Structure of Polyvanadotungstates. I. The Crystal Structure of α-$(CN_3H_6)_4V_2W_4O_{19}$

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Crystals of α-$(CN_3H_6)_4V_2W_4O_{19}$ are monoclinic, space group $P2_1$, with the cell dimensions, $a=14.85(2)$, $b=19.48(2)$, $c=9.48(1)$ Å, $\beta=92.6(2)°$. The X-ray structure determination showed that $V_2W_4O_{19}^{4-}$ anion has the hexaniobate-type structure consisting of 6 edge-shared MO_6 octahedra. Each M position is randomly occupied by vanadium and tungsten atoms with a 2:4 probability. This randomness makes it impossible to determine whether $V_2W_4O_{19}^{4-}$ anion has the *cis* or *trans* configuration or both. The final R value was 0.086 with anisotropic temperature factors for metals and isotropic factors for other lighter atoms.

In an acidic aqueous solution, the orthotungstate ion WO_4^{2-} is condensed to isopolytungstate polyanions and the metavanadate ion VO_3^- forms isopolyvanadates. Isopolytungstate anions have no tendency to form an infinite polymer structure in crystals, and the existence of discrete anions with formulas $W_6O_{19}^{2-}$,[1] $W_{10}O_{32}^{4-}$,[2] $H_2W_{12}O_{40}^{6-}$ (metatungstate),[3] and $H_2W_{12}O_{42}^{10-}$ (paratungstate)[4] has been reported in the solid phase. On the other hand, it is known that isopolyanions containing vanadium(V) very often have infinite chain or sheet structures in crystals. The crystals of KVO_3 contain chains of VO_4 tetrahedra connected by sharing corners, and $KVO_3 \cdot H_2O$ has a chain structure made of VO_5 trigonal bipyramids sharing edges.[5]

There are no discrete $V_3O_8^-$ nor $V_5O_{14}^{3-}$ ions in CsV_3O_8[6] and $K_3V_5O_{14}$[7] crystals. In $[V_3O_8^-]_\infty$, VO_6 octahedra form plane sheets by sharing edges, and in $[V_5O_{14}^{3-}]_\infty$, VO_5 square pyramids and VO_4 tetrahedra are bound by sharing corners. The only discrete isopolyvanadate ion which has been reported is $V_{10}O_{28}^{6-}$ built by VO_6 octahedra sharing edges.[8,9] But when vanadium(V) and tungsten(VI) are both present in an acidic solution, crystals of "polyvanadotungstates", which are sometimes called "mixed isopolyanions", may be obtained. It has been reported that the composition of the vanadotungstates varies with the pH and the constitution of the solution.[10–17] Table 1 gives the analytical formulas of vanadotungstate anions so far reported as salts in crystals. No crystal structure work has been published on the vanadotungstate salts and it has not yet known whether these mixed isopolyanions have polymeric structures like the polyvanadates or contain discrete polyanions.

The present paper reports the structure of the guanidinium salt of $V_2W_4O_{19}^{4-}$ polyanion, $(CN_3H_6)_4V_2W_4O_{19}$, obtained from single crystal X-ray diffraction.

Experimental

The guanidinium salt was obtained by mixing a solution of guanidinium perchlorate at pH 4—6 with that of $Na_4V_2W_4O_{19} \cdot 14H_2O$. The sodium salt was prepared by concentration of an aqueous solution at pH 4—6 containing sodium salts of vanadate and of tungstate in the ratio of 1:2.[15]

Repeated preparations revealed the existence of three different guanidinium salts, which are denoted here α, β and γ. The α and β forms, having the same chemical formula $(CN_3H_6)_4V_2W_4O_{19}$, always precipitate together from solution at pH 4—6 as needles-like orange crystals. After several recrystallizations, almost pure α-form was obtained but the β-form could not be prepared in a pure state. The γ form precipitates from the same solution after a week as polyhedral crystals, but loses water of crystallization quickly in air. The crystal data for the α- and β-forms are shown in Table 2.

TABLE 2. CRYSTAL DATA FOR α- AND β-$(CN_3H_6)_4V_2W_4O_{19}$

α-$(CN_3H_6)_4V_2W_4O_{19}$	β-$(CN_3H_6)_4V_2W_4O_{19}$
F.W. 1381.3	F.W. 1381.3
Monoclinic	Orthorhombic
$a=14.85(2)$ Å	$a=14.43$ Å
$b=19.48(2)$	$b=20.49$
$c=9.48(1)$	$c=9.26$
$\beta=92.6(2)°$	
$V=2733$ Å^3	$V=2738$ Å^3
Space group $P2_1$	Space group $Pnm2_1$, $Pn2_1m$ or $Pnmm$
$Z=2$ (for $[(CN_3H_6)_4V_2W_4O_{19}]_2$)	$Z=4$ (for $(CN_3H_6)_4V_2W_4O_{19}$)
$D_m=3.38$ g/cm^3	
$D_x=3.39$ g/cm^3	
μ(MoKα)$=199.0$ cm^{-1}	

Reflection data for a specimen of the pure α-form were collected on a Rigaku four-circle diffractometer with MoKα radiation monochromated by a graphite crystal ($\lambda=0.7107$ Å).

TABLE 1. FORMULAS OF VANADOTUNGSTATE ANIONS REPORTED AS SALTS

$V_3W_{18}O_{72}^{21-}$,	$V_6W_6O_{38}^{10-}$,	$V_6W_{12}O_{57}^{12-}$	Prandtl[10]
$V_2W_4O_{19}^{4-}$	$V_3W_3O_{19}^{5-}$,	$V_3W_7O_{31}^{5-}$	Rosenheim and Pieck[11]
$V_2W_4O_{19}^{4-}$	$V_8W_{16}O_{73}^{10-}$,	$V_4W_{20}O_{75}^{10-}$	Bekturov, Begalieva and I'lyasova[14]
$V_nW_{6-n}O_{19}^{-(n+2)}$ ($n=1,2$): $V_2W_4O_{19}^{4-}$, $VW_5O_{19}^{3-}$			Flynn and Pope[15–17]
$V^tV_nW_{12-n}O_{40}^{-(n+3)}$ ($n=2,3,4$): $V_3W_{10}O_{40}^{5-}$, $V_4W_9O_{40}^{6-}$, $V_5W_8O_{40}^{7-}$			

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An ω-2θ scan technique was employed and 2362 independent reflections whose intensities are larger than 3σ up to $2\theta=60°$ were obtained. The data were corrected for Lorentz and polarization factors but not for absorption. The dimensions of the specimen used were approximately $0.1\times0.08\times0.14$ mm.

Structure Determination

The structure was solved by the heavy atom method. Twelve metal atoms forming two independent octahedral M_6 units were easily located. The coordinates of these two polyanions are related by pseudo-two fold screw axes parallel to the *a* and *c* axes which cause the observed extra extinction rule: *h*00 and 00*l* are absent or very weak if *h* or *l* is odd.

The positions of oxygen peaks suggested that six MO_6 octahedra are connected in a compact way by sharing edges to form the M_6O_{19} polyanion. Each M_6O_{19} anion must contain two vanadium atoms in either the *trans*- or *cis*-configuration,[18] but it was impossible to distinguish vanadium from tungsten on the Fourier maps. The best agreement between F_o and F_c was obtained by assuming that the twelve metal positions (M1—M6, M1′—M6′) are randomly occupied by vanadium and tungsten atoms with a 2:4 probability. Thus our data could be explained by randomly orientated *trans*- or *cis*-$V_2W_4O_{19}^{4-}$, and no conclusion could be drawn about the configuration of the $V_2W_4O_{19}^{4-}$ anion.

All the 82 atoms—12 metal, 38 oxygen, 8 carbon, and 24 nitrogen (hydrogen atoms were excluded)—are crystallographically independent. Of these, 70 atoms could be located. Three guanidinium ions were omitted as described in the Results and Discussion.

The atomic parameters were refined to $R=0.086$ by the block-diagonal least-squares method, using anisotropic temperature factors for the metal atoms and isotropic ones for the other atoms. The final positional parameters and temperature factors are shown in Tables 3 and 4. The F_o-F_c table is held by the Chemical Society of Japan as Document No. 7505.

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]

Table 3. Final position coordinates ($\times10^4$) and isotropic temperature factors for O, C and N atoms[a]
(Anisotropic temperature factors for metal atoms are given in Table 4).

	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*
M(1)	−922 (3)	859 (3)	4451 (6)		O(4)′	5672 (44)	−3042 (33)	2935 (72)	2.2 (9)
M(2)	1317 (4)	1238 (3)	1303 (6)		O(5)′	3013 (43)	−1801 (34)	−820 (73)	2.1 (8)
M(3)	−282 (4)	2144 (3)	2436 (7)		O(6)′	6510 (84)	−538 (68)	5240 (74)	2.5 (10)
M(4)	775 (4)	−36 (3)	3244 (6)		O(13)′	3475 (31)	−403 (30)	3061 (53)	0.9 (7)
M(5)	−782 (4)	658 (3)	1012 (7)		O(14)′	4191 (49)	−2158 (39)	3777 (80)	2.5 (9)
M(6)	1166 (4)	1453 (3)	4680 (7)		O(15)′	3138 (54)	−1562 (43)	2094 (88)	2.2 (9)
M(1)′	3689 (4)	−1340 (3)	3836 (6)		O(16)′	4693 (31)	−1061 (25)	4907 (54)	1.1 (7)
M(2)′	5928 (4)	−983 (3)	586 (6)		O(23)′	5289 (43)	−105 (37)	500 (73)	2.4 (7)
M(3)′	4255 (4)	−89 (3)	1767 (6)		O(24)′	6112 (48)	−1886 (37)	931 (79)	2.3 (9)
M(4)′	5394 (4)	−2219 (3)	2550 (7)		O(25)′	4839 (48)	−1329 (40)	−673 (80)	2.2 (9)
M(5)′	3848 (4)	−1559 (3)	369 (7)		O(26)′	6505 (42)	−618 (33)	2358 (71)	1.8 (8)
M(6)′	5773 (4)	−765 (3)	3952 (7)		O(35)′	3594 (32)	−720 (26)	383 (55)	1.0 (7)
O(C)	152 (42)	989 (31)	2855 (69)	1.4 (9)	O(36)′	5201 (37)	52 (29)	3283 (62)	1.1 (7)
O(1)	−1758 (47)	881 (39)	5658 (78)	2.5 (9)	O(45)′	4407 (40)	−2276 (31)	1144 (66)	1.7 (8)
O(2)	2005 (44)	1356 (36)	−211 (73)	2.3 (9)	O(46)′	5979 (60)	−1757 (48)	3996 (85)	2.2 (10)
O(3)	−846 (62)	2888 (48)	1950 (100)	2.5 (10)	C(1)	974 (53)	7425 (48)	2230 (91)	1.0 (9)
O(4)	1070 (53)	−821 (42)	3751 (89)	2.5 (9)	N(11)	490 (84)	7011 (62)	1957 (80)	2.9 (10)
O(5)	−1394 (42)	285 (32)	−247 (71)	2.0 (8)	N(12)	1310 (62)	7589 (51)	3336 (82)	2.2 (10)
O(6)	1787 (35)	1713 (27)	5981 (60)	1.2 (7)	N(13)	1431 (63)	7780 (43)	1236 (78)	1.4 (9)
O(13)	−1169 (30)	1765 (22)	3827 (51)	1.1 (7)	C(2)	3483 (71)	6077 (51)	1657 (83)	0.9 (9)
O(14)	−270 (50)	71 (40)	4636 (82)	2.3 (9)	N(21)	4001 (57)	6068 (45)	566 (74)	1.4 (9)
O(15)	−1461 (40)	701 (31)	2762 (69)	1.8 (8)	N(22)	3160 (66)	6600 (52)	2613 (83)	1.7 (10)
O(16)	−5 (32)	1240 (26)	5518 (54)	1.2 (7)	N(23)	3351 (52)	5424 (39)	2225 (75)	1.1 (10)
O(23)	641 (46)	2092 (36)	1085 (75)	2.4 (8)	C(3)	6340 (71)	5274 (71)	3052 (91)	2.2 (10)
O(24)	1381 (46)	379 (35)	1490 (76)	2.6 (9)	N(31)	6575 (72)	5444 (58)	4391 (90)	2.5 (10)
O(25)	426 (42)	813 (35)	−195 (71)	2.1 (9)	N(32)	5680 (71)	4897 (58)	2541 (88)	2.4 (9)
O(26)	1938 (40)	1534 (31)	3126 (66)	1.7 (8)	N(33)	6710 (70)	5694 (56)	1911 (85)	2.9 (10)
O(35)	−1001 (41)	1580 (33)	1055 (69)	1.9 (7)	C(4)	3880 (74)	2543 (57)	2909 (90)	1.2 (10)
O(36)	464 (40)	2308 (31)	4020 (66)	1.7 (7)	N(41)	3913 (68)	2134 (55)	1600 (81)	1.4 (9)
O(45)	−224 (68)	−185 (55)	1558 (85)	2.7 (10)	N(42)	3606 (90)	2194 (78)	3744 (91)	2.7 (10)
O(46)	1422 (37)	403 (29)	4651 (62)	1.2 (7)	N(43)	4546 (90)	2948 (74)	2999 (100)	2.8 (11)
O(C)′	4790 (51)	−1192 (39)	2219 (83)	1.8 (9)	C(5)	1433 (83)	3754 (68)	2936 (91)	2.1 (9)
O(1)′	2827 (38)	−1529 (29)	4864 (62)	1.3 (7)	N(51)	1032 (82)	3749 (72)	4092 (92)	2.5 (10)
O(2)′	6827 (61)	−739 (48)	−622 (91)	2.4 (9)	N(52)	1738 (83)	3295 (61)	2371 (90)	2.6 (10)
O(3)′	3933 (60)	711 (45)	1678 (94)	2.5 (9)	N(53)	1543 (74)	4265 (58)	2343 (85)	2.3 (9)

a) The estimated standard deviations in parentheses here and elsewhere are in units of the last significant digit.

Table 4. Final anisotropic temperature factors for metals ($\times 10^4$) with their estimated standard deviations in parentheses

(The temperature factor is of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M(1)	20 (2)	13 (1)	49 (6)	−1 (1)	11 (3)	0 (2)
M(2)	21 (2)	12 (1)	37 (6)	−1 (1)	11 (3)	−2 (2)
M(3)	33 (3)	16 (1)	80 (8)	1 (2)	13 (4)	0 (3)
M(4)	23 (2)	11 (1)	60 (7)	2 (1)	8 (3)	1 (2)
M(5)	24 (2)	19 (1)	74 (8)	0 (1)	1 (3)	−3 (3)
M(6)	28 (3)	18 (1)	71 (8)	−3 (1)	4 (3)	−2 (3)
M(1)′	21 (2)	13 (1)	36 (6)	−1 (1)	2 (3)	−2 (2)
M(2)′	21 (2)	13 (1)	50 (7)	−1 (1)	11 (3)	0 (2)
M(3)′	24 (3)	11 (1)	60 (8)	2 (2)	9 (4)	2 (3)
M(4)′	40 (3)	17 (1)	78 (8)	3 (2)	11 (3)	1 (3)
M(5)′	27 (2)	18 (1)	75 (7)	−2 (1)	5 (3)	−2 (2)
M(6)′	26 (2)	19 (1)	73 (8)	0 (1)	3 (3)	−5 (3)

The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[21] A weighting scheme with $w=1$ for $|F_o|\geq 101.3$ and $w=0.4$ otherwise was employed.

Results and Discussion

In Fig. 1, the $M_6O_{19}^{4-}$ ion (M=(2V+4W)/6) is shown as a "coordination polyhedral model" consisting of 6 edge-shared MO_6 octahedra. This is identical with the "hexaniobate structure" found by Lindqvist in $Nb_6O_{19}^{8-}$ [22] and by Henning and Hüllen in $W_6O_{19}^{2-}$.[1]

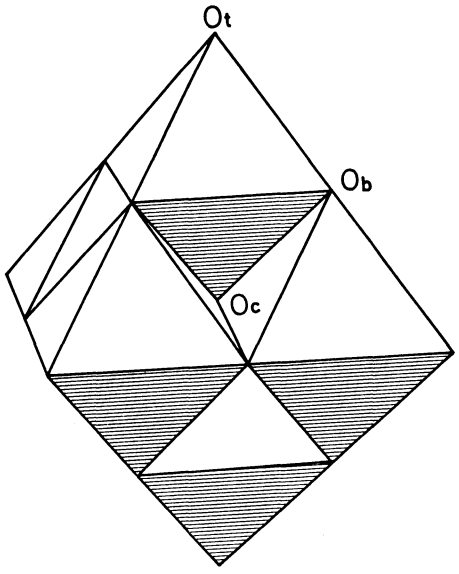

Fig. 1. The coordination polyhedral model of $M_6O_{19}^{4-}$ ion.

The distances between two adjacent metal atoms shown in Table 5 suggest that the M_6 octahedra are slightly deformed, but the reason for this is unknown. The metal atoms are not exactly at the center of each MO_6 octahedron but are displaced outward as if they are repulsing each other.

The oxygen atoms are classified according to the bonding pattern into three groups, Oc, Ob, and Ot. The M–Oc bond length ranges from 2.2 to 2.4 Å, M–Ob 1.78—2.08 Å, M–Ot 1.60—1.82 Å (Table 6). The Oc oxygen atoms at the center of the polyanions are bound to six metal atoms, Ob is bound to two metal atoms forming a bridge, and Ot is the terminal oxygen atom and is bonded to only one metal atom.

The bond lengths shown in Tables 5 and 6 should be understood as averaged values of W–W and V–W or V–O and W–O distances because of the randomness

Table 5. Metal–metal interatomic distances with their estimated standard deviations

M(1)—M(3)	3.316 (9) Å	M(1)′—M(3)′	3.263 (8) Å
M(4)	3.311 (8)	M(4)′	3.334 (9)
M(5)	3.301 (9)	M(5)′	3.335 (8)
M(6)	3.308 (9)	M(6)′	3.288 (9)
M(2)—M(3)	3.185 (8)	M(2)′—M(3)′	3.274 (8)
M(4)	3.215 (8)	M(4)′	3.168 (9)
M(5)	3.316 (9)	M(5)′	3.285 (9)
M(6)	3.248 (8)	M(6)′	3.239 (9)
M(3)—M(5)	3.266 (9)	M(3)′—M(5)′	3.202 (9)
M(6)	3.248 (9)	M(6)′	3.268 (9)
M(4)—M(5)	3.347 (9)	M(4)′—M(5)′	3.282 (9)
M(6)	3.246 (9)	M(6)′	3.169 (9)

Table 6. Metal–oxygen interatomic distances with their estimated standard deviations

(1) The distances of M–Oc			
M(1)–Oc	2.26 (6) Å	M(1)′–Oc′	2.31 (8) Å
M(2)	2.37 (6)	M(2)′	2.33 (8)
M(3)	2.23 (6)	M(3)′	2.21 (8)
M(4)	2.27 (6)	M(4)′	2.31 (8)
M(5)	2.42 (6)	M(5)′	2.38 (8)
M(6)	2.37 (6)	M(6)′	2.30 (8)
(2) The distances of M–Ot			
M(1)–O(1)	1.73 (7) Å	M(1)′–O(1)′	1.69 (6) Å
M(2)–O(2)	1.82 (7)	M(2)′–O(2)′	1.63 (9)
M(3)–O(3)	1.73 (9)	M(3)′–O(3)′	1.69 (7)
M(4)–O(4)	1.66 (8)	M(4)′–O(4)′	1.72 (8)
M(5)–O(5)	1.64 (7)	M(5)′–O(5)′	1.80 (9)
M(6)–O(6)	1.60 (6)	M(6)′–O(6)′	1.66 (8)
(3) The distances of M–Ob			
M(1)–O(13)	1.89 (5) Å	M(2)–O(23)	1.95 (7) Å
O(14)	1.82 (8)	O(24)	1.79 (7)
O(15)	1.78 (6)	O(25)	2.07 (7)
O(16)	1.82 (5)	O(26)	2.01 (6)
M(3)–O(13)	2.05 (5)	M(4)–O(14)	2.09 (8)
O(23)	1.95 (7)	O(24)	2.09 (7)
O(35)	1.98 (7)	O(45)	2.05 (8)
O(36)	1.85 (6)	O(46)	1.82 (6)
M(5)–O(15)	1.98 (6)	M(6)–O(16)	1.99 (5)
O(25)	2.05 (7)	O(26)	1.92 (6)
O(35)	1.90 (8)	O(36)	2.04 (6)
O(45)	1.83 (6)	O(46)	2.05 (6)
M(1)′–O(13)′	1.99 (5)	M(2)′–O(23)′	1.96 (7)
O(14)′	1.86 (7)	O(24)′	1.81 (7)
O(15)′	1.86 (8)	O(25)′	2.08 (8)
O(16)′	1.85 (5)	O(26)′	1.98 (7)
M(3)′–O(13)′	1.83 (5)	M(4)′–O(14)′	2.08 (8)
O(23)′	1.99 (7)	O(24)′	2.02 (7)
O(35)′	2.02 (5)	O(45)′	1.94 (6)
O(36)′	1.98 (6)	O(46)′	1.83 (9)
M(5)′–O(15)′	1.99 (8)	M(6)′–O(16)′	1.96 (5)
O(25)′	1.87 (8)	O(26)′	1.92 (6)
O(35)′	1.78 (5)	O(36)′	1.90 (6)
O(45)′	1.77 (6)	O(46)′	1.96 (9)

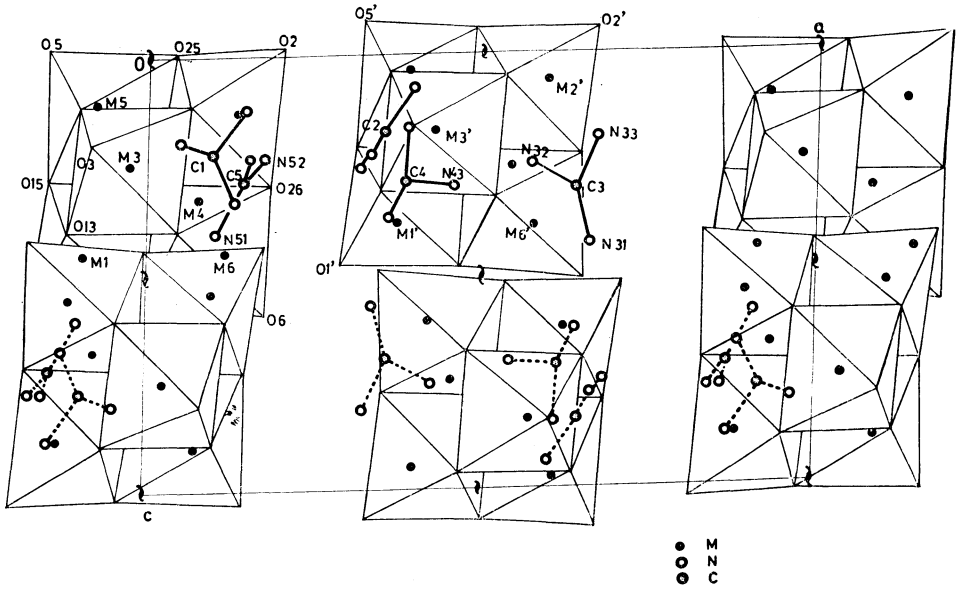

Fig. 2. A view of the structure as projected down the b axis. The dotted lines of guanidinium cations show that they are behind the anions.

already mentioned. In $W_6O_{19}^{2-}$, which has a similar structure, the W–W distances lie between 3.22 and 3.34 Å.[1] The $V_6O_{19}^{8-}$ ion seems to be too unstable to be isolated but V–V distances in the $V_{10}O_{28}^{6-}$ anion range from 3.05 to 3.19 Å.[8,9] It is understandable that the present crystals have intermediate values.

The guanidinium cation, $(CN_3H_6)^+$, has a flat triangular shape. Most of the NH groups form hydrogen bonds to Ob and Ot with O–N distances of 2.7—3.0 Å. Two diffuse peaks corresponding to guanidinium ions found in the Fourier map suggest a rotational disorder around the threefold axis. One of the guanidinium cations could not be found at all.

Flynn and Pope divided the vanadotungstates into two groups, namely the $Nv+Nw=6$ series and the $Nv+Nw=13$ series (Nv: number of vanadium atom, Nw: number of tungsten atom). They proposed the "hexaniobate structure" [22] for the first series, $V_nW_{6-n}O_{19}^{-(n+2)}$, and the Keggin structure $V^tV_nW_{12-n}O_{40}^{-(n+3)}$, for the second series, where V^t is the tetrahedrally coordinated central vanadium atom in a Keggin ion.[23] The present study, together with our unpublished structure determination of $K_7V_5W_8O_{40}\cdot 12H_2O$ crystals having the Keggin structure,[19] provides proof of Flynn and Pope's theory on the composition of vanadotungstates. The isopolytungstate, $W_{16}O_{19}^{2-}$ is unstable in aqueous solution and is easily hydrolyzed.[24] On the other hand, $V_2W_4O_{19}^{4-}$ is stable at pH 4—6 and $VW_5O_{19}^{3-}$ at 4. The latter ion will be isostructural to $W_6O_{19}^{2-}$ and to $V_2W_4O_{19}^{4-}$. The unstable $W_6O_{19}^{2-}$ ion seems to be stabilized by substitution of one or two tungsten atoms by vanadium.

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References

1) G. Henning and A. Hüllen, *Z. Kristallogr.*, **130**, 162 (1969).
2) J. Fuchs, H. Hartl, and W. Schiller, *Angew. Chem. Int. Edit.*, **12**, 409 (1973).
3) A. Kobayashi and Y. Sasaki, (to be published).
4) R. Allmann, *Acta Crystallogr.*, **B27**, 1393 (1971).
5) H. T. Evans, Jr., *Z. Krist.*, **114**, 257 (1960).
6) H. T. Evans, Jr. and S. Block, *Inorg. Chem.* **5**, 1808 (1966).
7) A. M. Byström and H. T. Evans, Jr., *Acta Chem. Scand.*, **13**, 377 (1959).
8) H. T. Evans, *Inorg. Chem.*, **5**, 967 (1966).
9) A. G. Swallow, F. R. Ahmed, and W. H. Barnes, *Acta Crystallogr.*, **21**, 397 (1966).
10) W. Prandtl, *Z. Anorg. Chem.*, **92**, 198 (1915).
11) A. Rosenheim and M. Pieck, *ibid.*, **98**, 223 (1916).
12) F. Chauveau, *Bull. Soc. Chim. Fr.*, **5**, 834 (1960).
13) F. Chauveau and P. Souchay, *ibid.*, **8**, 561 (1963).
14) A. B. Bekturov, D. U. Begalieva, and A. K. I'lyasova, *Russian J. Inorg. Chem.*, **15**, 1332 (1970).
15) C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **10**, 2524 (1971).
16) C. M. Flynn, Jr., and M. T. Pope, *ibid.*, **10**, 2745 (1971).
17) C. M. Flynn, Jr., and M. T. Pope, *ibid.*, **11**, 1950 (1972).
18) The assumption that these two crystallographically independent polyanions might have different chemical formula was ruled out by the aid of Raman spectroscopy. The Raman spectra of the crystals are almost identical to those of $Ag_4V_2W_4O_{19}\cdot 2H_2O$ which contains only one discrete $V_2W_4O_{19}^{4-}$ anion per unit cell.[19]
19) K. Nishikawa, A. Kobayashi, and Y. Sasaki, to be published.
20) "The Universal Crystallographic Computation Program System," Crystallographic Society of Japan (1967).
21) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham (1962), Vol. III.
22) I. Lindqvist, *Arkiv Kemi*, **5**, 247 (1953).
23) J. F. Keggin, *Proc. Roy. Soc.*, **A144**, 75 (1934).
24) K. F. Jahr, J. Fuchs, and R. Oberhauser, *Chem. Ber.*, **101**, 477 (1968).