The Crystal Structure of α-Barium 12-Tungstosilicate, α-$Ba_2SiW_{12}O_{40}$·$16H_2O$

Akiko Kobayashi and Yukiyoshi Sasaki

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received August 1, 1974)

α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$ is monoclinic, space group C2/c, with a=25.09(5), b=12.10(2), c=18.79(3) Å, β= 122.5(3)°; D_m=4.95 g cm^{-3} and D_x=4.78 g cm^{-3} for Z=4. The crystal consists of the well known Keggin ion $SiW_{12}O_{40}{}^{4-}$, having a SiO_4 tetrahedron in the center, bound by Ba^{2+} and water molecules to form a three-dimensional framework. Four water molecules could not be located on electron-density maps, which seem to be disordered or "*zeolitic*". The structural relationship of the Keggin ion to its isomer, the β-$SiW_{12}O_{40}{}^{4-}$ polyanion found in β-$K_4SiW_{12}O_{40}\cdot 9H_2O$, is discussed. Mutual transformation between α- and β-isomers can occur through rotation of a W_3O_{13} group which is a building-unit of both α- and β-polyanions.

It was already known in the last century, that 12-tungstosilicic acid and its salts had two isomers referred to as α- and β-forms (or normal and iso-forms).[1] Acidification of an aqueous solution containing sodium silicate and sodium tungstate gives the α-isomer of the $SiW_{12}O_{40}{}^{4-}$ ion, while addition of acid to sodium tungstate solution prior to mixing with sodium silicate yields the β-isomer.[2,3]

Recent absorption spectrophotometric and polarographic studies have revealed that a number of related compounds, such as 12-tungstoborate,[2] 12-tungstogermanate,[3] 12-molybdosilicate,[4,5] 12-molybdogermanate,[6] 12-molybdophosphate, and 12-molybdoarsenate,[7,9] show a similar isomerism. In order to clarify the structural relationships between these pairs of isomers, we have undertaken a series of single crystal X-ray diffraction studies.

To start with, we have chosen α- and β-salts of 12-tungstosilicic acid. Owing to the presence of many heavy tungsten atoms, these salts are not suitable for an accurate structure determination. However salts of this acid are favorable for comparative study, since both α- and β-isomers are stable even in aqueous solutions and both can be obtained as separate crystalline samples. Other acids, particularly β-polyanions containing molybdenum atoms, seem to be short lived in aqueous solutions and are quickly converted into the corresponding α-forms.[4-9] The present paper deals with the structure of the α-isomer of 12-tungstosilicate, α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$. The structure of a β-isomer, β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ was published elsewhere.[10]

The α-salts were widely believed to contain the well known "*Keggin molecules*", or more correctly "*Keggin polyanions*", even though a definite proof was lacking.[11] The guess was based on the fact that $CsHSiW_{12}O_{40}\cdot nH_2O$ (n=0 or 2) was isomorphous with $H_3PW_{12}O_{40}\cdot 5H_2O$[13] which was the first example of the "*Keggin structure*".[14]

Experimental

The α-form of 12-tungstosilicate was prepared by mixing a solution of sodium tungstate, sodium silicate and hydrochloric acid.[16] For purification, α-$SiW_{12}O_{40}{}^{4-}$ was treated with hydrochloric acid and extracted with ether, the extract was then converted to aqueous solution. The barium salt was obtained by neutralization of the polyacid solution with solid barium carbonate. The colorless tabular crystals were obtained from the neutral aqueous solution at >30 °C.

The α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$ crystals were chosen because of their stability in air and because of the absence of twin formation which is frequently encountered in heteropoly compounds. The crystals are stable at room temperature but begin to loose a part of the water of crystallization at 40 °C.

Thermogravimetric analysis and DTA have shown endothermic reactions at 120, 190 and 250 °C corresponding to the loss of eight, twelve and sixteen water molecules. For the purpose of the X-ray diffraction work a specimen in the form of an irregular rhombus with a maximum dimension of 0.25 mm was used. The intensities of reflections were measured on a Rigaku four-circle diffractometer with Mo*Kα* radiation. The ω-2θ scan technique was employed and 2952 significant independent reflections for which $|F_o|\geq 141.0$ (F_o :absolute scale) up to $2\theta=60°$ were obtained. The data were corrected for Lorentz and polarization effects. No corrections were made for absorption. The crystal data are as follows:

α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$
F. W. 3438.7
monoclinic
a = 25.09 (5) Å
b = 12.10 (2) Å
c = 18.79 (3) Å
β = 122.5 (3)°
V = 4813 Å^3
space group C2/c
Z = 4 (D_m = 4.95 g cm^{-3}, D_x = 4.78 g cm^{-3})
μ (Mo*Kα*: 0.7107 Å) = 320 cm^{-1}

Since Wilson's statistics indicated the presence of a center of symmetry, the space group C2/c was assumed. The structure was solved by the heavy atom method. The atomic positions and anisotropic temperature factors of tungsten, barium and silicon atoms were refined by the block-diagonal least-squares method. At this stage the R-value was reduced to 0.16. After several refinement cycles including oxygen atoms of the anion with isotropic temperature factors, the R value was reduced to 0.14. There are eight crystallographically independent water molecules, of which six were found by a difference Fourier synthesis. After several further cycles, the structure converged to R=0.13.

A weighting scheme, w=0.2 for $|F_o|\leq 253.0$ and w=1, otherwise was employed. Atomic scattering factors were taken from "International Tables for X-ray Crystallography,"[15] and those for W and Ba were corrected for anomalous dispersion.[15]

Results and Discussion

The atomic parameters and their estimated standard deviations are listed in Table 1. The final F_O-F_C table

Table 1. Atomic parameters and their estimated standard deviations

The positional parameters of all the atoms and their anisotropic thermal parameters have been multiplied by 10^4. The anisotropic temperature factor is of the form $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

	x	y	z	$B_{11}(B)$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si	0(0)	1045(64)	2500(0)	28(17)	80(58)	106(56)	0(0)	47(29)	0(0)
W_1	−205(2)	2967(3)	1045(3)	4(1)	27(2)	19(1)	0(1)	7(1)	4(2)
W_2	1177(2)	2924(3)	3238(3)	5(1)	26(2)	22(1)	−5(1)	9(1)	−2(2)
W_3	−83(2)	−1189(3)	1118(2)	5(1)	25(2)	17(1)	1(1)	8(1)	−2(2)
W_4	1163(2)	−1153(3)	3110(2)	5(1)	24(2)	18(1)	5(1)	9(1)	4(2)
W_5	1011(2)	777(3)	1733(2)	5(0)	25(2)	22(1)	2(1)	10(0)	5(2)
W_6	1298(1)	990(3)	4603(2)	4(1)	23(2)	14(1)	0(1)	5(1)	0(2)
Ba	2757(2)	927(5)	1660(4)	9(1)	24(3)	31(2)	0(2)	14(1)	1(3)
O_1	1754(31)	−2143(63)	3648(44)	1.9(1.1)					
O_2	596(36)	−1883(66)	2023(51)	2.6(1.4)					
O_3	−381(40)	−2167(80)	262(57)	3.3(1.6)					
O_4	1466(31)	−300(58)	2521(44)	1.8(1.1)					
O_5	544(30)	−321(57)	1054(43)	1.5(1.1)					
O_6	1475(38)	1171(77)	1360(54)	3.2(1.5)					
O_7	396(29)	1840(55)	1183(42)	1.5(1.1)					
O_8	1299(36)	1794(70)	2667(52)	2.7(1.4)					
O_9	415(34)	87(64)	2277(48)	2.2(1.2)					
O_{10}	435(29)	3278(53)	2171(42)	1.3(1.0)					
O_{11}	1735(34)	3956(73)	3356(48)	2.8(1.4)					
O_{12}	883(31)	3741(62)	3902(44)	2.1(1.2)					
O_{13}	109(32)	3877(65)	4542(45)	2.3(1.2)					
O_{14}	1682(31)	2126(63)	4293(44)	1.9(1.1)					
O_{15}	900(32)	2213(64)	4820(46)	2.1(1.2)					
O_{16}	1905(27)	695(53)	5583(39)	1.3(1.0)					
O_{17}	1459(32)	25(64)	3942(47)	2.0(1.2)					
O_{18}	682(29)	−47(57)	4482(42)	1.6(1.0)					
O_{19}	500(27)	1717(51)	3297(38)	1.1(0.9)					
O_{20}	496(34)	−1641(65)	3285(48)	2.3(1.3)					
$H_2O(1)$	1788(44)	2064(88)	290(62)	4.2(1.9)					
$H_2O(2)$	2254(34)	4557(64)	2159(48)	2.3(1.3)					
$H_2O(3)$	2171(40)	5997(89)	617(57)	3.9(1.7)					
$H_2O(4)$	1138(49)	4520(90)	678(69)	4.6(2.1)					
$H_2O(5)$	2765(46)	2288(90)	2811(65)	4.4(2.0)					
$H_2O(6)$	980(50)	5772(109)	1967(70)	5.4(2.3)					

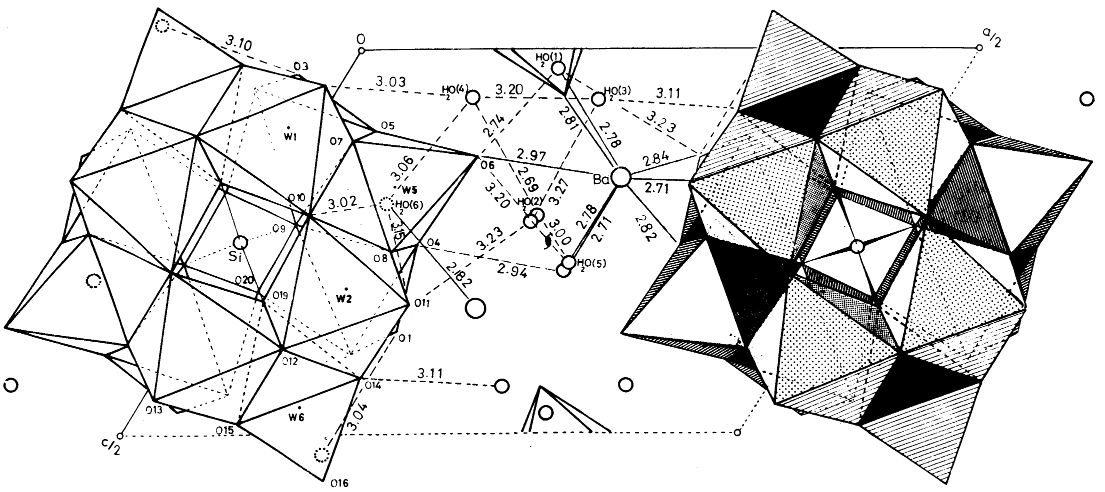

Fig. 1. A view of the structure as projected onto the (010) plane. Large circles represent Ba^{2+} ions and small circles water molecules. The coordination bonds around Ba^{2+} are designated by full lines, other close contacts by dotted lines.

is held by the office of the Chemical Society of Japan as Document No. 7504. The crystal structure projected along the b-axis is shown in Fig. 1. As is shown in this figure, the crystal consists of α-$SiW_{12}O_{40}^{4-}$ anions, Ba^{2+} cations and water molecules of crystallization. The center of the anion lies on a twofold rotation axis at $y=1/4$.

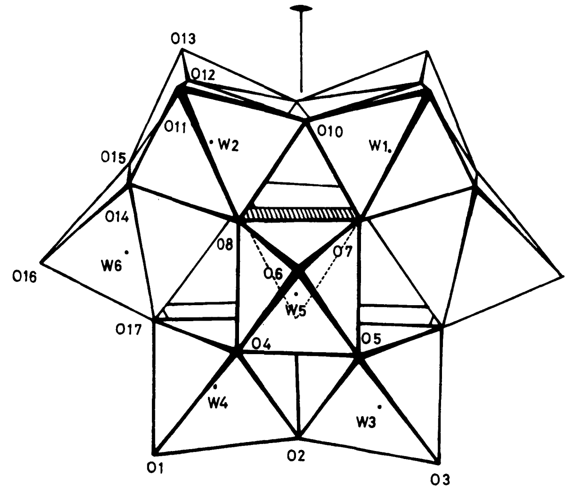

Fig. 2. A perspective view of the α-$SiW_{12}O_{40}^{4-}$ anion. Deformed octahedra represent WO_6 groups. The central SiO_4 tetrahedron, shaded on the figure, is only partly seen.

TABLE 2. INTERATOMIC DISTANCES (Å) AND ESTIMATED STANDARD DEVIATIONS[a)] WITHIN THE ANION, α-$SiW_{12}O_{40}^{4-}$

W_1-O_{10}	(Ob)[b)]	1.88(6)	W_2-O_{10}	(Ob)	1.91(5)
W_1-O_7	(Ob)	1.94(7)	W_2-O_8	(Ob)	1.86(10)
W_1-$O_{19'}$[c)]	(Oa)	2.31(8)	W_2-O_{19}	(Oa)	2.29(7)
W_1-$O_{15'}$	(Oc)	1.86(6)	W_2-O_{14}	(Oc)	1.94(7)
W_1-$O_{12'}$	(Oc)	1.99(9)	W_2-O_{12}	(Oc)	2.02(10)
W_1-$O_{13'}$	(Od)	1.67(9)	W_2-O_{11}	(Od)	1.80(9)
W_3-$O_{18'}$	(Ob)	1.90(6)	W_4-O_{17}	(Ob)	1.95(8)
W_3-$O_{20'}$	(Ob)	1.97(11)	W_4-O_{20}	(Ob)	1.96(10)
W_3-O_9	(Oa)	2.40(8)	W_4-O_9	(Oa)	2.25(7)
W_3-O_5	(Oc)	1.95(8)	W_4-O_4	(Oc)	1.94(9)
W_3-O_2	(Oc)	1.84(7)	W_4-O_2	(Oc)	1.96(7)
W_3-O_3	(Od)	1.80(10)	W_4-O_1	(Od)	1.75(7)
W_5-O_7	(Ob)	1.84(6)	W_6-O_{17}	(Ob)	1.90(9)
W_5-O_8	(Ob)	1.94(9)	W_6-O_{18}	(Ob)	1.91(8)
W_5-O_9	(Oa)	2.37(10)	W_6-O_{19}	(Oa)	2.35(5)
W_5-O_5	(Oc)	1.78(6)	W_6-O_{14}	(Oc)	1.94(9)
W_5-O_4	(Oc)	1.84(7)	W_6-O_{15}	(Oc)	1.95(9)
W_5-O_6	(Od)	1.72(12)	W_6-O_{16}	(Od)	1.68(5)
Si-O_9		1.75(11)			
Si-O_{19}		1.57(7)			

a) E.s.d.'s in parentheses in Tables 2 and 3 are in units of the last significant digit. b) Oa: the oxygen atom bound to one silicon and at the same time to three tungsten atoms. Ob: the oxygen atom bridging two tungsten atoms of two neighboring W_3O_{13} moieties. Oc: the bridging oxygen atom shared between two tungsten atoms belonging to a same W_3-O_{13} group. Od: the terminal oxygen atom bonded to only one tungsten atom. c) Atoms with a prime are associated with those in Table 1 by a twofold axis.

Structure of α-$SiW_{12}O_{40}^{4-}$ *Ion.* A perspective drawing of α-$SiW_{12}O_{40}^{4-}$ anion is presented in Fig. 2. Interatomic distances and their e.s.d.'s within the anion are listed in Table 2. The anion consists of a central SiO_4 tetrahedral group in which each of the oxygen atoms is replaced by a W_3O_{13} unit constructed from three WO_6 octahedra sharing edges. Thus, the anion has the expected Keggin structure. This result confirms the proposed model for the structure of this anion in aqueous solution from a liquid X-ray diffraction study.[16)] The structural relationships between α- and β-$SiW_{12}O_{40}^{4-}$ are now clear: the α-polyanion has the well known Keggin structure, whereas the β-anion has a lower symmetry and is a geometrical isomer of the Keggin structure. If a model of the α-polyanion is built with idealized polyhedra, a corresponding β-model can be obtained by a 60° rotation of one of the W_3O_{13} groups of the α-model.[10)] All the WO_6 octahedra in α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$ are distorted. The bond lengths of W–Oa, W–Ob, W–Oc, and W–Od are 2.2—2.4, 1.8—2.0, 1.7—2.0, and 1.6—1.8 Å respectively as are listed in Table 2. Oa represents the oxygen atom attached to one silicon atom and to three tungsten atoms, Ob is shared between tungsten atoms of different W_3O_{13} units, Oc is also bound to two tungsten atoms but belonging to the same unit, and Od is the unshared terminal oxygen atom bonded to only one metal atom. These classifications of the oxygen atoms conform to those given by Evans.[17)] These data seem to indicate that the octahedra are elongated in the direction of Oa, the oxygen atom attached to the central silicon atom, moreover the tungsten atoms are displaced outward from the diagonal line Oa—Od, as if the tungsten atoms are repulsing each other within a W_3O_{13} group, the Ob–W–Oc diagonal angles being 150(3)—161(3)°. Detailed discussion of the O–O distances was not possible, since the standard deviation was as large as 0.15 Å. The central SiO_4 tetrahedron is not quite regular. The bond distances are listed in Table 2.

Coordination Around Barium Cation. As shown in Table 3 and indicated by broken lines in Fig. 1, each barium ion is coordinated by eight oxygen atoms at distances of 2.7—2.9 Å, four from water molecules and four oxygen atoms (Od) from three adjacent $SiW_{12}O_{40}^{4-}$ anions. Table 3 shows oxygen-oxygen distances around $H_2O(1)$—$H_2O(6)$ and barium-oxygen distances. Six oxygen atoms form a distorted trigonal prism around a barium cation while the other two stick out of two rectangular faces of the prism.

Water of Crystallization. In general, crystals of polytungstates and polymolybdates contain many water molecules. Although it is important to clarify the role of these water molecules in the crystal structure, their position can not always be fixed with sufficient accuracy because of the presence of many heavy atoms. In the present case, twelve out of sixteen water molecules in the chemical formula, could be located while the remaining four are still missing. These water molecules might be "*zeolitic*", having large thermal vibration factors, and be correlated with the loss of water at a temperature as low as 40 °C.[18)] Of the twelve water

Table 3. Interatomic distances (Å) less than 3.5 Å outside the anion

Ba	O_1	(Od)[a]	2.84(8)				
	O_6	(Od)	2.97(10)				
	O_{11}	(Od)	2.71(9)				
	O_{16}	(Od)	2.81(6)				
	H_2O (1)		2.78(9)				
	H_2O (2)		2.78(9)				
	H_2O (5)		2.71(13)				
	H_2O (6)		2.82(9)				
H_2O (1)	O_1	(Od)	3.04(16)	H_2O (2)	O_4	(Oc)	2.94(12)
	O_1	(Od)	3.23(12)		O_6	(Od)	3.49(10)
	O_3	(Od)	3.10(15)		O_{11}	(Od)	3.23(15)
	O_6	(Od)	2.74(18)		H_2O (3)		3.29(15)
	O_{16}	(Od)	3.37(12)		H_2O (4)		2.69(11)
	O_{17}	(Ob)	3.35(14)		H_2O (5)		3.00(13)
	O_{18}	(Ob)	3.38(12)		H_2O (5)		3.31(13)
	O_{20}	(Ob)	3.44(10)		H_2O (6)		3.36(16)
H_2O (3)	O_{14}	(Oc)	3.11(14)	H_2O (4)	O_3	(Od)	3.35(14)
	O_{17}	(Ob)	3.29(13)		O_{13}	(Od)	3.03(16)
	H_2O (4)		3.20(18)		H_2O (6)		3.06(20)
	H_2O (5)		3.27(17)				
H_2O (5)	O_6	(Od)	3.20(11)	H_2O (6)	O_2	(Oc)	3.02(16)
	H_2O (6)		3.47(18)		O_{10}	(Ob)	3.42(15)
					O_{11}	(Od)	3.15(14)

a) Classification of oxygen atoms in the polyanion: see text and footnote of Table 2.

molecules whose position could be fixed, eight coordinate to two barium cations and at the same time some of them form hydrogen bonds with polyanions. The rest of the water molecules have some close contacts with the polyanion or with water molecules which are coordinated to barium ions. Thus barium cations and polyanions build up a three dimensional framework, accommodating water molecules in interstices.

Comparison of α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$ with α-$K_4SiW_{12}O_{40}\cdot 17H_2O$. The main difference between the crystal structures of the two tungstosilicates is that the barium salt consists of a three dimensional framework with mobile water molecules in interstices, while the potassium salt crystals contain one dimensional spiral chains made of alternate potassium cations and polyanions. There are large channels parallel to the spirals, and the three potassium ions and fifteen water molecules which could not be found by neutron and X-ray diffraction techniques are probably in random or mobile zeolitic state in these spaces; this structure explains the efflorescent nature of the potassium salt.

The calculations were performed on a HITAC 8700/8800 computer at the Computer Center of the University of Tokyo using a local version of UNICS.[20]

The authors wish to thank Dr. Hitoshi Iwasaki for reading through the manuscript and for his criticism. The work was financially supported by a Grant-in-aid for Cooperated Scientific Research of the Ministry of Education.

References

1) C. Marignac, *Ann. Chim. Phys.* [4], **3**, 44 (1864).
2) P. Souchay, *Bull. Soc. Chim. France* [5], **18**, 365 (1951).
3) P. Souchay, A. Tézé, and G. Hervé, *C. R. Acad. Sci. Ser. C*, **275**, 1073 (1972).
4) J. D. H. Strickland, *J. Amer. Chem. Soc.* **74**, 862 (1953).
5) R. Massart, *Ann. Chim.* [14], **3**, 507 (1968).
6) P. Souchay, A. Tézé, and C. Hervé, *Proceedings of XX I.C.C.C. Moscow* 1972.
7) P. Souchay, R. Content, and M. Fruchart, *C. R. Acad. Sci. Ser. C.* **264**, 976 (1967).
8) J. M. Fruchart and P. Souchay, *ibid.* **266**, 1571 (1968).
9) P. Souchay and R. Contant, *ibid.* **265**, 723 (1967).
10) K. Yamamura and Y. Sasaki, *Chem. Communn.*, **1973**, 648.
11) After our measurements were completed, we learned that the Keggin structure of the tungstosilicic acid had been acertained by Smith[12] in his structure determination of $K_4SiW_{12}O_{40}\cdot 17H_2O$ by X-ray and neutron diffraction techniques. However, our computation was continued due to our interest in the roles of divalent barium cation and of water of crystallization in the present polyanion crystals.
12) P. M. Smith, *Dissertation Abstr.*, **32**, 5136-B (1972).
13) J. A. Santos, *Proc. Roy. Soc.* **A150**, 309 (1935).
14) J. F. Keggin, *ibid.*, **A144**, 75 (1934).
15) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham (1962), Vol. III.
16) H. A. Levy, P. A. Agron, and M. D. Danford, *J. Chem. Phys.* **30**, 1486 (1959).
17) H. T. Evans, Jr., *Perspectives Struct. Chem.* **4**, 1 (1971).
18) This kind of water of crystallization is rather common in heteropolymetallate compounds. Apart from $K_4SiW_{12}O_{40}\cdot 17H_2O$,[12] $K_5CoW_{12}O_{40}\cdot 20H_2O$[19] and $(NH_4)_7Na_2[H_2GaW_{11}O_{40}]\cdot 15H_2O$[17] have been known to contain loosely bound water molecules which can not be located by X-ray diffraction techniques.
19) N. F. Yannoni, *Dissertation* (1961).
20) "UNICS: The Universal Crystallographic Computation Program System," Crystallographic Society of Japan (1967).