The Structure of Polyvanadotungstates. II. The Crystal Structure of $K_7V_5W_8O_{40}\cdot 12H_2O$

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(Received May 7, 1975)

Crystals of $K_7V_5W_8O_{40}\cdot 12H_2O$ are cubic, with the space group of P$\bar{4}$3m and with the cell dimension of a= 10.62(1) Å. The structure was determined by the single-crystal X-ray diffraction technique. All the non-hydrogen atoms were located, and the final R value was 0.057. The $V_5W_8O_{40}{}^{7-}$ anion has the Keggin structure, with a central VO_4 tetrahedron. The twelve outer metal positions are randomly occupied by four vanadium and eight tungsten atoms. A detailed discussion of the configuration isomers is impossible because of the orientational disorder. The present work, and the former X-ray structure determination of $V_2W_4O_{19}{}^{4-}$ show that polyvanadotungstates can be regarded as substituted homologues of isopolytungstates: $V_nW_{6-n}O_{19}{}^{(n+2)-}$ (n=1, 2) has a hexaniobate-type structure, and $V^tV_nW_{n-12}O_{40}{}^{(n+3)-}$ (n=2, 3, 4), the Keggin structure, where V^t represents the central vanadium atom.

When a solution of orthotungstate ($WO_4{}^{2-}$) and metavanadate ($VO_3{}^-$) salts is acidified, polyvanadotungstate crystals are precipitated.[1] Several species of polyvanadotungstates have been reported as salts, their composition varies with the pH, the constitution, and the concentration.[1-4] Recently, Pope and Flynn proposed, in their preparative studies,[5-7] that these polyvanadotungstate anions can be divided into two groups: $V_nW_{6-n}O_{19}{}^{(n+2)-}$($n$=1,2) and $V^tV_nW_{12-n}O_{40}{}^{(n+3)-}$(where V^t is the vanadium in the center of the tetrahedron, n=2,3,4). For the former series, we have determined the crystal structure of α-$(CN_3H_6)_4V_2W_4O_{19}$ and showed[8] that, as Pope proposed, it has the "*hexaniobate structure*"[9] shown in Fig. 1. This paper will report the structure of $K_7V_5W_8O_{40}\cdot 12H_2O$, which belongs to the latter series.

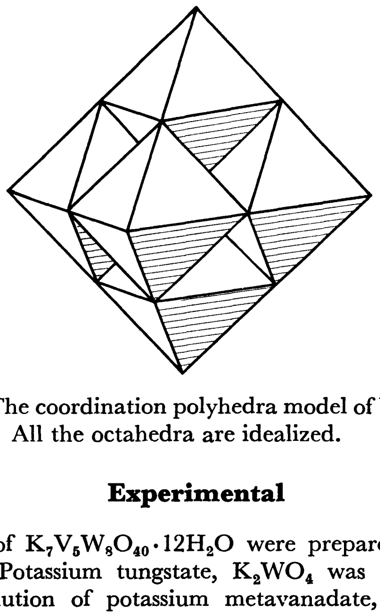

Fig. 1. The coordination polyhedra model of $V_2W_4O_{19}{}^{4-}$ anion. All the octahedra are idealized.

Experimental

Crystals of $K_7V_5W_8O_{40}\cdot 12H_2O$ were prepared by Pope's method.[7] Potassium tungstate, K_2WO_4 was added to an aqueous solution of potassium metavanadate, KVO_3; the mixture was acidified with formic acid to pH=3 and then heated until just before boiling. From the red-brown crystals obtained after cooling, a single crystal 0.2×0.2×0.15 mm in size was chosen for the X-ray diffraction experiments. The reflection data were collected on a Rigaku four-circle diffractometer with Mo$K\alpha$ radiation monochromatized by a graphite crystal (λ=0.7107 Å). The $\omega-2\theta$ scan technique was employed, and 256 independent reflections with intensities larger than 3σ were obtained to 2θ=60 °. The intensities were corrected for the Lorentz and polarization factors, but not for absorption. The crystal data are as follows:

$K_7V_5W_8O_{40}\cdot 12H_2O$

cubic

a = 10.62(1) Å

V = 1199 Å^3

space group P$\bar{4}$3m

Z = 1 (D_m=4.0 g cm^{-3}, D_x=3.97 g cm^{-3})

(Mo$K\alpha$) = 233.3 cm^{-1}

The conventional heavy atom method was used to solve the structure.** The positional parameters and anisotoropic thermal parameters for all the non-hydrogen atoms were refined by the block-diagonal, least-squares method to R= 0.057. No significant peak was found on the residual electron density map. The F_o—F_c table is kept by the Chemical Society of Japan as Document No. 7525. A weighting scheme of w=0.5 for $|F_o|<104.4$ and w=1 otherwise was employed. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography," but those for W and V were corrected for the anomalous dispersion.[10] 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.[11]

Results and Discussion

The Structure of the Polyanion. As is shown in Fig. 2, one unit cell contains one Keggin-type polyanion, $V^tM_{12}O_{40}{}^{7-}$, where V^t represents the central vanadium atom of the VO_4 tetrahedron and where M_{12} means 4V

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** The possible space groups observed in connection with the systematic extinctions are P$\bar{4}$3m, Pm3m, and P432. Considering the composition of the polyanion, the Patterson map was solved only by assuming the positional disorder of metal atoms. A trial structure obtained on the assumption of the P$\bar{4}$3m space group gave an R value of 0.27; however, Pm3m and P432 gave 0.8—0.9.

TABLE 1. FINAL POSITIONAL COORDINATES ($\times 10^4$) AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$)[a)]
(The temperature factor is of the form: $\exp[-h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M[b)]	2351 (2)	2351 (2)	−30 (2)	18 (2)	18 (2)	36 (2)	−5 (1)	3 (7)	3 (7)
V[t]	0	0	0	28 (5)	28 (5)	28 (5)	0	0	0
Oa[c)]	948(110)	948(110)	−948(110)	58(47)	58(47)	58(47)	24(58)	24(58)	24(58)
Ob	1101 (35)	2806 (50)	2806 (50)	40(28)	38(28)	38(45)	35(32)	35(32)	21(32)
Oc	1428 (40)	1428 (40)	−3211 (49)	53(35)	53(35)	34(49)	23(46)	0(32)	0(32)
Od	3476 (30)	3476 (30)	182 (44)	39(24)	39(24)	30(65)	9(31)	11(22)	11(22)
K(1)	5000	0	0	24(19)	33(13)	33(13)	0	0	0
K(2)	5000	5000	1423 (37)	58(17)	58(17)	124(40)	0	0	0
H_2O	3113 (47)	3113 (47)	5234(100)	161(51)	161(51)	86(53)	30(65)	80(74)	80(74)

a) The estimated standard deviations in parantheses here and elsewhere are in units of the last significant digit.
b) $M=\dfrac{4V+8W}{12}$, see text. c) The Evans classification of oxygen atoms in the Keggin structure (see text).[12)]

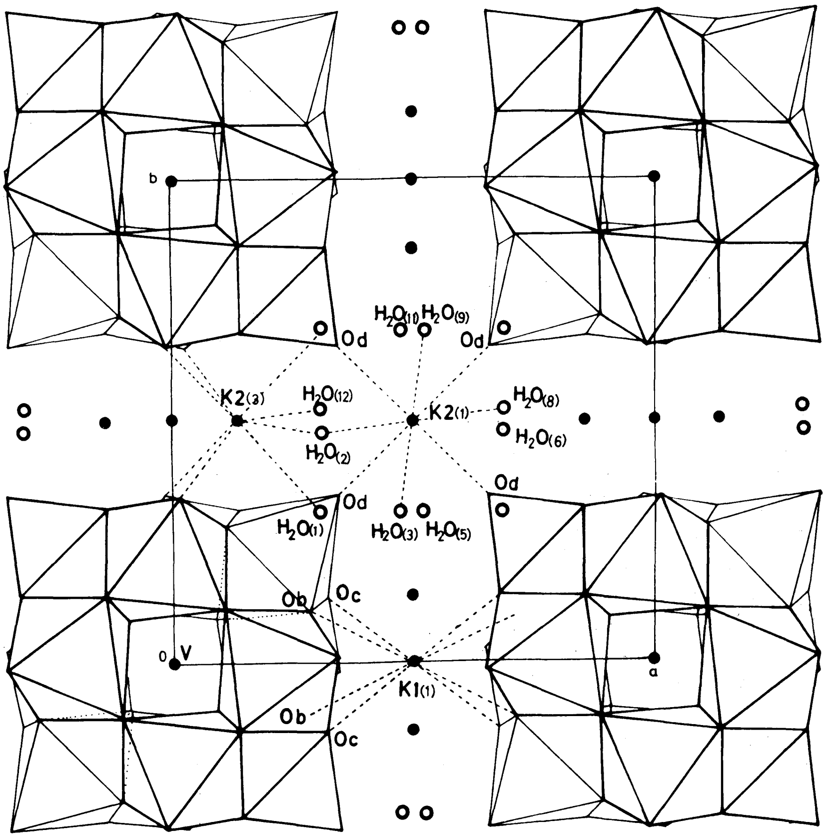

Fig. 2. A view of the structure as projected down the c axis. The $V_5W_8O_{40}{}^{7-}$ anion has three two fold axes parallel to the crystal axes. The coordination bonds around K^+ are designated by dotted lines.

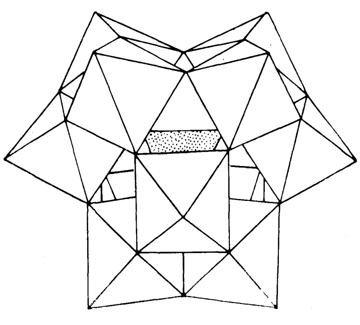

Fig. 3. The coordination polyhedral model of Keggin structure.

and 8W atoms randomly mixed. In Fig. 3 the polyanion is shown as a coordination polyhedral model. Three MO_6 octahedra link together by sharing edges to form a M_3O_{13} unit with a trigonal symmetry (Fig. 4). Four such M_3O_{13} units link in a T_d symmetry with a central hetero-atom by sharing corners to build the structure known as the Keggin ion.[13)]

The twelve metal positions are occupied by four vanadium and eight tungsten atoms with a 4:8 probability. The space-group symmetry requires that twelve metal positions are crystallographically equivalent; it is impossible to discriminate the 38 possible isomers with a different distribution of four vanadium and eight tung-

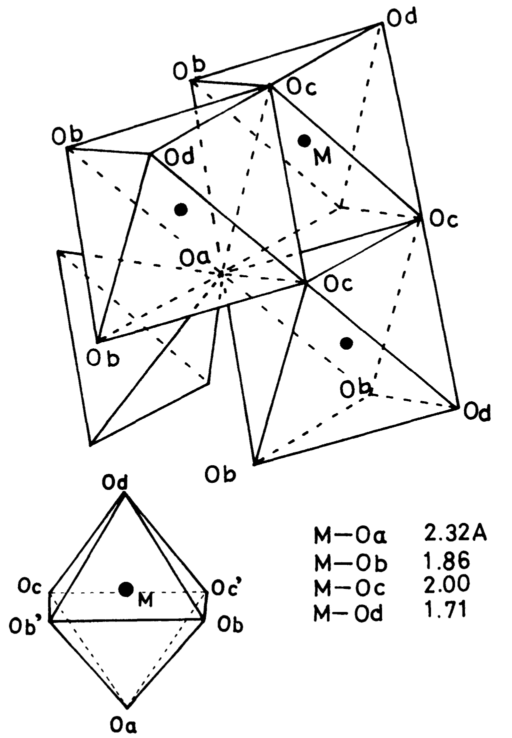

Fig. 4. The coordination polyhedral model of M_3O_{13} unit and central VO_4 tetrahedron and MO_6 octahedron. The classification of the oxygen atoms conform to those given by Evans.[12]

sten atoms on the twelve metal positions in a $V^tM_{12}O_{40}{}^{7-}$ anion. The assumption that the sample is a mixed crystal of many configurational isomers cannot be definitely ruled out on the basis of the present diffraction data. There is no evidence for the tungsten atoms being randomly mixed in the central vanadium position.

Oxygen atoms in the polyanion are classified into four groups—Oa, Ob, Oc, and Od, as is shown in Fig. 4. Oa is the oxygen atom bound to one central vanadium atom and to three metal atoms, while Ob is shared by two metal atoms of different M_3O_{13} units. Oc is bound to two metal atoms in the same M_3O_{13} unit. Od is the terminal oxygen atom combined with only one metal.

TABLE 2. INTERATOMIC DISTANCES (d/Å) AND ESTIMATED STANDARD DEVIATIONS WITHIN THE ANION $V_5W_8O_{40}{}^{7-}$

(1) The metal–metal interatomic distances	
M–M (in M_3O_{10} unit)	3.486 (9)
M–M (nearest M–M in different M_3O_{13} units)	3.578(11)
M–V^t	3.532 (9)
(2) The distances between metal and oxygen atoms	
M–Oa	2.32(12)
M–Ob	1.86 (5)
M–Oc	2.00 (5)
M–Od	1.71 (4)
V^t–Oa	1.75(12)
(3) The distances between oxygen atoms	
Oa–Ob	2.94(13)
Oa–Oc	2.51(13)
Ob–Oc	2.74 (8)
Oc–Od	2.78 (8)

The M–O distances in Table 2 (2) are the weighted average of the W–O and V–O distances, since the M in each position is occupied by randomly distributed V and W atoms. All the MO_6 octahedra are deformed. The M atom is not at the center of the octahedra, but near Od; it is displaced 0.35 Å outside the plane made by two Ob and two Oc atoms. Three Oc atoms form a triangle 0.43 Å inside the plane which three Od atoms make. On the other hand, one Oa and six Ob atoms form an almost perfect plane.

The $V^tV_4W_{12}O_{40}{}^{7-}$ is the sole example of the Keggin structure containing a vanadium (V) atom in the center as V^t. From the standpoint of vanadium structure chemistry, it is interesting to see whether or not the V^t-$(Oa)_4$ tetrahedron is deformed, because, in general, VO_4 has a remarkable tendency to deviate from the tetrahedral symmetry. For instance, Evans reported that, in VO_4 (tetrahedron),[14] VO_5 (trigonal bipyramid), or VO_6 (octahedron),[15] two V–O bonds are always shorter, suggesting the existence of bent O–V–O bondings stronger than other V–O bonds. Banks, Greenblatt, and Post, in their structure study of K_3VO_4, found that the deformation of $VO_4{}^{3-}$ is more remarkable than that of $AsO_4{}^{3-}$.[16] In the present case, however, the polyanion apparently has the T_d symmetry. As a result, such a deformation of the $V(Oa)_4$ tetrahedron, if it occurred at all, must have been smeared out by the orientational disorder. Though the large observed standard deviations in the positional and thermal parameters of the Oa atoms, and consequently the large errors in the V–Oa distances, are consistent with this model of the random orientation of the deformed polyanion, there is no difinite proof of it.

TABLE 3. BOND ANGLES (φ/°) AND ESTIMATED STANDARD DEVIATIONS WITHIN A MO_6 UNIT

Oa–M–Ob	88.8 (35)
Oa–M–Oc	70.6 (34)
Oa–M–Od	162.8 (34)
Ob–M–Ob′	87.2 (24)
Ob–M–Oc	159.3 (22)
Ob–M–Oc′	90.7 (22)
Ob–M–Od	103.6 (23)
Oc–M–Oc′	84.1 (20)
Oc–M–Od	97.0 (20)

Potassium Ions and Water of Crystallization. One unit cell contains seven potassium ions, of which three, K(1), the 3d sites, are at (1/2, 0, 0; 0, 1/2, 0; 0, 0, 1/2). Other four ions, K(2), are distributed among the sixfold positions, 6g ($\pm x$, 1/2, 1/2; 1/2, $\pm x$, 1/2; 1/2, 1/2, $\pm x$) with equal probability. This assumption explains the peak heights on Fourier maps [K(1): K(2): O (oxygen atom of H_2O)=4: 2: 1] and gives reasonable temperature factors and the lowest R value. Both K(1) and K(2) are coordinated by eight oxygen atoms, as is shown in Fig. 2. The K(1) is surrounded by four Oc and four Ob atoms, and K(2), by four water molecules and four terminal Od atoms of the polyanions. Table 4 shows the K–O distances. The coordination numbers of potassium ions by oxygen atoms are known to be 6, 7, 8, 9, 10, and 12,[17] and for the 8 coordination, the K–O

Table 4. Interatomic distances (d/Å) shorter than 3.5 Å outside the polyanion

K(1)–Ob	2.86 (4)
K(1)–Oc	2.87 (5)
K(2)–Od	2.64 (6)
K(2)–H_2O	2.70 (8)
H_2O–H_2O	3.13(10)
Oc–H_2O	3.38 (8)

distance has been reported to be in the range from 2.66 to 3.10 Å.[17] The present data of bond lengths seem to be typical.

Water of Crystallization. Water molecules are used only as ligands to potassium cations. There is no hydrogen bonding between the oxygen of the polyanion and water molecules (the shortest distance, H_2O–Oc, is 3.38 Å).

Comparison with Isopolyvanadates and Isopolytungstate. Isopolytungstates in the solid phase have always been found in the solid phase as discrete polyanions, such as $W_6O_{19}^{2-}$,[18] $W_{10}O_{32}^{4-}$,[19] $H_2W_{12}O_{42}^{10-}$ (paratungstate),[20] and $H_2W_{12}O_{40}^{4-}$ (metatungstate)[21]. No infinite polymer has been reported; these polyanions seem all to exist in aqueous solutions. On the other hand, all the isopolyvanadate crystals so far studied, with the sole exception of $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ crystals containing discrete $V_{10}O_{28}^{6-}$ [15] anions, have infinite polymeric structures.

The CsV_3O_8 crystals contain a plane sheet consisting of VO_6 octahedra-sharing edges,[22] $K_3V_5O_{14}$ consists of VO_5 square pyramids, and VO_4 of tetrahedra bound by sharing corners.[23] The equilibria of isopolyvanadates in an aqueous solution are fairly complicated. The following species have been reported:[24] VO_2^+, $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$, $HV_6O_{17}^{3-}$, $HV_2O_7^{3-}$, $V_2O_7^{4-}$, HVO_3, VO_3^-, H_3VO_4, $H_2VO_4^-$, HVO_4^{2-}, and VO_4^{3-}. However, the existence of any infinite polymer in the aqueous phase has never been proved.

We have already determined the structures of the five polyvanadotungstates, $(CN_3H_6)_4V_2W_4O_{19}$,[8] $K_7V_5W_8O_4\cdot 12H_2O$, $Ag_4V_2W_4O_{19}$,[25] and $(CN_3H_6)_5HV_2^{IV}W_4O_{19}$,[26] but no isopolyvanadate-like infinite polymer has been found; the structures are always similar to those of the isopolytungstates.

These results support Pope's proposal[5–7] that all the polyvanadotungstates form two homologous series, $V_nW_{6-n}O_{19}^{(n+2)-}$ (n=1,2) and $V^tV_nW_{12-n}O_{40}^{(n+3)-}$ (n=2,3,4). According to him, the two series are derived from the hexatungstate $W_6O_{19}^{2-}$ with the hexaniobate structure and from the hypothetical heteropolytungstate, $V^tW_{12}O_{40}^{3-}$, which is a Keggin ion as a result of the partial replacement of W(VI) by V(V). The Keggin ions are stable in acidic solutions, and the niobate-type anion, $V_2W_4O_{19}^{4-}$, is reversibly converted to a Keggin ion, $V_4W_9O_{40}^{6-}$, on acidification.

In the both series, a lower pH stabilizes polyanions containing fewer vanadium atoms. This may be correlated with the facts that the basicity of V(V) is stronger than that of W(VI) and that the VO_2^+ cation is stable in acidic media.

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