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Crystal Structure of Pentapotassium Disodium Hexatungstoantimonate(V) Dodecahydrate, $K_5Na_2[SbW_6O_{24}]\cdot 12H_2O$

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The crystal structure of $K_5Na_2[SbW_6O_{24}]\cdot 12H_2O$ has been determined. Final R = 0.081 for 890 observed independent reflections collected by diffractometry. Crystal data as follows; trigonal, space group $R\bar{3}m$, a = 9.794(1) Å, α = 84.72(1) °, Z = 1. The heteropolyanion has a structure with point symmetry D_{3d} ($\bar{3}$m), of the ideal Anderson-type heteropolyanion. The Sb-W and W-W distances are 3.259(2) and 3.259(3) Å. Three types of W-O (W-O_t, W-O_b and W-O_c) distances are 1.73(2), 1.95(4) and 2.20(3) Å. The Sb-O distance is 1.97(3) Å.

Introduction

The Anderson-type[1] heteropolyanion is typical XM_6 (X:heteroatom, M: Mo and W) heteropolyoxometalate species having D_{3d} point symmetry. The structural studies of Anderson-type hexamolybdoheteropolyanions such as $[TeMo_6O_{24}]^{6-}$[2], $[IMo_6O_{24}]^{5-}$[3], $[H_6CrMo_6O_{24}]^{3-}$[4], $[H_6CoMo_6O_{24}]^{3-}$[5], $[H_{4.5}PtMo_6O_{24}]^{3.5-}$[6] and hexatungstoheteropolyanions such as $[MnW_6O_{24}]^{8-}$[7], $[PtW_6O_{24}]^{8}$ and $[H_3PtW_6O_{24}]^{5-}$[9] polyanions had been reported. These Anderson-type structures consist of central XO_6 octahedron with six MO_6 octahedra surrounding it on a plane always sharing their edges. However, the hexamolybdoantimonate(V) polyanion, $[H_2SbMo_6O_{24}]^{5-}$[10] has the bent structure with C_{2v} (2mm) point symmetry. This heteropolyanion has the same framework as the $[Mo_7O_{24}]^{6-}$[11] and $[H_4PtMo_6O_{24}]^{4-}$[6] polyanions. We report in this paper the structure of the $[SbW_6O_{24}]^{7-}$ polyanion which is the ideal Anderson-type heteropolyanion.

Experimental

The title compound was prepared by mixing $K[Sb(OH)_6]$ and K_2WO_4 solutions (adding a small portion of NaCl) in the molar ratio of Sb : W = 1 : 6, adjusting the pH to 5.4 with dilute HNO_3 solution. After concentrating on the water bath, filtering and cooling at room temperature, colourless, transparent rectangular crystals of $K_5Na_2[SbW_6O_{24}]\cdot 12H_2O$ were separated from the solution. A summary of crystal data, together with the details concerning intensity measurements, is given in Table 1. Intensities of standard reflections remained constant throughout data collection. The structure was solved by heavy-atom method; Sb and W atoms were located from three-dimensional Patterson maps, remaining atoms from successive difference Fourier maps; structure refined by block-diagonal least squares based on F with anisotropic thermal parameters for all atoms; atomic scattering factors from *International Tables for X-ray Crystallography* [12] including f′ and f″ for Sb and W. Calculations carried out with *UNICS III*[13] on the *HITAC M-280H* computer at the *Computer Center of the University of Tokyo*. The final atomic parameters are given in Table 2.*

Discussion

The $[SbW_6O_{24}]^{7-}$ polyanion has D_{3d} ($\bar{3}$m) symmetry. It is isostructural with the ideal Anderson-type heteropolytungstate anions such as $[MnW_6O_{24}]^{8-}$[6] and $[PtW_6O_{24}]^{8-}$[7]. Figure 1 shows the crystal structure projected on the (111) plane. In this figure, there are several overlaps between the atoms such as Na-Sb-Na, Aq2-Oc-Aq1 and K-Ob. The W atoms are located

* The final Fo-Fc and anisotropic thermal parameter tables (total 9 pp.) are available as supplementary materials from the auther.

Table 1. Summary of Crystal Data, Intensity Collection and Least-Squares Refinement Stactistics

formula	$K_5Na_2[SbW_6O_{24}]\cdot 12H_2O$
fw	2066.33
space group	trigonal R$\bar{3}$m
a, Å	9.794(1)
α, deg	84.72(1)
V, Å^3	928.2(2)
Z	1
μ (Mo Kα), cm^{-1}	209.98
density, gcm^{-3} calcd.	3.698
radiation	Mo Kα (graphite monochrom)
crystal size, mm	0.10 × 0.12 × 0.13
cell-constant determination	25 reflections (40°<2θ 45°)
reflection measured	+h max 13, +k max 9, ±l max 13
2θ range, deg	3 — 60
scan type	ω — 2θ
scan speed, deg min^{-1}	2
scan range, deg	2θ (1.3 + 0.6 tan θ)
standard reflection	3/50
no. of unique reflections	992
no. of unique reflections	890 |F ≥ 3σ(F)|
R	0.081
wR	0.095
w^{-1}	σ^2(Fo) + (0.02Fo)^2
$(\Delta/\sigma)_{max.}$	0.010
final $\Delta\rho$ excursions (e Å^{-3})	17 (the maximum values are near W)
diffractometer	Rigaku AFC

Table 2. Positional Parameters (×10^4) and Isotropic Thermal Parameters (Å^2×10^2 for Sb and W; ×10 for O, K and Na) with e.s.d's in parentheses

	No. of positions (Wyckoff notation)	x	y	z	$B_{iso.}$
Sb	1(a)	0	0	0	71(13)
W	6(f)	2469(2)	-2469(2)	0	89(3)
O_b	6(h)	947(41)	947(41)	-3417(26)	20(7)
O_c	6(h)	-1260(31)	-1260(31)	973(26)	13(6)
O_t	12(i)	-1192(20)	2818(19)	-3676(19)	19(4)
K	6(h)	-3418(14)	-3418(14)	1182(11)	19(2)
Na	2(c)	2553(55)	2553(55)	2553(55)	22(9)
Aq 1	6(h)	1008(52)	1008(52)	3833(40)	38(12)
Aq 2	6(h)	4157(37)	4157(37)	1573(33)	23(8)

at the corners of the regular hexagon and the Sb atom is located at its center. All the Sb and W atoms are octahedrally surrounded by the O atoms. This heteropolyanion has three types of O atoms, denoted O_t, O_b and O_c, where O_t is the terminal O atom bound to a W atom, Ob is the bridging atom between two W atoms, and O_c is the central atom coordinated to the Sb and W atoms. The $W(O_b)_2(O_c)_2(O_t)_2$ octahedra are joined to the central $Sb(O_c)_6$ octahedron by edge sharing. In-

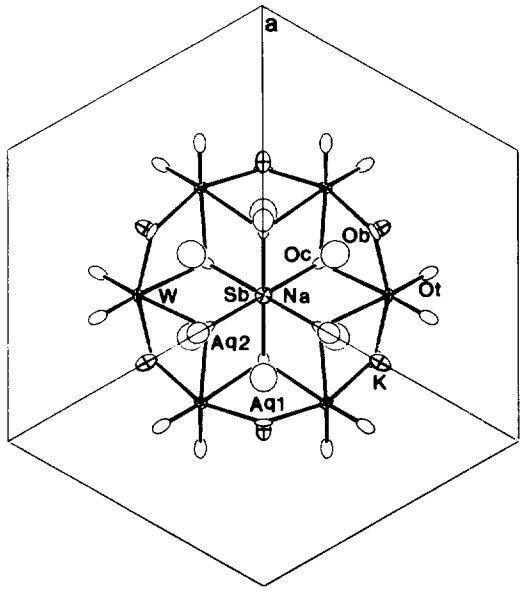

Figure 1. A view of the crystal structure projected on the (111) plane.

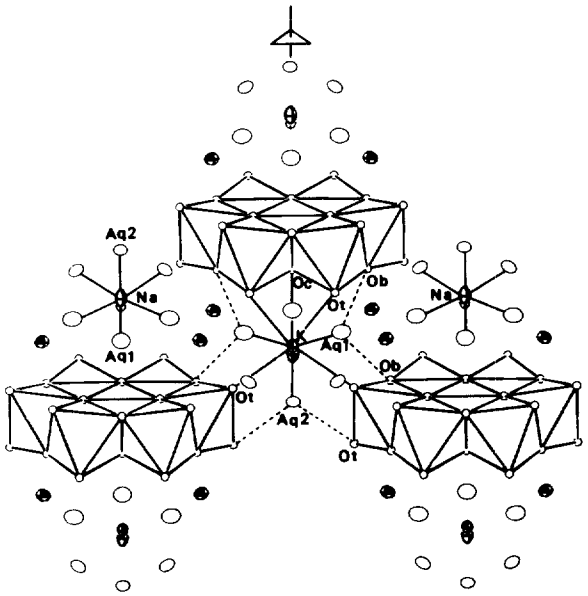

Figure 2. Some possible hydrogen bonds and the coordination feature.

teratomic distances and angles of the polyanion are listed in Table 3. The molecular dimensions of the $[SbW_6O_{24}]^{7-}$ polyanion agree well with those of the isostructural $[MnW_6O_{24}]^{8-6}$ and $[PtW_6O_{24}]^{8-7}$ polyanions, except small variations caused by the different ionic radii and charges of the heteroatoms.

During the course of the refinement, the temperature factor of the K atom was found to be larger than the ordinary value. Although the multiplicity of the K atoms coordination (x,x,z) is 6/12 in the R$\bar{3}$m space group, a reasonable temperature factor was obtained by reducing occupancy factor of K to 5/6. The elemental analysis data of K (calc. : 9.4%, found: 10.0%) also support this occupancy factor. Thus, we established the correct stoichiometry as K_5Na_2 $[SbW_6O_{24}]\cdot 12H_2O$ assuming that five K^+ ions randomly occupy the six positions. Figure 2 shows the possible hydrogen bonds and the coordination features of Na^+ and K^+ ions in the

Table 3. Interatomic Distances (Å) and Angles (°) in the $[SbW_6O_{24}]^{7-}$ Anion

(a) Distances. The prime (') refers to the atoms on the opposite side of the W_6 plane

Sb–W	3.259(2)	Sb–O_c	1.,95(3)
W–W	3.259(3)	W–O_c	2.20(3)
W–O_b	1.95(4)	W–O_t	1.73(2)
O_c–O_c	2.95(5)	O_c–O_c'	2.55(6)
O_c–O_b	2.88(4)	O_c–O_b'	2.49(4)
O_c–O_t	2.84(3)	O_b–O_t	2.67(4)
O_b–O_t'	2.83(5)	O_t–O_t	2.78(4)

(b) Angles. *anti* indicates that the two O atoms are on opposite sides of the W_6 plane, *syn* indicates that they are on the same side.

W–O_c–W	95.9(10)	W–O_c–Sb	103.5(14)
W–O_b–W	113.7(16)		
O_c–Sb–O_c(*syn*)	98.2(12)	O_c–Sb–O_c(*anti*)	81.8(12)
O_c–W–O_c(*anti*)	71.2(10)	O_c–W–O_b(*syn*)	87.9(13)
O_c–W–O_b(*anti*)	73.7(13)	O_c–W–O_t(*syn*)	92.1(10)
O_c–W–O_t(*anti*)	158.6(10)	O_b–W–O_b(*anti*)	157.6(15)
O_b–W–O_t(*syn*)	93.0(12)	O_b–W–O_t(*anti*)	100.4(13)
O_t–W–O_t(*anti*)	107.1(9)		

Table 4. Na^+–O and K^+–O Distances (Å) less than 3.2 Å

Na – Aq 1	2.42(7)	K – O_c	3.11(4)
Aq $1^{i,ii}$	2.42(7)	$O_t^{i,ii}$	2.80(2)
Aq 2	2.40(7)	$O_t^{vi,vii}$	2.85(2)
Aq $2^{i,ii}$	2.40(7)	Aq $1^{iii,v}$	3.06(5)
		Aq 2^{iv}	3.02(4)

Symmetry code: (i) x,z,y; (ii) z,x,y; (iii) −z,−y,−x; (iv) −x,−y,−z; (v) −x,−z,−y; (vi) −y,−1−z,−x; (vii) −1−z,−y,−x.

crystal. The Na^+ ion is coordinated octahedrally by six water molecules as $[Na(Aq1)_3(Aq2)_3]^+$. The K^+ ion is coordinated to eight oxygen atoms as $[K(Aq1)_2(Aq2)(O_c)(O_t)_4]^+$. The $[K_3Na(Aq)_6]^{4+}$ cluster with 3mm point symmetry are placed at all of the tetrahedral cavities in the anionic packing. The Na^+-O and K^+-O distances less than 3.2 Å are given in Table 4. All water molecules form hydrogen bonds with the oxygen atoms in the polyanions. The distances of Aq1–O_b are 2.91(7) and 2.68(6) Å (adjacent layer anion) and the Aq2–O_t distance is 2.95(4) Å (two different anions in the adjacent layer). The heteropolyanions are joined to one another through the water molecules and the K^+ ions.

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