

Multicomponent Polyanions. 29. The Structure of Trisodium Bis(tetramethylammonium) Monohydrogenhexamolybdodiarisenate Heptahydrate

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Abstract

$[\text{N}(\text{CH}_3)_4]_2\text{Na}_3\text{HMo}_6\text{As}_2\text{O}_{26} \cdot 7\text{H}_2\text{O}$ is triclinic, $P\bar{1}$, with $a = 8.200$ (1), $b = 22.779$ (3), $c = 12.002$ (2) Å, $\alpha = 118.82$ (1), $\beta = 91.58$ (1), $\gamma = 76.58$ (1)°, $Z = 2$. The final $R = 0.037$ for 4959 independent reflexions. The structure contains $\text{HMo}_6\text{As}_2\text{O}_{26}^{6-}$ anions consisting of six MoO_6 octahedra joined in a hexagonal ring by sharing edges, and with one AsO_4 tetrahedron attached on each side of the ring. The anion is protonated and the H atom is attached to one of the unshared arsenate O atoms. The mean Mo–Mo distances are 3.27, 5.65 and 6.52 Å. The Mo–O distances are distributed in three different groups, depending on coordination, with mean values of 1.71, 1.91 and 2.34 Å. The As–O distances vary between 1.649 and 1.725 Å. The anions are joined in a three-dimensional framework mainly by O–Na–O and O–Na–H₂O–Na–O links, with all Na^+ ions directly coordinated to the anions. The structure is a superstructure with an approximate repetition of the anions and $[\text{N}(\text{CH}_3)_4]^+$ cations after $b/2$. The repetition is broken by the Na^+ ions and water molecules, basically as a result of the anion protonation.

Introduction

Aqueous equilibria $p\text{H}^+ + q\text{MoO}_4^{2-} + r\text{HAsO}_4^{2-} \rightleftharpoons (\text{H}^+)_p(\text{MoO}_4^{2-})_q(\text{HAsO}_4^{2-})_r$ have been studied by potentiometric and spectrophotometric methods (298 K, 3.0 M NaClO_4 medium; Pettersson, 1975; Lyhamn & Pettersson, 1980). These investigations established the formation of two series of complexes which, in (p,q,r) notation, consist of (8,5,2) and $(p,6,2)$ with $p = 10, 11, 12$ (colourless complexes), and $(p,9,1)$ with $p = 14, 15, 16, 17$ (yellow complexes). From a large-angle X-ray scattering (LAXS) investigation (Johansson, Pettersson & Ingri, 1978) the $(p,9,1)$ complexes with $p = 14, 15$ and 16 were shown to have the same basic structure as the $\text{Mo}_9\text{AsO}_{31}(\text{OH}_2)_3^{3-}$ anion [corresponding to (17,9,1)] found in $\text{Na}_3\text{Mo}_9\text{AsO}_{31}(\text{OH}_2)_3 \cdot 12\text{--}13\text{H}_2\text{O}$ (Johansson, 1980). Raman data also showed these anions to be

present in solution and, furthermore, indicated the presence of a dimerized (17,9,1) complex, $\text{Mo}_{18}\text{As}_2\text{O}_{62}^{6-}$ (Lyhamn & Pettersson, 1979). The Na^+ salt of this dimer is isomorphous with the P analogue $\text{Na}_6\text{Mo}_{18}\text{P}_2\text{O}_{62} \cdot 24\text{H}_2\text{O}$ (Strandberg, 1975).

For the $(p,6,2)$ complexes, Pettersson (1975) suggested the anion structure found in the present work, *i.e.* a ring of six edge-sharing MoO_6 octahedra with one AsO_4 tetrahedron on each side [formula $\text{H}_n\text{Mo}_6\text{As}_2\text{O}_{26}^{(6-n)-}$, $n = 0\text{--}2$]. This structure was supported in an ^{17}O NMR investigation (Filowitz & Klemperer, 1976) and is isostructural with the anions $\text{Mo}_8\text{O}_{26}^{4-}$ (Fuchs & Hartl, 1976) and $\text{Mo}_6\text{V}_2\text{O}_{26}^{6-}$ (Björnberg, 1979). The same basic anion structure has also been found for the anion $(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}^{4-}$, in which the terminal O atom in each arsenate tetrahedron has been replaced by a CH_3 group (Kwak, Rajković, Stalick, Pope & Quicksall, 1976). However, the $\text{Mo}_6\text{As}_2\text{O}_{26}$ structure does not explain the LAXS data of a (12,6,2) solution (Johansson *et al.*, 1978). Among several models tested, the best fit seems to be obtained for a structure based on the $[(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{25}\text{H}_2]^{4-}$ anion, with C_6H_5 replaced by O atoms (Johansson, Pettersson & Ingri, 1980). This anion contains six MoO_6 octahedra, which form a ring with one face-, two corner- and three edge-sharings and with two $\text{C}_6\text{H}_5\text{AsO}_3$ tetrahedra capping, sharing the O atoms with Mo (Matsumoto, 1978). In the molybdoarsenate system the $\text{H}_4\text{Mo}_{12}\text{As}_4\text{O}_{50}^{4-}$ anion has also been found (Nishikawa & Sasaki, 1975). In the present work the structure for the (11,6,2) complex is reported.

Experimental

Crystal preparation and data

An aqueous solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and HClO_4 in molar ratios $\text{H}^+:\text{MoO}_4^{2-}:\text{HAsO}_4^{2-} = 11:6:2$ and with $[\text{Mo}]_{\text{tot}} = 0.5$ M was prepared for the crystallization. To this solution was added $[\text{N}(\text{CH}_3)_4]\text{I}$ in amounts equivalent to a molar compensation by tetramethylammonium ions of half the negative charge of the (11,6,2) complex.

Table 1. *Crystal data for* $[\text{N}(\text{CH}_3)_4]_2\text{Na}_3\text{HMo}_6\text{As}_2\text{O}_{26} \cdot 7\text{H}_2\text{O}$

Triclinic, space group $P\bar{1}$		
$a = 8.200$ (1) Å*	$V = 1901.2$ (5) Å ³	
$b = 22.779$ (3)	$Z = 2$	
$c = 12.002$ (2)	$M_r = 1485.85$	
$\alpha = 118.82$ (1)°	$D_x = 2.60$ Mg m ⁻³	
$\beta = 91.58$ (1)	$D_m = 2.59$	
$\gamma = 76.58$ (1)	$\mu(\text{Mo } K\alpha) = 3.85$ mm ⁻¹	

* Throughout this paper, numbers in parentheses represent the e.s.d.'s and refer to the last decimal place.

Colourless acicular crystals were formed within a week by evaporation at room temperature. The crystals slowly decompose in air, and were sealed in a glass capillary during the X-ray investigation. The density was determined by flotation in bromoform/carbon tetrachloride. Weissenberg photographs indicated triclinic symmetry, and the space group $P\bar{1}$ was established in the structure determination. Cell parameters were obtained by least-squares refinement from 25 reflexions ($20^\circ < 2\theta < 48^\circ$) automatically centred on a Syntex R3 four-circle diffractometer. Crystal data are listed in Table 1.

Data collection and reduction

Intensities were collected at 298 K on the diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite crystal ($\lambda = 0.71069$ Å). They were collected by the θ - 2θ scan method (2θ scan rate between 3 and 8° min⁻¹, 2θ scan width 2.6° plus the α_1 - α_2 dispersion, background measured on each side of the reflexion for a total time equal to the scan time). Three standard reflexions were measured at an interval of 50 reflexions. 8684 unique reflexions with $2\theta \lesssim 57^\circ$ were measured; of these, 4959 with $I > 3\sigma(I)$ were considered observed, where $\sigma(I) = (\text{TI} + \text{BI}/\text{TR}^2)^{1/2} \times \text{scan rate}$ (TI = total scan intensity, BI = total background intensity, TR = time ratio scan/background). The size of the crystal was approximately 0.13 × 0.15 × 0.20 mm. An empirical absorption correction was applied, based on the measurement of 11 reflexions evenly distributed in $(\sin \theta)/\lambda$, each reflexion being rotated around its diffraction vector in steps of 10°. The relative transmission factor varied from 1.0 to 0.669 [$\mu(\text{Mo } K\alpha) = 3.85$ mm⁻¹]. The intensities and the $\sigma(I)$ were also corrected for Lorentz and polarization effects.

Structure determination and refinement

From a Patterson synthesis based on subcell data ($b = 11.389$ Å, odd k removed and even halved) the Mo and As atoms were located, and routine heavy-

Table 2. *Fractional atomic coordinates* ($\times 10^4$; for Mo and As $\times 10^5$)

For the O atoms O(*i*), O(*ij*) and OAs(*ij*) the index indicates that the atom is bonded to Mo atoms *i* or *j*, and As indicates that it is also bonded to an As atom.

	<i>x</i>	<i>y</i>	<i>z</i>
Mo(1)	44635 (11)	25875 (4)	23889 (9)
Mo(2)	65050 (11)	11491 (4)	23013 (9)
Mo(3)	69464 (11)	11046 (4)	49704 (9)
Mo(4)	54077 (12)	24770 (4)	77169 (9)
Mo(5)	34401 (11)	39070 (4)	77744 (9)
Mo(6)	30102 (11)	39799 (4)	51492 (9)
As(1)	68109 (12)	27622 (4)	51330 (9)
As(2)	31248 (12)	22765 (4)	49197 (10)
O(1)	5915 (10)	2474 (4)	1266 (7)
O'(1)	2559 (9)	2790 (4)	1892 (8)
O(12)	4573 (9)	1645 (3)	1892 (7)
O(16)	4601 (8)	3495 (3)	3674 (7)
OAs(12)	6419 (8)	2309 (3)	3574 (6)
OAs(16)	2877 (8)	2781 (3)	4212 (7)
O(2)	8001 (9)	1078 (3)	1242 (6)
O'(2)	6097 (10)	346 (3)	1580 (7)
O(23)	7945 (8)	1081 (3)	3521 (7)
OAs(23)	4691 (8)	1541 (3)	4131 (7)
O(3)	8726 (9)	992 (3)	5694 (7)
O'(3)	6472 (10)	322 (4)	4260 (8)
O(34)	5338 (9)	1559 (3)	6454 (7)
OAs(34)	6913 (8)	2269 (3)	5857 (6)
O(4)	7262 (10)	2278 (4)	8311 (8)
O'(4)	3851 (10)	2614 (4)	8787 (7)
O(45)	5372 (8)	3402 (3)	8134 (7)
OAs(45)	3391 (9)	2737 (3)	6504 (7)
O(5)	3849 (9)	4703 (3)	8503 (7)
O'(5)	1909 (9)	3966 (4)	8797 (7)
O(56)	1989 (8)	3989 (3)	6561 (7)
OAs(56)	5191 (8)	3494 (3)	5917 (6)
O(6)	3483 (9)	4766 (3)	5844 (7)
O'(6)	1203 (9)	4081 (4)	4432 (8)
OAs1	8625 (8)	2968 (3)	5201 (7)
OAs2	1306 (9)	2003 (3)	4814 (7)
Na(1)	9996 (5)	3090 (2)	3526 (4)
Na(2)	8211 (6)	2834 (2)	641 (4)
Na(3)	40 (6)	1918 (2)	7083 (5)
Aq(1)	7582 (9)	3738 (3)	3062 (8)
Aq(2)	9600 (8)	2139 (4)	1666 (8)
Aq(3)	7870 (11)	3767 (4)	205 (8)
Aq(4)	913 (10)	2261 (4)	9324 (8)
Aq(5)	9647 (9)	3079 (4)	7692 (8)
Aq(6)	2509 (10)	1124 (4)	6661 (9)
Aq(7)	2448 (10)	1143 (4)	-10 (8)
N(1)	2254 (11)	4803 (4)	2188 (9)
C(1)	3912 (16)	4270 (6)	1629 (14)
C(2)	863 (15)	4440 (6)	1905 (13)
C(3)	1995 (15)	5278 (6)	1621 (12)
C(4)	2285 (19)	5254 (7)	3595 (13)
N(2)	7866 (11)	176 (4)	7809 (8)
C(5)	6264 (16)	724 (6)	8354 (13)
C(6)	9344 (16)	501 (6)	8088 (12)
C(7)	8088 (18)	-293 (6)	8400 (14)
C(8)	7845 (16)	-262 (6)	6382 (11)

atom methods yielded the positions of the anion O and non-hydrogen atoms of the $[\text{N}(\text{CH}_3)_4]^+$ cation. After expanding to the full structure ($b = 22.779$ Å, all atoms repeated at $y + \frac{1}{2}$, all data) the remaining non-hydrogen

atoms were located. Full-matrix least-squares refinement with isotropic temperature factors gave $R = 0.08$. With anisotropic thermal parameters the refinement converged at $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.037$ and $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2} = 0.041$. A weighting scheme, $w = 1/\sigma^2(F_o)$, was applied in which $\sigma^2(F_o)$ was modified to $\sigma^2(F_o) = \sigma^2(F_o) + (0.012F_o)^2$. In the final cycle the parameter shifts were $< 0.1\sigma$. A final difference synthesis showed no anomalies. Mo^{3+} , As, O^- (anion atoms), Na^+ , O, N and C scattering factors were used and account was taken of the real and imaginary parts of anomalous dispersion (*International Tables for X-ray Crystallography*, 1974).

The computer programs were those supplied with the Syntex R3 crystallographic system, and the computations were made on a Data General Nova 3 computer. Final atomic positional and thermal parameters are given in Table 2.*

Description and discussion of the structure

The structure consists of $\text{HMo}_6\text{As}_2\text{O}_{26}^{5-}$ anions joined in a three-dimensional framework. In the [100] and [001] directions they are connected by O—Na—O and O—Na—H₂O—Na—O links as well as by hydrogen bonds, while $[\text{N}(\text{CH}_3)_4]^+$ cations link in the [010] direction (Fig. 1).

The $\text{HMo}_6\text{As}_2\text{O}_{26}^{5-}$ anion

The anion consists of six MoO_6 octahedra joined in a flat hexagonal ring by sharing edges. On each side the ring is capped by one AsO_4 tetrahedron, which has three O atoms in common with the Mo atoms (Fig. 2). An H atom is attached to one of the unshared arsenate atoms OAs2. As can be seen in Table 3, the anion is regular [approximate $\bar{3}m$ (D_{3d}) symmetry, disregarding the H atom] with mean Mo—Mo distances of 3.27, 5.65 and 6.52 Å. The MoO_6 octahedra are distorted with the characteristic 2 + 2 + 2 distribution of Mo—O distances, with mean values of 1.71 (terminal), 1.91 (shared by two Mo atoms) and 2.34 Å (shared by two Mo and one As atom). The distances compare well with those found in similar heteropolyanions, e.g. $\text{HMo}_3\text{P}_2\text{O}_{23}^{5-}$ (Hedman & Strandberg, 1979) or $(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}^{4-}$ (Kwak *et al.*, 1976). The AsO_4 tetrahedra are slightly distorted (Table 3) as a joint result of protonation and of having two Mo atoms coordinated to three of the O atoms. For the latter the

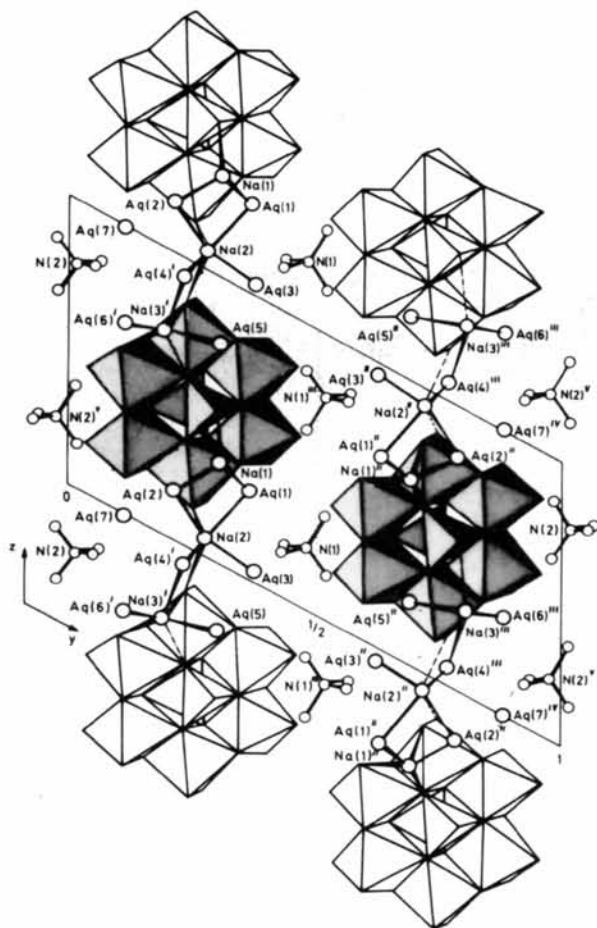


Fig. 1. The structure projected on the yz plane. The subcell is indicated by a dotted line. Dashed lines indicate bonds to anions on $x + 1$ compared with those drawn, and dashed-dotted lines indicate long Na—O distances. The superscripts indicate the symmetry operations: (') $x + 1, y, z$; (") $2 - x, 1 - y, 1 - z$; (""') $1 - x, 1 - y, 1 - z$; (iv) $1 - x, 1 - y, -z$; (v) $1 - x, -y, 1 - z$.

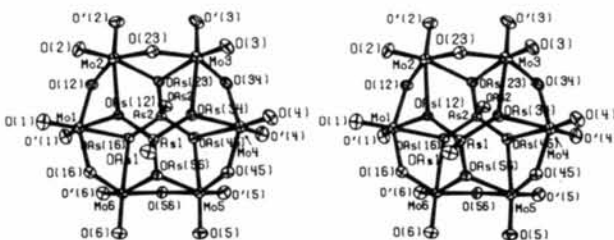


Fig. 2. A stereoscopic view of the $\text{HMo}_6\text{As}_2\text{O}_{26}^{5-}$ anion. The thermal ellipsoids are scaled to include 50% probability (ORTEP II; Johnson, 1976).

mean As—O distance is 1.71 Å, which is longer than in most orthoarsenates, e.g. 1.669–1.670 Å in $\text{Na}_3\text{AsO}_4 \cdot (\text{NaOH})_{0.25} \cdot 12\text{H}_2\text{O}$ (Tillmanns & Baur, 1971). For the unshared O atoms the difference in distances [As(1)—OAs1 1.649 (7), As(2)—OAs2 1.725 (7) Å] clearly indicates the protonation of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35316 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

OAs2. This is comparable to the differences found in, for example, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 1.662 to 1.728 Å (Baur & Khan, 1970) or $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$, 1.672 to 1.729 Å (Ferraris, 1969). Furthermore, As(2) seems to

be displaced nearer to the Mo_6O_{24} ring than is As(1), as indicated by the increased $\text{OAs}(ij)\text{—As}(2)\text{—OAs}(ij)$ and decreased $\text{OAs2—As}(2)\text{—OAs}(ij)$ angles as compared with the As(1) values. The mean As(2)—Mo

Table 3. Distances (Å) and angles (°) within the $\text{HMo}_6\text{As}_2\text{O}_{26}^{4-}$ anion

Mo(1)—Mo(2)	3.268 (1)	Mo(2)—Mo(4)	5.684 (1)	As(1)—Mo(1)	3.668 (1)	As(2)—Mo(1)	3.681 (1)
Mo(2)—Mo(3)	3.261 (1)	Mo(2)—Mo(6)	5.674 (1)	Mo(2)	3.668 (1)	Mo(2)	3.681 (1)
Mo(3)—Mo(4)	3.270 (1)	Mo(3)—Mo(5)	5.625 (1)	Mo(3)	3.661 (2)	Mo(3)	3.635 (2)
Mo(4)—Mo(5)	3.251 (2)	Mo(4)—Mo(6)	5.639 (2)	Mo(4)	3.722 (1)	Mo(4)	3.682 (1)
Mo(5)—Mo(6)	3.240 (1)	Mo(1)—Mo(4)	6.538 (1)	Mo(5)	3.696 (1)	Mo(5)	3.705 (1)
Mo(6)—Mo(1)	3.285 (1)	Mo(2)—Mo(5)	6.537 (1)	Mo(6)	3.653 (1)	Mo(6)	3.734 (2)
Mo(1)—Mo(3)	5.631 (2)	Mo(3)—Mo(6)	6.499 (2)			As(1)—As(2)	3.415 (1)
Mo(1)—Mo(5)	5.649 (1)						
Mo(6)—Mo(1)—Mo(2)	119.96 (4)	Mo(2)—Mo(3)—Mo(4)	120.99 (4)	Mo(4)—Mo(5)—Mo(6)	120.63 (4)		
Mo(1)—Mo(2)—Mo(3)	119.17 (4)	Mo(3)—Mo(4)—Mo(5)	119.23 (4)	Mo(5)—Mo(6)—Mo(1)	119.97 (4)		
	O(1)	O'(1)	O(12)	O(16)	OAs(12)	OAs(16)	
Mo(1)	1.706 (8)	1.699 (8)	1.910 (8)	1.921 (7)	2.296 (7)	2.373 (7)	
O(1)		2.707 (11)	2.778 (12)	2.730 (10)	2.976 (11)		
OAs(16)		2.799 (11)	2.825 (10)	2.681 (10)	2.839 (10)		
O(12)		2.744 (12)			2.570 (10)		
O(16)		2.774 (10)			2.714 (11)		
O(1)—Mo(1)—		105.3 (4)	100.2 (4)	97.5 (4)	95.0 (3)		
OAs(16)—Mo(1)—		85.1 (3)	81.8 (3)	76.5 (3)	74.9 (3)		
O(12)—Mo(1)—		98.8 (4)			74.7 (3)		
O(16)—Mo(1)—		99.9 (4)			79.6 (3)		
	O(2)	O'(2)	O(12)	O(23)	OAs(12)	OAs(23)	
Mo(2)	1.715 (7)	1.717 (8)	1.921 (8)	1.897 (7)	2.312 (7)	2.346 (7)	
O(2)		2.697 (11)	2.765 (11)	2.733 (10)	2.885 (10)		
OAs(23)		2.969 (10)	2.806 (10)	2.612 (10)	2.800 (10)		
O(12)		2.776 (11)			2.570 (10)		
O(23)		2.783 (10)			2.757 (11)		
O(2)—Mo(2)—		103.6 (4)	98.8 (3)	98.2 (3)	90.3 (3)		
OAs(23)—Mo(2)—		92.6 (3)	81.6 (3)	75.2 (3)	73.9 (3)		
O(12)—Mo(2)—		99.3 (4)			74.1 (3)		
O(23)—Mo(2)—		100.6 (4)			81.2 (3)		
	O(3)	O'(3)	O(23)	O(34)	OAs(23)	OAs(34)	
Mo(3)	1.709 (8)	1.702 (9)	1.915 (7)	1.923 (7)	2.332 (7)	2.326 (8)	
O(3)		2.704 (11)	2.759 (11)	2.749 (11)		2.858 (12)	
OAs(23)		2.898 (12)	2.612 (10)	2.807 (10)		2.871 (10)	
O(23)		2.783 (12)				2.766 (10)	
O(34)		2.740 (11)				2.632 (11)	
O(3)—Mo(3)—		104.9 (4)	99.0 (4)	98.2 (4)		88.8 (3)	
OAs(23)—Mo(3)—		90.5 (3)	75.2 (3)	81.9 (3)		76.1 (3)	
O(23)—Mo(3)—		100.4 (4)				80.8 (3)	
O(34)—Mo(3)—		98.0 (4)				75.9 (3)	
	O(4)	O'(4)	O(34)	O(45)	OAs(34)	OAs(45)	
Mo(4)	1.720 (9)	1.702 (8)	1.915 (8)	1.909 (8)	2.365 (7)	2.334 (7)	
O(4)		2.722 (12)	2.761 (11)	2.769 (12)	2.943 (11)		
OAs(45)		2.892 (11)	2.758 (12)	2.621 (10)	2.824 (10)		
O(34)		2.729 (11)			2.632 (11)		
O(45)		2.800 (12)			2.758 (10)		
O(4)—Mo(4)—		105.4 (4)	98.7 (4)	99.3 (4)	90.8 (3)		
OAs(45)—Mo(4)—		90.1 (4)	80.3 (3)	75.6 (3)	73.9 (3)		
O(34)—Mo(4)—		97.8 (4)			75.1 (3)		
O(45)—Mo(4)—		101.5 (4)			79.6 (3)		
	O(5)	O'(5)	O(45)	O(56)	OAs(45)	OAs(56)	
Mo(5)	1.704 (8)	1.718 (8)	1.901 (7)	1.907 (7)	2.358 (8)	2.333 (7)	
O(5)		2.705 (12)	2.755 (11)	2.775 (10)		2.995 (10)	
OAs(45)		2.841 (11)	2.621 (10)	2.786 (11)		2.839 (10)	
O(45)		2.792 (11)				2.765 (10)	
O(56)		2.713 (11)				2.581 (10)	
O(5)—Mo(5)—		104.5 (4)	99.5 (4)	100.3 (4)		94.5 (3)	
OAs(45)—Mo(5)—		86.9 (3)	75.1 (3)	80.8 (3)		74.5 (3)	
O(45)—Mo(5)—		100.9 (4)				80.9 (3)	
O(56)—Mo(5)—		96.8 (4)				74.2 (3)	

Table 3 (cont.)

	O(6)	O'(6)	O(16)	O(56)	OAs(16)	OAs(56)		
Mo(6)	1.708 (8)	1.718 (8)	1.905 (7)	1.899 (7)	2.429 (8)	2.291 (7)		
O(6)		2.726 (11)	2.763 (11)	2.811 (11)		2.953 (11)		
OAs(16)		2.845 (12)	2.681 (10)	2.785 (10)		2.904 (10)		
O(16)		2.759 (10)				2.723 (10)		
O(56)		2.710 (11)				2.581 (10)		
O(6)—Mo(6)—		105.5 (4)	99.6 (4)	102.3 (4)		94.1 (3)		
OAs(16)—Mo(6)—		84.8 (3)	75.3 (3)	79.0 (3)		75.9 (3)		
O(16)—Mo(6)—		99.1 (4)				80.4 (3)		
O(56)—Mo(6)—		96.9 (4)				75.4 (3)		
	OAs1	OAs(12)	OAs(34)	OAs(56)	OAs2	OAs(16)	OAs(23)	OAs(45)
As(1)	1.649 (7)	1.711 (7)	1.708 (8)	1.720 (7)	1.725 (7)	1.706 (8)	1.700 (7)	1.710 (7)
OAs1		2.753 (10)	2.728 (10)	2.771 (10)	OAs2	2.770 (11)	2.724 (10)	2.775 (10)
OAs(12)			2.799 (10)	2.790 (10)	OAs(16)		2.827 (11)	2.818 (10)
OAs(34)				2.787 (11)	OAs(23)			2.830 (10)
OAs1—As(1)—		110.0 (4)	108.6 (4)	110.7 (4)	OAs2—As(2)—	107.7 (4)	105.4 (4)	107.8 (4)
OAs(12)—As(1)—			109.9 (3)	108.9 (3)	OAs(16)—As(2)—		112.2 (4)	111.2 (4)
OAs(34)—As(1)—				108.8 (3)	OAs(23)—As(2)—			112.2 (4)

and As(1)—Mo distances are 3.69 and 3.68 Å, respectively. Another indication of the protonation is the short OAs2—OAs1' hydrogen-bond distance of 2.591 (11) Å. This hydrogen bond links the anions into continuous chains extended in the [100] direction.

The sodium—oxygen arrangement, the water hydrogen bonds and tetramethylammonium cations

The three crystallographically different Na⁺ ions are all coordinated to anion O atoms (Fig. 1). Na(1) links two anions in the [100] direction by binding to O'(1), O'(6) and OAs(16) in one anion and OAs1 in the other. Two water O atoms complete a distorted octahedral arrangement around Na(1). A similar arrangement, but with four water and two anion O atoms {O(1) and O'(4), binding along [001]}, is found around Na(2), while for Na(3) three water and two anion O atoms [O(3) and O(4)] are found at a short distance with two additional O atoms, OAs(34) and OAs2', further away. The coordination is capped octahedral. The short Na—O distances vary between 2.259 and 2.645 Å, with the two long distances slightly above 3 Å (Table 4).

The Na—O polyhedra are internally joined by common edges to trimers (Fig. 1), with schematic composition Na₃O₉(H₂O)₆. Together with numerous hydrogen bonds (distances given in Table 4) they constitute the main binding forces in the [100] and [001] directions. With one exception, the H atoms all seem to be directed towards anion O atoms or to the only water molecule [Aq(7)] not coordinated to Na⁺. All unshared and seven shared anion O atoms are, in this way, parts of Na—O or hydrogen bonds.

The [N(CH₃)₄]⁺ cations have the usual tetrahedral geometry with C—N—C angles ranging from 106 to 112° and an average N—C distance of 1.51 Å (Table 5).

Table 4. Sodium—oxygen and hydrogen-bond distances (Å)

The superscripts refer to the following symmetry operations:

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

Na(1)—Aq(2)	2.325 (9)	OAs2—OAs1 ^{iv}	2.591 (11)
Aq(1)	2.404 (10)	O(16)	2.818 (11)
O'(6) ⁱ	2.421 (9)	Aq(1)	
OAs1	2.488 (8)	O(6) ^v	2.910 (12)
OAs(16) ^j	2.537 (8)	Aq(7) ^j	2.837 (12)
O'(1) ⁱ	2.645 (9)	Aq(2)	
		O(2)	2.841 (12)
Na(2)—Aq(3)	2.380 (11)	Aq(5) ⁱⁱⁱ	2.881 (12)
Aq(4) ⁱⁱ	2.444 (10)	Aq(3)	
O(1)	2.483 (10)	O(5) ^v	3.027 (13)
Aq(2)	2.506 (10)	O'(4)	2.889 (12)
Aq(1)	2.602 (9)	Aq(4)	
O(4) ⁱⁱⁱ	2.636 (9)	O(7) ^{vi}	3.023 (14)
		O'(1) ^{vi}	3.117 (11)
Na(3)—Aq(6)	2.259 (11)	O'(5) ⁱ	2.881 (11)
Aq(5) ^{iv}	2.321 (11)	Aq(5)	
O(3) ^{iv}	2.440 (9)	OAs1	2.990 (11)
O(4) ^{iv}	2.488 (10)	O(34)	2.787 (12)
Aq(4)	2.547 (10)	Aq(6)	
OAs2	3.047 (10)	O'(3) ^{vii}	2.832 (13)
OAs(34) ^{iv}	3.058 (9)	O(12)	2.783 (11)
		Aq(7)	
		O'(2) ^{viii}	2.925 (12)

Table 5. Distances (Å) and angles (°) in the [N(CH₃)₄]⁺ cations

N(1)—C(1)	1.507 (17)	N(2)—C(5)	1.487 (17)
C(2)	1.499 (17)	C(6)	1.512 (17)
C(3)	1.508 (17)	C(7)	1.520 (19)
C(4)	1.499 (16)	C(8)	1.513 (14)
C(1)—N(1)—C(2)	108.9 (10)	C(5)—N(2)—C(6)	110.0 (10)
C(1)—N(1)—C(3)	109.8 (10)	C(5)—N(2)—C(7)	110.7 (10)
C(1)—N(1)—C(4)	109.9 (10)	C(5)—N(2)—C(8)	109.8 (10)
C(2)—N(1)—C(3)	110.4 (10)	C(6)—N(2)—C(7)	108.0 (10)
C(2)—N(1)—C(4)	111.8 (10)	C(6)—N(2)—C(8)	110.1 (10)
C(3)—N(1)—C(4)	106.0 (10)	C(7)—N(2)—C(8)	108.3 (10)

The superstructure

The anion possesses an approximate centre of inversion which is situated near $\frac{1}{2}, \frac{1}{4}, \frac{1}{2}$. Together with the crystallographic centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ this results in an apparent translation of the anion by $b/2$ (Fig. 1). Furthermore, the two independent $[\text{N}(\text{CH}_3)_4]^+$ cations are also situated as if repeated by $b/2$. However, the Na–H₂O arrangement is not repeated in this way, even if some individual atoms may be considered to be. This may be explained by the protonation of the anions, with the H atom pointing alternately in the $-x$ and $+x$ directions for anions at y and $y + \frac{1}{2}$, respectively. The conditions for Na⁺ coordination to the arsenate O atoms are thus different, with the given result. The number of reflexions with $I > 3\sigma(I)$ [$I > 2\sigma(I)$] was 3558 [3777] for k even and 1401 [1898] for k odd. The intensity was $< 10\sigma(I)$ for 75% of the k odd reflexions and the maximum value was $55\sigma(I)$.

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X-ray and NMR Studies of the Interaction Between Pd^{II} and S-Methyl-L-cysteine Methyl Ester

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Abstract

Both X-ray and NMR results indicated that S-methyl-L-cysteine methyl ester (SmcOMe) is coordinated to Pd^{II} through the S and N donors. X-ray studies were performed on crystals of the 1:1 ligand–metal complex. Crystals of dichloro(S-methyl-L-cysteine methyl ester)palladium(II) monohydrate are tetragonal, space

group $P4_12_12$, with $a = b = 8.309(3)$, $c = 33.860(9)$ Å, $Z = 8$. The structure was refined to $R = 0.062$ for 823 counter reflections. The coordination around Pd is slightly distorted square planar and involves the S and N atoms of the amino acid molecule and two Cl atoms. The five-membered chelate ring has an envelope-like conformation. The absolute configuration of the ligand was assigned as (3*R*,*S**R*) with reference to the known *R* configuration of L-cysteine.

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