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Synthesis and Crystal Structure of $[(CH_3)_4N]_6[H_3BiW_{18}O_{60}]$

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A novel heteropolytungstate salt $[(CH_3)_4N]_6[H_3BiW_{18}O_{60}]$ is prepared and its crystal structure is determined : monoclinic, $P2_1/c$, a=13.986(7) Å, b=15,134(2), c=23.250(8), β=115.32(3)°, Z=2. The anion has the same framework as that found in 18-tungstoarsenate(III)($AsW_{18}O_{60}$). The Bi atom is coordinated by three O atoms and is on the apex of BiO_3 trigonal pyramid.

Several heteropolytungstates incorporating the group 5B trivalent elements as heteroatoms have been investigated.[1)] Some crystal structures of heteropolytungstates salts containing As(III) or Sb(III) were determined by X-ray diffractions.[2 ,3)] These heteroatoms are bonded to three oxygen atoms constructing XO_3 trigonal pyramids. Recently we have synthesized a new 18-tungstobismuthate salt and analysed its crystal structure. This is the first structural study of BiO_3^{3-} monomeric oxoaninon form included in a Bi oxy-compound.

The preparation of $[(CH_3)_4N]_6[H_3BiW_{18}O_{60}]$ is as follows. H_2WO_4(14.2 g : 57 mmol) and NaOH (4.5 g) were dissolved in 100 cm^3 of hot water (60-70 °C). Acetic acid was added to the solution to adjust pH at 4. $Bi(NO_3)_3\cdot5H_2O$ (2.5 g : 5.1 mmol) was dissolved in 20 cm^3 CH_3COOH/CH_3COONa (pH 4) buffer solution and was added to the tungstate solution. The mixture became pale yellow after heating on a water bath (90 °C) for 4 h. A solution of $(CH_3)_4NBr$ (5.0 g) in 300 cm^3 water was added to the mixture dropwise and then the solution was filtered. Slightly yellow colored prismatic crystals were obtained from the filtrate after a few days with slow evaporation at 37 °C.

A single crystal with dimensions 0.30 x 0.38 x 0.38 mm^3 was subjected to a X-ray diffraction measurement. Crystallographic data: FW=4926.1, monoclinic, $P2_1/c$, a=13.986(7), b=15.134(2), c=23.250(8) Å, β=115.32(3)°, V=4448(3) $Å^3$, Dx=3.68 g cm^{-3}, μ=257.3 cm^{-1} (for Mo Kα), Z=2. Intensity data were collected on a RIGAKU AFC-5 automated four-circle diffractometer at Engineering Research Institute, Faculty of Engineering, The University of Tokyo, with graphite monochromated Mo Kα radiation. No decreases of standard reflections were observed.

A total 3592 of independent reflections with $F\geqq3\sigma(F)$ in the range $4° < 2\theta < 55°$

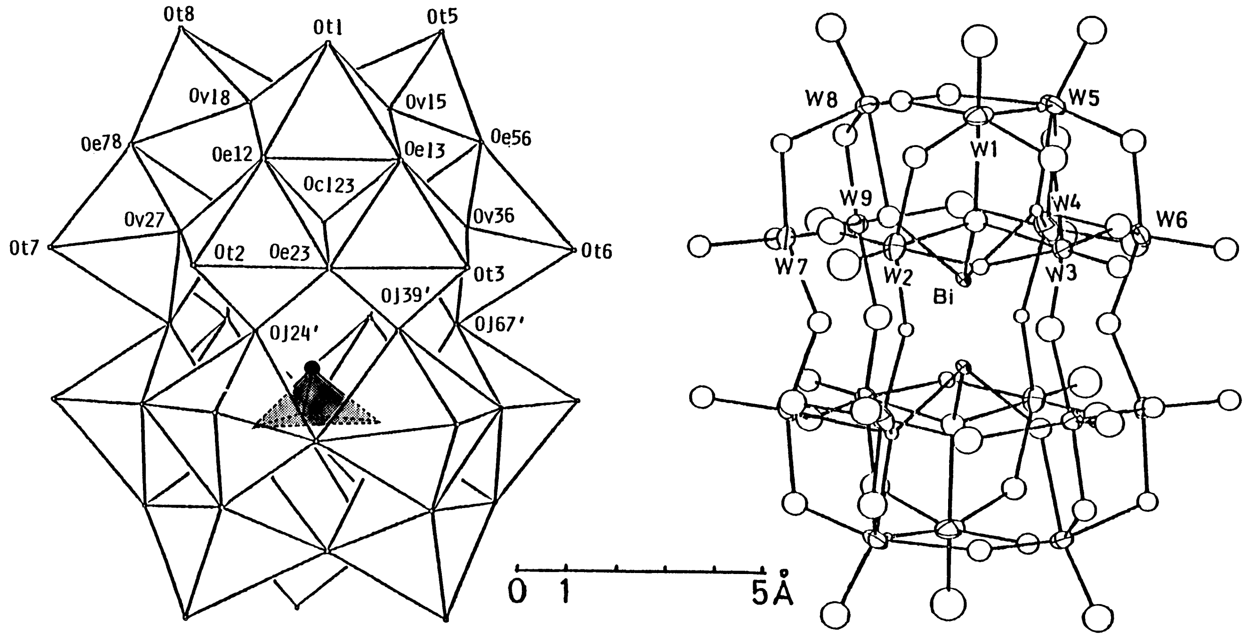
Table 1. Positional parameters (x 10^3; for Bi and W x 10^4) and isotropic thermal parameters (A^2) with e.s.d.'s in parentheses

Atom	x	y	z	Beq[b]/Biso	Atom	x	y	z	Biso
Bi[a]	480(4)	242(3)	380(2)	1.6	Ov(15)	255(2)	20(2)	225(1)	0.3(0.5)
W(1)	1445(3)	729(2)	2312(1)	3.9	Ov(18)	149(4)	195(4)	190(3)	4.3(1.2)
W(2)	-1059(3)	838(2)	1237(2)	3.3	Ov(27)	-75(4)	182(4)	88(3)	4.2(1.2)
W(3)	185(2)	-1085(2)	1608(1)	2.6	Ov(38)	151(4)	-145(3)	154(2)	3.1(1.0)
W(4)	2983(3)	-52(3)	291(2)	3.6	Ov(49)	266(5)	113(4)	17(3)	4.6(1.3)
W(5)	3551(3)	327(2)	1799(2)	4.0	Ov(58)	313(4)	165(3)	146(2)	2.8(0.9)
W(6)	2359(2)	-1517(2)	1125(2)	3.0	Oj(24')	-164(3)	29(2)	38(2)	1.1(0.7)
W(7)	-327(3)	2513(2)	299(1)	2.8	Oj(39')	-57(5)	-127(4)	73(3)	4.8(1.3)
W(8)	2098(3)	2434(2)	1401(1)	3.2	Oj(67')	107(3)	-163(3)	32(2)	2.0(0.8)
W(9)	1578(2)	2118(2)	-115(1)	2.5	Oi(123)	48(4)	20(4)	129(2)	3.6(1.1)
Ot(1)	206(5)	105(5)	318(3)	6.1(1.6)	Oi(456)	213(3)	-8(3)	89(2)	1.4(0.7)
Ot(2)	-209(5)	120(5)	137(3)	6.4(1.6)	Oi(789)	96(3)	154(3)	54(2)	2.2(0.8)
Ot(3)	-22(4)	-198(3)	190(2)	3.2(1.0)	N(1)	380(5)	333(5)	360(3)	4.1(1.4)
Ot(4)	370(4)	-8(4)	-9(3)	4.4(1.2)	C(11)	428(7)	258(6)	343(4)	4.1(1.7)
Ot(5)	487(4)	32(3)	243(2)	3.6(1.0)	C(12)	414(6)	327(6)	435(4)	3.9(1.7)
Ot(6)	277(4)	-258(3)	125(2)	2.8(0.9)	C(13)	380(10)	425(9)	345(6)	8.7(3.5)
Ot(7)	-116(4)	340(4)	16(3)	3.9(1.1)	C(14)	246(10)	301(8)	334(6)	7.5(3.0)
Ot(8)	281(4)	332(4)	191(2)	3.7(1.1)	N(2)	-69(7)	48(7)	352(4)	7.3(2.3)
Ot(9)	201(4)	270(4)	-50(3)	4.1(1.2)	C(21)	-79(10)	139(8)	330(6)	7.4(2.9)
Oe(12)	-3(4)	110(4)	203(2)	3.6(1.1)	C(22)	-102(7)	-24(6)	307(4)	4.7(1.9)
Oe(13)	104(4)	-44(3)	236(2)	3.4(1.0)	C(23)	-143(15)	48(14)	369(9)	14.6(6.2)
Oe(23)	-103(3)	-38(3)	152(2)	2.4(0.8)	C(24)	47(20)	42(18)	408(12)	19.6(8.8)
Oe(45)	400(4)	30(3)	117(2)	2.6(0.9)	N(3)	-425(7)	276(6)	150(4)	6.6(2.1)
Oe(46)	311(4)	-125(3)	59(2)	3.4(1.0)	C(31)	-367(16)	203(15)	201(10)	15.8(7.0)
Oe(56)	345(4)	-89(4)	181(3)	4.4(1.2)	C(32)	-465(8)	311(7)	176(5)	6.0(2.4)
Oe(78)	80(4)	314(3)	104(2)	2.7(0.9)	C(33)	-458(12)	221(10)	98(7)	10.0(4.0)
Oe(79)	33(4)	285(3)	-16(2)	2.7(0.9)	C(34)	-314(16)	311(14)	162(10)	15.2(6.6)
Oe(89)	244(4)	273(3)	68(2)	3.0(1.0)					

[a] The occupancy of Bi atom is 0.5.

[b] $Beq=(8/3)\pi^2\Sigma_{ij}U_{ij}a_i{*}a_j{*}\ a_i.a_j.$

were used for structure determination and refinements. Intensities were corrected for absorption. The positions of Bi and W atoms were determined from three-dimensional Patterson functions. All the other atoms except hydrogen were located from successive Fourier syntheses. The positional and thermal parameters were refined by block-diagonal least squares.[4] The R value $(\Sigma||Fo|-|Fc||/\Sigma|Fo|)$ of 0.099 at the present stage was obtained by using anisotropic temperature factors for W and Bi atoms.



(a) (b)

Fig. 1. The molecular structure of $[H_3BiW_{18}O_{60}]^{6-}$ polyanion.
(a) Polyhedral representation.
(b) ORTEP Plotting with 30% probability ellipsoids.

Table 2. Comparison of mean distances (Å) and angles (°) in $[XW_{18}O_{60}]$ polyanions

X=	Bi	As	X=	Bi	As
W-W intra	3.31(1)	3.32(2)	W - Ov	1.97(15)	1.92(2)
W-W inter	3.69(4)	3.70(1)	W - Oj	1.94(5)	1.90(2)
W-W joint	3.63(1)	3.66(2)	W - Oi	2.27(6)	2.30(5)
W-X	3.63(2)	3.59(5)	Oi- Oi	2.88(4)	2.81(4)
W - Ot	1.71(10)	1.72(2)	X - Oi	2.11(5)	1.87(4)
W - Oe	1.93(7)	1.94(3)	Oi-X-Oi'	86.3(2.6)	97.5(2.1)

Figure 1 shows the structure of $[H_3BiW_{18}O_{60}]^{6-}$ molecule which has crystallographically a center of symmetry. The framework of WO_6 octahedra consists of two equivalent W_9O_{33} half units which have C_{3v} symmetry. Each of them is derived from the Keggin type $(XM_{12}O_{40})$ structure by removal of a edge-shared W_3O_{13} moiety. These half units are linked to each other by sharing six oxygen (Oj) atoms and the whole molecule has approximate D_{3d} symmetry if H and Bi atoms are neglected. There is one Bi atom disordered between two possible sites which are distant by 1.85 Å from each other. The heteroatom is bonded to only three oxygen atoms (Oi). Each of the Oi atoms is coordinated to three W atoms. The BiO_3 moiety is regarded as discrete "bismuthite anion" like as phosphite or arsenite. This trigonal pyramidal bond of Bi-O is rarely found in bismuth oxy-compounds, in which the Bi atom is coordinated by 5 or 6 O atoms at distances less than 2.7 Å.$^{5)}$ The other oxygen atoms in the anion are simply classified in three types. Ot (terminal) oxygen atom is bonded to one W atom. Oe and Ov oxygen atoms which are coordinated to two W atoms are located at edge-shared and vertex-shared points of WO_6 octahedra, respectively. The anion has the same framework that found in the $[H_2AsW_{18}O_{60}]^{7-}$ polyanion.$^{3)}$ The mean distances and angles within the 18-tungsto-bismuthate(III) and arsenate(III) molecules are given in Table 2. The distances of Bi-Oi (2.11 Å) are longer than those of As-Oi bonds (1.87 Å). The Oi-Bi-Oi' angles (86.3 °) are smaller, and the BiO_3 pyramid has sharper apex than that of the AsO_3. There are small differences in W-W and W-O bonds between the two polyanions. The change of heteroatoms effect XO_3 moieties significantly and little influence is observed in the W-O common frameworks.

References

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