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The Crystal Structure of Hexakis(isopropylammonium) Dihydrogenoctamolybdate(6−) Dihydrate, $(C_3H_{10}N)_6[H_2Mo_8O_{28}].2H_2O$

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$(C_3H_{10}N)_6[H_2Mo_8O_{28}].2H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 10{\cdot}66$ (1), $b = 12{\cdot}29$ (1), $c = 9{\cdot}65$ (2) Å, $\alpha = 104{\cdot}6$ (2), $\beta = 82{\cdot}1$ (5), $\gamma = 96{\cdot}5$ (2)° and $Z = 1$. The structure was determined by the heavy-atom method and refined by the least-squares method to $R = 0{\cdot}033$ for 4511 observed reflexions. The unit cell contains a $[H_2Mo_8O_{28}]^{6-}$ complex anion, six $(C_3H_{10}N)^+$ cations and two water molecules. The $[H_2Mo_8O_{28}]^{6-}$ anion is composed of MoO_6 octahedra sharing edges (with two protons at two apices of octahedra) and belongs to a new structural family of octamolybdate isopolyanions.

Introduction

Crystals of the title compound, obtained from an aqueous solution of isopropylamine and ammonium heptamolybdate, are colourless and transparent, but turn reddish violet on exposure to ultraviolet rays; they are bleached again on heating. ESR measurements suggested that a reduction of some of the Mo^{VI} ions to Mo^V is responsible for the induction of a colour centre (Yamase, Hayashi & Ikawa, 1974). In order to obtain a clue to the reduction mechanism, the structure determination of this substance has been undertaken.

Experimental

The symmetry and approximate cell dimensions of the crystals were determined from oscillation and Weissenberg photographs. The more accurate cell dimensions were obtained by least-squares calculations based on the 2θ values of 19 reflexions measured on a Philips automated four-circle diffractometer (Mo $K\alpha$ radiation). The crystal data are in Table 1.

Intensities were measured with a crystal of dimensions 0·1 × 0·1 × 0·1 mm on the Philips four-circle diffractometer in the ω–2θ mode (with graphite-monochromated Mo $K\alpha$ radiation). Of the 5814 reflexions

Table 1. *Crystal data*

$(C_3H_{10}N)_6[H_2Mo_8O_{28}].2H_2O$		a	10·66 (1) Å
FW	806·2	b	12·29 (1)
Crystal system	Triclinic	c	9·65 (2)
Space group	$P\bar{1}$	α	104·6 (2)°
Z	1	β	82·1 (5)
D_x	2·22 g cm^{-3}	γ	96·5 (2)
μ(Mo $K\alpha$)	20·6 cm^{-1}	V	1207 (2) Å^3

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scanned within the range $2\theta < 56°$, 4559 with $|F| > 3\sigma$ were used for the structure analysis. However, 48 of the 4559 reflexions were rejected during the structure refinement, since they were found to have been systematically allotted values too small owing to a sudden change in the orientation of the specimen during the measurement. The intensities were corrected for Lorentz and polarization factors, but no corrections were made for absorption or extinction effects.

Structure determination

The structure was solved by the heavy-atom method. The Mo atoms were easily located from the Patterson function, and the remaining non-hydrogen atoms were located from a series of difference Fourier syntheses. The positions of the non-hydrogen atoms obtained were refined by the full-matrix least-squares procedure, with first isotropic and then anisotropic thermal motion being assumed. A difference Fourier synthesis at this stage revealed 24 H atoms of the 33 atoms in the asymmetric unit, the positional and isotropic thermal parameters of these atoms being refined in the later cycles. The final conventional R value was 0·033 for the 4511 reflexions. Unit weight was given to all reflexions. The atomic scattering factors for Mo, N, C and O, and the corrections for anomalous scattering of Mo were taken from *International Tables for X-ray Crystallography* (1962). For H, the values given by Stewart, Davidson & Simpson (1965) were used. The final atomic parameters are listed in Table 2.* Selected bond lengths and angles are listed in Table 3 together with their estimated standard deviations.

Description of the structure and discussion

The crystal structure viewed along the c axis is shown in Fig. 1. The repeat unit consists of a $[H_2Mo_8O_{28}]^{6-}$ anion, six $(C_3H_{10}N)^+$ cations and two water molecules. These constituents are held together by several hydrogen bonds. A schematic drawing of the structure of the $[H_2Mo_8O_{28}]^{6-}$ anion is given in Fig. 2, neglecting the two H atoms. All the Mo atoms are octahedrally surrounded by O atoms, and the MoO_6 coordination octahedra are joined together by sharing edges to form the Mo_8O_{28} group. As shown in Table 3, the bond lengths between the Mo and O atoms shared by two or more neighbouring MoO_6 octahedra (1·77–2·41 Å) are longer than those between the Mo and unshared O atoms (1·70–1·73 Å), with the exception of Mo(4)–O(6^{i}) (1·97 Å). The Mo atoms are shifted from the centres of their respective octahedra towards the unshared O atoms owing to the repulsion between

Table 2. *Final atomic parameters*

(*a*) Non-hydrogen atoms (×10⁴)

	x	*y*	*z*
Mo(1)	3008 (1)	3285 (1)	3979 (1)
Mo(2)	5367 (1)	2332 (1)	5049 (1)
Mo(3)	5471 (1)	4958 (1)	3200 (1)
Mo(4)	7167 (1)	4014 (1)	7388 (1)
O(1)	1384 (4)	3296 (4)	4380 (5)
O(2)	3232 (5)	2347 (4)	2333 (5)
O(3)	3521 (4)	2333 (3)	5053 (4)
O(4)	3017 (4)	4565 (3)	6261 (4)
O(5)	3438 (4)	4668 (3)	3385 (4)
O(6)	3334 (5)	4908 (4)	778 (4)
O(7)	5276 (5)	1349 (4)	6060 (5)
O(8)	5739 (4)	1608 (4)	3292 (5)
O(9)	5025 (4)	3721 (3)	7130 (4)
O(10)	5016 (4)	3883 (3)	4402 (4)
O(11)	5781 (4)	4085 (4)	1529 (4)
O(12)	7049 (5)	2931 (4)	8248 (5)
O(13)	6997 (4)	3087 (4)	5419 (4)
O(14)	8749 (4)	4394 (4)	7041 (6)
O(*WA*)	5982 (6)	1497 (4)	199 (6)
C(1)	2518 (7)	2075 (6)	9211 (7)
C(2)	2752 (10)	841 (7)	8525 (11)
C(3)	1820 (8)	2615 (8)	8323 (9)
C(4)	7922 (8)	475 (7)	6961 (10)
C(5)	8823 (9)	−45 (9)	7684 (12)
C(6)	8203 (12)	280 (12)	5362 (12)
C(7)	8643 (8)	3298 (7)	2224 (8)
C(8)	9097 (10)	2141 (7)	2024 (11)
C(9)	9149 (10)	3900 (8)	1041 (9)
N(1)	3785 (6)	2735 (5)	9453 (6)
N(2)	6574 (6)	44 (5)	7329 (7)
N(3)	8997 (6)	4027 (5)	3669 (6)

(*b*) Hydrogen atoms (×10³, except *B*)

The H atoms bonded to C(5), C(6) and N(2) were not revealed.

	x	*y*	*z*	*B* (Å²)
H(C1)	204 (8)	206 (7)	1001 (9)	5·2 (19)
H(C2)1	331 (8)	60 (7)	929 (8)	6·3 (19)
H(C2)2	207 (8)	56 (7)	853 (9)	6·5 (19)
H(C2)3	322 (8)	78 (7)	757 (9)	6·3 (19)
H(C3)1	97 (8)	227 (7)	832 (8)	3·3 (19)
H(C3)2	186 (7)	339 (7)	891 (9)	5·2 (19)
H(C3)3	234 (8)	253 (7)	749 (9)	4·9 (19)
H(N1)1	377 (8)	350 (7)	984 (9)	5·4 (19)
H(N1)2	400 (8)	278 (7)	840 (9)	7·2 (19)
H(N1)3	421 (7)	237 (7)	995 (8)	5·5 (19)
H(C4)	796 (7)	138 (7)	743 (8)	4·2 (19)
H(C7)	755 (8)	324 (7)	229 (8)	6·2 (19)
H(C8)1	996 (8)	223 (7)	210 (8)	7·6 (19)
H(C8)2	865 (8)	200 (7)	282 (9)	6·3 (19)
H(C8)3	867 (8)	179 (7)	128 (9)	7·3 (19)
H(C9)1	1000 (8)	388 (7)	130 (9)	6·9 (19)
H(C9)2	896 (8)	338 (7)	17 (9)	4·5 (19)
H(C9)3	878 (8)	450 (7)	130 (9)	7·4 (19)
H(N3)1	881 (8)	475 (7)	378 (8)	5·9 (19)
H(N3)2	972 (8)	393 (7)	389 (9)	5·6 (19)
H(N3)3	863 (8)	365 (7)	436 (9)	6·4 (19)
H(*WA*)1	642 (7)	211 (7)	0 (9)	6·7 (19)
H(*WA*)2	585 (7)	155 (7)	133 (8)	6·3 (19)
H(O6)	344 (8)	519 (7)	8 (8)	4·9 (19)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33541 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances* (Å) *and bond angles* (°)

(*a*) Mo–O bond distances

Mo(1)–O(1)	1·721 (6)	Mo(3)–O(4^{i})	1·754 (6)
–O(2)	1·716 (6)	–O(5)	2·146 (5)
–O(3)	1·912 (6)	–O(9^{i})	1·875 (5)
–O(4)	2·362 (7)	–O(10)	1·950 (6)
–O(5)	1·916 (5)	–O(10^{i})	2·414 (8)
–O(10)	2·241 (6)	–O(11)	1·708 (6)
Mo(2)–O(3)	1·967 (5)	Mo(4)–O(5^{i})	2·138 (6)
–O(7)	1·720 (6)	–O(6^{i})	1·972 (7)
–O(8)	1·719 (7)	–O(9)	2·308 (5)
–O(9)	2·300 (8)	–O(12)	1·722 (6)
–O(10)	2·233 (5)	–O(13)	1·975 (6)
–O(13)	1·910 (6)	–O(14)	1·709 (6)

(*b*) O–O distances and O–Mo–O angles in MoO_6 octahedra

Mo(1)O_6	O(1)–O(2)	2·72 (1)	104·9 (5)
	–O(3)	2·90 (1)	105·8 (4)
	–O(4)	2·76 (1)	83·8 (5)
	–O(5)	2·82 (1)	101·6 (3)
	O(2)–O(3)	2·69 (1)	95·5 (3)
	–O(5)	2·77 (1)	99·3 (3)
	–O(10)	3·08 (1)	101·5 (5)
	O(3)–O(4)	2·78 (1)	80·4 (2)
	–O(10)	2·49 (1)	73·2 (3)
	O(4)–O(5)	2·78 (1)	80·4 (2)
	–O(10)	2·65 (1)	70·4 (5)
	O(5)–O(10)	2·45 (1)	71·9 (3)
Mo(2)O_6	O(3)–O(7)	2·74 (1)	95·7 (4)
	–O(8)	2·81 (1)	98·9 (5)
	–O(9)	2·84 (1)	82·9 (5)
	–O(10)	2·49 (1)	72·4 (3)
	O(7)–O(8)	2·74 (1)	105·6 (3)
	–O(9)	2·87 (1)	89·8 (2)
	–O(13)	2·79 (1)	100·3 (4)
	O(8)–O(10)	2·88 (1)	92·7 (3)
	–O(13)	2·77 (1)	99·1 (5)
	O(9)–O(10)	2·69 (1)	72·8 (2)
	–O(13)	2·55 (1)	73·9 (4)
	O(10)–O(13)	2·81 (1)	85·0 (3)
Mo(3)O_6	O(4^{i})–O(9^{i})	2·79 (1)	100·5 (3)
	–O(10)	2·79 (1)	97·6 (3)
	–O(10^{i})	2·65 (1)	77·3 (4)
	–O(11)	2·73 (1)	103·9 (4)
	O(5)–O(9^{i})	2·53 (1)	77·6 (3)
	–O(10)	2·45 (1)	73·5 (3)
	–O(10^{i})	2·97 (1)	81·2 (5)
	–O(11)	2·91 (1)	97·3 (5)
	O(9^{i})–O(10^{i})	2·69 (1)	76·5 (2)
	–O(11)	2·85 (1)	105·4 (3)
	O(10)–O(10^{i})	2·70 (1)	75·6 (2)
	–O(11)	2·84 (1)	101·8 (3)
Mo(4)O_6	O(5^{i})–O(6^{i})	2·62 (1)	79·2 (2)
	–O(9)	2·53 (1)	69·2 (3)
	–O(13)	2·77 (1)	84·7 (3)
	–O(14)	2·83 (1)	94·2 (3)
	O(6^{i})–O(9)	2·93 (1)	85·9 (5)
	–O(12)	2·64 (1)	91·1 (3)
	–O(14)	2·88 (2)	103·0 (5)
	O(9)–O(12)	2·90 (1)	90·8 (4)
	–O(13)	2·55 (1)	72·7 (5)
	O(12)–O(13)	2·79 (1)	97·9 (2)
	–O(14)	2·76 (1)	107·1 (4)
	O(13)–O(14)	2·72 (1)	94·8 (5)

Table 3 (*cont.*)

(*c*) Bond distances and angles in $(C_3H_{10}N)^+$ cations

C(1)–C(2)	1·53 (1)	C(2)–C(1)–C(3)	114·2 (7)
C(1)–C(3)	1·52 (1)	C(2)–C(1)–N(1)	108·5 (7)
C(1)–N(1)	1·51 (1)	C(3)–C(1)–N(1)	109·1 (7)
C(4)–C(5)	1·54 (2)	C(5)–C(4)–C(6)	115·0 (9)
C(4)–C(6)	1·49 (1)	C(5)–C(4)–N(2)	109·8 (8)
C(4)–N(2)	1·50 (1)	C(6)–C(4)–N(2)	109·2 (9)
C(7)–C(8)	1·51 (1)	C(8)–C(7)–C(9)	115·5 (8)
C(7)–C(9)	1·52 (1)	C(8)–C(7)–N(3)	108·3 (8)
C(8)–N(3)	1·53 (1)	C(9)–C(7)–N(3)	109·4 (7)

The superscript (i) refers to the symmetry position $(1-x, 1-y, 1-z)$.

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 3·27 to 3·49 Å. To keep the crystal electrically neutral, two protons must be attached to the Mo_8O_{28} group. It was revealed from the difference Fourier map that these protons are bonded to O(6) and its crystallographic equivalent, O(6^{i}). This explains the longer Mo(4)–O(6^{i}) distance.

Several kinds of isopolymolybdate anions have so far been reported; among these, $[Mo_8O_{26}]^{4-}$ (Lindqvist, 1950) and $[Mo_7O_{24}]^{6-}$ (Evans, 1968) are known as examples of discrete polyanions. If we disregard the two H atoms, the $[H_2Mo_8O_{28}]^{6-}$ anion in this crystal is constructed from eight MoO_6 octahedra sharing edges, as in the case of $[Mo_8O_{26}]^{4-}$. However, the configurations of the MoO_6 octahedra are quite different in these two anions. The same type of arrangement of

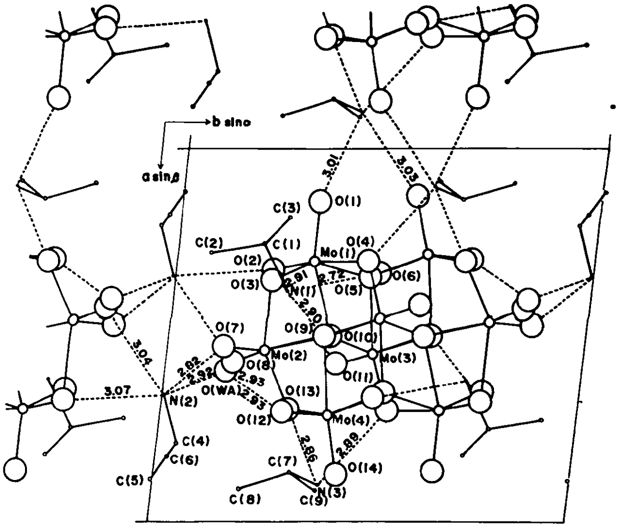

Fig. 1. The crystal structure viewed down the *c* axis. Hydrogen bonds are indicated as broken lines.

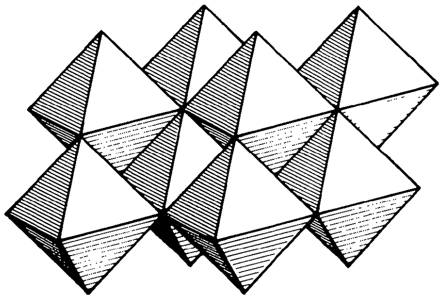
Fig. 2. The linkage of MoO_6 octahedra in the Mo_8O_{28} group.

MoO_6 as in $[H_2Mo_8O_{28}]^{6-}$ is found in an infinite chain of Mo_8O_{27} in crystals of $(NH_4)_6Mo_8O_{27}.4H_2O$ (Boschen, Buss & Krebs, 1974). The chain is constructed from the Mo_8O_{28} groups by sharing O atoms, corresponding to O(6) and its crystallographic equivalent in $[H_2Mo_8O_{28}]^{6-}$, of neighbouring groups.

All the C—C and C—N bond lengths in the three independent isopropylammonium cations are normal within experimental error. In each cation, 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 of the polyanions and/or to water molecules. The water molecules are also bonded to the polyanion by weak hydrogen bonds. Thus, the crystal is held together mainly by the three-dimensional hydrogen-bond system shown with broken lines in Fig. 1.

When the crystals are irradiated with ultraviolet rays, some of the Mo^{VI} ions are reduced to Mo^{V}. ESR spectra of the irradiated crystals exhibit three hyperfine lines (1:2:1) owing to a superhyperfine interaction with two magnetically-equivalent H atoms (Yamase, 1978). The structure obtained suggests that the paramagnetic centre is produced at the Mo(4) site where a hydroxide group was originally coordinated, and that the two magnetically equivalent H atoms are probably bound to $O(6^i)$ and O(13) in positions *trans* to each other in the $Mo(4)O_6$ octahedron. A detailed discussion of the reduction mechanism is given elsewhere (Yamase, 1978).

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A Redetermination of the Crystal Structures of α-Calcium Formate, α-Strontium Formate and Barium Formate by X-ray Analyses

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The crystal structure of α-calcium formate was refined to $R = 0{\cdot}022$, and the result affords a good complement to the neutron analysis on the same compound [Burger, Fuess & Mason (1977). *Acta Cryst.* B**33**, 1968–1970]. The crystal structures of α-strontium formate and barium formate reported by previous workers were revised and refined to $R = 0{\cdot}034$ and 0·027 respectively. These two formates are not isostructural, but the crystal structure of barium formate can be approximately transformed to that of α-strontium formate by a reorientation of one of the two independent formate groups in the asymmetric unit. The numbers of O atoms around the cations are (7 + 1) for α-calcium formate, 8 for α-strontium formate, and (8 + 1) for barium formate, where the additional terms are the number of O atoms situated at greater distances. The mean interatomic distances between the cations and their immediate neighbours are 2·421 Å for Ca^{2+}—O, 2·613 Å for Sr^{2+}—O, and 2·794 Å for Ba^{2+}—O.