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The Crystal Structure of α-$K_8SiW_{11}O_{39}\cdot 13H_2O$

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α-$K_8SiW_{11}O_{39}\cdot 13H_2O$ is cubic with the space group $P\bar{4}3m$ and $a=10.654(1)$ Å; $D_m=4.40$ g cm^{-3}, $D_x=4.42$ g cm^{-3} for $Z=1$. The crystal contains a discrete $SiW_{11}O_{39}{}^{8-}$ ion, which is almost identical to α-$SiW_{12}O_{40}{}^{4-}$ anion in shape and in size but one tungsten atom and the exterior terminal oxygen atom are absent. The position of the vacant hole could not be located because of the seemingly high symmetry of T_d of the polyanion caused by the orientational randomness of the anions. The silicon atom at the center of the polyanion lies on the origin of the cubic lattice and the potassium cations linking α-$SiW_{11}O_{39}{}^{8-}$ ions are at the middle points of adjacent polyanions.

The 11-tungstosilicate salts were first prepared by Marignac,[1] however he described the compounds as 10-tungstosilicates, $M_8{}^{I}SiW_{10}O_{36}$. Most of the 10-tungstosilicates given in the Gmelin's Handbook[2] are now believed to be 11-tungstosilicates.

This heteropoly anion can be regarded as an hydrolytic degradation product of α-$SiW_{12}O_{40}{}^{4-}$ anion and the reaction is as follows;

$$\alpha\text{-}SiW_{12}O_{40}{}^{4-} + 6OH^- \rightleftharpoons \alpha\text{-}SiW_{11}O_{39}{}^{8-} + WO_4{}^{2-} + 3H_2O$$

This reaction is reversible and addition of acid to a solution of α-$SiW_{11}O_{39}{}^{8-}$ in the presence of $WO_4{}^{2-}$ yields α-$SiW_{12}O_{40}{}^{4-}$ immediately. Even in the absence of $WO_4{}^{2-}$, α-$SiW_{12}O_{40}{}^{4-}$ is formed on acidification from α-$SiW_{11}O_{39}{}^{8-}$.

Recent investigation by Souchay *et al.*[3] has shown that the α-$SiW_{11}O_{39}{}^{8-}$ anion is an important intermediate product in the formation of α-$SiW_{12}O_{40}{}^{4-}$ and the reaction proceeds as follows;

$$SiO(OH)_3{}^- + 11WO_4{}^{2-} + 15H^+ \longrightarrow \alpha\text{-}SiW_{11}O_{39}{}^{8-} + 9H_2O$$

$$\alpha\text{-}SiW_{11}O_{39}{}^{8-} + WO_4{}^{2-} + 6H^+ \longrightarrow \alpha\text{-}SiW_{12}O_{40}{}^{4-} + 3H_2O$$

On the other hand, addition of acidified sodium silicate to a solution of acidified sodium tungstate gives β-$SiW_{11}O_{39}{}^{8-}$ and β-$SiW_{12}O_{40}{}^{4-}$ as is shown in Fig. 1. As for the structure of α- and β-$SiW_{12}O_{40}{}^{4-}$, we have already published the results.[5–7] Recently the formation of three isomers of β-$SiW_{11}O_{39}{}^{8-}$, β_1, β_2, and β_3, through $SiW_9O_{34}{}^{10-}$ and $HSiW_9O_{34}{}^{9-}$ have been reported by Contant *et al.*[4] However these isomers are outscope of the present study. The reaction

$$SiW_{11}O_{39}{}^{8-} + M^{n+} \longrightarrow SiW_{11}MO_{40}{}^{(8-n)-}$$

where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Fe(III), Cr(III), V(IV), V(V), and Mo(VI) were reported[8] and the resultant $SiW_{11}MO_{40}{}^{(8-n)-}$ anions have Keggin structure,[9] in which one of the twelve tungsten atoms is substituted by M. But lanthanide cations (Ln) may be too large to be included in the Keggin structure and form salts of the type $K_{10}Ln(SiW_{11}O_{39})_2\cdot nH_2O$.[10]

Present crystal-structure determination of α-$K_8SiW_{11}O_{39}\cdot 13H_2O$ have revealed that the structure of the α-$SiW_{11}O_{39}{}^{8-}$ is very similar to that of α-$SiW_{12}O_{40}{}^{4-}$, which has the Keggin structure, but one tungsten atom and its terminal oxygen atom are missing.

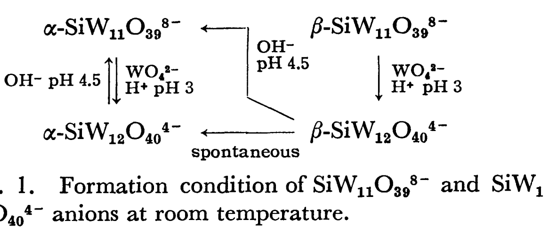

Fig. 1. Formation condition of $SiW_{11}O_{39}{}^{8-}$ and $SiW_{12}O_{40}{}^{4-}$ anions at room temperature.

Experimental

Potassium hydroxide was added to a hot concentrated solution of α-$K_4SiW_{12}O_{40}$ with mole-ratio of 6: 1; the pH of the solution was increased to 4.5. The crystals of α-$K_8SiW_{11}O_{39}\cdot 13H_2O$ were precipitated on cooling and was recrystallized from water. They are colorless, stable in air and more resistant to reduction that the α-$SiW_{12}O_{40}{}^{4-}$.

Preliminary oscillation and Weissenberg photographs showed that the crystal is cubic. No systematic absence of the reflections was observed, therefore three space groups, $P\bar{4}3m$, $P432$, and $Pm3m$ were possible, however further structure analysis determined the space group to be $P\bar{4}3m$. The intensities of the reflections up to $2\theta=60°$ were measured on the Rigaku four-circle diffractometer with graphite-monochromated Mo*K*α radiation ($\lambda=0.71069$ Å). The ω-2θ scan technique was employed and a total of 312 independent reflections, whose intensities were larger than 3σ, were used for the structure analysis. The data were corrected for Lorentz and polarization factors. No corrections were made for absorption and extinction effects. The crystal used for intensity measurement was of the dimensions 0.1×0.1×0.1 mm and the crystal data are as follows;

α-$K_8SiW_{11}O_{39}\cdot 13H_2O$
F.W. = 3220.7
cubic $P\bar{4}3m$
$a = 10.654(1)$ Å
$V = 1209.3$ Å^3
$Z = 1$
$D_m = 4.40$ g cm^{-1}, $D_x = 4.42$ g cm^{-1}
$\mu = 302.0$ cm^{-1} (for Mo*K*α radiation)

Structure Determination

The structure was solved by the heavy atom method. The three dimensional Patterson map could not be at

Table 1. Atomic parameters

Positional and thermal parameters ($\times 10^4$) with their estimated standard deviations in parentheses. The β_{ij}'s are defined by: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	2349(2)	2349(2)	38(10)	25(1)	25(1)	54(3)	−5(2)	−0(4)	−0(4)
Si	0(0)	0(0)	0(0)	72(34)	72(34)	72(34)	0(0)	0(0)	0(0)
O(1)	877(50)	877(50)	−877(50)	50(39)	50(39)	50(39)	−19(41)	19(41)	19(41)
O(2)	3328(65)	1412(41)	−1412(41)	77(70)	90(46)	90(46)	22(40)	−22(40)	33(67)
O(3)	2908(46)	1120(32)	1120(32)	45(49)	28(24)	28(24)	−4(28)	−4(28)	1(34)
O(4)	3438(39)	3438(39)	285(69)	36(29)	36(29)	89(119)	19(40)	−16(37)	−16(37)
K	5000(0)	0(0)	0(0)	11(21)	108(26)	108(26)	0(0)	0(0)	0(0)

first solved with the three possible space groups assuming eleven tungsten atoms per molecule, but satisfactory solution was obtained assuming that eleven tungsten atoms occupy the twelve tungsten positions of the Keggin structure[9] with equal statistical weight and that the space group is $P\bar{4}3m$. All the other atoms, except five potassium cations and thirteen water molecules, were located from the Fourier synthesis based on the coordinates of tungsten atoms. The structure was refined by the block diagonal least-squares technique with a local version of UNICS[11] program. A weighting scheme, $w=0.2$ for $|F_o|<41$ and $w=1$ otherwise, was employed. At the last stage of the refinement, the temperature factors were assumed to be anisotropic and the last R value, $R=\sum||F_o|-|F_c||/\sum|F_o|$, was 0.069.

The atomic scattering factors used were taken from the International Tables for X-Ray Crystallography.[12] The calculations were performed on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo. The atomic coordinates and the temperature factors are listed in Table 1. The final F_o-F_c table is kept at the office of Chemical Society of Japan as Document No. 7607.

Results and Discussion

The structure of the α-$SiW_{11}O_{39}^{8-}$ anion results from removing one WO_6 octahedron from the α-$SiW_{12}O_{40}^{4-}$, which has the Keggin structure, and is illustrated in Fig. 2 as a coordination polyhedra model. The result of the structure determination has shown that α-$SiW_{11}O_{39}^{8-}$ is required to have T_d symmetry and Keggin structure. This apparent high symmetry is effected by orientational randomness of the polyanions in the crystal. The α-$SiW_{11}O_{39}^{8-}$ anion can be regarded as a "deficient Keggin ion," in which one of the twelve equivalent positions of metals and its terminal oxygen, is vacant. This deficient Keggin ion lies in the crystal with its vacant site oriented randomly to one of the twelve positions and with the statistical weight of 11/12. The deformation of the Keggin structure caused by the removal of one tungsten atom could not be studied in detail because of this randomness. The standard deviations of the coordinates of the heavy atoms and the thermal parameters are not so large and accordingly it is inferred that the α-$SiW_{11}O_{39}^{8-}$ is not much deformed from the α-$SiW_{12}O_{40}^{4-}$. The tungsten-oxygen and silicon-oxygen interatomic distances given in Table 2 should be understood as average values for this hypothetical Keggin ion and agree well with those of the α-$SiW_{12}O_{40}^{4-}$ anion.[5]

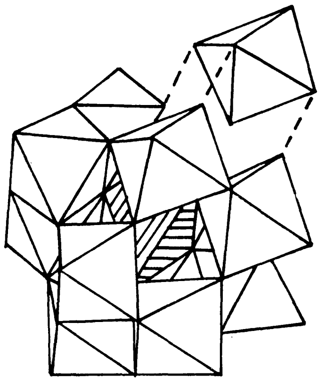

Fig. 2. The structure of the α-$SiW_{11}O_{39}^{8-}$ anion and its structural relation to the α-$SiW_{12}O_{40}^{4-}$ anion.

Table 2. Interatomic distances with their estimated standard deviations

W—O(1)	2.422(54)Å	O(2)—O(3)	2.752(85)
O(2)	2.114(70)	O(4)	2.817(101)
O(3)	1.843(50)	O(3)—O(4)	2.684(89)
O(4)	1.662(74)	Si—O(1)	1.617(53)
O(1)—O(2)	2.733(87)	K—O(2)	2.774(70)
O(3)	3.045(72)	K—O(3)	2.795(49)

Three equivalent potassium cations per formula unit were located and are shown in Fig. 3. The potassium ion is octacoordinated by four O(2) and four O(3) in the form of skewed antiprism. The molecular center is at the origin of the cubic cell and the potassium atoms lie at the middle points of the cell edges. There are large straight channels through the center of the unit cell parallel to the three axes and on the Fourier map low electron-density peaks were found in this space, however they could not be interpreted even by assuming random distribution of the unlocated five potassium cations and/or water molecules. Similar situation was encountered when Baker *et al.* solved the crystal structure of ammonium salt of $Co^{III}Co^{II}W_{11}O_{40}^{9-}$, in which he could not locate the ammonium cations and water of crystallization probably because of the disorder in the channels and large pockets formed by the exterior oxygens of the anions.[13] Although this anion is not exactly the same as that of the present compound because the former has the Keggin structure with one

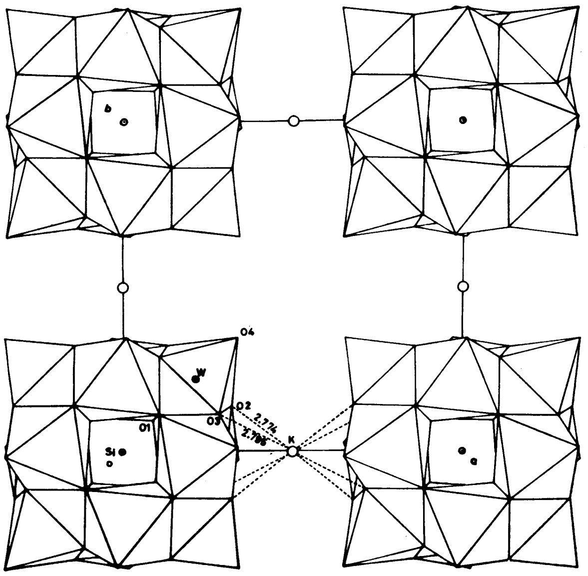

Fig. 3. The crystal structure of α-$K_8SiW_{11}O_{39}\cdot 13H_2O$ showing the coordination around potassium atoms.

of the twelve tungstens replaced by Co^{II}, their crystal structures resemble each other; the ammonium salt of $Co^{III}Co^{II}W_{11}O_{40}{}^{9-}$ is cubic with the space group Fm3m, the cell constant is just the double of that of the present compound and $Z=8$. The arrangement of anions is an enlarged NaCl type, with the Na^+ ions replaced by a set of Keggin units having one unique orientation and the Cl^- ions replaced by Keggin units with an orientation at right angles to the first set. Therefore if there have not been for the two sets of orientations, the unit-cell dimensions would be the half and the arrangement of the anions would be the same as in the present compound. Single crystal X-ray work of $(NH_4)_7Na_2[GaH_2W_{11}O_{40}]\cdot 15H_2O$, $(NH_4)_{7.3}H_{2.7}[Co^{II}Co^{II}W_{11}O_{40}]\cdot 17H_2O$, $Rb_{6.5}Co_{0.4}H_{2.7}[Co^{II}Co^{II}W_{11}O_{40}]\cdot 15H_2O$, $K_{6.5}H_{2.5}[Co^{II}Co^{II}W_{11}O_{40}]\cdot 13H_2O$, $K_7H[Co^{III}Co^{III}W_{11}O_{40}]\cdot 14H_2O$[13,14] have shown that these compounds are isomorphous with the ammonium salt of $Co^{III}Co^{II}W_{11}O_{40}{}^{9-}$ in spite of their various number of cations and water of crystallization. The unit-cell edge of $(NH_4)_7Na_2[GaH_2W_{11}O_{40}]\cdot 15H_2O$ shrinks reversibly and continuously with increasing temperature. From these facts, fairly high degree of freedom in the arrangement of cations and water molecules in the channels can be inferred. In the crystal-structure analysis of $K_4SiW_{12}O_{40}\cdot 17H_2O$,[15] some of the potassium atoms could not be located and some works[7,14,16] have reported that crystals of heteropoly acids often contain zeolitic water. These facts suggest that the unlocated potassium atoms and water molecules in the present crystal are a characteristic result of disorder in the cavities between the polyanions.

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