The Crystal Structure of β-$K_4SiW_{12}O_{40}\cdot 9H_2O$, Containing an Isomer of the Keggin Ion

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β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ is orthorhombic, with the space group Pnma and $a=20.62(1)$, $b=15.57(1)$, $c=12.95(1)$ Å, $D_m=4.88$ g cm^{-3} and $D_x=5.04$ g cm^{-3} for $Z=4$. The crystal contains a discrete β-$SiW_{12}O_{40}^{4-}$ polyanion, a geometrical isomer of the α-$SiW_{12}O_{40}^{4-}$ with the well known Keggin structure. The idealized Keggin ion has a T_d symmetry, but the β-isomer has only a C_s symmetry. Mutual transformation between the α- and β-structures is possible through a 60° rotation of one of the four W_3O_{13} units, which make a cage around a SiO_4 tetrahedron in both structures. The other possible geometrical isomers of the Keggin structure are discussed.

The 12-tungstosilicic acid and its salts were first synthesized in 1863 by Marignac. Later he reported the existence of two isomers, "*silicotungstic acid*" and "*tungstosilicic acid*" or "*iso-silicotungstic acid*," and found that all the salts also always have two forms, the crystal habit and solubility different from one to another.[1] Similar isomers have also been found in 12-tungstoboric acid, $H_5BW_{12}O_{40}$, and its salts.[2] Though at the begining of this century, Copaux claimed to have confirmed these results,[3,4] the existence of such isomerism was still often regarded as doubtful because of the close resemblance in the chemical properties of each pair of isomers.

Some early workers naturally contrived structural models of the two isomers. Pfeiffer proposed two isomeric structures based upon a Werner-type isomerism of an octahedral coordination around the silicon atom.[5] Pauling thought that one was a dimer of the other.[6] However, no one went beyond speculations. Though, in 1934, Keggin[7] first solved, by the powder X-ray diffraction technique, the structure of $PW_{12}O_{40}^{3-}$, which is isomorphous with $BW_{12}O_{40}^{5-}$ and $SiW_{12}O_{40}^{4-}$, successive similar X-ray investigations of the 12-tungstoborates[8,9] denied the existence of any isomerism in the $BW_{12}O_{40}^{5-}$ polyanion.

Recently, however, these isomers were confirmed by Souchay with the aid of modern physicochemical techniques, together with synthetic works; they were named the α- and β-forms.[10-17] In addition to the 12-tungstosilicate[10] and 12-tungstoborate[11] mentioned above, 12-tungstogermanate,[10] 12-molybdosilicate,[12,13] 12-molybdogermanate,[14] 12-molybdophosphate,[15,16] and 12-molybdoarsenate[15,17] have also been reported to have similar kinds of isomers.

The β-isomers are generally unstable compared to the corresponding α-isomers.[10-17] In 1909 Copaux examined the crystals prepared by Marignac 40 years before and found that the β-tungstosilicic acid samples had been transformed into the α-form in an appreciable amount. When the β-crystals are placed in contact with a saturated aqueous solution in a sealed tube, the transition is completed within one hour at 150 °C.[3] In an aqueous solution, the rate of the transformation depends on the kind of the hetero atom; the stability lies in this order; Si>Ge>P>As.

The 12-heterotungstates are generally more stable than the corresponding 12-heteromolybdates. The transformation from β to α is considerably retarded by the addition of an organic solvent, such as alcohol or dioxane. The present authors have found that the addition of a small amount of a base to an aqueous solution of the β-form accelerates its transformation. The polarographic studies of the α and β isomers show that the β-isomer is more easily reduced than the corresponding α-isomer.[10,11,13,16,17] The features of their polarographic curve are independent of the kind of hetero atom except in the case of β-12-tungstoborate. The polarogram and also the UV absorption spectra suggest that the β-12-tungstoborate anion differs from other β-isomers in its structure.

The crystal-structure determination of β-12-heteropoly acids or their salts has been considered to be indispensable to the elucidation of the structural relation between α and β isomers. With this in mind, β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ has been subjected to X-ray crystal structure analysis, since it appeared suitable for a structural study because of its stability in air and because of the relatively low amount of water of crystallization.

Experimental

Originally β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ was prepared in a very low yield, together with the main product, α-$K_4SiW_{12}O_{40}\cdot 17H_2O$.[1] Recently Souchay, Tézé, and Hervé reported a new synthetic method which gives almost pure β-$SiW_{12}O_{40}^{4-}$.[10] The β-$SiW_{12}O_{40}^{4-}$ was prepared by the acidification of sodium tungstate, followed by the addition of acidified water glass, while the acidification of the mixed solution of sodium tungstate and water glass solutions gave α-$SiW_{12}O_{40}^{4-}$. For purification, β-$SiW_{12}O_{40}^{4-}$ was extracted with hydrochloric acid and ether; then the ether was removed from the extract according to the procedure applied to the α-isomer (see Ref. 18 for the details). The addition of a saturated solution of potassium chloride precipitates β-$K_4SiW_{12}O_{40}\cdot 9H_2O$. The precipitate was recrystallized from water in order to remove a small amount of the α-isomer. The β-isomer is slightly more soluble in water than the α-form.

The crystals of β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ thus prepared are faint yellow, rhombic, and stable in air, while the α-isomer is colorless.

Preliminary oscillation and Weissenberg photographs showed that the crystal is orthorhombic, with the space group Pnma. The crystals quite often gave smeared reflection spots. A specimen was chosen which gave well-shaped reflection spots, its size being $0.1\times 0.12\times 0.07$ mm. The intensities of the reflections were measured on a Rigaku four-circle

* Formerly Kazuko Yamamura in Ref. 21.

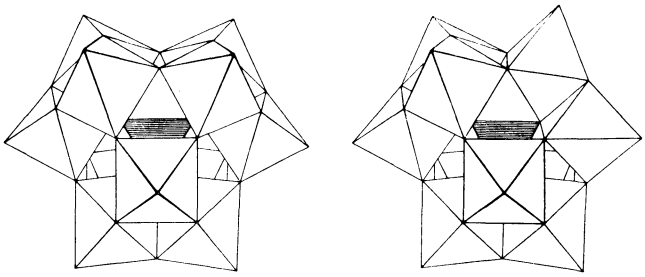
diffractometer with Mo$K\alpha$ radiation (λ=0.71069 Å). The ω–2θ scan technique was employed; 2007 independent reflections, for which $|F_o| \geqq 110$ (F_o: absolute scale) up to $2\theta=60°$, were obtained. The data were corrected for Lorentz and polarization factors. Though the crystals have a large μ value, no absorption correction could be made bacause of the irregular shape of the sample and because of its brittleness, which made polishing of the specimen practically impossible. The unit-cell dimensions and their standard deviations are a=20.62(1), b=15.57(1), c=12.95(1) A; V=4157 Å^3 at 23 °C, D_m=4.88, D_x=5.04 g cm^{-3} for Z=4, F.W. 3157.3, μ(Mo$K\alpha$)=376.2 cm^{-1}.

Solution and Refinement of the Structure

The structure was solved by the heavy atom method. All the coordinates of the atoms of the polyanion were obtained by several Fourier syntheses. Refinements were carried out with anisotropic temperature factors for the tungsten and potassium atoms and with isotropic ones for all the oxygen and silicon atoms to the final R value of 0.138. A weighting scheme, w=0.2 if $|F_o| < 150$ and w=1 otherwise, was employed. The atomic scattering factors were taken from Ref. 19, and corrections for anomalous dispersion were made for the tungsten, potassium, and silicon atoms.[20] The atomic parameters and their estimated standard deviations are listed in Table 1. The F_c—F_o table is kept at the office of this Bulletin as Document No. 7523. A preliminary report of this work has already been published elsewhere.[21] All the calculations were performed on a HITAC 8700/8800 Computer at the Computer Centre of the University of Tokyo, using a local version of UNICS.[22]

Description of the Structure and Discussion

A recent investigation of α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$[23] and α-$K_4SiW_{12}O_{40}\cdot 17H_2O$[24] proved that the α-$SiW_{12}O_{40}^{4-}$ anion has the well-known Keggin structure[7]



α β

Fig. 1. Polyhedral models of α- and β-$SiW_{12}O_{40}^{4-}$ polyanions. The central SiO_4 tetrahedra are shaded. The model α represents the Keggin structure found in α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$.[23]

Table 1. Atomic parameters

(a) Positional and thermal parameters for tungsten and potassium atoms (×10^4), with their estimated standard deviations in parentheses. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	2764 (2)	5224 (3)	6114 (4)	4 (1)	24 (2)	17 (2)	1 (1)	0 (1)	−5 (2)
W(2)	1610 (2)	6300 (3)	7331 (3)	3 (1)	21 (2)	23 (2)	−1 (1)	1 (1)	−1 (2)
W(3)	3121 (2)	6310 (3)	8283 (3)	3 (1)	19 (2)	17 (2)	1 (1)	−1 (1)	1 (2)
W(4)	4416 (3)	7500 (0)	6895 (5)	2 (1)	20 (3)	17 (4)	0 (0)	−2 (2)	0 (0)
W(5)	4066 (2)	6428 (4)	4712 (4)	4 (1)	24 (2)	21 (2)	1 (1)	3 (1)	−3 (2)
W(6)	2783 (3)	7500 (0)	3248 (5)	7 (1)	36 (4)	13 (4)	0 (0)	−2 (2)	0 (0)
W(7)	1622 (2)	6428 (4)	4515 (3)	5 (1)	23 (2)	20 (2)	−3 (1)	−4 (1)	0 (2)
K(1)	21(20)	2500 (0)	7037(41)	16(10)	19(17)	81(41)	0 (0)	−12(17)	0 (0)
K(2)	7023(24)	7500 (0)	4908(49)	18(13)	52(31)	96(50)	0 (0)	−12(19)	0 (0)
K(3)	301(14)	4896(25)	2482(30)	9 (5)	65(20)	75(26)	3(10)	26(10)	−27(22)

(b) Positional and isotropic thermal parameters for the silicon and oxygen atoms (×10^4).

	x	y	z	B/Å^2		x	y	z	B/Å^2
Si	2756(25)	7500 (0)	5922(43)	2.3 (9)	O(13)	3278 (37)	6649(56)	3721 (65)	2.2(16)
O (1)	909(41)	5902(56)	7982(64)	2.3(15)	O(14)	4297(140)	7500 (0)	4263(242)	11.9(88)
O (2)	1362(51)	6642(76)	5983(90)	4.5(24)	O(15)	4454 (53)	5714(81)	3887 (93)	4.7(25)
O (3)	2709(37)	6606(55)	6586(64)	2.2(15)	O(16)	4630 (32)	6717(51)	6019 (59)	1.5(13)
O (4)	2214(29)	6224(42)	8435(48)	0.7(10)	O(17)	3631 (41)	7500 (0)	5681 (70)	0.5(15)
O (5)	1573(55)	7500 (0)	7714(89)	1.8(20)	O(18)	3518 (28)	5710(44)	5425 (51)	0.6(11)
O (6)	1892(35)	5321(51)	6838(61)	1.6(13)	O(19)	5152 (40)	7500 (0)	7689 (72)	0.4(14)
O (7)	1034(29)	5787(46)	3924(53)	0.8(11)	O(20)	3952 (37)	6536(55)	7505 (68)	2.3(16)
O (8)	1199(45)	7500 (0)	4109(83)	1.0(17)	O(21)	3410 (55)	5910(78)	9393 (87)	4.7(24)
O (9)	2075(32)	6633(49)	3244(58)	1.4(13)	O(22)	2986 (47)	7500 (0)	8642 (85)	1.3(19)
O(10)	2218(39)	5673(54)	5044(62)	2.0(14)	O(23)	3163 (32)	5234(46)	7530 (46)	1.2(12)
O(11)	2358(76)	7500 (0)	5074(126)	4.3(35)	O(24)	2882 (33)	4251(48)	5794 (57)	1.4(13)
O(12)	3026(95)	7500 (0)	1918(158)	6.5(48)					

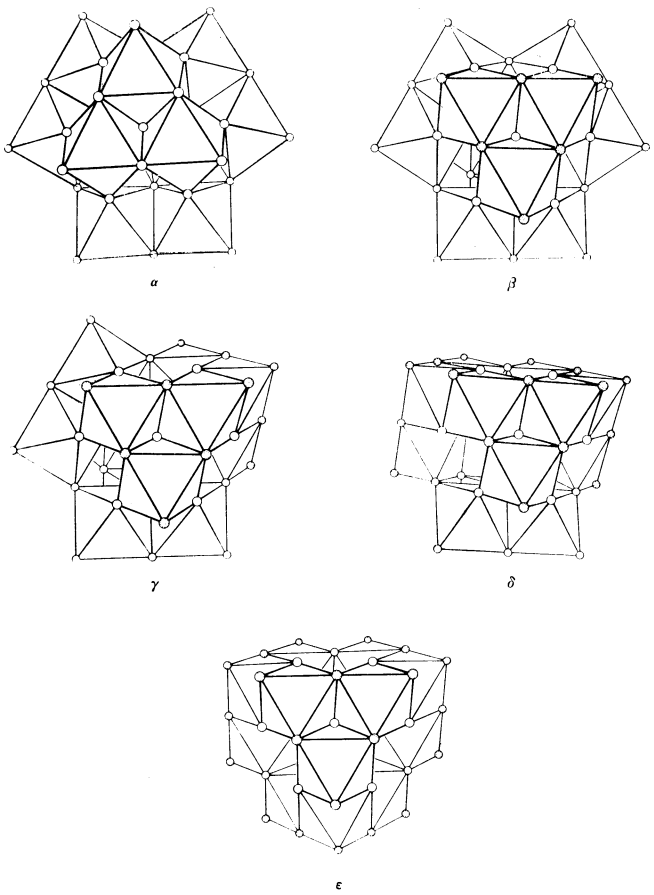


Fig. 2. Five possible isomeric structures of the Keggin structure. The models $A^tB_{12}O_{40}$ are constructed by idealized regular tetrahedra A^tO_4 and BO_6 octahedra. White and dotted balls represent oxygen atoms. The β, γ, δ, and ε (Jahr structure) models are made by rotating one, two, three, and all the four W_3O_{13} moieties of the α (Keggin structure) by 60°. The W_3O_{13} units with dotted balls are rotated parts.

(*cf.* Fig. 1α and 2α). The present work has revealed that the β-$SiW_{12}O_{40}^{4-}$ anion has the structure shown in Figs. 1β and 2β. Note that the β-isomer results from a 60° rotation about the threefold axis of one of the trigonal edge-sharing W_3O_{13} units of the α-isomer and from reattachment again *via* corner sharing. The possibility of such geometrical isomers has been predicted by Baker and Figgis[24] on the basis of stoichiometric and structural speculations.

Table 2 lists the interatomic distances within the anion, along with their standard deviations.

The central SiO_4 tetrahedron is largely distorted, the Si–O distances ranging from 1.37 to 1.83 Å. Each WO_6 octahedron is also greatly distorted. The oxygen atoms are classified into four groups, which will be called O_a, O_b, O_c, and O_d. The positions of these types of oxygen atoms are indicated in Fig. 3, which represents one of the W_3O_{13} units and the central SiO_4 tetrahedron. The O_a oxygen atoms are shared between three WO_6 octahedra and one SiO_4 tetrahedron. The O_b oxygen atoms are shared between adjacent W_3O_{13} units. The O_c oxygen atoms are shared between $2WO_6$ octahedra in a W_3O_{13} unit. The O_d oxygen atoms are unshared with other

Table 2. Interatomic distances within the anion with their estimated standard deviations

W(1)–O(18)	b	1.94 (6) Å	W(5)–O(14)	c	1.83(12) Å
O (6)	c	2.03 (7)	O(17)	a	2.27 (6)
O(23)	c	2.01 (7)	O(15)	d	1.73(12)
O(10)	b	1.92 (8)	O(18)	b	1.84 (6)
O (3)	b	2.24 (8)	O(13)	b	2.10 (8)
O(24)	d	1.58 (7)	O(16)	c	2.10 (7)
W(2)–O (2)	b	1.90(11)	W(6)–O (9)	c	1.99 (7)
O (5)	b	1.93 (3)	O(12)	d	1.79(20)
O (6)	c	1.75 (7)	O(11)	a	2.53(16)
O (1)	d	1.78 (8)	O(13)	b	1.78 (8)
O (4)	c	1.90 (6)	W(7)–O (2)	b	2.00(11)
O (3)	b	2.50 (7)	O (7)	d	1.75 (6)
W(3)–O (3)	b	2.40 (8)	O(10)	b	1.83 (8)
O(21)	d	1.68(11)	O (8)	c	1.95 (5)
O (4)	c	1.88 (5)	O(11)	a	2.36(11)
O(22)	b	1.93 (3)	O (9)	b	1.92 (7)
O(20)	b	2.02 (8)	Si–O(11)	a	1.37(17)
O(23)	c	1.94 (7)	O(17)	a	1.83 (9)
W(4)–O(16)	c	1.72 (7)	O (3)	b	1.64 (8)
O(19)	d	1.83(68)			
O(17)	a	2.25 (8)			
O(20)	b	1.94 (8)			

O (1)–O (2)	2.99(14)	O (9)–O (9)′	2.70(15)
O (4)	2.79(10)	O(10)	2.79(11)
O (5)	2.86(10)	O(11)	2.79(16)
O (6)	2.67(11)	O(12)	2.93(19)
O (2)–O (3)	2.88(13)	O(13)	2.55(10)
O (5)	2.65(15)	O(10)–O(11)	2.85 (8)
O (6)	2.57(14)	O(18)	2.72 (9)
O (7)	3.07(13)	O(24)	2.77(11)
O (8)	2.79(15)	O(11)–O(13)	2.90(16)
O(10)	2.62(13)	O(17)	2.73(17)
O(11)	2.71(17)	O(12)–O(13)	2.74(19)
O (3)–O (3)′	2.78(17)	O(13)–O(13)′	2.64(17)
O (4)	2.67(10)	O(14)	2.58(26)
O (5)	3.09(12)	O(15)	2.83(13)
O (6)	2.63(11)	O(17)	2.96(11)
O(10)	2.67(11)	O(18)	2.70(10)
O(11)	2.51(15)	O(14)–O(15)	2.84(14)
O(17)	2.63(10)	O(16)	2.67(28)
O(18)	2.65(10)	O(17)	2.29(31)
O(20)	2.82(11)	O(15)–O(16)	3.20(14)
O(22)	3.06(12)	O(18)	2.77(13)
O(23)	2.63(11)	O(16)–O(16)′	2.43(16)
O (4)–O (5)	2.56 (9)	O(17)	2.43(10)
O (6)	2.59(10)	O(18)	2.89 (9)
O(21)	2.80(12)	O(19)	2.71(34)
O(22)	2.55 (8)	O(20)	2.40(11)
O(23)	2.75 (9)	O(17)–O(18)	2.82 (6)
O (6)–O(10)	2.48(11)	O(20)	2.88(11)
O(23)	2.77(10)	O(18)–O(23)	2.92 (9)
O(24)	2.96(10)	O(24)	2.65 (9)
O (7)–O (8)	2.70 (7)	O(19)–O(20)	2.90(70)
O (9)	2.66 (9)	O(20)–O(20)′	3.00(17)
O(10)	2.85(10)	O(21)	2.86(14)
O (8)–O (9)	2.51(10)	O(22)	2.89(12)
O(11)	2.69(18)	O(23)	2.59(10)
		O(21)–O(22)	2.80(12)
		O(23)	2.68(13)
		O(23)–O(24)	2.78(10)

Prime refers to the transformation x, 0.5 $-y$, z.

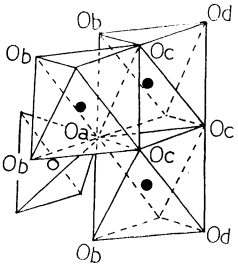


Fig. 3. One of the W_3O_{13} units in β-$SiW_{12}O_{40}^{4-}$ with the central SiO_4 tetrahedron (see text).

polyhedra. The O_a–O_c edges are shared between two WO_6 octahedra. The W–O distances are W–O_a 2.24—2.53, W–O_b 1.74—2.10, W–O_c 1.75—2.10, and W–O_d 1.59—1.80 Å. These values show that the tungsten atoms are off-centered in the respective WO_6 octahedron and that all the tungsten atoms are displaced toward the outside of the anion. Similar displacements have been observed for the tungsten atoms in $PW_{12}O_{40}^{3-}$,[7] $CoW_{12}O_{40}^{5-}$,[26] and α-$SiW_{12}O_{40}^{4-}$,[23,24] and also for the molybdenum atoms in $TeMo_6O_{24}^{6-}$,[26] $As_4Mo_{12}O_{50}^{8-}$,[28] and $CeMo_{12}O_{42}^{8-}$,[29] such displacement is considered to be a characteristic feature of not only Keggin-type structures but also of other types of heteropolymolybdates and heteropolytungstates.

The crystal structure projected along the b and c axes are presented in Figs. 4 and 5 respectively. Two anions lie on the crystallographic mirror plane at $y=1/4$, and other two, on the mirror plane at $y=3/4$. The rotated W_3O_{13} unit is dipicted as W6–W7–W7^{I}. An attempt to locate the water molecules was not successful, since many

Table 3. Interanionic and inter cation-anion distances (less than 3.5 Å)

O (1)^{III}	–O(19)^{I}	3.06(42) Å
	O(16)^{I}	3.20(11)
O (2)^{III}	–O(19)^{I}	3.31(63)
O (4)^{IV}	–O(24)^{I}	3.16 (9)
O (5)^{III}	–O(19)^{I}	2.97(81)
O (7)	–O(21)^{III}	2.94(13)
O (9)	–O(23)^{III}	3.09(10)
	O(24)^{III}	3.47(10)
O(10)	–O(21)^{III}	2.90(14)
O(21)^{III}	–O(24)^{III}	3.23(13)
K (1)^{III}	–O(14)	3.22(31)
K (2)	–O (4)^{IV}	2.96 (7)
	O(22)^{IV}	2.74(11)
	O(24)^{I}	2.88 (7)
K (3)^{II}	–O (1)^{III}	2.85 (9)
	O(15)	2.80(12)

Roman numeral superscripts refer to the following transformations of the coordinates:

I	$1-x$,	$1-y$,	$1-z$
II	$0.5+x$,	y,	$0.5-z$
III	$0.5-x$,	$1-y$,	$-0.5+z$
IV	$0.5+x$,	y,	$1.5-z$
V	$1-x$,	$-0.5+y$,	$1-z$
VI	$0.5+x$,	$0.5-y$,	$1.4-z$

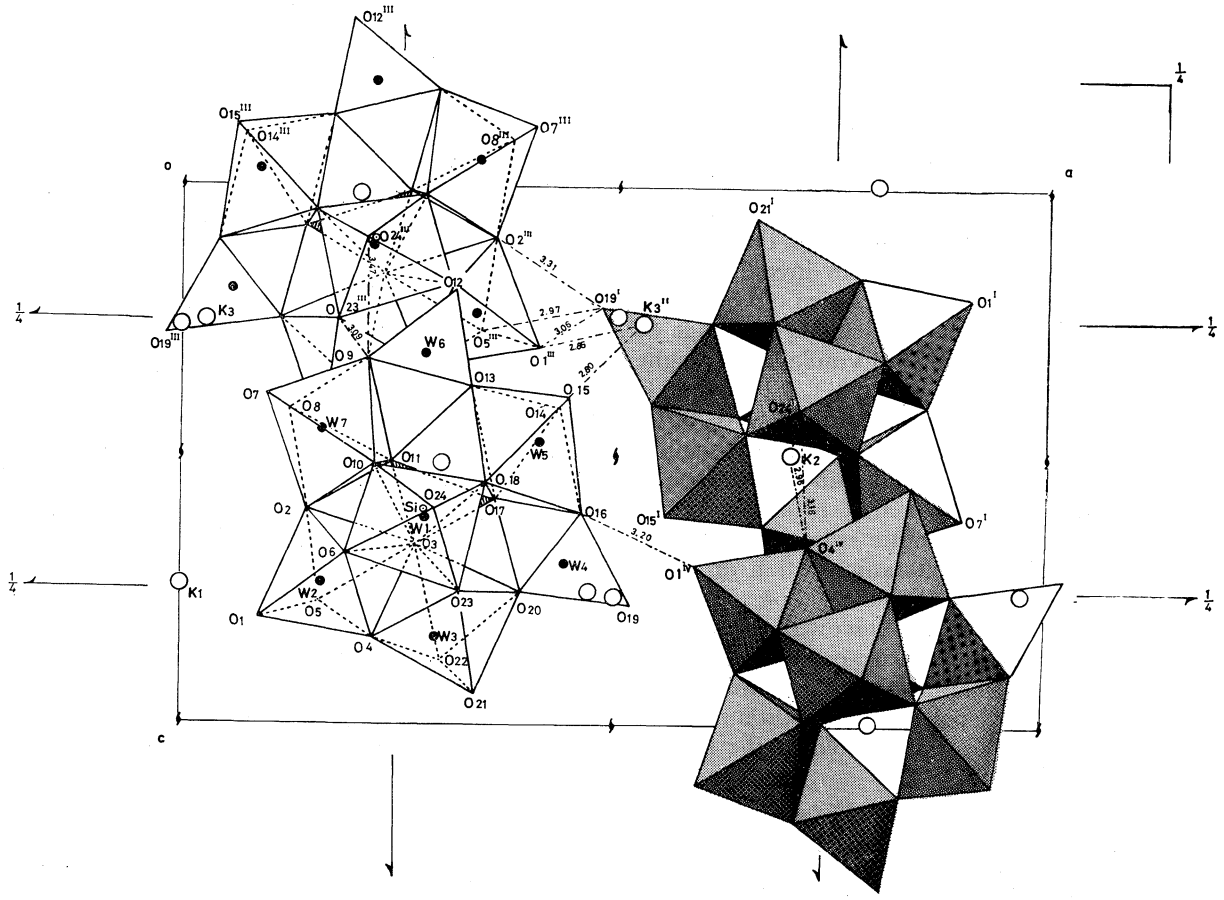


Fig. 4. The crystal structure of β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ projected along the b axis.

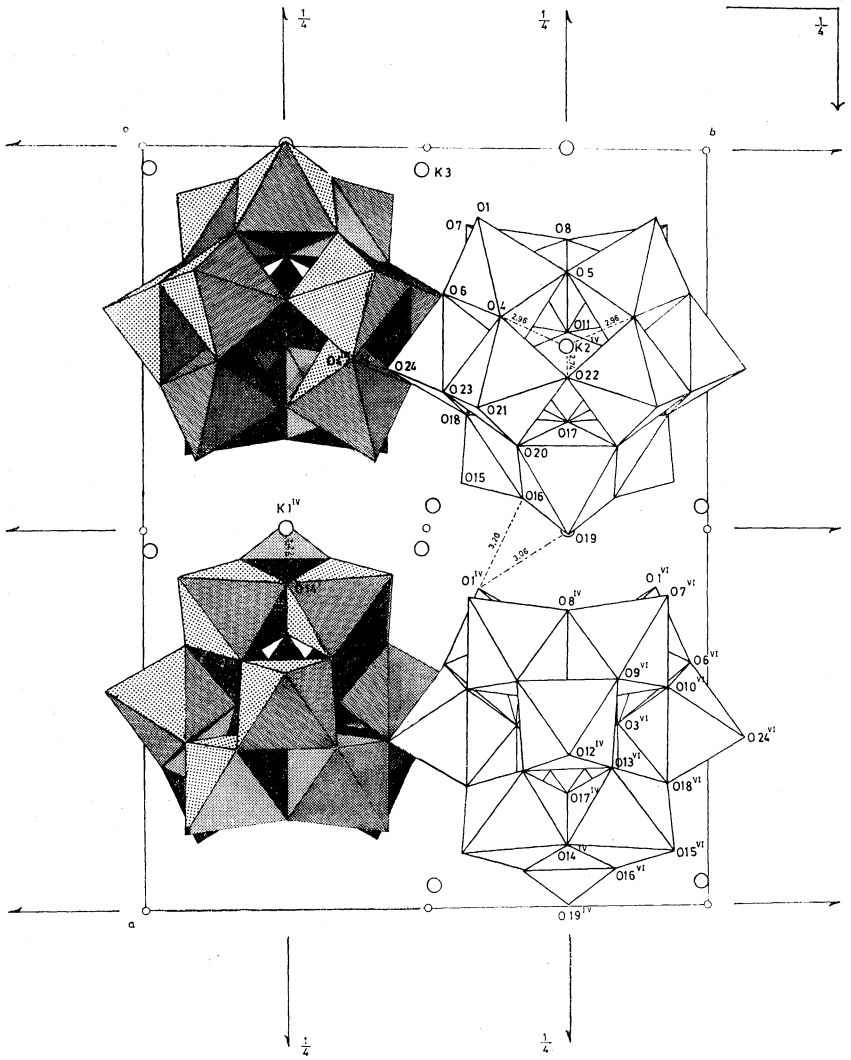


Fig. 5. The crystal structure of β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ projected along the c axis.

electron density peaks, which were lower than those of the anion oxygens, were smeared out in the cavities between the polyanions. In order to investigate the crystal water, thermal analysis was carried out on β-$K_4SiW_{12}O_{40}\cdot 9H_2O$. The results confirm the presence of a total of nine water molecules per formula unit (weight loss at 230 °C: calcd 5.1%, obsd 4.9%). The crystals begin to lose the water at a temperature as low as 70 °C, which, together with the X-ray diffraction study, suggest that the present crystals possibly contain mobile zeolitic water. It has been established that heteropoly compounds very often contain zeolitic water in the crystals.[11,29] Interanionic and interanion-cation distances less than 3.5 Å are listed in Table 3. Some parts of adjacent anions seem to come in contact with one another directly. All the potassium ions are partly coordinated by anion oxygens, the remaining coordination numbers being presumably completed by the addition of the water oxygens, which were not located in the present work.

The structural relationship between the α- and β-isomers has been clarified for the first time by this investigation, though with large standard deviations of the positions of the light elements, as is shown in Tables 1 and 2.

On the Other Possible Geometrical Isomer of the Keggin Structure

Figure 2 shows all five possible isomers of $SiW_{12}O_{40}^{4-}$ or the Keggin ion in general. The models are constructed of idealized octahedra (WO_6) and tetrahedra (SiO_4). In the β-model, one W_3O_{13} of the Keggin ion (α) is rotated by 60°; such a reorientation of two, three, and all four W_3O_{13} moieties leads to γ, δ, and ε isomers successively. The ε model was once proposed for 12-heteropolyanions by Jahr[31] and later found by Johansson in the $Al^tO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ ion,[32,33] where Al^tO_4 denotes AlO_4 tetrahedron and where the other 12 aluminum atoms are surrounded by an octahedral array of 6 oxygen atoms.

None of the five isomers can be optically active, and a close-packing of the oxygen atoms is realized only in δ and ε. If we use A, B, and C to label the layers of oxygen atoms, as is common in discussions of the close-packing (ABAB for a hexagonal close-packing and ABCABC for a cubic one), the arrangements of the oxygen atom layers in δ and ε are ABCB and ABCA. In both anions, the A and B layers both contain 12 atoms and C, 10, while the last B layer in δ and the last A in ε contain 6 oxygen atoms each. One isomer of $BW_{12}O_{40}^{4-}$, which gives

unique polarographic waves among all the 12-heteropoly acids, might have a γ, δ, or ε structure; an X-ray diffraction study of the crystals containing this anion is highly desirable.

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