

Structure of Pentapotassium Dihydrogenhexamolybdoantimonate Heptahydrate

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Abstract. $K_5[H_2SbMo_6O_{24}] \cdot 7H_2O$, $M_r = 1405 \cdot 1$, monoclinic, $P2_1/a$, $a = 20 \cdot 783$ (4), $b = 10 \cdot 105$ (1), $c = 15 \cdot 085$ (2) Å, $\beta = 112 \cdot 15$ (1)°, $U = 2934$ (1) Å³, $Z = 4$, $D_m = 3 \cdot 20$, $D_x = 3 \cdot 18$ Mg m⁻³, $\lambda(Mo K\alpha) = 0 \cdot 71069$ Å, $\mu = 4 \cdot 16$ mm⁻¹, $F(000) = 2648$, $T = 298$ K, $R = 0 \cdot 057$ for 5889 unique reflections. The structure contains the discrete polyanion $[H_2SbMo_6O_{24}]^{5-}$, the configuration of which differs from that of $[TeMo_6O_{24}]^{6-}$ and $[IMo_6O_{24}]^{5-}$, but is identical to that of $[Mo_7O_{24}]^{6-}$. Two polyanion molecules are paired by hydrogen bonds, and the positions of the H atoms were estimated from anomalies in Mo–O distances.

Introduction. We obtained four new heteropolyanions containing Sb^v and Mo^{vi}: $K_5[H_2SbMo_6O_{24}] \cdot 7H_2O$, $K_6[H_2Sb_6Mo_4O_{36}] \cdot 7H_2O$, $(NH_4)_7[H_{10}Sb_5Mo_5O_{36}] \cdot nH_2O$ and $K_6[H_{12}Sb_4Mo_{10}O_{50}] \cdot 8H_2O$; their crystal structures have been determined. Sb^vO₆ coordination has been expected to develop a novel stereochemistry for the heteropolyoxometallates, because no example of an Sb^vO₄ tetrahedron has so far been reported, whereas most oxo compounds of pentavalent P and As assume fourfold coordination. There is, therefore, no analogy between the molybdoantimonates and -phosphates or -arsenates. Because hexamolybdoantimonate is structurally different from the other three, we report it here separately.

Experimental. Hot aqueous solution containing $KSb(OH)_6$ and K_2MoO_4 in the ratio 1:6, pH 5–6 adjusted by adding 2M HCl at ca 323 K; monoclinic crystals isolated at room temperature; colourless single crystal with dimensions 0.1 × 0.3 × 0.3 mm mounted on a Rigaku automated four-circle diffractometer, graphite-monochromated Mo K α , data collected up to $2\theta = 60^\circ$, $0 < h < 18$, $0 < k < 8$, $0 < l < 10$, θ - 2θ scan mode; three standard reflections varied within $\pm 3\%$. Lorentz and polarization effects were corrected, but no absorption correction was made. Of 7607 reflections,

5889 independent with $|F| > 3\sigma(|F|)$ used for structure analysis. From Patterson function one Sb and six Mo atoms were located and successive Fourier syntheses gave all non-hydrogen atoms. Refinement was on all atoms with anisotropic thermal parameters by block-diagonal least squares. $R = 0 \cdot 057$ and $S = 1 \cdot 40$ for 5889 unique reflections; no significant peaks higher than $0 \cdot 2 e \text{ \AA}^{-3}$ in final difference map; unit-weight minimization of F ; complex atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on a HITAC M200-H/M280-H computer at the Computer Centre of the University of Tokyo, using UNICSIII (Sakurai & Kobayashi, 1979). Atomic parameters are listed in Table 1. §

Discussion. All the atoms are at general positions. Fig. 1 shows the structure of the polyanion molecule, and relevant interatomic distances are given in Table 2. The configuration of the hexamolybdoantimonate ion has been assumed from its constitution to be identical to that of $[TeMo_6O_{24}]^{6-}$ (Evans, 1974) or $[IMo_6O_{24}]^{5-}$ (Kondo, Kobayashi & Sasaki, 1980), where all the metal atoms are coplanar. However, this determination proved that $[H_2SbMo_6O_{24}]^{5-}$ takes the same 'bent' structure as the well known $[Mo_7O_{24}]^{6-}$ (Sjöbom & Hedman, 1973). The O atoms may be classified into five groups with respect to their coordination numbers. Two O atoms, namely O(S135) and O(S246), are shared by Sb and three Mo atoms, and another two O atoms coordinate to Sb and two Mo atoms. Of the eight O atoms shared by two metal atoms, two connect Sb and Mo, and the others bridge two Mo atoms. The remaining twelve O atoms are bonded to only one Mo atom to form a *cis* terminal coordination. A total of 24 O atoms make up an approximate hexagonal closest packing. Mo–O distances vary from 1.71 to 2.47 Å, while Sb–O vary from 1.95 to 2.01 Å. Each MoO₆ octahedron can be described as having (2+2+2)

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§ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51126 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and equivalent isotropic thermal parameters; fractional coordinates are multiplied by 10⁴, except for Sb and Mo by 10⁵

$$B_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B _{eq} (Å ²)
Sb	-1178 (3)	4171 (6)	32760 (4)	0.8
Mo(1)	3323 (4)	-26611 (8)	39587 (6)	1.1
Mo(2)	-12932 (4)	-19647 (8)	25596 (6)	1.1
Mo(3)	10783 (4)	3303 (8)	22991 (6)	1.0
Mo(4)	-5396 (5)	8594 (9)	9495 (6)	1.1
Mo(5)	15415 (4)	-3913 (9)	45770 (6)	1.1
Mo(6)	-17916 (5)	10318 (9)	17756 (7)	1.3
K(1)	1964 (2)	6549 (3)	2899 (2)	2.4
K(2)	-891 (2)	4404 (3)	3485 (2)	2.3
K(3)	2406 (2)	-470 (3)	1216 (2)	2.8
K(4)	1429 (2)	3360 (3)	4696 (2)	3.1
K(5)	-1346 (2)	6970 (3)	-187 (2)	3.2
O(S135)	621 (4)	-869 (7)	3274 (5)	1.1
O(S246)	-829 (4)	-254 (7)	2045 (5)	1.0
O(S12)	-448 (4)	-1066 (7)	3851 (5)	1.0
O(S34)	198 (4)	1476 (7)	2434 (5)	1.1
O(12)	-420 (4)	-2906 (7)	2745 (5)	1.3
O(34)	245 (3)	-286 (7)	1267 (5)	1.2
O(15)	973 (4)	-1560 (7)	5006 (5)	1.3
O(26)	-1848 (3)	-421 (7)	2571 (5)	1.2
O(35)	1581 (4)	855 (7)	3629 (5)	1.2
O(46)	-1201 (4)	1975 (7)	1295 (5)	1.3
O(S5)	596 (4)	1074 (7)	4468 (5)	1.3
O(S6)	-847 (4)	1664 (7)	3290 (5)	1.3
O(1)a	46 (5)	-3605 (8)	4684 (6)	2.0
O(1)b	933 (4)	-3610 (8)	3715 (6)	2.0
O(2)a	-1610 (5)	-3013 (8)	3206 (7)	2.3
O(2)b	-1696 (4)	-2455 (8)	1392 (6)	1.9
O(3)a	1324 (4)	1604 (8)	1749 (6)	2.0
O(3)b	1595 (4)	-981 (8)	2267 (6)	2.0
O(4)a	-315 (5)	2167 (9)	386 (6)	2.6
O(4)b	-1136 (4)	-88 (9)	56 (6)	2.0
O(5)a	1981 (4)	532 (9)	5572 (6)	2.1
O(5)b	2123 (4)	-1558 (8)	4506 (6)	1.9
O(6)a	-2220 (5)	2312 (9)	2074 (7)	2.7
O(6)b	-2391 (4)	441 (9)	697 (6)	2.0
Ow(1)	183 (6)	4032 (9)	2918 (9)	3.7
Ow(2)	-1252 (6)	4696 (9)	1340 (8)	3.5
Ow(3)	1814 (6)	3860 (10)	3073 (8)	3.9
Ow(4)	14 (6)	6888 (9)	1232 (7)	3.0
Ow(5)	1903 (5)	5851 (10)	5780 (7)	3.0
Ow(6)	1764 (6)	6844 (11)	947 (7)	3.5
Ow(7)	621 (6)	4431 (11)	1107 (9)	4.0

(1.75 and 1.76 Å). The sum of the bond valences (Brown & Altermatt, 1985) about the O atoms is estimated to be close to 2.0, the largest deviation being 1.2 for O(S5) and O(S6) in this structure. This indicates that the neutralization of charge is not sufficient for O(S5) and O(S6). On the other hand, as shown in Fig. 2, O(S5)—O(S12)' and O(S6)—O(15)' are shown to be the shortest (2.7 Å) among the O—O intermolecular contacts of polyanions. Therefore, hydrogen bonds may exist, and we presume that the H atoms bond to O(S5) and O(S6). By this interaction the two anion molecules are paired, lowering the molecular

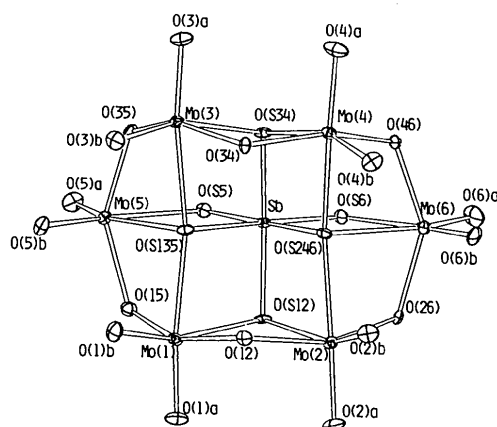


Fig. 1. ORTEP (Johnson, 1976) view of the [H₂SbMo₆O₂₄]⁵⁻ anion. The thermal ellipsoids are scaled to enclose 30% probability.

Table 2. Interatomic distances (Å) in [H₂SbMo₆O₂₄]⁵⁻

Sb—Mo(1)	3.299 (1)	Sb—Mo(2)	3.307 (1)	Sb—Mo(3)	3.335 (1)
Sb—Mo(4)	3.311 (1)	Sb—Mo(5)	3.363 (1)	Sb—Mo(6)	3.417 (1)
Mo(1)—Mo(2)	3.315 (1)	Mo(3)—Mo(4)	3.252 (1)	Mo(1)—Mo(5)	3.268 (1)
Mo(2)—Mo(6)	3.274 (1)	Mo(3)—Mo(5)	3.282 (1)	Mo(4)—Mo(6)	3.286 (2)
Mo(1)—Mo(3)	4.554 (1)	Mo(2)—Mo(4)	4.401 (1)		
Sb—O(S135)	2.013 (8)	Sb—O(S246)	2.006 (6)	Sb—O(S12)	1.979 (8)
Sb—O(S34)	1.954 (9)	Sb—O(S5)	1.966 (6)	Sb—O(S6)	1.977 (8)
Mo(1)—O(S135)	2.275 (8)	Mo(1)—O(S12)	2.249 (8)	Mo(1)—O(12)	1.923 (6)
Mo(1)—O(15)	1.980 (7)	Mo(1)—O(1)a	1.718 (10)	Mo(1)—O(1)b	1.720 (9)
Mo(2)—O(S246)	2.255 (8)	Mo(2)—O(S12)	2.264 (6)	Mo(2)—O(12)	1.973 (8)
Mo(2)—O(26)	1.944 (7)	Mo(2)—O(2)a	1.729 (11)	Mo(2)—O(2)b	1.714 (8)
Mo(3)—O(S135)	2.364 (9)	Mo(3)—O(S34)	2.238 (9)	Mo(3)—O(34)	1.944 (6)
Mo(3)—O(35)	1.954 (7)	Mo(3)—O(3)a	1.710 (9)	Mo(3)—O(3)b	1.718 (9)
Mo(4)—O(S246)	2.260 (9)	Mo(4)—O(S34)	2.273 (6)	Mo(4)—O(34)	1.908 (7)
Mo(4)—O(46)	1.993 (9)	Mo(4)—O(4)a	1.728 (10)	Mo(4)—O(4)b	1.735 (8)
Mo(5)—O(S135)	2.218 (6)	Mo(5)—O(S5)	2.416 (8)	Mo(5)—O(15)	1.946 (9)
Mo(5)—O(35)	1.930 (8)	Mo(5)—O(5)a	1.710 (8)	Mo(5)—O(5)b	1.720 (9)
Mo(6)—O(S246)	2.290 (8)	Mo(6)—O(S6)	2.470 (6)	Mo(6)—O(26)	1.928 (8)
Mo(6)—O(46)	1.900 (9)	Mo(6)—O(6)a	1.724 (11)	Mo(6)—O(6)b	1.740 (8)

coordination (Wells, 1975); thus the polyanion is referred to as type II (Pope, 1983). The change in Mo—O distance depends on the coordination number of the O atom, except that Mo(1)—O(S5) and Mo(2)—O(S6) are much longer than all the other Mo—O bonds. Corresponding Mo—O distances in [Mo₇O₂₄]⁶⁻ exceed 2.5 Å; however, those on opposite sides are very short

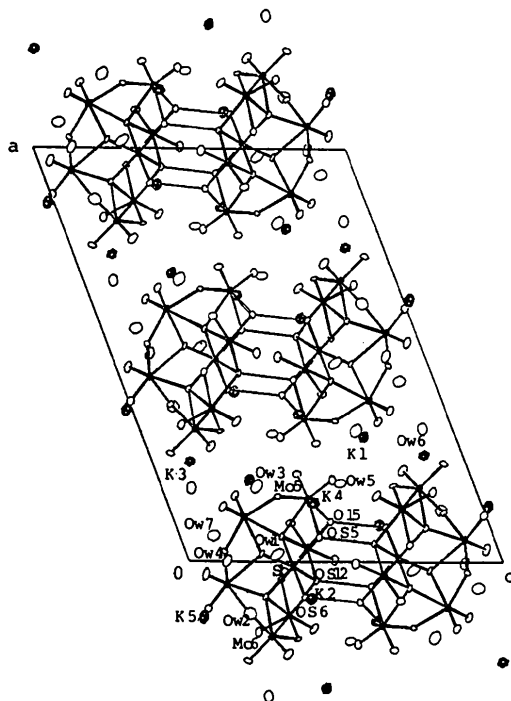


Fig. 2. Structure projected along b, showing anion-anion contacts.

symmetry from C_{2v} to C_1 . Recently, $[\text{SbW}_6\text{O}_{24}]^{7-}$ (Lee & Sasaki, 1987) has been shown to adopt D_{3d} symmetry and to have the same structure as $[\text{TeMo}_6\text{O}_{24}]^6$. It is not definite which configuration the proton-free anion $[\text{SbMo}_6\text{O}_{24}]^{7-}$ should take. However, the distribution of Mo—O distances and the estimated positions of the H atoms favour this 'bent' structure for the protonated form $[\text{H}_2\text{SbMo}_6\text{O}_{24}]^{5-}$.

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Die Struktur des Erdalkalimetall-Oxocuprats, $M_{10}\text{Cu}_{17}\text{O}_{29}$

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Abstract. Bismuth calcium copper strontium oxide, $\text{Bi}_{0,31}\text{Ca}_{5,64}\text{Sr}_{4,05}\text{Cu}_{17}\text{O}_{29}$, $M_r = 2189,95$, incommensurate composite crystal, orthorhombic, approximate space group $F222$, $a = 12,811(2)$, $b = 11,3446(5)$, $c = 5 \times 3,9035(2)$ [$\approx 7 \times 2,755(2)$] Å, $V = 2836,6(4)$ Å³, $Z = 4$, $D_x = 5,128$ Mg m⁻³, $\lambda(\text{Mo } K\alpha_1) = 0,70930$ Å, $\mu = 22,8$ mm⁻¹, $F(000) = 4069,72$, $T = 295$ K, final $R = 0,024$ for 1006 unique observed reflections. Zigzag chains (unit length 3,9035 Å) of edge-shared CuO_4 squares are connected through common corners to form a plane net of Cu_2O_3 parallel to (100). Between the Cu_2O_3 nets, straight chains (unit length 2,755 Å) of edge-shared CuO_4 squares run parallel to [001]. Counter ions are accommodated between the net and the straight chain of cuprate groups. Bi is not an essential element of the compound.

Einleitung. Um Einkristalle des Supraleiters im System Bi–Sr–Ca–Cu–O (Maeda, Tanaka, Fukutomi & Asano, 1988) herzustellen, wurde ein Gemisch von $\text{Bi}_2\text{O}_3 + 2\text{SrCO}_3 + 2\text{CaCO}_3 + 6\text{CuO}$ bis zu 1273 K erhitzt und langsam gekühlt. In der Reaktionsmasse fanden wir neben den glimmerartigen Kristallen des Supraleiters gut ausgebildete prismatische Kristalle der vorliegenden Verbindung. Eine Analyse mit der

Elektronenmikroskopie EMX-SM7 der Fa. Shimadzu ergab die Werte Cu 46,89, Sr 15,38, Ca 9,82 und Bi 2,78 Gew.-%, die zu einer Formel wie $\text{Ca}_{5,64}\text{Sr}_{4,05}\text{Bi}_{0,31}\text{Cu}_{17}\text{O}_y$ führten. Im wesentlichen handelt es sich hierbei um einen Mischkristall der Oxocuprate $M_{10}\text{Cu}_{17}\text{O}_y$ mit Ca und Sr als M-Element. Röntgenographisch erwies sich der Kristall als ein Kompositkristall aus zwei Teilen, die zueinander nicht kommensurable Perioden parallel [001] aufweisen. Da die Satellitenreflexe sehr schwach waren, erfolgte eine Strukturbestimmung nach der gewöhnlichen Methode. Als ein weiteres Beispiel derartiger Kristalle soll hier 'LaCrS₃' genannt werden (Kato, Kawada & Takahashi, 1977; Otero-Diaz, FitzGerald, Williams & Hyde, 1985).

Experimentelles. Abmessung des röntgenographisch untersuchten Kristalls 0,10 × 0,11 × 0,56 mm. Gitterparameter aus 2θ -Werten ($69 < 2\theta < 90^\circ$) von 25 Reflexen des 3,9035 Å-Gitters und 12 Reflexen des 2,755 Å-Gitters gemessen auf Einkristalldiffraktometer AFC-5 der Fa. Rigaku. Intensitäten von 3851 Reflexen mit $l \equiv 0 \pmod{5}$ oder $l \equiv 0 \pmod{7}$ bis zu $(\sin\theta)/\lambda = 0,997$ Å⁻¹ gemessen auf dem gleichen Diffraktometer, Indexgrenzen $-25 \leq h \leq 25$, $-22 \leq k \leq 22$, $0 \leq l \leq 30$; ω -Scan für $2\theta < 30^\circ$, $\omega/2\theta$ -Scan für $2\theta \geq 30^\circ$, Scan-Breite und -Geschwindigkeit $1,1^\circ + 0,5^\circ \tan\theta$ bzw. 2° min^{-1} für ω -Kreis. Drei Standardreflexe 83 mal gemessen mit Standardabweichungen von 0,34 bis 0,51%.

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