BUSING, W. R., JOHNSON, C. K., ELLISON, R. D., THIESSEN, W. E. & LEVY, H. A. (1973). *ORXFLS*3. *World List of Crystallographic Computer Programs*, 3rd ed., Accession No. 84. *J. Appl. Cryst.* **6**, 309–346.

COHEN, S. H. & GUSANANO, E. A. (1967). *Proc. Soc. Exp. Biol. Med.* **126**, 79–83.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

CURZON, M. E. J., ADKINS, B. L., BIBBY, B. G. & LOSEE, F. L. (1970). *J. Dent. Res.* **49**, 526–528.

HIRSHFELD, F. L. & RABINOVICH, D. (1973). *Acta Cryst.* A**29**, 510–513.

International Tables for X-ray Crystallography (1967). Vol. II, 2nd ed. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.

KHUDOLOZKIN, V. O., URUSOV, V. S. & TOBELKO, K. I. (1972). *Geochem. Int.* **9**, 827–833.

KHUDOLOZKIN, V. O., URUSOV, V. S. & TOBELKO, K. I. (1973). *Geochem. Int.* **10**, 266–269.

LENGEMANN, F. W. (1957). *Proc. Soc. Exp. Biol. Med.* **94**, 64–66.

LITTLE, M. F. & BARRETT, K. (1976*a*). *Caries Res.* **10**, 297–307.

LITTLE, M. F. & BARRETT, K. (1976*b*). *Arch. Oral Biol.* **21**, 651–657.

MACKIE, P. E., ELLIOTT, J. C. & YOUNG, R. A. (1972). *Acta Cryst.* B**28**, 1840–1848.

NEUMAN, W. R. & NEUMAN, M. W. (1958). *The Chemical Dynamics of Bone Mineral.* Chicago Univ. Press.

PRENER, J. S. (1967). *J. Electrochem. Soc.* **114**, 77–83.

SCHNELL, E., KIESEWETTER, W., KIM, Y. H. & HAYEK, E. (1971). *Monatsh. Chem.* **102**, 1327–1336.

STARKEY, W. E. & FLETCHER, W. (1969). *Arch. Oral Biol.* **14**, 169–179.

STEADMAN, L. T., BRUDEVOLD, F. & SMITH, F. A. (1958). *J. Am. Dent. Assoc.* **57**, 340–344.

SUDARSANAN, K. & YOUNG, R. A. (1969). *Acta Cryst.* B**25**, 1534–1543.

SUDARSANAN, K. & YOUNG, R. A. (1972). *Acta Cryst.* B**28**, 3668–3670.

SUDARSANAN, K. & YOUNG, R. A. (1974). *Acta Cryst.* B**30**, 1381–1386.

SUDARSANAN, K. & YOUNG, R. A. (1978). *Acta Cryst.* B**34**, 1401–1407.

URUSOV, V. S. & KHUDOLOZKIN, V. O. (1974). *Geochem. Int.* **11**, 1048–1053.

Acta Cryst. (1980). B**36**, 1530–1536

Multicomponent Polyanions.

28. The Structure of $K_7Mo_8V_5O_{40}.\sim 8H_2O$, a Compound Containing a Structurally New Potassium-Coordinated Octamolybdopentavanadate Anion

BY ARNE BJÖRNBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

(*Received* 6 *December* 1979; *accepted* 12 *March* 1980)

Abstract

The crystal structure of $K_7Mo_8V_5O_{40}.\sim 8H_2O$ has been determined from X-ray diffraction data collected with a Syntex $P2_1$ automatic four-circle diffractometer and Mo $K\alpha$ radiation. The monoclinic ($P2_1/n$) unit cell has $a = 19{\cdot}435$ (4), $b = 20{\cdot}237$ (5), $c = 12{\cdot}769$ (3) Å, $\beta = 108{\cdot}29$ (2)°, $Z = 4$. The structure was refined to R 0·070 based on 7418 independent reflexions. The structure is built up from $[Mo_8V_5O_{40}]^{7-}$ anions which are linked together by K^+ ions and water molecules in a three-dimensional framework. The anion consists of edge-sharing MoO_6 octahedra forming an eight-membered ring in a two-up–two-down fashion. VO_5 trigonal bipyramids fill the gaps between the pairs of octahedra, and the fifth V atom is found in a VO_4 tetrahedron in the center of the anion, which within experimental error possesses $\bar{4}$ symmetry. For edge-sharing polyhedra the Mo—Mo distances vary between 3·302 (2) and 3·377 (2) Å, and the Mo—V distances between 3·426 (3) and 3·524 (3) Å. The Mo—O distances within the octahedra are 1·680 (11)–2·386 (10) Å. The VO_5 trigonal bipyramids all have one extremely long V—O distance (>2·7 Å). There is a K^+ ion situated in the large void at each of the two sides of the anion ring, coordinating eight anion O atoms which form a bi-peaked hexagonal pyramid. The remaining five K^+ ions all coordinate 5–8 anion and water O atoms.

Introduction

The interpretation of data from potentiometric EMF measurements in the system $H^+—MoO_4^{2-}—HVO_4^{2-}$ is difficult due to the formation of several different

0567-7408/80/071530-07$01.00

polynuclear complexes (Pettersson, 1979). To clarify and support the results from these studies, crystallization experiments followed by X-ray structure investigations were started. The difficulty of the interpretation of EMF data was explained, as these experiments yielded a number of different phases with Mo/V ratios between 4:8 and 10:3 (Björnberg, 1980). Since more than one of these can crystallize from the same starting solution, the great abundance of reports of various molybdovanadates in early literature is easily understood (Mellor, 1964).

More recent investigations of molybdovanadates are scarce. Heteropolyanions containing P^V and V^V as well as Mo^{VI} or W^{VI} have been thoroughly investigated (Weakley, 1974, and references therein), but among all-metal heteropolyvanadates only a limited number have been studied. Before the present series of investigations, the structurally known heteropolyvanadates with pentavalent V, not containing P^V, belonged to one of three types: $V_xM_{13-x}O_{40}$ (Nishikawa, Kobayashi & Sasaki, 1975*a*, $M = W$), $V_xM_{6-x}O_{19}$ (Nishikawa, Kobayashi & Sasaki, 1975*b*, $M = W$) or $MV_{13/14}O_{38/40}$ (Evans & Konnert, 1978, $M =$ Al, Mn or Ni).

The object of this study is the structure of $K_7Mo_8V_5O_{40}.\sim8H_2O$, which is *not* a Keggin (1934) structure although the composition is correct for a Keggin anion. There is no earlier report of an 8:5 molybdovanadate; the closest is a 13:8 complex (Isenburg, 1901).

Experimental

Crystal preparation, analysis and data

In a typical preparation 3·60 g of MoO_3 was dissolved in 50 ml of hot 0·50*M* KOH, and 5·85 g of NH_4VO_3 was dissolved in 60 ml of hot water. The vanadate solution was poured into the molybdate solution and 12·5 ml of 2*M* HCl added. 7·46 g of KCl was dissolved in this solution, which was filtered at about 313 K. Overnight, yellow acicular crystals, growing in thistle-like arrangements, were formed. The crystals are mechanically fragile as well as unstable in air, and during the X-ray exposures they were sealed, with part of the mother liquor, in a Lindemann-glass capillary. Water analysis was performed by heating on a thermobalance and gave 6·9 wt% H_2O (calculated for 8 H_2O: 6·9 wt%).

From Weissenberg and precession photographs the crystals were found to be monoclinic, and systematic extinctions $0k0$: $k = 2n + 1$ and $h0l$: $h + l = 2n + 1$ uniquely determined the space group as $P2_1/n$. The density was determined by flotation in a diiodomethane/chloroform solution. Crystal data are given in Table 1.

Table 1. *Crystal data for* $K_7Mo_8V_5O_{40}.\sim8H_2O$

Monoclinic, space group $P2_1/n$ (No. 14)

$a = 19{\cdot}435\ (4)$ Å
$b = 20{\cdot}237\ (5)$
$c = 12{\cdot}769\ (3)$
$\beta = 108{\cdot}29\ (2)°$
$Z = 4$
$V = 4768{\cdot}4$ Å^3
$M_r = 2079{\cdot}07$
$D_x = 2{\cdot}896$ Mg m^{-3}
$D_m = 2{\cdot}89\ (1)$
$\mu(\text{Mo } K\alpha) = 3{\cdot}692$ mm^{-1}

Data collection and reduction

A crystal 0·3 × 0·18 × 0·10 mm was chosen. The data were collected at the Department of Inorganic Chemistry, University of Göteborg, and Chalmers University of Technology, Göteborg, on a Syntex $P2_1$ automatic four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The cell parameters were determined by least squares from the setting angles for 15 reflexions.

In the collection of intensities the $\theta/2\theta$ scan method was used, and the 2θ scan speed was allowed to vary between 2 and 8° min^{-1} depending on the intensity of the measured reflexion.

11467 independent reflexions were collected in the region $(\sin\theta)/\lambda < 0{\cdot}65$ Å^{-1}. No separate background measurements were made during the data collection. A profile analysis based on the Lehmann & Larsen (1974) method was instead applied to the 96-step profile measured for each reflexion (program *LELA*; Lindqvist & Ljungström, 1979). Correction was made for Lorentz and polarization effects. 7418 reflexions with $F_o^2 \geq 3\sigma(F_o^2)$ were considered observed and were used in the subsequent calculations. Absorption correction was applied with an 8 × 6 × 4 Gaussian grid [$\mu(\text{Mo } K\alpha) = 3{\cdot}692$ mm^{-1}] and the transmission factor varied between 0·576 and 0·699.

Structure determination and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970). The 214 reflexions with $E \geq 2{\cdot}50$ were used for sign determination with the $\sum_2$ relationship. A basis set consisting of seven reflexions was used: one determined by the $\sum_1$ formula, three for definition of the origin and three being varied in the *MULTAN* procedure. The *E* maps based on the set with the best figures of merit revealed all eight Mo atoms, and heavy-atom methods gave the positions of all the other non-hydrogen atoms. Block-matrix least-squares refinement with isotropic temperature factors gave $R = 0{\cdot}099$ which decreased to 0·073 when anisotropic temperature factors were applied. In a difference synthesis calculated at this stage a number of peaks corresponding to an electron density of about

2·5 e Å^{-3} or less could be found. Most of these appeared in positions situated at very reasonable hydrogen-bond and K–O bond distances from atoms already included in the model. A refinement of the occupancy factors of 14 water O atom positions was performed, but did not give chemically significant results. Consequently, only nine of the probable water O atom positions were included in the final model, with no attempt to determine the occupancy factor of each position (which was set equal to one). Moreover, K(7) appears to be distributed between two positions, K(7) and K(7)″. A refinement of the occupancy factors of these two positions gave 0·53 (2) and 0·44 (2) respectively. The occupancy factors were therefore set at 0·55 and 0·45, making the sum equal to 1. Refinement finally converged at R = 0·070 (R_w = 0·073), with $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $\sum w(|F_o| - |F_c|)^2$ was minimized.

In the final cycle the parameter shifts were less than 0·08σ. Mo^{3+}, V^{2+}, K^+, O^- (anion O atoms) and O scattering factors were used and account was taken of the real and imaginary parts of the anomalous-dispersion correction (*International Tables for X-ray Crystallography*, 1974). The computer programs were those provided with the Syntex $R3$ Crystallographic System, the Data General NOVA3 computer of which was also used for the computations.

Final atomic positional parameters are given in Table 2.*

Description and discussion of the structure

The structure is built up from $[Mo_8V_5O_{40}]^{7-}$ anions (Figs. 1 and 2). These anions contain eight MoO_6 octahedra which share edges in a two-up–two-down fashion to form a puckered ring of octahedron pairs. VO_5 trigonal bipyramids are fitted in by sharing two edges of the same pyramid with the MoO_6 octahedra. These twelve metal atoms thus form two six-membered

Table 2. *The fractional atomic coordinates* (× 10^4; *for* Mo *and* V × 10^5)

Numbers and letters in the O atom designation denote the metal atom(s) to which each O atom is coordinated.

	x	*y*	*z*
Mo(1)	77199 (6)	12102 (6)	31837 (9)
Mo(2)	85517 (7)	23813 (6)	22355 (10)
Mo(3)	96451 (6)	33329 (6)	42358 (10)
Mo(4)	87428 (7)	44550 (6)	51752 (10)
Mo(5)	69602 (7)	44099 (6)	39207 (10)
Mo(6)	61072 (7)	32492 (6)	48934 (10)
Mo(7)	72328 (8)	23284 (7)	68964 (11)
Mo(8)	81329 (7)	12136 (6)	59574 (10)
V(*a*)	94627 (12)	16119 (11)	46884 (19)
V(*b*)	81257 (13)	40644 (11)	23431 (19)
V(*c*)	76200 (18)	40017 (15)	67020 (25)
V(*d*)	63533 (12)	15400 (11)	44419 (18)
V(*e*)	78930 (11)	28212 (10)	45633 (17)
O(1)	6982 (5)	1361 (5)	2059 (8)
O′(1)	7828 (6)	0384 (5)	3194 (9)
O(12*a*)	8492 (5)	1478 (4)	2644 (8)
O(12*e*)	7846 (5)	2349 (4)	3436 (7)
O(2)	7770 (6)	2456 (5)	1181 (7)
O′(2)	9186 (6)	2296 (5)	1600 (9)
O(23*a*)	9378 (5)	2406 (4)	3914 (7)
O(23*b*)	8668 (5)	3306 (4)	2687 (7)
O(3)	10208 (5)	3232 (5)	5549 (8)
O′(3)	10226 (6)	3422 (5)	3494 (9)
O(34*b*)	9345 (5)	4229 (5)	4279 (8)
O(34*e*)	8658 (5)	3318 (4)	4888 (7)
O(4)	9323 (6)	4300 (5)	6446 (9)
O′(4)	8775 (6)	5282 (5)	5043 (9)
O(45*b*)	7868 (5)	4347 (4)	3552 (7)
O(45*c*)	7847 (5)	4351 (5)	5505 (8)
O(5)	6384 (5)	4217 (5)	2654 (8)
O′(5)	6873 (7)	5241 (5)	4038 (10)
O(56*c*)	6374 (6)	4151 (5)	4860 (9)
O(56*e*)	7118 (5)	3273 (4)	4239 (7)
O(6)	5586 (6)	3123 (5)	3584 (9)
O′(6)	5515 (6)	3322 (6)	5624 (10)
O(67*c*)	7040 (6)	3241 (5)	6426 (8)
O(67*d*)	6400 (5)	2309 (4)	5216 (8)
O(7)	8012 (7)	2443 (6)	7933 (9)
O′(7)	6604 (6)	2204 (6)	7539 (9)
O(78*d*)	7337 (5)	1436 (5)	6482 (8)
O(78*e*)	7943 (5)	2345 (4)	5674 (7)
O(8)	8865 (5)	1398 (5)	7058 (8)
O′(8)	8090 (6)	0382 (5)	5962 (9)
O(18*a*)	8600 (5)	1315 (5)	4798 (7)
O(18*d*)	7233 (5)	1284 (4)	4325 (7)
O(*a*)	9966 (5)	1777 (6)	5926 (8)
O′(*a*)	9864 (6)	1022 (6)	4226 (9)
O(*b*)	7400 (6)	3869 (6)	1363 (9)
O′(*b*)	8564 (6)	4618 (5)	1845 (9)
O(*c*)	8374 (8)	3812 (8)	7630 (10)
O′(*c*)	7272 (8)	4569 (7)	7258 (12)
O(*d*)	5846 (6)	1694 (5)	3186 (8)
O′(*d*)	5965 (6)	0954 (5)	4925 (9)
K(1)	5752 (2)	0589 (2)	1725 (3)
K(2)	6372 (2)	2760 (2)	1966 (3)
K(3)	9427 (2)	2770 (2)	7174 (3)
K(4)	6733 (4)	−0271 (3)	5456 (5)
K(5)	9583 (4)	0871 (4)	1872 (7)
K(6)	8204 (5)	6525 (4)	5291 (5)
K(7)	5271 (6)	1878 (6)	6374 (8)
K(7)″	5225 (19)	1083 (18)	6509 (20)
Aq(1)	8897 (4)	−0343 (4)	4716 (7)
Aq(2)	4598 (10)	0406 (11)	3907 (15)
Aq(3)	3914 (19)	3508 (12)	4474 (14)
Aq(4)	0098 (10)	−0378 (9)	2897 (26)
Aq(5)	1135 (13)	1043 (13)	2971 (21)
Aq(6)	1261 (10)	2110 (11)	4718 (17)
Aq(7)	4468 (12)	2034 (14)	4497 (22)
Aq(8)	7121 (20)	−1600 (10)	5465 (17)
Aq(9)	1654 (20)	4329 (10)	2687 (22)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35123 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

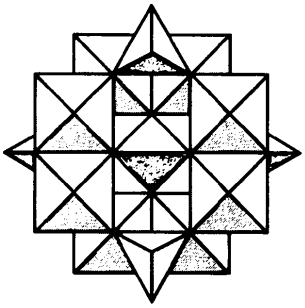

Fig. 1. The $[Mo_8V_5O_{40}]^{7-}$ anion drawn with idealized polyhedra.

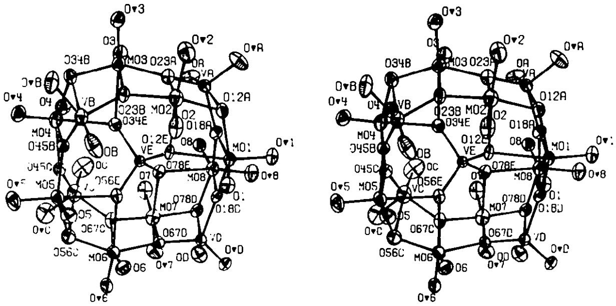

Fig. 2. A stereoscopic drawing of the $[Mo_8V_5O_{40}]^{7-}$ anion. The thermal ellipsoids are scaled to enclose 50% probability (Johnson, 1976).

rings which are sandwiched on top of each other with a slight mutual twist. The fifth V atom is found in the center of the anion inside a VO_4 tetrahedron which shares each corner with two MoO_6 octahedra. The anion is unusual in that it contains no two-coordinated O atoms. All O atoms are either terminal or three-coordinated. The anions are joined in a three-dimensional framework by K^+ ions and hydrogen bonds from the water molecules. The closest distance between O atoms in adjacent anions is 2·97 (2) Å, which implies that the anions are not in van der Waals contact with each other. The sum of two oxygen van der Waals radii is 2·8 Å (Pauling, 1960).

The $[Mo_8V_5O_{40}]^{7-}$ *anion*

The MoO_6 *octahedra.* As is shown in Table 3, the MoO_6 octahedra are noticeably distorted. The usual variation in Mo—O lengths according to coordination number is shown quite clearly, with Mo—O distances for terminal O atoms between 1·68 and 1·71 Å, while all the Mo—O distances for three-coordinated O atoms are 1·90 Å or longer. The long Mo—O bonds are also distributed as expected, with distances to O atoms *trans* to the terminal O atoms longer than 2·21 Å. These O atoms are, of course, situated on the octahedron edges pointing towards the center of the anion. The remaining two O atoms of each octahedron are at intermediate distances with Mo—O lengths between 1·90 and 1·99 Å. There is a slight systematic variation: when an O atom shared with a V atom is in an apical position of the VO_5 trigonal bipyramid, the Mo—O distance is a few hundredths of an ångström shorter than for an O atom in an equatorial position (see below). As a whole, the configuration of O atoms around the Mo atoms is in accordance with those found in other structures (Strandberg, 1974). As in all polyanions, the metal atoms are displaced within their O atom coordination figures in a direction away from the center of the anion.

The VO_4 *and* VO_5 *groups.* The central VO_4 tetrahedron is fairly regular. Perfectly regular VO_4 tetrahedra have been found in cubic Keggin (1934) structures, and this has often been accounted for by ascribing the regularity to rotational disorder of the anion (Nishikawa, Kobayashi & Sasaki, 1975*a*). This seems unlikely in the present structure, as the O atoms of the VO_4 tetrahedron show no anomalies in their thermal parameters. In solution, the VO_4^{3-} anion is probably very close to regular (Tillmanns & Baur, 1971), and the anion ring apparently makes an attractive site for a VO_4 tetrahedron.

The VO_5 trigonal bipyramids are similar to the same groups in the $[Mo_4V_8O_{36}]^{8-}$ anion (Björnberg, 1979). Four of the O atoms make up a tetrahedron showing the usual pattern (Evans, 1966) of two short and two long bonds. The fifth O atom in each group is situated a long way from the V atom, the V—O length in all four cases being 2·71–2·86 Å. This distance is at the limit of making the five-coordination uncertain. As is the case in $[Mo_4V_8O_{36}]^{8-}$, the Mo—O distances for these O atoms are longer than for O atoms coordinated only to two Mo atoms. This supports the description of the V atoms as being five-coordinate. As was mentioned above, the Mo—O length for these apical (with respect to the VO_5 groups) O atoms is slightly shorter than for O atoms in equatorial positions in the VO_5 bipyramids, which shows the weakness of the V—O bond of the apical O atoms.

The terminal O atoms can be divided into two distinct groups: one with the atoms pointing away from the plane of the anion ring (henceforth called 'axial' O atoms, denoted without primes) and the other with the atoms pointing from their respective metal atom in a direction parallel to the ring plane (henceforth called 'equatorial' O atoms, denoted with primes). There seems to be no systematic relation between Mo—O (or V—O) length and the axial or equatorial position of the O atom.

Bond distances within the anion are given in Table 3.

The mechanism behind the formation of the $[Mo_8V_5O_{40}]^{7-}$ anion is not easily understood. All the V atoms have tetrahedral or near-tetrahedral coordination figures, which makes it probable that the anion is formed rapidly upon acidification of the

Table 3. *Distances* (Å) *and angles* (°) *within the* $[Mo_8V_5O_{40}]^{7-}$ *anion*

	O(1)	O′(1)	O(12*a*)	O(18*d*)	O(18*a*)	O(12*e*)
Mo(1)–	1·709 (10)	1·685 (10)	1·916 (10)	1·977 (9)	2·238 (9)	2·329 (8)
O(1)–		2·687 (14)	2·803 (15)	2·784 (13)		2·840 (13)
O(18*a*)–		2·840 (14)	2·712 (13)	2·535 (13)		2·819 (13)
O′(1)–			2·763 (14)	2·791 (14)		
O(12*e*)–			2·550 (13)	2·865 (13)		
O(1)–Mo(1)–		104·7 (5)	101·1 (4)	97·8 (4)	162·7 (4)	88·0 (4)
O(18*a*)–Mo(1)–		91·7 (4)	81·1 (4)	73·7 (4)		76·2 (3)
O′(1)–Mo(1)–			100·0 (5)	99·0 (4)		166·7 (4)
O(12*e*)–Mo(1)–			73·1 (4)	83·0 (3)		

	O(3)	O′(3)	O(34*b*)	O(23*a*)	O(23*b*)	O(34*e*)
Mo(3)–	1·702 (10)	1·696 (11)	1·911 (10)	1·956 (9)	2·272 (9)	2·320 (10)
O(3)–		2·663 (14)	2·795 (14)	2·764 (13)		2·868 (14)
O(23*b*)		2·885 (15)	2·771 (13)	2·513 (13)		2·818 (13)
O′(3)--			2·772 (15)	2·792 (14)		
O(34*e*)			2·538 (14)	2·830 (13)		
O(3)–Mo(3)–		103·2 (5)	101·2 (5)	97·9 (4)	163·2 (4)	89·6 (4)
O(23*b*)–Mo(3)–		92·1 (4)	82·5 (4)	72·5 (4)		75·7 (3)
O′(3)–Mo(3)–			100·2 (5)	99·5 (5)		166·6 (4)
O(34*e*)–Mo(3)–			73·0 (4)	82·4 (4)		

	O(5)	O′(5)	O(56*c*)	O(45*b*)	O(45*c*)	O(56*e*)
Mo(5)–	1·699 (10)	1·701 (11)	1·967 (11)	1·968 (9)	2·210 (10)	2·339 (9)
O(5)–		2·695 (15)	2·827 (15)	2·762 (14)		2·823 (14)
O(45*c*)–		2·847 (15)	2·749 (16)	2·507 (13)		2·818 (13)
O′(5)–			2·747 (16)	2·855 (15)		
O(56*e*)–			2·567 (14)	2·902 (13)		
O(5)–Mo(5)–		104·8 (6)	100·6 (5)	97·5 (4)	161·9 (4)	87·2 (4)
O(45*c*)–Mo(5)–		92·5 (5)	82·1 (4)	73·5 (4)		76·5 (3)
O′(5)–Mo(5)–			96·7 (5)	102·0 (5)		165·4 (5)
O(56*e*)–Mo(5)–			72·6 (4)	84·2 (3)		

	O(7)	O′(7)	O(78*d*)	O(67*c*)	O(67*d*)	O(78*e*)
Mo(7)–	1·685 (12)	1·690 (13)	1·911 (9)	1·942 (9)	2·247 (10)	2·386 (10)
O(7)–		2·666 (18)	2·790 (15)	2·757 (15)		2·851 (14)
O(67*d*)		2·874 (15)	2·684 (13)	2·508 (13)		2·872 (14)
O′(7)–			2·734 (16)	2·810 (15)		
O(78*e*)–			2·568 (14)	2·890 (14)		
O(7)–Mo(7)–		104·4 (6)	101·5 (5)	98·7 (5)	162·4 (5)	87·1 (5)
O(67*d*)–Mo(7)–		92·7 (5)	80·0 (4)	73·2 (4)		76·5 (3)
O′(7)–Mo(7)–			98·6 (5)	101·2 (5)		166·9 (5)
O(78*e*)–Mo(7)–			72·4 (4)	83·1 (4)		

	O(*a*)	O′(*a*)	O(18*a*)	O(23*a*)	O(12*a*)
V(*a*)–	1·611 (10)	1·634 (12)	1·826 (10)	1·866 (9)	2·712 (9)
O(*a*)–		2·611 (16)	2·755 (14)	2·772 (14)	
O(12*a*)–		2·942 (15)	2·712 (13)	2·713 (13)	
O′(*a*)–			2·835 (15)	2·941 (15)	
O(18*a*)–				3·081 (13)	
O(*a*)–V(*a*)–		107·1 (6)	106·4 (5)	105·5 (5)	171·8 (5)
O(12*a*)–V(*a*)–		81·1 (5)	70·3 (4)	69·9 (4)	
O′(*a*)–V(*a*)–			109·9 (5)	114·2 (5)	
O(18*a*)–V(*a*)–				113·1 (4)	

	O(*c*)	O′(*c*)	O(45*c*)	O(67*c*)	O(56*c*)
V(*c*)–	1·615 (14)	1·607 (16)	1·858 (10)	1·875 (11)	2·813 (11)
O(*c*)–		2·554 (22)	2·803 (16)	2·814 (18)	
O(56*c*)–		3·128 (18)	2·749 (16)	2·727 (14)	
O′(*c*)–			2·833 (18)	2·873 (17)	
O(45*c*)–				3·169 (14)	
O(*c*)–V(*c*)–		104·9 (8)	107·4 (6)	107·2 (6)	169·6 (6)
O(56*c*)–V(*c*)–		85·5 (6)	68·6 (4)	67·8 (4)	
O′(*c*)–V(*c*)–			109·4 (6)	111·0 (6)	
O(45*c*)–V(*c*)–				116·2 (5)	

	O(2)	O′(2)	O(12*a*)	O(23*b*)	O(23*a*)	O(12*e*)
Mo(2)–	1·690 (10)	1·685 (13)	1·914 (9)	1·950 (9)	2·239 (9)	2·357 (10)
O(2)–		2·654 (17)	2·780 (13)	2·756 (13)		2·845 (13)
O(23*a*)–		2·868 (14)	2·713 (13)	2·513 (13)		2·846 (14)
O′(2)–			2·731 (15)	2·828 (15)		
O(12*e*)–			2·550 (13)	2·860 (13)		
O(2)–Mo(2)–		103·7 (5)	100·7 (4)	98·2 (4)	162·8 (4)	87·7 (4)
O(23*a*)–Mo(2)–		92·9 (5)	81·2 (4)	73·4 (4)		76·5 (3)
O′(2)–Mo(2)–			98·6 (5)	101·9 (5)		166·8 (5)
O(12*e*)–Mo(2)–			72·5 (4)	82·6 (4)		

	O(4)	O′(4)	O(45*c*)	O(34*b*)	O(45*b*)	O(34*e*)
Mo(4)–	1·689 (11)	1·685 (11)	1·927 (11)	1·931 (10)	2·241 (9)	2·327 (9)
O(4)–		2·662 (15)	2·743 (16)	2·784 (14)		2·821 (14)
O(45*b*)–		2·865 (14)	2·507 (13)	2·736 (14)		2·821 (12)
O′(4)–			2·796 (15)	2·719 (15)		
O(34*e*)–			2·873 (14)	2·538 (14)		
O(4)–Mo(4)–		104·2 (4)	98·4 (5)	100·3 (5)	162·6 (4)	87·7 (4)
O(45*b*)–Mo(4)–		92·6 (4)	73·5 (4)	81·6 (4)		76·2 (3)
O′(4)–Mo(4)–			101·3 (4)	97·3 (5)		165·7 (4)
O(34*e*)–Mo(4)–			84·4 (4)	72·5 (4)		

	O(6)	O′(6)	O(56*c*)	O(67*d*)	O(67*c*)	O(56*e*)
Mo(6)–	1·680 (11)	1·701 (13)	1·901 (10)	1·992 (9)	2·211 (10)	2·364 (10)
O(6)–		2·683 (16)	2·785 (15)	2·736 (14)		2·844 (15)
O(67*c*)–		2·821 (17)	2·727 (14)	2·508 (13)		2·845 (13)
O′(6)–			2·752 (16)	2·828 (15)		
O(56*e*)–			2·567 (14)	2·899 (13)		
O(6)–Mo(6)–		105·0 (5)	102·0 (5)	96·0 (5)	161·8 (5)	87·7 (4)
O(67*c*)–Mo(6)–		91·3 (5)	82·7 (4)	73·1 (4)		76·8 (3)
O′(6)–Mo(6)–			99·5 (5)	99·6 (5)		166·6 (5)
O(56*e*)–Mo(6)–			73·1 (4)	83·0 (4)		

	O(8)	O′(8)	O(78*d*)	O(18*a*)	O(18*d*)	O(78*e*)
Mo(8)–	1·699 (10)	1·685 (10)	1·921 (10)	1·976 (9)	2·266 (9)	2·329 (9)
O(8)–		2·671 (15)	2·827 (15)	2·773 (13)		2·830 (13)
O(18*d*)–		2·879 (14)	2·714 (13)	2·535 (13)		2·827 (13)
O′(8)–			2·782 (15)	2·772 (15)		
O(78*e*)–			2·568 (14)	2·850 (13)		
O(8)–Mo(8)–		104·3 (5)	102·5 (4)	97·7 (4)	162·1 (4)	87·8 (4)
O(18*d*)–Mo(8)–		92·4 (4)	80·3 (4)	73·0 (4)		75·9 (3)
O′(8)–Mo(8)–			100·8 (5)	98·1 (5)		167·6 (5)
O(78*e*)–Mo(8)–			73·6 (4)	82·5 (4)		

	O(*b*)	O′(*b*)	O(23*b*)	O(45*b*)	O(34*b*)
V(*b*)–	1·615 (12)	1·650 (12)	1·836 (9)	1·856 (9)	2·857 (10)
O(*b*)–		2·633 (18)	2·759 (15)	2·826 (14)	
O(34*b*)–		3·103 (14)	2·771 (13)	2·736 (14)	
O′(*b*)–			2·848 (13)	2·955 (15)	
O(23*b*)–				3·026 (13)	
O(*b*)–V(*b*)–		107·5 (6)	106·0 (5)	108·8 (5)	170·1 (5)
O(34*b*)–V(*b*)–		82·3 (4)	68·4 (4)	67·1 (3)	
O′(*b*)–V(*b*)–			109·4 (5)	114·7 (5)	
O(23*b*)–V(*b*)–				110·1 (4)	

	O(*d*)	O′(*d*)	O(67*d*)	O(18*d*)	O(78*d*)
V(*d*)–	1·627 (10)	1·628 (10)	1·830 (9)	1·836 (10)	2·713 (10)
O(*d*)–		2·628 (15)	2·770 (14)	2·757 (14)	
O(78*d*)--		2·947 (15)	2·684 (13)	2·714 (13)	
O′(*d*)–			2·859 (14)	2·878 (15)	
O(67*d*)–				3·061 (13)	
O(*d*)–V(*d*)–		107·7 (5)	106·4 (5)	105·4 (5)	170·9 (4)
O(78*d*)–V(*d*)–		81·4 (4)	69·3 (4)	70·3 (4)	
O′(*d*)–V(*d*)–			111·4 (5)	112·2 (5)	
O(67*d*)–V(*d*)–				113·2 (4)	

Table 3 (*cont.*)

	O(12*e*)	O(34*e*)	O(45*e*)	O(78*e*)
V(*e*)–	1·706 (9)	1·734 (10)	1·700 (10)	1·693 (9)
O(12*e*)–		2·817 (13)	2·732 (13)	2·804 (13)
O(34*e*)–			2·846 (14)	2·773 (13)
O(56*e*)–				2·761 (13)
O(12*e*)–V(*e*)–		110·0 (5)	106·7 (4)	111·2 (5)
O(34*e*)–V(*e*)–			112·0 (4)	108·1 (4)
O(56*e*)–V(*e*)–				109·0 (5)

	Mo(2)	Mo(3)	Mo(4)	Mo(5)	Mo(6)	Mo(7)
Mo(1)	3·305 (2)	5·577 (2)			5·993 (2)	5·595 (2)
Mo(2)		3·368 (2)	5·565 (2)	5·935 (2)		
Mo(3)			3·315 (2)	5·552 (2)		
Mo(4)				3·331 (2)	5·583 (2)	6·001 (2)
Mo(5)					3·332 (2)	5·585 (2)
Mo(6)						3·360 (2)

	Mo(8)	V(*a*)	V(*b*)	V(*c*)	V(*d*)	V(*e*)
Mo(1)	3·377 (2)	3·426 (3)	5·972 (3)		3·572 (3)	3·671 (2)
Mo(2)	5·591 (2)	3·448 (3)	3·518 (3)		6·054 (3)	3·695 (3)
Mo(3)	5·993 (2)	3·566 (3)	3·503 (3)	5·918 (4)		3·706 (3)
Mo(4)		6·000 (3)	3·524 (3)	3·475 (4)		3·669 (2)
Mo(5)			3·542 (3)	3·476 (3)	6·005 (3)	3·656 (2)
Mo(6)	5·564 (2)		6·061 (3)	3·469 (4)	3·563 (3)	3·727 (3)
Mo(7)	3·302 (2)	6·042 (3)		3·494 (3)	3·454 (3)	3·730 (3)
Mo(8)		3·547 (3)		5·859 (3)	3·456 (3)	3·667 (2)
V(*e*)		3·875 (3)	3·921 (3)	3·789 (4)	3·925 (3)	

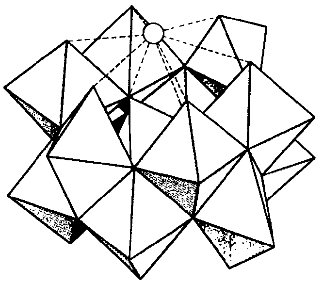

Fig. 3. A schematic drawing showing the position and coordination to the anion of the K(2) ion.

molybdovanadate solution. {The $[Mo_4V_8O_{36}]^{8-}$ anion, which is formed if crystals of $K_7Mo_8V_5O_{40}.\sim 8H_2O$ are dissolved in water and left to crystallize (Björnberg, 1979), contains octahedrally coordinated V atoms.}

The potassium ions and water molecules

As usual, most of the K^+ ions coordinate 7–11 anion or water O atoms within a distance of 3·25 Å. The coordination figures are rather irregular, and the structure as a whole is probably formed by the possibility of packing the anions in an energetically favorable way and by the formation of hydrogen bonds from water molecules, rather than by bonds in preferred directions from K^+ ions. K(2) and K(3), however, are two exceptions to this pattern. The axial terminal O atoms of the anion form six-membered rings around the cavities on each side of the anion. K(2) and K(3) are situated near the centers of these rings, also coordinating two O atoms of the central VO_4 tetrahedron (Fig. 3). The K^+ ions are displaced slightly outward from the plane of the axial O atoms; the distances from K(2) and K(3) to the least-squares planes through the O atoms are 0·601 (4) and 0·648 (4) Å respectively. The coordination around K(2) and K(3) is completed by water molecules and O atoms from neighboring anions.

It seems probable that these two K^+ ions are important for the stability of the anion. The $[V_5W_8O_{40}]^{7-}$ anion described by Nishikawa *et al.* (1975*a*) has a similar formula, but that is a Keggin anion. The present structure has not been observed for any other anion, while the Keggin structure has been

Table 4. K—O *distances* (Å) *less than* 3·4 Å

The superscripts refer to the following symmetry operations:

(i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$
(ii) $1\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
(iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
(iv) $1-x, -y, 1-z$
(v) $1\frac{1}{2}-x, y-\frac{1}{2}, 1\frac{1}{2}-z$
(vi) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$
(vii) $1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(viii) $2-x, 1-y, 1-z$
(ix) $1\frac{1}{2}-x, \frac{1}{2}+y, 1\frac{1}{2}-z$
(x) $1-x, 1-y, 1-z$
(xi) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$
(xii) $x-1, y, z$
(xiii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z.$

K(1)—O(4$^{\mathrm{i}}$)	2·70 (1)	K(3)—O(*a*)	2·95 (1)	K(5)—Aq(4)	2·88 (2)	K(7)—Aq(7)	2·44 (3)
O′(*b*$^{\mathrm{ii}}$)	2·73 (1)	O(8)	2·97 (1)	O(12*a*)	2·88 (2)	O′(7)	2·64 (2)
O′(4$^{\mathrm{ii}}$)	2·76 (1)	O(34*e*)	3·04 (1)	O′(*a*)	2·90 (1)	O′(2$^{\mathrm{xi}}$)	2·78 (2)
O(1)	2·77 (1)	O(78*e*)	3·04 (1)	Aq(5)	2·92 (3)	O′(3$^{\mathrm{xi}}$)	2·80 (2)
O(3$^{\mathrm{i}}$)	2·84 (1)	O(3)	3·08 (1)	O′(2)	2·98 (1)	O(67*d*)	3·13 (2)
O(*d*)	2·88 (1)	O(*c*)	3·12 (2)	O′(5$^{\mathrm{ii}}$)	2·99 (2)	O′(6)	3·16 (2)
O(34*b*$^{\mathrm{ii}}$)	3·02 (1)	O(4)	3·22 (1)	Aq(3$^{\mathrm{vi}}$)	3·18 (2)	O′(*d*)	3·21 (2)
		O(7)	3·26 (1)	O′(6$^{\mathrm{vi}}$)	3·21 (2)		
K(2)—O(56*e*)	2·99 (1)	O(*d*$^{\mathrm{iii}}$)	2·87 (1)				
O(12*e*)	3·01 (1)	Aq(7$^{\mathrm{iii}}$)	2·97 (3)	K(6)—O′(4)	2·81 (1)	K(7)″—O′(3$^{\mathrm{xii}}$)	2·72 (3)
O(*d*)	3·02 (1)	O(6$^{\mathrm{iii}}$)	3·01 (1)	O(2$^{\mathrm{vii}}$)	2·90 (1)	Aq(9)	2·84 (5)
O(6)	3·02 (1)			O(1$^{\mathrm{vii}}$)	2·93 (1)	O′(*d*$^{\mathrm{i}}$)	2·84 (3)
O(1)	3·06 (1)	K(4)—Aq(8)	2·79 (2)	Aq(6$^{\mathrm{viii}}$)	2·95 (2)	Aq(2$^{\mathrm{xiii}}$)	3·10 (4)
O(5)	3·08 (1)	O′(*b*$^{\mathrm{ii}}$)	2·82 (1)	O(3$^{\mathrm{viii}}$)	2·96 (1)	Aq(7$^{\mathrm{i}}$)	3·18 (4)
O(2)	3·24 (1)	O′(8)	2·84 (1)	O′(7$^{\mathrm{ix}}$)	3·01 (1)		
O(*b*)	3·25 (1)	O′(*d*)	2·86 (1)	Aq(9$^{\mathrm{x}}$)	3·05 (3)		
O(*a*$^{\mathrm{i}}$)	2·80 (1)	Aq(2$^{\mathrm{iv}}$)	2·96 (2)			K(7)″—K(7)	1·62 (4)
Aq(6$^{\mathrm{i}}$)	2·82 (2)	O′(*c*$^{\mathrm{v}}$)	2·97 (2)				
O(3$^{\mathrm{i}}$)	3·14 (1)	O(*c*$^{\mathrm{v}}$)	3·13 (2)				

Table 5. *Probable hydrogen-bond distances* (Å)

The superscripts refer to the following symmetry operations:

(i) $2-x, -y, 1-z$
(ii) $x-\frac{1}{2}, -\frac{1}{2}-y, z-\frac{1}{2}$
(iii) $1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(iv) $1\frac{1}{2}-x, y-\frac{1}{2}, -z-\frac{1}{2}$
(v) $1\frac{1}{2}-x, \frac{1}{2}+y, -z-\frac{1}{2}$
(vi) $x, y, 1+z$
(vii) $1\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Aq(1)—O′($a^{\rm i}$)	2·73 (2)
O′(1)	2·78 (1)
O(b)	2·94 (2)
O′(8)	2·95 (2)
Aq(2)—O′($d^{\rm ii}$)	2·79 (2)
O(c)	2·90 (2)
Aq(3)—O($7^{\rm iii}$)	2·91 (3)
O′($6^{\rm i}$)	3·02 (4)
Aq(4)—O($5^{\rm i}$)	2·86 (2)
O(8)	2·87 (2)
Aq(5)—O′(c)	2·92 (3)
Aq($6^{\rm iv}$)	3·06 (3)
Aq(6)—Aq($5^{\rm v}$)	3·06 (3)
O(2)	3·07 (2)
Aq(7)—O($7^{\rm v}$)	3·09 (3)
O($c^{\rm v}$)	3·16 (3)
Aq(8)—O($7^{\rm vi}$)	2·89 (3)
O($2^{\rm vii}$)	2·90 (2)
O(b)	2·93 (3)
O($c^{\rm vi}$)	3·00 (3)
Aq(9)—O(78d)	2·80 (3)
O′($c^{\rm iv}$)	3·04 (3)

found for a number of different complexes. The two K^+ ions seem to be the stabilizing agents preventing the relocation of O atoms necessary to form the more condensed structure of a Keggin anion.

All the water molecules seem to be engaged in hydrogen bonds to anion O atoms or to other water molecules. The anions are packed to form layers parallel to the xz plane, with comparatively few bonds between these layers. This explains the needle-like shape and poor mechanical properties of the crystals. K–O lengths are given in Table 4 and probable hydrogen-bond lengths in Table 5.

I thank Professor Nils Ingri for valuable advice, for his interest and for the facilities placed at my disposal, Dr Britt Hedman for help with computational and other problems and Drs Oliver Lindqvist and Evert Ljungström for the use of the Syntex $P2_1$ diffractometer and for help with the data processing. The English of this paper has been corrected by Dr Michael Sharp. This work is part of a program financially supported by the Swedish Natural Science Research Council.

References

Björnberg, A. (1979). *Acta Cryst.* B**35**, 1989–1995.
Björnberg, A. (1980). Accepted for publication.
Evans, H. T. Jr (1966). *Inorg. Chem.* **5**, 967–976.
Evans, H. T. Jr & Konnert, J. A. (1978). *Am. Mineral.* **63**, 863–868.
Germain, G., Main, P. & Woolfson, M. M. (1970). *Acta Cryst.* B**26**, 274–285.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–83, 149. Birmingham: Kynoch Press.
Isenburg, A. (1901). *Beiträge zur Kenntnis der Vanadinmolybdate*, PhD Thesis, Bern.
Johnson, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
Keggin, J. F. (1934). *Proc. R. Soc. London Ser. A*, **144**, 75–100.
Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.
Lindqvist, O. & Ljungström, E. (1979). *J. Appl. Cryst.* **12**, 134.
Mellor, J. W. (1964). *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, pp. 780–784. London: Longmans.
Nishikawa, K., Kobayashi, A. & Sasaki, Y. (1975*a*). *Bull. Chem. Soc. Jpn*, **48**, 3152–3155.
Nishikawa, K., Kobayashi, A. & Sasaki, Y. (1975*b*). *Bull. Chem. Soc. Jpn*, **48**, 889–892.
Pauling, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
Pettersson, L. (1979). Personal communication.
Strandberg, R. (1974). Dissertation, Univ. of Umeå.
Tillmanns, E. & Baur, W. H. (1971). *Acta Cryst.* B**27**, 2124–2132.
Weakley, T. J. R. (1974). *Struct. Bonding (Berlin)*, **18**, 131–176.