

Structure of the Tetrahydrogentetramolybdotetraarsenate(V)(4–) Poly-anion

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Abstract. $\text{Na}_4[\text{H}_4\text{As}_4\text{Mo}_4\text{O}_{26}] \cdot 6\text{H}_2\text{O}$, triclinic, $P\bar{1}$, $a = 10.136$ (6), $b = 10.697$ (8), $c = 7.744$ (5) Å, $\alpha = 111.68$ (6), $\beta = 85.06$ (6), $\gamma = 118.77$ (5)°, $U = 679.6$ (6) Å³, FW 1303.5, $Z = 1$, $D_m = 3.18$, $D_x = 3.19$ Mg m⁻³, $\mu = 7.065$ mm⁻¹ (for Mo K α); $R = 0.051$, $R_w = 0.062$ for 3402 reflections. The structure contains the discrete heteropolyanion $[\text{H}_4\text{As}_4\text{Mo}_4\text{O}_{26}]^{4-}$ which consists of four MoO_6 octahedra forming a pair of Mo_2O_{10} groups and four AsO_4 tetrahedra bridging the groups with corner sharing. Protonation at the four terminal O atoms of AsO_4 is observed.

Introduction. A preparative description of heteropoly complexes with the ratio As:Mo = 1:1 was reported as early as 1892 (Friedheim & Mach, 1892). Later, Contant (1973) proposed the existence of the 1:1 heteropolyanion only in a strongly acidified solution containing a large excess of HAsO_4^{2-} , but its structure has been entirely unknown.

The sodium salt, $\text{Na}_4[\text{H}_4\text{As}_4\text{Mo}_4\text{O}_{26}] \cdot 6\text{H}_2\text{O}$, crystallized as colourless triclinic parallelepipeds from an aqueous solution (pH = 2) of the stoichiometric quantities of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ on the addition of NaCl.

All the X-ray diffraction intensities were measured on a Philips automatic four-circle diffractometer in the ω - 2θ scan mode using graphite-monochromated Mo K α radiation. The intensities were corrected for the absorption effect and 3402 independent reflections [$6^\circ < 2\theta < 60^\circ$, $|F_o| > 3\sigma(|F_o|)$] were used. The dimensions of the crystal were $0.28 \times 0.20 \times 0.10$ mm. The structure was solved by the usual heavy-atom method. Atomic scattering factors and corrections for anomalous scattering were taken from *International Tables for X-ray Crystallography* (1974). Anisotropic temperature factors were applied to all the non-hydrogen atoms. Refinements were made by the block-diagonal least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 0.2$ for $|F_o| < 15$ and $w = 1/[\sigma(|F_o|)^2 + c|F_o|^2]$ otherwise. The parameter c was estimated to be 0.02 from the

fluctuation of the intensities of the standard reflections during the data collection and $\sigma(|F_o|)$ was from counting statistics. The final R and R_w values were 0.051 and 0.062, respectively, where $R_w = \sum w|F_o| - |F_c| / \sum w|F_o|$. All the calculations were performed on

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å² $\times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mo(1)	1496 (1)	3111 (1)	3942 (1)	17 (1)
Mo(2)	3476 (1)	6818 (1)	4627 (1)	19 (1)
As(1)	2705 (1)	694 (1)	3899 (1)	22 (1)
As(2)	5076 (1)	4500 (1)	2582 (1)	14 (1)
Na(1)	1499 (4)	4636 (4)	51 (5)	36 (2)
Na(2)	2167 (4)	638 (4)	-575 (5)	36 (1)
O(1)	182 (5)	1597 (6)	2156 (7)	26 (2)
O(2)	514 (6)	3469 (7)	5776 (8)	34 (3)
O(3)	2459 (6)	7252 (6)	6381 (8)	30 (2)
O(4)	3408 (7)	7690 (6)	3227 (8)	33 (3)
O(5)	1967 (5)	4761 (5)	3172 (7)	21 (2)
O(6)	2042 (5)	1941 (5)	5004 (7)	22 (2)
O(7)	5408 (6)	8475 (6)	6232 (8)	30 (2)
O(8)	3369 (5)	2971 (5)	2301 (7)	20 (2)
O(9)	5011 (6)	6099 (6)	2859 (8)	28 (2)
O(10)	3692 (5)	5213 (5)	5802 (7)	21 (2)
O(11)	5879 (6)	4082 (6)	555 (7)	29 (2)
O(12)	1818 (6)	-508 (6)	1810 (7)	28 (2)
O(13)	2377 (7)	-156 (7)	5505 (9)	36 (3)
Aq(1)	1127 (6)	6506 (6)	-421 (8)	29 (2)
Aq(2)	1338 (6)	2151 (6)	-1405 (7)	28 (2)
Aq(3)	4582 (8)	742 (8)	-870 (9)	46 (3)

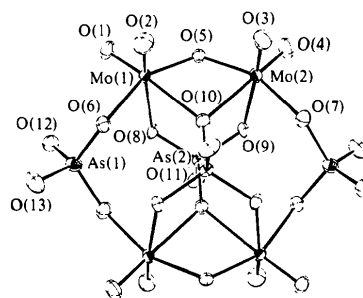


Fig. 1. The structure of the $[\text{H}_4\text{As}_4\text{Mo}_4\text{O}_{26}]^{4-}$ anion. The thermal ellipsoids are scaled to enclose 50% probability.

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Table 2. *Interatomic distances (Å) and angles (°) in the [H₄As₄Mo₄O₂₆]⁴⁻ anion*

	O(1)	O(2)	O(5)	O(6)	O(8)	O(10)
Mo(1)—	1.702 (4)	1.696 (6)	1.902 (6)	2.014 (7)	2.227 (5)	2.330 (5)
O(1)—		2.711 (8)	2.780 (7)	2.829 (9)	2.825 (7)	
O(10)—		2.838 (7)	2.552 (9)	2.894 (7)	2.793 (7)	
O(2)—			2.781 (9)	2.643 (10)		
O(8)—			2.764 (9)	2.683 (8)		
O(1)—Mo(1)—		105.9 (3)	100.9 (2)	98.8 (2)	90.9 (2)	165.7 (2)
O(2)—Mo(1)—			101.1 (3)	90.4 (3)	161.2 (3)	88.2 (2)
O(5)—Mo(1)—				153.4 (3)	83.7 (2)	73.4 (2)
O(6)—Mo(1)—					78.3 (2)	83.2 (2)
O(8)—Mo(1)—						75.6 (2)

	O(4)	O(3)	O(5)	O(7)	O(9)	O(10)
Mo(2)—	1.695 (8)	1.696 (6)	1.917 (4)	1.993 (5)	2.212 (7)	2.318 (7)
O(4)—		2.668 (9)	2.731 (8)	2.821 (10)	2.800 (11)	
O(10)—		2.885 (10)	2.552 (9)	2.951 (8)	2.781 (9)	
O(3)—			2.751 (7)	2.636 (8)		
O(9)—			2.739 (7)	2.781 (8)		
O(4)—Mo(2)—		103.8 (3)	98.1 (3)	99.5 (3)	90.6 (3)	164.5 (3)
O(3)—Mo(2)—			99.0 (2)	90.8 (2)	165.1 (3)	90.5 (3)
O(5)—Mo(2)—				157.2 (2)	82.8 (2)	73.4 (2)
O(7)—Mo(2)—					82.6 (2)	86.1 (2)
O(9)—Mo(2)—						75.7 (2)

Table 2 (cont.)

	O(6)	O(7)'	O(12)	O(13)
As(1)—	1.698 (6)	1.690 (6)	1.637 (5)	1.720 (8)
O(6)—		2.857 (8)	2.787 (7)	2.588 (11)
O(7)'—			2.710 (7)	2.732 (9)
O(12)—				2.816 (10)
O(6)—As(1)—		114.9 (3)	113.4 (3)	98.4 (3)
O(7)'—As(1)—			109.1 (2)	106.5 (3)
O(12)—As(1)—				114.0 (3)

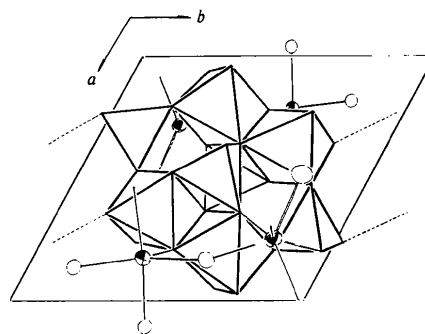
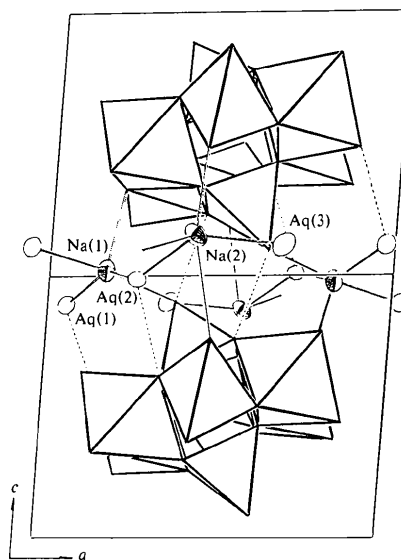
	O(8)	O(9)	O(10)'	O(11)
As(2)—	1.672 (4)	1.677 (7)	1.684 (6)	1.714 (6)
O(8)—		2.801 (8)	2.807 (6)	2.720 (7)
O(9)—			2.803 (11)	2.707 (9)
O(10)'—				2.653 (9)
O(8)—As(2)—		113.6 (3)	113.6 (3)	106.9 (2)
O(9)—As(2)—			113.1 (3)	105.9 (3)
O(10)'—As(2)—				102.7 (3)

	Mo(1)	Mo(2)	As(1)	As(2)
Mo(1)—		3.317 (3)	3.342 (3)	3.434 (3)
Mo(2)—			6.022 (5)	3.437 (3)
As(1)—				4.077 (4)
Mo(1)'—	6.241 (1)	5.267 (1)	6.105 (1)	3.719 (1)
Mo(2)'—		6.208 (3)	3.460 (1)	3.688 (1)
As(1)'—			7.612 (1)	4.300 (1)
As(2)'—				3.506 (1)

The prime refers to the symmetry operation $1 - x, 1 - y, 1 - z$.

HITAC 8800/8700 and M200H computers at the Computer Centre of the University of Tokyo with a local version of *UNICS* (Sakurai, 1967). The final atomic coordinates are given in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36290 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 2. A view of the crystal structure projected along the c^* axis.Fig. 3. A view of the crystal structure projected along the b^* axis.

Discussion. The structure determination revealed a new type of heteropolymolybdate anion $[\text{H}_4\text{As}_4\text{Mo}_4\text{O}_{26}]^{4-}$ which consists of four MoO_6 octahedra forming a pair of edge-shared dimers and four AsO_4 tetrahedra bridging the Mo_2O_{10} groups with corner sharing (Fig. 1). Two $\text{As}(1)\text{O}_4$ tetrahedra have two terminal O atoms but the other two $\text{As}(2)\text{O}_4$ tetrahedra have only one terminal O. Interatomic distances and angles in the $[\text{H}_4\text{As}_4\text{Mo}_4\text{O}_{26}]^{4-}$ anion are listed in Table 2. The anion represents a partial structure of $[\text{H}_6\text{As}_6\text{V}_4\text{O}_{30}]^{4-}$ consisting of VO_6 octahedra and AsO_4 which contains two more tetrahedra (Durif & Averbuch-Pouchot, 1979). The MoO_6 octahedra are highly distorted; Mo—O distances fall into five groups according to the type of O. The average Mo—O bond distances for these five groups are given in Table 3. Views of the crystal structure are shown in Figs. 2 and 3.

Table 4 shows O—O distances which are shorter than 3 Å and suggests hydrogen bonding through protons between two O atoms. The terminal oxygen O(11) bound to As(2) seems to be protonated and a hydrogen bond is directed to bridging oxygen O(9) of the neighbouring polyanion. The protonation at O(13), one of two terminal O atoms attached to As(1), is deduced from the As—O(13) bond length (1.720 Å) which is longer than As—O(12) (1.637 Å). These data accord with the observation in the crystal structure study of $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ by Worzala (1968). Another hydrogen bond is suggested between O(13) and O(4), a Mo-bound terminal O, of a neighbouring polyanion. The coordination spheres around the Na^+ cations are shown in Fig. 4 and bond lengths are given in Table 5. The Na^+ ions are bound to water molecules, O atoms bridging two Mo atoms, O atoms bridging the As and Mo atoms, terminal O atoms of $\text{Mo}(1)\text{O}_6$ octahedra, and to two terminal O atoms of $\text{As}(1)\text{O}_4$ tetrahedra. The protonated terminal O(13) is also coordinated to

Table 3. Comparison of the average Mo—O distances (Å)

$[\text{H}_2\text{As}_2\text{Mo}_6\text{O}_{26}]^{4-}$		$[\text{H}_4\text{As}_4\text{Mo}_4\text{O}_{26}]^{4-}$	
Mo— O_a	1.71	Mo=O	1.70
Mo— O_b	1.92	Mo—O...Mo	1.91
		Mo—O...As(1)*	2.00
		Mo—O...As(2)†	2.22
		Mo—O...As(2)	2.32
Mo— O_c	2.37		

* As(1) has two terminal O atoms.

† As(2) has one terminal O atom.

Table 4. Probable hydrogen-bond distances (Å)

Aq(1)—O(3) ⁱ	2.905 (9)	Aq(3)—O(4) ^{iv}	2.937 (10)
—O(12) ⁱⁱ	2.767 (8)	—O(7) ^v	3.038 (11)
Aq(2)—O(6) ⁱ	2.765 (8)	—O(11)	2.920 (10)
—O(12) ⁱⁱⁱ	2.788 (8)	—Aq(3) ^{vi}	2.851 (20)
O(11)—O(9) ^v	2.776 (10)	O(13)—O(4) ^{vii}	2.917 (11)

The superscripts refer to the following symmetry operations:

(i)	$x, y, z - 1$	(v)	$x, y - 1, z - 1$
(ii)	$x, 1 + y, z$	(vi)	$1 - x, -y, -z$
(iii)	$-x, -y, -z$	(vii)	$x, y - 1, z$
(iv)	$1 - x, 1 - y, -z$		

Table 5. Na—O distances (Å) less than 3.0 Å

Na(1)—O(5)	2.446 (7) Å	Na(2)—O(1) ⁱⁱⁱ	2.397 (5) Å
—O(11) ⁱ	2.432 (7)	—O(8)	2.471 (6)
—Aq(1)	2.359 (9)	—O(12)	2.486 (8)
—Aq(1) ⁱⁱ	2.378 (6)	—O(13) ^v	2.853 (8)
—Aq(2)	2.401 (8)	—Aq(2)	2.431 (10)
		—Aq(3)	2.391 (10)

The superscripts refer to the following symmetry operations:

(i)	$1 - x, 1 - y, -z$	(iii)	$-x, -y, -z$
(ii)	$-x, 1 - y, -z$	(iv)	$x, y, z - 1$

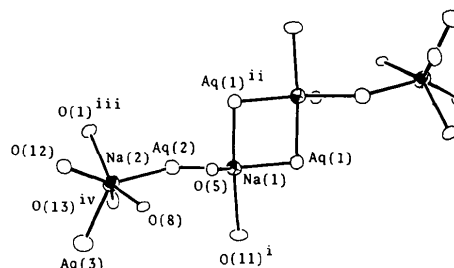


Fig. 4. Sodium—oxygen arrangement.

Na(2). Na(1) is pentacoordinated and Na(2) is hexacoordinated and four Na^+ ions form a unit to link polyanions and waters of crystallization.

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