^{17}O Nuclear Magnetic Resonance Structure Determinations of $As_2Mo_6O_{26}^{6-}$ and $(PhAs)_2Mo_6O_{24}^{4-}$

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Summary The solution structures of $As_2Mo_6O_{26}^{6-}$ and $(PhAs)_2Mo_6O_{24}^{4-}$ have been determined by ^{17}O n.m.r. spectroscopy, thus establishing a new structural class of heteropolyanions.

Although 1:3 arsenomolybdates were first synthesized many years ago, no structural studies have been reported.[1] Using ^{17}O n.m.r. spectroscopy,[2,3] we have determined the solution structures of $As_2Mo_6O_{26}^{6-}$ (**1**) and $(PhAs)_2Mo_6O_{24}^{4-}$ (**2**). Both species were synthesized from aqueous solutions of sodium molybdate and the appropriate arsenic oxoacid in stoicheiometric proportions by stoicheiometric addition of HCl. Anion (**1**) was isolated as a hydrated sodium salt, while anion (**2**) was isolated as an anhydrous tetrabutylammonium salt.†

When $Na_6As_2Mo_6O_{26}\cdot 8H_2O$ is dissolved in 2 atom % ^{17}O-enriched water and heated to 70 °C, its ^{17}O n.m.r. spectrum exhibits resonances at −819, −386, and −102 p.p.m. (Figure 1a). This spectrum is most easily interpreted by comparison with the spectrum of $TeMo_6O_{24}^{6-}$, which has resonances at −807, −383, and −180 p.p.m.[3] Using the previously established chemical shift scale[3] and knowledge of the $TeMo_6O_{24}^{6-}$ structure[4] (Figure 2a), the resonance at −819 p.p.m. is assigned to dioxo terminal oxygens and the resonance at −386 is assigned to oxygens bonded to two molybdenums, each of which has two terminal

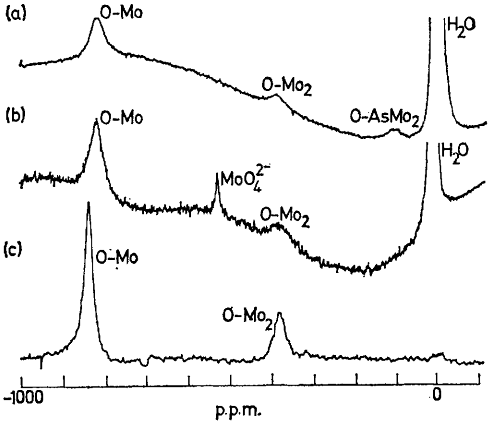

Figure 1. 13·5 MHz ^{17}O n.m.r. spectra of (a) $Na_6As_2Mo_6O_{26}\cdot 8H_2O$ in H_2O at 70 °C; (b) $Na_4(PhAs)_2Mo_6O_{24}$ + Na_2MoO_4 in H_2O at 25 °C; (c) $(Bu^n{}_4N)_4(PhAs)_2Mo_6O_{24}$ in MeCN at 80 °C.

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† Satisfactory elemental analyses were obtained for both compounds.

oxygens. To be consistent with the structure shown in Figure 2b, two further types of oxygens must be accounted for: the six O–AsMo$_2$ triply bridging oxygens, and the two O–As terminal oxygens. The resonances for these oxygens are unresolved and appear at -102 p.p.m. The failure to resolve these resonances is hardly surprising since the terminal and bridging oxygen resonances in AsO(OEt)$_3$ are observed at -110 and -73 p.p.m., respectively. We note further that the resonance at -102 p.p.m. is observed only at high temperatures. At 25 °C, it is not observed, owing to quadrupole broadening.

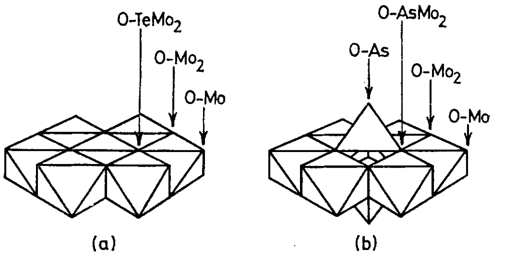

FIGURE 2. Structures of (a) $TeMo_6O_{24}^{6-}$ and (b) $As_2Mo_6O_{26}^{6-}$. For each anion, the linking of the co-ordination polyhedra are shown. In addition, nonequivalent types of oxygens are identified by the atoms which they are bonded to.

Partial acidification of ^{17}O-enriched phenylarsonic acid and sodium molybdate (1:3 mol ratio) in ^{17}O-enriched water at 25 °C yields a solution, the ^{17}O n.m.r. spectrum of which (Figure 1b) has resonances at -820, -532, and -385 p.p.m. The resonance at -532 p.p.m. is due to MoO_4^{2-}, and the remaining resonances are due to the heteropolymolybdate formed. Following complete (stoicheiometric) acidification, a tetrabutylammonium salt may be precipitated the ^{17}O n.m.r. spectrum of which in MeCN at 80 °C is shown in Figure 1c. The resonances observed at -850 and -398 p.p.m. are shifted slightly downfield from the resonances observed in aqueous solution. The close correspondence between these resonances and the resonances observed for (**1**) allows assignment of a structure to (**2**) which is isomorphic to that of (**1**). This is obtained by replacing the two O–As terminal oxygens in (**1**) (Figure 2b) by phenyl groups. In contrast to (**1**), the resonances for the O–AsMo$_2$ oxygens in (**2**) are not observed either at high or at low temperatures.

Owing to steric constraints, this new structural class of 2:6 heteropolymolybdates is not expected to have many members in addition to arsenomolybdates. Viewing the structure as a Mo_6O_{24} ring of edge sharing MoO_6 octahedra capped above and below by $RAsO_3$ tripods, the facial O–O distance between the centrally located oxygens must have a distance compatible with the tripod ligands. This facial O–O distance is known to be 2·8 Å in $TeMo_6O_{24}^{6-}$ and 2·9 Å in $H_6CrMo_6O_{24}^{3-}$.[4,5] Comparison with the O–O distances in H_3AsO_4[6] (2·7 Å) and $PhAsO_3H_2$[7] (2·8 Å) shows the steric compatibility of $RAsO_3$ tripod capping ligands and the Mo_6O_{24} ring. When smaller tripod ligands such as RPO_3^{2-} or SO_3^{2-} are incorporated into heteropolymolybdates, 2:5 complexes are formed[8] which involve capping of a smaller ring of five MoO_6 octahedra which share edges and corners.[9] If large tetrahedra such as IO_4^- are condensed with MoO_4^{2-}, octahedral co-ordination of the heteroatom is preferred, resulting in a 1:6 complex, *i.e.*, $IMo_6O_{24}^{5-}$.

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[1] The compound $Na_6As_2Mo_6O_{26}\cdot xH_2O$ was first prepared by Pufahl (O. Pufahl, Doctoral Dissertation, Berlin, 1888). The ionic formula $As_2Mo_6O_{26}^{6-}$ was determined by Contant (R. Contant, *Bull. Soc. chim. France*, 1973, 3277). Pettersohn very recently confirmed Contant's formula, and proposed the correct structure on the basis of stoicheiometry alone (L. Pettersohn, *Acta Chem. Scand.*, 1975, **A29**, 677). The isolation of 1:3 arsenomolybdates containing arylarsonates was first reported by A. Rosenheim and R. Bilecki (*Ber.*, 1913, **46**, 539).

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