

The Structure of Hexaguanidinium Octadecamolybdiarsenate Enneahydrate, (CH₆N₃)₆[As₂Mo₁₈O₆₂].9H₂O

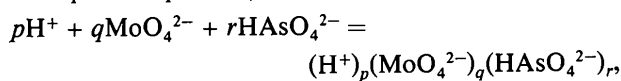
BY HIKARU ICHIDA AND YUKIYOSHI SASAKI

Department of Chemistry and Research Centre for Spectrochemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

(Received 2 November 1982; accepted 21 December 1982)

Abstract. $M_r = 3391.4$, trigonal, $R3$, $a = 12.772$ (1) Å, $\alpha = 104.21$ (1)°, $V = 1851$ Å³, $Z = 1$, $D_x = 3.10$, $D_m = 3.04$ Mg m⁻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 [As₂Mo₁₈O₆₂]⁶⁻, referred to as the Dawson type, which is regarded as the dimer of [AsMo₉O₃₁(OH)₂]³⁻ derived from the Keggin type, [AsMo₁₂O₄₀]³⁻. The polyanion consists of eighteen MoO₆ octahedra forming two Mo₃O₁₃ and six Mo₂O₁₀ units and two interior AsO₄ 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 MoO₆ 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 AsO₄ tetrahedra are not regular and the As–O bond lengths vary from 1.65 to 1.75 Å.

Introduction. The Dawson (1953) type heteropolyanion, [X₂M₁₈O₆₂]⁶⁻ ($X = \text{As, P}$ and $M = \text{Mo, W}$), is closely connected with the Keggin (1934) type, [XM₁₂O₄₀]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 [As₂Mo₁₈O₆₂]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% H₃AsO₄ were poured into 100 ml of the solution containing 29.0 g of Na₂MoO₄.2H₂O; 6 M HNO₃ 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 CH₂I₂/CHCl₃.

Weissenberg photographs showed rhombohedral symmetry; space group $R3$ was determined during the structure analysis; lattice constants were obtained by least squares from 24 reflexions ($15^\circ < \theta < 17^\circ$), crystal 0.26 × 0.18 × 0.16 mm; Rigaku automated four-circle diffractometer, Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation monochromated by a graphite plate; 13945 reflexions, layers $hk0-hk17$, $\theta-2\theta$ scan mode, $2\theta_{\text{max}} = 65^\circ$, 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.

$[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion

This anion exhibits the Dawson (1953) type structure, $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{6-}$ ($\text{X} = \text{As}, \text{P}$ and $\text{M} = \text{Mo}$ and W) regarded as the dimer of $[\text{XM}_9\text{O}_{31}(\text{OH}_2)_3]^{3-}$, having three MO_6 octahedra removed from three of four M_3O_{13} units of the well-known Keggin (1934) molecule

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38309 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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)

$$B_{eq} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	x	y	z	B_{eq} (\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)
OH(1)	4051 (10)	2895 (10)	8525 (10)	42 (4)
OH(2)	1676 (10)	2326 (11)	8447 (9)	43 (4)
OH(3)	417 (9)	5686 (10)	9695 (10)	39 (4)

$[\text{XM}_{12}\text{O}_{40}]^{3-}$. Therefore the structure consists of two M_3O_{13} and six M_2O_{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 molybdophosphate 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

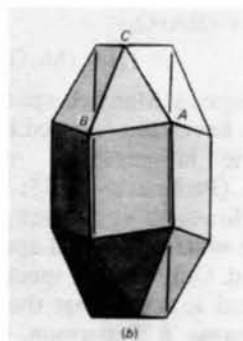
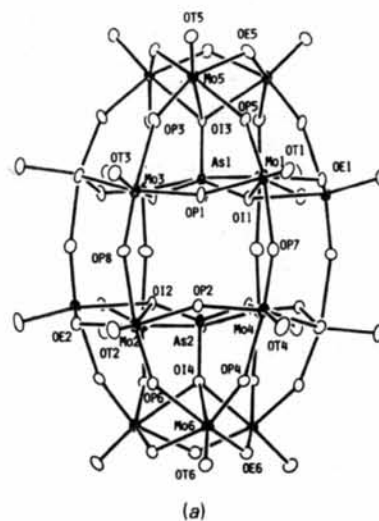


Fig. 1. (a) The structure of the $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion. The thermal ellipsoids are scaled to enclose 30% probability. (b) The skeleton made by the Mo atoms, showing the D_3 symmetry and three sites A, B and C (see text).

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.

We thank Professor Nils Ingri for his valuable advice and interest in this work.

References

D'AMOUR, H. (1976). *Acta Cryst.* B32, 729–740.

D'AMOUR, H. & ALLMANN, R. (1976). *Z. Kristallogr.* 143, 1–13.

BAUR, W. H. & KAHN, A. A. (1970). *Acta Cryst.* B26, 1584–1596.

DAWSON, B. (1953). *Acta Cryst.* 6, 113–126.

GARVEY, J. F. & POPE, M. T. (1978). *Inorg. Chem.* 17, 1115–1118.

ICHIDA, H., KOBAYASHI, A. & SASAKI, Y. (1980). *Acta Cryst.* B36, 1382–1387.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KEGGIN, J. F. (1934). *Proc. R. Soc. London Ser. A*, 144, 75–100.

LYHAMN, L. & PETTERSSON, L. (1979). *Chem. Scr.* 12, 142–152.

LYHAMN, L. & PETTERSSON, L. (1980). *Chem. Scr.* 16, 52–61.

PETTERSSON, L. (1975). *Acta Chem. Scand. Ser. A*, 29, 677–689.

SAKURAI, T. (1967). *The Universal Crystallographic Computation Program System*. Crystallographic Society of Japan.

STRANDBERG, R. (1975). *Acta Chem. Scand. Ser. A*, 29, 350–358.

WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 529. Oxford: Clarendon Press.

Acta Cryst. (1983). C39, 533–536

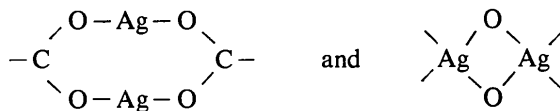
catena-Bis(μ -benzoato-O, O', μ -O)-bis(pyridin)-disilber(I), [Ag₂(C₅H₅N)₂(C₇H₅O₂)₂]

VON MARTINA HEDRICH UND HANS HARTL

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34/36,
D-1000 Berlin 33, Bundesrepublik Deutschland

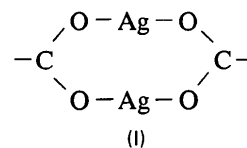
(Eingegangen am 3. November 1982; angenommen am 5. Januar 1983)

Abstract. $M_r = 616.171$, monoclinic, $P2_1/c$, $a = 24.337$ (6), $b = 5.733$ (1), $c = 17.287$ (6) Å, $\beta = 110.54$ (2)°, $V = 2258$ (2) Å³, $Z = 4$, $D_x = 1.81$ Mg m⁻³, Zr-filtered Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 17.4$ cm⁻¹, $F(000) = 1216$, $T = 298$ K, $R = 0.059$ 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) Å (molecule I) and 2.90 (2) Å (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 $\text{Ag}L_2$ tritt häufig in Gegenwart einzähliger Liganden mit den Bindungseigenschaften harter Basen (vor allem O- und N-haltige Liganden) auf. Weiche Basen bzw. mehrzählige Liganden bevorzugen die höheren Koordinationszahlen 3 bzw. 4 am Ag^I. So betragen die Bindungswinkel N–Ag–N z.B. in Diamminsilber(I)-sulfat (Corey & Wyckoff, 1934) oder Bis(pyridin)-silber(I)-nitrat-I-hydrat (Menchetti,

Rossi & Tazzoli, 1970) angenähert 180°. In Komplexverbindungen mit Carboxylatgruppen als zweizählige 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 & Femi-Onadeko, 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