

Structure of Hexakis(isopropylammonium) Diformyloctamolybdate

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(Received 8 February 1988; accepted 19 December 1988)

Abstract. $[\text{NH}_3(\text{C}_3\text{H}_7)]_6[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]$, $M_r = 1640.31$, triclinic, space group $P1$, $a = 10.254$ (5), $b = 10.638$ (8), $c = 12.627$ (3) Å, $\alpha = 111.89$ (4), $\beta = 100.37$ (3), $\gamma = 94.05$ (5)°, $V = 1242.888$ (3) Å³, $Z = 1$, $D_x = 2.19$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71073$ Å, $\mu = 19.9$ cm⁻¹. $T = 290$ K, $F(000) = 806$, $R = 0.034$, $wR = 0.055$ for 4304 observed [$I/\sigma(I) \geq 3.0$] reflections. The unit cell contains a $[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]^{6-}$ complex anion and six $[\text{NH}_3(\text{C}_3\text{H}_7)]^+$ cations. The complex anion is composed of MoO_6 octahedra sharing edges with two formyl groups at two apices of the octahedra.

Introduction. The partial oxidation of hydrocarbons under the catalysis of molybdenum oxides appears to depend upon the ease with which carboxylic acids bind to the oxide surface. On UV irradiation, carboxylated molybdate clusters turn from colourless to reddish brown, resulting in a Mo^{V} EPR signal (Chen, You, Han & Sui, 1988). Because they serve as models of surface complexes, and provide a clue to the photo-reduction mechanism, such organic molybdenum adducts have received renewed attention (MaCarron, Whitney & Chase, 1984). However, little structural information is available for this kind of compound. In this paper, the structure determination of $[\text{NH}_3(\text{C}_3\text{H}_7)]_6[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]$ is described.

Experimental. The preparation method follows Adams, Klemperer & Liu (1979). Slow addition of HCOOH (1.6 ml) to a solution of $[\text{NH}_3(\text{C}_3\text{H}_7)]_6(\text{Mo}_7\text{O}_{24}) \cdot 4\text{H}_2\text{O}$ (9.5 g) in water (20 ml) at 303 K without stirring yields a supersaturated solution from which colourless crystals are deposited after warming the solution to 323 K and allowing it to cool slowly to room temperature. The molecular structure proposed is consistent with IR and elemental analysis. A plate crystal, dimensions $0.15 \times 0.2 \times 0.3$ mm, was selected for data collection.

Data were collected with a CAD-4 four-circle diffractometer in the ω - 2θ mode (with graphite-monochromated $\text{Mo } K\alpha$ radiation). $2^\circ < 2\theta < 50^\circ$. hkl ranges: h -12 to 12; k -12 to -12; l 0-15. Maximum

value of $(\sin\theta)/\lambda$ is 0.59 \AA^{-1} . 4570 unique reflections Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 25 reflections.

The structure was solved by direct methods, using *MULTAN*11/82 (Main *et al.*, 1982), based on 4304 reflections with $I \geq 3\sigma(I)$ (266 unobserved reflections). The intensities were corrected for absorption effects with maximum and minimum transmission factors 99.9% and 77.7% respectively, and then for Lorentz and polarization factors. Programs *PSI* (semi-empirical absorption correction curve) and *EAC* (apply empirical absorption correction to data) were used for empirical absorption correction. Source of programs: North, Phillips & Mathews (1968). All non-H atoms were refined with anisotropic thermal parameters. The H atoms were fixed in their idealized positions. Final refinement was on F by least-squares methods. A weighting scheme of the form $w = 1/[\sigma(I) + (PF)^2]$, with $P = 0.05$, was used, and found to be satisfactory by a weight analysis. Final $R = 0.034$, $wR = 0.055$, with maximum Δ/σ in the final refinement cycle of 0.02. Max. and min. heights in final difference Fourier synthesis, 1.125 and $-0.597 \text{ e \AA}^{-3}$. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1,* and selected bond lengths and angles in Table 2.

Discussion. The structure of $[\text{NH}_3(\text{C}_3\text{H}_7)]_6[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]$ is similar to that of $(\text{NH}_4)_6[\text{Mo}_8\text{O}_{28}(\text{CHO})_2] \cdot 2\text{H}_2\text{O}$. The asymmetric unit consists of a $[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]^{6-}$ anion and six $[\text{NH}_3(\text{C}_3\text{H}_7)]^+$ cations. These constituents are held together by several hydrogen bonds. A view of the $[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]^{6-}$ anion is given in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51392 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Coordinates of non-H atoms ($\times 10^4$) and B_{eq}

	x	y	z	$B_{eq}(\text{\AA}^2)$
Mo(1)	5466.3 (3)	1638.1 (3)	5067.8 (3)	2.204 (7)
Mo(2)	3930.5 (3)	-382.7 (4)	2178.2 (3)	2.944 (8)
Mo(3)	2394.4 (3)	1933.6 (3)	3821.7 (3)	3.191 (8)
Mo(4)	6593.3 (3)	-1306.2 (3)	3354.7 (3)	2.772 (7)
O(1)	4701 (2)	-752 (2)	3833 (2)	2.33 (5)
O(2)	4543 (3)	1709 (3)	3680 (2)	2.73 (6)
O(3)	6939 (3)	1058 (3)	4674 (2)	2.70 (6)
O(4)	3408 (2)	1520 (3)	5196 (2)	2.61 (6)
O(5)	2314 (3)	92 (3)	2807 (2)	3.11 (6)
O(6)	5845 (3)	-451 (3)	2344 (2)	3.11 (6)
O(7)	6003 (3)	3306 (3)	5992 (3)	3.21 (6)
O(8)	3763 (3)	348 (4)	1187 (3)	4.90 (9)
O(9)	3268 (3)	-2063 (3)	1415 (3)	4.22 (8)
O(10)	2253 (4)	2733 (3)	2876 (3)	5.12 (9)
O(11)	839 (3)	1794 (3)	4105 (3)	4.58 (9)
O(12)	6190 (4)	-2957 (3)	2430 (3)	4.68 (8)
O(13)	8278 (3)	-907 (4)	3468 (3)	4.45 (8)
O(14)	3103 (3)	3892 (3)	5192 (3)	4.96 (9)
O(15)	2809 (3)	5958 (3)	6311 (3)	5.08 (9)
C(1)	2492 (5)	4889 (5)	5446 (5)	4.9 (1)
N(11)	8102 (4)	1566 (4)	2710 (3)	3.9 (1)
C(11)	8137 (5)	1172 (4)	1434 (4)	3.8 (1)
C(12)	8717 (5)	-137 (5)	1028 (5)	5.0 (1)
C(13)	8875 (6)	2290 (6)	1263 (5)	5.4 (1)
N(21)	835 (3)	8453 (4)	3513 (3)	3.49 (9)
C(21)	792 (5)	6971 (5)	2808 (4)	4.4 (1)
C(23)	206 (9)	6152 (6)	3438 (6)	8.1 (2)
N(31)	5396 (4)	-4158 (4)	-2552 (4)	5.1 (1)
C(31)	5708 (7)	-3886 (9)	-1343 (6)	11.2 (2)
C(32)	6988 (8)	-4263 (9)	-911 (6)	8.9 (2)
C(33)	4820 (9)	-3310 (10)	-686 (6)	14.0 (3)

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$)

(a) O—Mo—O angles in MoO_6 octahedra					
Mo(1) O_6	O(1)—O(1')	75.39 (9)	Mo(2) O_6	O(1)—O(2)	73.02 (9)
	O(2)	77.4 (1)		O(5)	86.1 (1)
	O(3)	77.5 (1)		O(6)	71.7 (1)
	O(4)	80.6 (1)		O(8)	160.9 (1)
	O(7)	177.4 (1)		O(9)	91.8 (1)
	O(1')—O(2)	141.4 (1)		O(2)—O(5)	73.4 (1)
	O(3)	98.7 (1)		O(6)	85.5 (1)
	O(4)	73.3 (1)		O(8)	91.0 (1)
	O(7)	102.1 (1)		O(9)	160.3 (2)
	O(2)—O(3)	101.5 (1)		O(3)—O(6)	153.1 (1)
	O(4)	75.8 (1)		O(8)	99.6 (2)
	O(7)	104.9 (1)		O(9)	93.5 (1)
	O(3)—O(4)	157.9 (1)		O(6)—O(8)	97.2 (2)
	O(7)	103.1 (1)		O(9)	101.9 (1)
	O(4)—O(7)	98.7 (1)		O(8)—O(9)	105.9 (2)
Mo(3) O_6	O(2)—O(4)	69.5 (1)	Mo(4) O_6	O(1)—O(3)	70.6 (1)
	O(5)	75.3 (1)		O(4)	73.1 (1)
	O(10)	90.4 (2)		O(6)	74.4 (1)
	O(11)	164.4 (2)		O(12)	103.7 (1)
	O(14)	88.7 (1)		O(13)	151.2 (1)
	O(4)—O(5)	89.7 (1)		O(3)—O(4)	80.1 (1)
	O(10)	153.8 (1)		O(6)	78.1 (1)
	O(11)	96.9 (2)		O(12)	174.3 (1)
	O(14)	75.6 (1)		O(13)	80.6 (1)
	O(5)—O(10)	101.8 (1)		O(4)—O(6)	145.3 (1)
	O(11)	97.7 (1)		O(12)	99.1 (1)
	O(14)	161.4 (1)		O(13)	101.4 (2)
	O(10)—O(11)	104.8 (2)		O(6)—O(12)	100.0 (2)
	O(14)	87.5 (2)		O(13)	101.3 (2)
	O(11)—O(14)	95.4 (1)		O(12)—O(13)	105.1 (2)
(b) Bond distances and angle in the —CHO group					
O(14)—C(1)	1.240 (6)				
O(15)—C(1)	1.219 (5)				
O(14)—C(1)—O(15)	127.3 (5)				
(c) Bond distances and angles in the $[\text{NH}_3(\text{C}_3\text{H}_7)]^+$ cations					
N(11)—C(11)	1.515 (6)	N(11)—C(11)—C(12)	108.3 (4)		
C(11)—C(12)	1.501 (7)	N(11)—C(11)—C(13)	111.0 (3)		
C(11)—C(13)	1.469 (8)	N(12)—C(11)—C(13)	113.1 (5)		
N(21)—C(21)	1.487 (6)	N(21)—C(21)—C(22)	111.2 (5)		
C(21)—C(22)	1.512 (7)	N(21)—C(21)—C(23)	108.1 (4)		
C(21)—C(23)	1.54 (1)	N(22)—C(21)—C(23)	110.2 (5)		
N(31)—C(31)	1.414 (9)	N(31)—C(31)—C(32)	115.5 (6)		
C(31)—C(32)	1.47 (1)	N(31)—C(31)—C(33)	118.5 (7)		
C(31)—C(33)	1.37 (1)	C(32)—C(31)—C(33)	126.0 (7)		

The MoO_6 coordination octahedra share edges to form the Mo_8O_{28} group. The bond lengths between the Mo and O atoms shared by two or more neighbouring MoO_6 octahedra [1.756–2.416 (3) \AA] are longer than those between Mo and the unshared O atoms [1.678–1.718 (3) \AA], with the exception of O(14) and Mo(3) (2.124 \AA). The Mo atoms are shifted from the centres of their respective octahedra towards the unshared O atoms owing to the repulsion between the neighbouring Mo^{VI} atoms with large positive charges. In fact, Mo—Mo distances between the edge-sharing octahedra are much longer than the edges of the octahedra, ranging from 3.261–3.467 (1) \AA . To keep the crystal electrically neutral, two —CHO groups must be attached to the MoO_6 group. It was revealed by the structure determination that two —CHO groups are bonded to O(14) and its crystallographic equivalent O(14'). This explains the longer Mo(3)—O(14) distance.

The bond strengths can be derived from the expression $s = (d/1.882)^{-6}$ (Bart & Ragaini, 1979) where d is the bond length in \AA . The bond order (BO) can be evaluated from the expression $\text{BO} = \sum(s)$. The bond strengths and bond orders of the Mo—O interactions are listed in Table 3. The structure of $[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]^{6-}$ $\{ = [\text{Mo}_8\text{O}_{26}(\text{CHOO})_2]^{6-} \}$ is analogous to a number of other octamolybdate anions: $(\text{H}_2\text{Mo}_8\text{O}_{28})^{6-} = [\text{Mo}_8\text{O}_{26}(\text{HO})_2]^{6-}$, $[\text{Mo}_8\text{O}_{26}(\text{C}_5\text{H}_5\text{N})_2]^{4-}$, and the octamolybdate condensation polymer itself, $(\text{Mo}_8\text{O}_{27})_n^{6-} = (\text{Mo}_8\text{O}_{26}\text{O}_{27})_n^{6-}$. A general description of these octamolybdates would be $[\text{Mo}_8\text{O}_{26}(\text{X})_2]^{2n-4}$, where n is the normal charge of the coordinated base X.

All the C—C and C—N bond lengths in the three independent isopropylammonium cations are normal within experimental error. The C—C—N angles are close to the tetrahedral values, whereas the C—C—C angle is significantly larger than 109.5°. All the NH_3 groups act as donors of hydrogen bonds to the O atoms

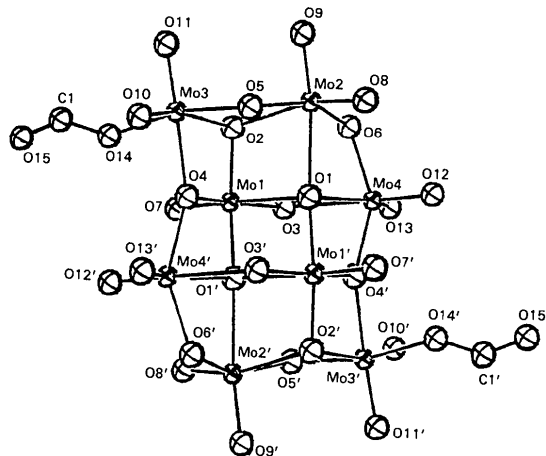
Fig. 1. The structure of the $[\text{Mo}_8\text{O}_{28}(\text{CHO})_2]^{6-}$ anion.

Table 3. Bond distances (Å), strengths and orders (BO) for MoO₆ octahedra

(a) Mo—O distances			
Mo(1)—O(1)	2.416 (2)	Mo(2)—O(1)	2.282 (3)
—O(1')	1.972 (3)	—O(2)	2.274 (2)
—O(2)	1.867 (3)	—O(5)	1.982 (3)
—O(3)	1.756 (3)	—O(6)	1.947 (3)
—O(4)	2.145 (3)	—O(8)	1.694 (4)
—O(7)	1.704 (2)	—O(9)	1.702 (3)
Mo(3)—O(2)	2.266 (3)	Mo(4)—O(1)	2.191 (3)
—O(4)	2.068 (3)	—O(3)	2.402 (2)
—O(5)	1.887 (3)	—O(4)	1.927 (3)
—O(10)	1.699 (4)	—O(6)	1.913 (3)
O(11)	1.705 (3)	—O(12)	1.678 (3)
—O(14)	2.124 (3)	—O(13)	1.718 (3)
(b) Bond strengths and orders			
	<i>s</i>		<i>s</i>
Mo(1)—O(1)	0.203	Mo(2)—O(1)	0.315
—O(1')	0.756	—O(2)	0.321
—O(2)	1.049	—O(5)	0.733
—O(3)	1.516	—O(6)	0.816
—O(4)	0.456	—O(8)	1.880
—O(7)	1.815	—O(9)	1.828
BO	5.815		5.893
	<i>s</i>		<i>s</i>
Mo(3)—O(2)	0.328	Mo(4)—O(1)	0.402
—O(4)	0.568	—O(3)	0.231
—O(5)	0.984	—O(4)	0.868
—O(10)	1.847	—O(6)	0.907
—O(11)	1.809	—O(12)	1.991
—O(14)	1.484	—O(13)	1.728
BO	6.020		6.127

of the polyanions. Thus, the crystal is held together mainly by the three-dimensional hydrogen-bond system. On UV irradiation, the H atoms in appropriate positions form bonds with O atoms, converting Mo^{VI}=O to Mo^V-OH. This causes the colour change from colourless to reddish brown.

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Acta Cryst. (1989). **C45**, 415–418

Structure of the Orthorhombic Form of the Barium Salt of Lasalocid A

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(Received 20 June 1988; accepted 17 October 1988)

Abstract. Ba²⁺·(C₃₄H₅₃O₈)₂²⁻·H₂O, *M_r* = 1334.94, orthorhombic, *P*2₁2₁2₁, *a* = 23.192 (4), *b* = 18.775 (5), *c* = 16.893 (2) Å, *V* = 7356 (2) Å³, *Z* = 4, *D_x* = 1.205 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 5.62 cm⁻¹, *F*(000) = 2832, *T* = 294 K, *R* = 0.047 for 4125 observed reflections. The salt, which was prepared from aqueous acetone, forms a 'head-to-tail' dimer having a pseudo twofold symmetry, with the polar oxygen groups directed towards the interior of the molecule to wrap the metal ion and the non-polar groups towards the exterior. The metal ion is ninefold coordinated by eight oxygen atoms of the two crystallographically independent ionophores and a water molecule, with the metal—O distances in the range 2.631 (5)–3.022 (5) Å.

Introduction. Antibiotic lasalocid A (1) is a naturally occurring ionophore which has been most extensively studied by X-ray diffraction methods (Duesler & Paul, 1983). A feature of special interest in lasalocid A's structural chemistry is its propensity to form a variety of structures: monomers, 'head-to-tail' or 'head-to-head' dimers, or polymers. In order to reveal further the whole structural aspects of lasalocid A to explain the mechanisms of metal ion uptake and release by lasalocid A, we have tried to prepare variable metal complexes from solvents of different polarity, since the solvent conditions used for crystallization are important factors affecting lasalocid A structures (Duesler & Paul, 1983). We report here the structure of a barium salt crystallized in the orthorhombic form from aqueous acetone. The 'head-to-tail' dimeric structure with a pseudo twofold symmetry is essentially the same as that

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