

The Structure of Hexaguanidinium Octadecamolybdodiarsenate Enneahydrate, $(\text{CH}_6\text{N}_3)_6[\text{As}_2\text{Mo}_{18}\text{O}_{62}].9\text{H}_2\text{O}$

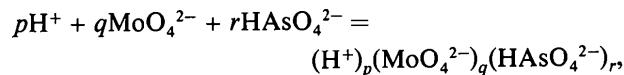
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Abstract. $M_r = 3391.4$, trigonal, $R\bar{3}$, $a = 12.772$ (1) Å, $\alpha = 104.21$ (1)°, $V = 1851$ Å³, $Z = 1$, $D_x = 3.10$, $D_m = 3.04$ Mgm⁻³, $\mu(\text{Mo } K\alpha) = 3.94$ mm⁻¹, $T = 298$ K, $F(000) = 1606$. $R = 0.041$ based on 3560 independent reflexions. The structure contains the discrete heteropolyanion $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$, referred to as the Dawson type, which is regarded as the dimer of $[\text{AsMo}_9\text{O}_{31}(\text{OH}_2)_3]^{3-}$ derived from the Keggin type, $[\text{AsMo}_{12}\text{O}_{40}]^{3-}$. The polyanion consists of eighteen MoO_6 octahedra forming two Mo_3O_{13} and six Mo_2O_{10} units and two interior AsO_4 tetrahedra. The Mo atoms deviate from point group $\bar{6}$ considerably and the molecule has only 32 (D_3) symmetry. The molecule is shorter along the principal axis and greater in diameter than the P analogue. There are two kinds of coordination for MoO_6 octahedra. The Mo–O bond distances range from 1.69 to 2.34 Å, intricately depending on the coordinations and also the dissymmetric configuration. As expected three asymmetric and two symmetric loops made by oxygen bridges are observed. The AsO_4 tetrahedra are not regular and the As–O bond lengths vary from 1.65 to 1.75 Å.

Introduction. The Dawson (1953) type heteropolyanion, $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{6-}$ ($\text{X} = \text{As}$, P and $\text{M} = \text{Mo}$, W), is closely connected with the Keggin (1934) type, $[\text{XM}_{12}\text{O}_{40}]^{3-}$, in terms not only of the structure, but also the aqueous equilibria,



in the lowest pH regions. Many complicated molybdoarsenate polyanions have been revealed by potentiometric and spectrometric investigations of the aqueous-equilibria system (Pettersson, 1975; Lyhamn & Pettersson, 1980). However, any direct evidence for the presence of these most condensed species has not yet been demonstrated. Only Raman spectra of the solution have been reported to imply that the $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion exists (Lyhamn & Pettersson, 1979). Earlier, it was known preparatively that the Dawson-type anion is exceptionally more stable than the Keggin type in the molybdoarsenate systems. The correct structure of this anion is of fundamental interest in relation to the

structural chemistry of heteropoly compounds. It is also necessary to understand the small change caused by placement of the different elements in the formally common site, as well as the behavior of identical elements in the slightly different sites.

Experimental. 2.7 ml of 60% H_3AsO_4 were poured into 100 ml of the solution containing 29.0 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; 6 M HNO_3 was added to adjust the pH to ca 2. The deep-yellow solution was treated with an aqueous solution of guanidinium chloride (1.0 g) by gentle addition. Within a week, deep-yellow rhombohedral crystals were obtained. Their density was measured by flotation in $\text{CH}_2\text{I}_2/\text{CHCl}_3$.

Weissenberg photographs showed rhombohedral symmetry; space group $R\bar{3}$ was determined during the structure analysis; lattice constants were obtained by least squares from 24 reflexions ($15^\circ < \theta < 17^\circ$), crystal $0.26 \times 0.18 \times 0.16$ mm; Rigaku automated four-circle diffractometer, $\text{Mo } K\alpha$ ($\lambda = 0.7107$ Å) radiation monochromated by a graphite plate; 13945 reflexions, layers $hk0-hk17$, $\theta-2\theta$ scan mode, $2\theta_{\max} = 65^\circ$, Lorentz-polarization corrections; three standard reflexions were measured every fifty to monitor electronic fluctuation and to check any crystal deterioration; absorption correction applied (transmission factor varied from 0.35 to 0.57); arithmetic mean values for the equivalent reflexions were calculated and reduced to 4082 unique reflexions, of which 3560 with $|F_o|^2 > 3\sigma(|F_o|^2)$ were regarded as observed and used for solution and refinement of the structure.

With the Dawson-type structure assumed, six crystallographically independent Mo atoms and two As atoms were located from a Patterson function. Successive Fourier syntheses and block-diagonal least-squares refinement yielded all the non-hydrogen atoms. However, one of the two guanidinium ions was revealed to be disordered. When two positions with 50% occupancy for each were assigned (except for one N atom common to both locations) the refinement with anisotropic thermal parameters converged at $R = 0.041$ and $R_w = 0.040$; $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2$. In the final cycle, the parameter shifts were smaller than 0.1σ . The atomic scattering factors and the real parts of

the anomalous scattering for all the atoms were from *International Tables for X-ray Crystallography* (1974). The computer programs were the local versions of *UNICS* (Sakurai, 1967), and computations were made on the HITAC 8800/8700 and HITAC M-200H computers at the Computer Centre of the University of Tokyo.*

Discussion. Final atomic parameters are given in Table 1.

[As₂Mo₁₈O₆₂]⁶⁻-anion

This anion exhibits the Dawson (1953) type structure, [X₂M₁₈O₆₂]⁶⁻ ($X = \text{As}$, P and $M = \text{Mo}$ and W) regarded as the dimer of $[XM_9O_{31}(\text{OH}_2)_3]^{3-}$, having three MO_6 octahedra removed from three of four $M_3\text{O}_{13}$ units of the well-known Keggin (1934) molecule

$[XM_{12}\text{O}_{40}]^{3-}$. Therefore the structure consists of two $M_3\text{O}_{13}$ and six $M_2\text{O}_{10}$ (or two M_6 rings) units, which are linked to each other by point-sharing and together surround two XO_4 tetrahedra. Unlike the analogue of W , it was pointed out that the symmetry of $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ was a dissymmetric one, $32(D_3)$, reduced from $\bar{6}m2(D_{3h})$ (d'Amour, 1976). It has been confirmed that only the molybdochosphate anion of the $[\text{P}_2\text{M}_{18}\text{O}_{62}]^{6-}$ ions shows the Pfeiffer effect in some chiral solvents (Garvey & Pope, 1978). Also in $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ the Mo and terminal O atoms were found to be displaced from the mirror planes and to fulfill the twofold symmetry of $\bar{6}m2$ within experimental error. It is thought that only rotation axes are required to conserve the bond strengths in this system. As a result of the dissymmetric configuration there are three different sites for Mo atoms, designated *A* [Mo(1), (2)], *B* [Mo(3), (4)] and *C* [Mo(5), (6)] in Fig. 1. As-Mo and Mo-Mo distances and related angles in Table 2 describe this structure as well as the difference between the sites *A* and *B* which are chemically

Table 1. Positional parameters ($\times 10^5$ for As and Mo, $\times 10^4$ for others) and thermal parameters B_{eq} ($\times 10^2$ for As and Mo, $\times 10$ for others)

	x	y	z	$B_{eq} (\text{\AA}^2)$
As(1)	37034 (12)	37034 (21)	37034 (21)	99 (5)
As(2)	62630 (21)	62630 (21)	62630 (21)	98 (5)
Mo(1)	21093 (8)	32685 (8)	55016 (8)	125 (2)
Mo(2)	68323 (8)	44578 (8)	78163 (8)	129 (2)
Mo(3)	43960 (8)	19671 (8)	53996 (8)	123 (2)
Mo(4)	45200 (8)	57074 (8)	79665 (8)	128 (2)
Mo(5)	16198 (8)	9468 (8)	28594 (8)	125 (2)
Mo(6)	76917 (8)	75703 (9)	93046 (8)	139 (2)
O(1)	3145 (7)	4297 (7)	4649 (6)	15 (2)
O(2)	6551 (6)	5074 (6)	6265 (6)	12 (2)
O(3)	2622 (13)	2622 (13)	2622 (13)	9 (3)
O(4)	7372 (14)	7372 (14)	7372 (14)	15 (3)
OE(1)	1416 (6)	4368 (6)	5186 (7)	14 (2)
OE(2)	4115 (7)	7063 (6)	7896 (7)	15 (2)
OE(3)	487 (6)	1568 (7)	1982 (7)	18 (2)
OE(4)	7781 (7)	8999 (7)	9220 (7)	17 (2)
OP(1)	3380 (7)	2722 (7)	5828 (6)	15 (2)
OP(2)	5435 (6)	4739 (6)	7816 (6)	13 (2)
OP(3)	2909 (7)	1085 (7)	3879 (7)	15 (2)
OP(4)	6189 (7)	6939 (6)	8921 (6)	15 (2)
OP(5)	1438 (7)	2126 (7)	4180 (6)	15 (2)
OP(6)	7667 (6)	5889 (7)	8702 (6)	14 (2)
OP(7)	3269 (7)	4684 (7)	6902 (7)	17 (2)
OP(8)	5648 (7)	2931 (6)	6489 (6)	17 (2)
OT(1)	1341 (7)	2838 (7)	6321 (7)	19 (3)
OT(2)	6965 (7)	3699 (7)	8719 (7)	22 (3)
OT(3)	4117 (7)	829 (7)	5858 (7)	18 (2)
OT(4)	4240 (8)	5636 (8)	9181 (7)	24 (3)
OT(5)	707 (7)	-278 (6)	2831 (7)	16 (2)
OT(6)	8183 (7)	7772 (7)	10713 (7)	20 (3)
C(1)	6277 (11)	1454 (11)	9972 (11)	25 (4)
C(2)	3870 (10)	8555 (10)	9950 (10)	18 (4)
C(2')	5400 (10)	8139 (10)	11000 (9)	16 (3)
N(1)	6493 (8)	660 (8)	10470 (9)	18 (3)
N(2)	7164 (9)	2367 (9)	10211 (10)	24 (3)
N(3)	5236 (10)	1339 (11)	9312 (12)	36 (4)
N(4)	4269 (8)	7901 (8)	10539 (8)	19 (3)
N(5)	2764 (8)	8289 (9)	9454 (9)	22 (3)
N(6)	4597 (8)	9469 (8)	9866 (8)	19 (3)
N(5')	5768 (8)	7396 (8)	11461 (9)	21 (3)
N(6')	6158 (8)	9074 (8)	10989 (8)	19 (3)
OW(1)	4051 (10)	2895 (10)	8525 (10)	42 (4)
OW(2)	1676 (10)	2326 (11)	8447 (9)	43 (4)
OW(3)	417 (9)	5686 (10)	9695 (10)	39 (4)

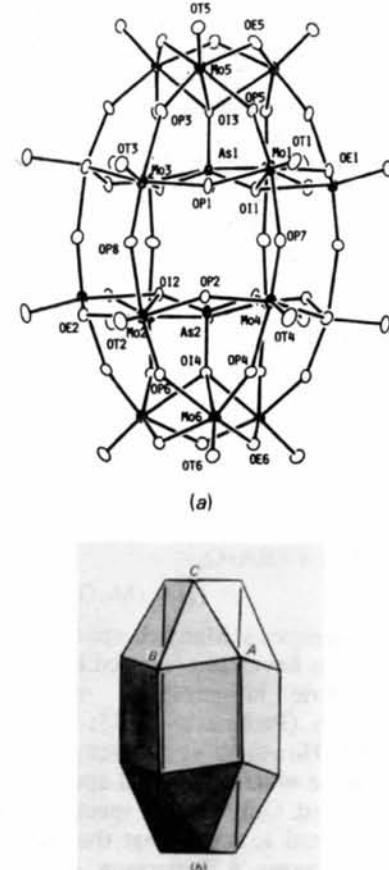


Fig. 1. (a) The structure of the $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion. The thermal ellipsoids are scaled to enclose 30% probability. (b) The skeleton made by the Mo atoms, showing the D_3 symmetry and three sites *A*, *B* and *C* (see text).

Table 2. Distances (\AA) and angles ($^\circ$) with their estimated standard deviations $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion

Mo(1)–Mo(3)'	3.382 (2)	O/I(1)'–OT(3)	3.970 (13)	OP(3)–Mo(3)–OP(8)	166.9 (3)
Mo(2)–Mo(4)''	3.365 (2)	OP(3)–OE(1)''	2.721 (12)	OP(3)–Mo(3)–OT(3)	90.4 (4)
Mo(5)–Mo(5)'	3.387 (2)	OP(3)–OP(1)	2.650 (10)	OE(1)''–Mo(3)–OP(1)	153.7 (4)
Mo(6)–Mo(6)'	3.380 (2)	OP(3)–OP(8)	3.908 (9)	OE(1)''–Mo(3)–OP(8)	95.1 (3)
Mo(1)–Mo(3)	3.711 (2)	OP(3)–OT(3)	2.759 (12)	OE(1)''–Mo(3)–OT(3)	97.7 (4)
Mo(1)–Mo(5)	3.703 (1)	OE(1)''–OP(1)	3.749 (13)	OP(1)–Mo(3)–OP(8)	96.5 (3)
Mo(2)–Mo(4)	3.708 (1)	OE(1)''–Mo(2)'	2.741 (10)	OP(1)–Mo(3)–OT(3)	102.7 (4)
Mo(2)–Mo(6)	3.707 (1)	Mo(5)–Mo(5)'–Mo(5)''	60.00	OP(8)–Mo(3)–OT(3)	102.7 (4)
Mo(3)–Mo(5)	3.848 (1)	Mo(6)–Mo(6)'–Mo(6)''	60.00		
Mo(4)–Mo(6)	3.855 (1)				
Mo(1)–Mo(4)	3.848 (1)	Mo(1)–OE(1)–Mo(3)'	122.7 (5)	Mo(4)–OI(2)'	2.300 (9)
Mo(2)–Mo(3)	3.864 (1)	Mo(2)–OE(2)–Mo(4)''	121.2 (5)	Mo(4)–OP(4)	2.154 (6)
As(1)–As(2)	4.040 (3)	Mo(5)–OE(3)–Mo(5)'	122.3 (4)	Mo(4)–OE(2)	1.949 (11)
As(1)–O(1)	1.668 (9)	Mo(6)–OE(4)–Mo(6)'	121.0 (4)	Mo(4)–OP(2)	1.907 (9)
As(1)–O(3)	1.707 (12)	Mo(1)–OP(1)–Mo(3)	153.2 (4)	Mo(4)–OP(7)	1.774 (6)
As(2)–O(2)	1.648 (9)	Mo(2)–OP(2)–Mo(4)	153.2 (4)	Mo(4)–OT(4)	1.694 (11)
As(2)–O(4)	1.750 (12)	Mo(3)–OP(3)–Mo(5)	155.0 (4)	O/I(2)’–OP(4)	2.817 (10)
Mo(1)–As(1)	3.478 (3)	Mo(4)–OP(4)–M.O(6)	157.3 (4)	O/I(2)’–OE(2)	2.505 (13)
Mo(2)–As(2)	3.484 (3)	Mo(1)–OP(5)–Mo(5)'	147.9 (5)	O/I(2)’–OP(2)	2.871 (12)
Mo(3)–As(1)	3.574 (3)	Mo(2)–OP(6)–Mo(6)	146.3 (5)	O/I(2)’–OP(7)	2.874 (12)
Mo(4)–As(2)	3.543 (3)	Mo(1)–OP(7)–Mo(4)	164.2 (5)	O/I(2)’–OT(4)	3.965 (14)
Mo(5)–As(1)	3.573 (2)	Mo(2)–OP(8)–Mo(3)	161.3 (5)	OP(4)–OE(2)	2.713 (12)
Mo(6)–As(2)	3.602 (2)			OP(4)–OP(2)	2.621 (10)
O/I(1)–O/I(1)'	2.747 (18)	O/I(1)–As(1)–O/I(1)'	110.9 (5)	OP(4)–OP(7)	3.900 (9)
O/I(1)–O/I(3)	2.730 (16)	O/I(1)–As(1)–O/I(3)	108.0 (5)	OP(4)–OT(4)	2.778 (13)
O/I(2)–O/I(2)'	2.735 (18)	O/I(2)–As(2)–O/I(2)'	112.1 (5)	OE(2)–OP(2)	3.749 (12)
O/I(2)–O/I(4)	2.727 (16)	O/I(2)–As(2)–O/I(4)	106.7 (5)	OE(2)–OP(7)	2.799 (10)
				OE(2)–OT(4)	2.743 (14)
Mo(1)–O/I(1)	2.284 (9)	OP(1)–OP(5)	2.624 (10)	Mo(5)–O/I(3)	2.339 (16)
Mo(1)–OP(7)	2.112 (6)	OP(1)–OT(1)	2.855 (14)	Mo(5)–OP(5)	2.070 (8)
Mo(1)–OE(1)	1.906 (9)	OP(5)–OT(1)	2.706 (12)	Mo(5)–OE(3)'	2.045 (9)
Mo(1)–OP(1)	1.914 (9)	O/I(1)–Mo(1)–OP(7)	77.5 (3)	Mo(5)–OE(3)''	1.820 (10)
Mo(1)–OP(5)	1.783 (6)	O/I(1)–Mo(1)–OE(1)	72.1 (3)	Mo(5)–OP(3)	1.769 (8)
Mo(1)–OT(1)	1.698 (10)	O/I(1)–Mo(1)–OP(1)	84.0 (4)	Mo(5)–OT(5)	1.692 (8)
O/I(1)–OP(7)	2.755 (12)	O/I(1)–Mo(1)–OP(5)	89.9 (3)	O/I(3)–OP(5)	2.876 (20)
O/I(1)–OE(1)	2.482 (13)	O/I(1)–Mo(1)–OT(1)	165.3 (4)	O/I(3)–OE(3)	2.545 (16)
O/I(1)–OP(1)	2.822 (13)	O/I(7)–Mo(1)–OE(1)	83.1 (3)	O/I(3)–OE(3)''	2.545 (16)
O/I(1)–OP(5)	2.894 (10)	O/I(7)–Mo(1)–OP(1)	80.3 (3)	O/I(3)–OP(3)	2.860 (20)
O/I(1)–OT(1)	3.950 (13)	O/I(7)–Mo(1)–OP(5)	165.0 (3)	O/I(3)–OT(5)	4.016 (18)
OP(7)–OE(1)	2.668 (11)	O/I(7)–Mo(1)–OT(1)	91.8 (4)	OP(5)–OE(3)'	2.604 (11)
OP(7)–OP(1)	2.601 (12)	O/E(1)–Mo(1)–OP(1)	153.3 (4)	OP(5)–OE(3)''	3.797 (12)
OP(7)–OP(5)	3.861 (9)	O/E(1)–Mo(1)–OP(5)	100.9 (3)	OP(5)–OP(3)	2.603 (13)
OP(7)–OT(1)	2.751 (10)	O/E(1)–Mo(1)–OT(1)	96.9 (4)	OP(5)–OT(5)	2.911 (10)
O/E(1)–OP(1)	3.716 (13)	O/P(1)–Mo(1)–OP(5)	90.4 (3)	OE(3)–OE(3)''	2.695 (19)
O/E(1)–OP(5)	2.846 (11)	O/P(1)–Mo(1)–OT(1)	104.3 (4)	OE(3)–OP(3)	3.716 (12)
O/E(1)–OT(1)	2.701 (13)	O/P(5)–Mo(1)–OT(1)	102.0 (4)	OE(3)–OT(5)	2.871 (13)
Mo(2)–O/I(2)	2.287 (9)	OP(2)–OP(6)	2.666 (10)	Mo(6)–O/I(4)	2.339 (17)
Mo(2)–OP(8)	2.153 (6)	OP(2)–OT(2)	2.799 (13)	Mo(6)–OP(6)	2.085 (8)
Mo(2)–OE(2)''	1.921 (9)	OP(6)–OT(2)	2.727 (13)	Mo(6)–OE(4)''	2.050 (9)
Mo(2)–OP(2)	1.905 (9)	O/I(2)–Mo(2)–OP(8)	78.5 (3)	Mo(6)–OE(4)	1.832 (9)
Mo(2)–OP(6)	1.787 (7)	O/I(2)–Mo(2)–OE(2)''	72.5 (4)	Mo(6)–OP(4)	1.777 (8)
Mo(2)–OT(2)	1.682 (11)	O/I(2)–Mo(2)–OP(2)	82.0 (3)	Mo(6)–OT(6)	1.684 (8)
O/I(2)–OP(8)	2.811 (11)	O/I(2)–Mo(2)–OP(6)	89.2 (3)	O/I(4)–OP(6)	2.869 (21)
O/I(2)–OE(2)''	2.505 (13)	O/I(2)–Mo(2)–OT(2)	166.2 (4)	O/I(4)–OE(4)''	2.572 (17)
O/I(2)–OP(2)	2.764 (12)	O/P(8)–Mo(2)–OE(2)''	83.3 (3)	O/I(4)–OE(4)	2.572 (17)
O/I(2)–OP(6)	2.882 (10)	O/P(8)–Mo(2)–OP(2)	80.4 (3)	O/I(4)–OP(4)	2.846 (21)
O/I(2)–OT(2)	3.941 (13)	O/P(8)–Mo(2)–OP(6)	166.4 (3)	O/I(4)–OT(6)	4.005 (19)
OP(8)–OE(2)''	2.713 (10)	O/P(8)–Mo(2)–OT(2)	89.2 (4)	OP(6)–OE(4)''	2.597 (11)
OP(8)–OP(2)	2.625 (11)	O/E(2)''–Mo(2)–OP(2)	152.0 (4)	OP(6)–OE(4)	3.823 (12)
OP(8)–OP(6)	3.912 (9)	O/E(2)''–Mo(2)–OP(6)	98.5 (3)	OP(6)–OP(4)	2.600 (13)
OP(8)–OT(2)	2.715 (11)	O/E(2)''–Mo(2)–OT(2)	100.0 (5)	OP(6)–OT(6)	2.859 (10)
O/E(2)''–OP(2)	3.712 (13)	O/P(2)–Mo(2)–OP(6)	92.4 (3)	OE(4)''–OE(4)	2.706 (19)
O/E(2)''–OP(6)	2.810 (11)	O/P(2)–Mo(2)–OT(2)	102.4 (4)	OE(4)''–OP(4)	3.724 (12)
O/E(2)''–OT(2)	2.765 (14)	O/P(6)–Mo(2)–OT(2)	103.6 (4)	OE(4)''–OT(6)	2.824 (13)
Mo(3)–O/I(1)''	2.319 (9)	OP(1)–OP(8)	2.736 (12)	Guanidinium ions	
Mo(3)–OP(3)	2.171 (6)	OP(1)–OT(3)	2.807 (13)	C(1)–N(1)	1.37 (2)
Mo(3)–OE(1)''	1.948 (9)	OP(8)–OT(3)	2.696 (10)	C(1)–N(2)	1.32 (2)
Mo(3)–OP(1)	1.902 (9)	O/I(1)''–Mo(3)–OP(3)	78.1 (3)	C(1)–N(3)	1.34 (2)
Mo(3)–OP(8)	1.763 (6)	O/I(1)''–Mo(3)–OE(1)''	70.6 (3)	C(2)–N(4)	1.36 (2)
Mo(3)–OT(3)''	1.688 (9)	O/I(1)''–Mo(3)–OP(1)	86.1 (4)	C(2)–N(5)	1.32 (2)
O/I(1)''–OP(3)	2.829 (11)	O/I(1)''–Mo(3)–OP(8)	88.9 (3)	C(2)–N(6)	1.35 (2)
O/I(1)''–OE(1)''	2.483 (13)	O/I(1)''–Mo(3)–OT(3)	164.3 (4)	C(2)’–N(4)	1.34 (2)
O/I(1)''–OP(1)	2.896 (13)	O/P(3)–Mo(3)–OE(1)''	82.5 (3)	C(2)’–N(5)'	1.35 (2)
O/I(1)''–OP(8)	2.887 (12)	O/P(3)–Mo(3)–OP(1)	80.9 (3)	C(2)’–N(6)'	1.35 (2)
				N(1)–C(1)–N(2)	115.4 (11)
				N(2)–C(1)–N(3)	121.6 (12)
				N(3)–C(1)–N(1)	122.9 (12)
				N(4)–C(2)–N(5)	119.7 (11)
				N(5)–C(2)–N(6)	119.7 (12)
				N(6)–C(2)–N(4)	120.6 (11)
				N(4)–C(2)’–N(5)'	118.1 (11)
				N(5)’–C(2)’–N(6)'	120.1 (11)
				N(6)’–C(2)’–N(4)	121.7 (12)

Symmetry code: None x, y, z , (') y, z, x , (") z, x, y .

identical. Compared to the values estimated from the results of $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ (Strandberg, 1975), the corresponding angles agree; however, $X\text{--Mo}$ and $\text{Mo}\text{--Mo}$ distances except $\text{Mo}(\text{C})\text{--Mo}(\text{C})$ are greater than those

of the P analogue by $0.02 \sim 0.06 \text{ \AA}$. The distance $\text{As}\text{--As}$ (4.040 \AA) is shorter than $\text{P}\text{--P}$ (4.154 \AA), and, moreover, the separations of the horizontal planes formed by two $\text{Mo}(A,B)_6$ rings are 0.47 and 0.46 \AA ,

respectively. Thus the oval skeleton of $[As_2Mo_{18}O_{62}]^{6-}$ is shorter than that of the phosphate by *ca* 0.08 Å along the direction of the principal axis and greater by 0.07 Å in diameter. Consequently the displacement of Mo(C) atoms from the point group 6, 16·7°, is also greater than the 15·4° in the P analogue (though the deviation from 6 has been reported to be rather small). Even then, both geometries are quite similar especially the Mo–Mo–Mo and Mo–O–Mo angles, except for Mo–OI–Mo, directly reflecting the size of the XO_4 group. The variation of the angles about the point-sharing O atoms Mo–OP–Mo is not as small, but the edge-sharing Mo–OE–Mo are constant in both molecules.

MoO_6 octahedra

The considerable deviation from 32 symmetry invalidates the conventional classification of Mo–O bonds into four, simply according to their coordination numbers. The Mo_3O_{13} unit of site C is isostructural to those of the Keggin molecules with reduced symmetry 23 (T) $[PMo_{12}O_{40}]^{3-}$ (d'Amour & Allmann, 1976) and $[SiMo_{12}O_{40}]^{4-}$ (Ichida, Kobayashi & Sasaki, 1980). The Mo(C) O_6 octahedra are asymmetric in terms of the Mo–OE and Mo–OP bond lengths, namely 2.078 (8), 2.048 (3), 1.826 (6) and 1.773 (4) Å, respectively, and may be described as having (1 + 2 + 2 + 1) coordination.* In sites A and B there are three different Mo–OP bonds, 2.148 (22), 1.907 (4) Å [which is very close to the 1.929 (4) of its opposite Mo–OE], and 1.777 (9) Å (being opposite to the first). This distribution of Mo–O bonds in these sites may not be very different from those often found in numerous stable polymolybdate anions, *i.e.* (2 + 2 + 2).* Thus the loop made by the Mo–O–Mo bridging consists of Mo–O bonds on the Mo_6 rings equivalent in length, whereas all the other bridging O atoms coordinate strongly to one Mo atom and weakly to the other, making asymmetric *trans*-bridging loops. Table 3 lists these mean bond lengths compared to those obtained from $[P_2Mo_{18}O_{62}]^{6-}$ (Strandberg, 1975). Although both anions show the same trend in Mo–O distances, the contrast between the two kinds of coordinations for MoO_6 , (1 + 2 + 2 + 1) and (2 + 2 + 2), is more pronounced in the molybdoarsenate anion. Unlike the Keggin type this anion has the anisotropic structure containing Mo_2O_{10} units with the stable coordination, which can delocalize the strain arising from enlargement of XO_4 under the restriction of the consistency between the molecular symmetry and the oxidation states of the atoms.

AsO_4 tetrahedra

As–OI bonds and OI–As–OI angles imply anisotropy of the tetrahedra resulting from the difference in

coordination numbers. The AsO_4 of this anion resembles that of $HAAsO_4^{3-}$ (Baur & Kahn, 1971) among the arsenates and polymolybdoarsenates previously reported. It suggests that the relation between the OI coordinated to three Mo atoms and others bonded to two is similar to that of the protonated O and others, *i.e.* terminal O atoms.

Guanidinium ions and water molecules

Fig. 2 shows the crystal structure along [111]. One of the crystallographically independent guanidinium ions is disordered on two sites. The bond lengths and

Table 3. Mo–O bond lengths in the $[X_2Mo_{18}O_{62}]^{6-}$ anions

	As*	P†
Sites A and B (M_6 ring)		
Mo–OT	1.691 (6) Å	1.684 (7) Å
Mo–OP ^a	1.777 (9)	1.772 (17)
Mo–OP ^b	1.907 (4)	1.886 (7)
Mo–OE	1.929 (4)	1.914 (16)
Mo–OP ^c	2.148 (22)	2.125 (11)
Mo–OI	2.298 (14)	2.334 (16)
Site C		
Mo–OT	1.688 (6)	1.686 (7)
Mo–OP ^d	1.773 (4)	1.781 (8)
Mo–OE ^d	1.826 (6)	1.834 (5)
Mo–OE ^e	2.048 (3)	2.036 (9)
Mo–OP ^a	2.078 (8)	2.060 (11)
Mo–OI	2.339 (17)	2.389 (17)

Notes: (a) shared by M_6 ring and site C or by two M_6 rings. (b) Shared within the same M_6 ring. (c) In the *trans* position to (a). (d) In the *cis* position to (c). (e) In the *trans* position to (d).

* Present work. †Strandberg (1975).

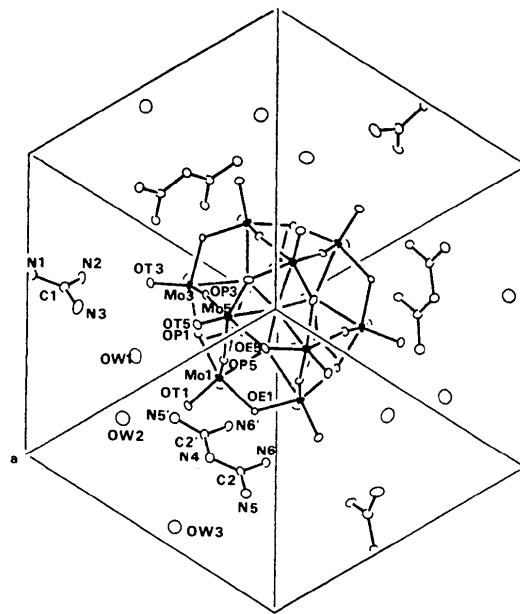


Fig. 2. A view of the crystal structure projected along the [111] axis.

The representation is taken from Wells (1975).

angles are nevertheless normal. There are hydrogen bonds between the O atoms of the anion and water molecules and the N atoms of the cations.

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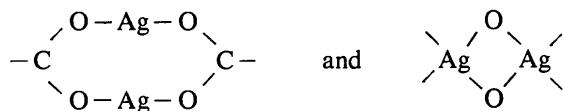
catena-Bis(μ -benzoato-O,O', μ -O)-bis(pyridin)-disilber(I), $[\text{Ag}_2(\text{C}_5\text{H}_5\text{N})_2(\text{C}_7\text{H}_5\text{O}_2)_2]$

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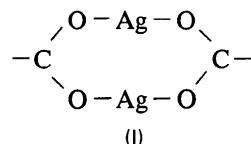
(Eingegangen am 3. November 1982; angenommen am 5. Januar 1983)

Abstract. $M_r = 616 \cdot 171$, monoclinic, $P2_1/c$, $a = 24 \cdot 337 (6)$, $b = 5 \cdot 733 (1)$, $c = 17 \cdot 287 (6) \text{ \AA}$, $\beta = 110 \cdot 54 (2)^\circ$, $V = 2258 (2) \text{ \AA}^3$, $Z = 4$, $D_x = 1 \cdot 81 \text{ Mg m}^{-3}$, Zr-filtered Mo $K\alpha$, $\lambda = 0 \cdot 7107 \text{ \AA}$, $\mu = 17 \cdot 4 \text{ cm}^{-1}$, $F(000) = 1216$, $T = 298 \text{ K}$, $R = 0 \cdot 059$ for 1935 observed reflexions. Ag is coordinated in a distorted tetrahedron to one N and three O atoms, shortest Ag–Ag distances being 2.85 (2) \AA (molecule I) and 2.90 (2) \AA (molecule II). The property of one carboxylate oxygen bridging two neighbouring Ag atoms leads to a polymeric structure of infinite chains composed of eight- and four-membered rings:



Einleitung. Die Koordinationszahl des Silber(I) in seinen Komplexverbindungen hängt sehr empfindlich von der Natur der Liganden ab. Der lineare Typ Ag_2L_2 tritt häufig in Gegenwart einzähniger Liganden mit den Bindungseigenschaften harter Basen (vor allem O- und N-haltige Liganden) auf. Weiche Basen bzw. mehrzähnige Liganden bevorzugen die höheren Koordinationszahlen 3 bzw. 4 am Ag⁺. So betragen die Bindungswinkel N–Ag–N z.B. in Diamminsilber(I)-sulfat (Corey & Wyckoff, 1934) oder Bis(pyridin-silber(I)-nitrat-l-hydrat) (Menchetti,

Rossi & Tazzoli, 1970) angenähert 180°. In Komplexverbindungen mit Carboxylatgruppen als zweizähnige Liganden tritt häufig die dimere, ringförmige Baueinheit



mit Winkeln O–Ag–O von ungefähr 160° auf. Die Abweichungen von der Linearität sind hier auf Ag–Ag-Abstossung zurückzuführen (z.B. Charbonnier, Faure & Loiseleur, 1981; Blakeslee & Hoard, 1956). In Silbersalzen von Aminosäuren stehen neben der Carboxylatgruppe noch zusätzlich N-haltige Koordinationsstellen zur Verfügung. In diesen Verbindungen sind sowohl die linearen Koordinationen O–Ag–O, N–Ag–N und O–Ag–N unter Ausbildung von Ketten, als auch der Koordinationstyp (1) möglich (Acland & Freeman, 1971; Rao & Viswamitra, 1972).

In Gegenwart eines zusätzlichen weichen Liganden, wie z.B. Triphenylphosphin (Blues, Drew & Femionadeko, 1977) oder Benzol (Hunt, Lee & Amma, 1974) bleibt die Einheit (1) erhalten, die Koordinationszahl am Silber wird aber vergrößert und die Winkel O–Ag–O bekommen Werte in der Größenordnung der Tetraederwinkel. In der vorliegenden Arbeit soll am