17}O resonances for terminal oxygens in (1) and (2) lie in the -800 to -900 p.p.m. range whereas the corresponding resonances for (3) and (4) lie in the -900 to -1000 p.p.m. range, characteristic of monoxo terminal oxygens.[6] As has been pointed out elsewhere,[8] (1) and (2) may be represented by the formulae $(AsO_4{}^{3-})_2(Mo_6O_{18})$ and $(PhAsO_3{}^{2-})_2(Mo_6O_{18})$ which specify the cluster sub-units obtained when the very weak bonds ($d_{Mo-O} > 2{\cdot}2$ Å) *trans* to terminal oxygens are broken. Thus (1) and (2) are best viewed as clusters resulting from a weak association of two arsonate anions and a neutral Mo_6O_{18} ring of distorted MoO_4 tetrahedra sharing corners. Analogous dissection of (3) or (4) yields four arsenate anions and a cationic $Mo_{12}O_{34}{}^{4+}$ cage of distorted MoO_4 tetrahedra sharing corners. The cationic nature of this molybdate cage framework renders (3) and (4) easily reducible and acid stable relative to (1) and (2). Comparison of the bonding scheme in the Mo_6O_{18} and $Mo_{12}O_{34}{}^{4+}$ frameworks reveals the cause of the increased terminal oxygen bond order in (3) and (4) relative to (1) and (2) which is responsible for the ^{17}O chemical shift differences mentioned above. In the Mo_6O_{18} ring, hexavalency at Mo^{VI} is satisfied by two double bonds to the two terminal oxygens and two single bonds to the two bridging oxygens at each molybdenum. An analogous bonding scheme in the $[Mo_{12}O_{34}]^{4+}$ cage would lead to three single bonds to each O_C [see Figure (a)], *i.e.*, localization of the four units of net positive charge on the four triply bridging oxygens. This situation is clearly disfavoured owing to the high electronegativity of oxygen. Consequently, the $Mo-O_C$ bond order is < 1, and the $Mo-O_A$ bond order is > 2 in order to achieve hexavalency at molybdenum. Such a bonding scheme, even if carried to the extreme of placing the net positive charge solely on the 24 terminal oxygens, ensures that the formal charge on the terminal oxygens cannot exceed $+1/6$. The scheme is also consistent with the bond lengths observed in (3).[4]

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