

Fig. 3. Enchaînement des polyèdres $[(\text{NH}_4)\text{O}_8 + (\text{E})\text{Te}^{\text{IV}}]$ parallèlement à l'axe y (ORTEP, Johnson, 1965).

l'ensemble des atomes d'oxygène. En effet, excepté la distance $\text{Te}(1)\text{—O}(1)$ courte, où l'atome $\text{O}(1)$ est aussi lié à un atome d'hydrogène, les autres distances Te—O sont nettement plus longues et voisines. Les polyèdres $[(\text{NH}_4)\text{O}_8 + \text{E}]$ ainsi définis sont réunis le long de l'axe y pour former des doubles chaînes (Fig. 3), nettement individualisées les unes des autres (Fig. 1).

Etant donné l'arrangement structural des cations ammonium d'une part, et des groupements hydroxyles peu rigides d'autre part, nous nous attacherons à dégager les caractéristiques de conductivité électrique de ce composé.

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Multicomponent Polyanions.

22. The Molecular and Crystal Structure of $\text{K}_8\text{Mo}_4\text{V}_8\text{O}_{36} \cdot 12\text{H}_2\text{O}$, a Compound Containing a Structurally New Heteropolyanion

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Abstract

$\text{K}_8\text{Mo}_4\text{V}_8\text{O}_{36} \cdot 12\text{H}_2\text{O}$ is monoclinic, space group $C2/c$, with $a = 23.255$ (2), $b = 11.708$ (1), $c = 18.453$ (8) Å, $\beta = 114.11$ (2)°, $Z = 4$. Refinement resulted in a final R of 0.055, based on 6798 independent reflexions. The structure contains discrete $\text{Mo}_4\text{V}_8\text{O}_{36}^{8-}$ anions consisting of twelve edge-sharing polyhedra. Two MoO_6 and four VO_6 octahedra form a ring around an inversion center. This ring is capped on each side by a VO_5 square

pyramid. The remaining two Mo and V atoms are attached at the edge of the ring in MoO_6 octahedra and VO_5 trigonal bipyramids. The MoO_6 octahedra are separated from one another and share no O atoms. The structure is held together by $\text{O—K}^+\text{—O}$ bonds as well as by hydrogen bonds. One water molecule is distributed between two different positions. The Mo—O distances vary between 1.69 and 2.38 Å, and the V—O distances between 1.61 and 2.76 Å. Each K^+ ion is surrounded by eight to ten anion or water O atoms within 3.24 Å.

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Introduction

The chemistry of Mo-containing iso- and heteropolyanions has been the subject of extensive studies (Evans, 1971; Weakley, 1974). Considerable attention has been given to heteropoly complexes containing tetrahedrally coordinated heteroatoms such as P^v, As^v, Si^{iv} and Ge^{iv}, and the structures of many of these complexes have been determined. The chemistry of all-metal heteropoly complexes is, however, somewhat less well systematized. Although several complexes have been found both in aqueous solution and in the solid phase (Evans, 1971; Pettersson, 1974), much remains to be revealed concerning the structures of such complexes and the mechanisms behind their formation. Since V^v is expected to be five- or six-coordinated in aqueous solutions with pH \lesssim 6, the molybdovanadates formed in slightly acidic solutions are likely to belong to this kind of complex. Since, in addition, the isopolyvanadates are fairly well known (Baes & Mesmer, 1976), an investigation of aqueous equilibria and crystal structures of the molybdovanadates was initiated.

Many molybdovanadates have been reported with Mo/V ratios between 6:1 and 1:8 (Mellor, 1964). The interpretation of data, obtained in the e.m.f. investigation of the molybdovanadate system in the ionic medium 3M NaClO₄, is difficult due to the formation of several different polynuclear complexes. Moreover, the total concentration of V^v cannot be varied to the desired extent due to the low solubility of the vanadates in slightly acidic solutions (Pettersson, 1979). It was therefore considered necessary to perform X-ray structure analyses of the crystalline phases obtainable in the system to facilitate the search for and the establishment of the aqueous complexes. E.m.f. data, in the pH range where the first molybdovanadate complexes are formed (pH \sim 7), indicated high nuclearity and a low Mo/V ratio. The present structure investigation has been performed on a phase obtained in this region and the discrete Mo₄V₈O₃₆⁸⁻ ions found are thus in accordance with the e.m.f. results.

Several investigations (Weakley, 1974) employing different techniques have been made on phosphomolybdovanadates. Among them are the recordings of X-ray powder patterns. These anions have the formula PV_xMO_{12-x}O₄₀^{(3+x)-} ($x = 1, 2, 3$) and are all assumed to

have the Keggin (1934) structure. No single-crystal structure determination of these compounds or of 'pure' molybdovanadates has, however, been published previously. Structure determinations have been performed on heteropolyvanadates containing heteroatoms other than Mo (Nishikawa, Kobayashi & Sasaki, 1975a,b).

This paper presents the crystal structure of K₈Mo₄V₈O₃₆·12H₂O. A compound which probably has the same anion, but with Ba²⁺ instead of K⁺ as the cation, was reported by von Euler-Chelpin (1895).

Experimental

Crystal preparation and analyses

In a typical preparation, 3.60 g MoO₃ was dissolved in 50 ml of hot 0.50M KOH, and 5.85 g NH₄VO₃ was dissolved in 60 ml of hot water. The vanadate solution was poured into the molybdate solution and 12.5 ml 2.0 M HCl was added. 7.46 g KCl was dissolved in this solution, which was filtered at about 313 K. Overnight, yellow acicular crystals growing in thistle-like arrangements were formed; they were redissolved in water, and, after a few days, yellow acicular crystals of a compound other than that previously formed appeared in this solution. The crystals are unstable in air and during the X-ray exposures they were enclosed, together with part of the mother liquor, in a sealed glass capillary.

Water analysis was performed by heating to constant weight at 513 K and gave 11.4% H₂O (calc. 11.4%).

Crystal data

Weissenberg and precession photographs showed the crystal system to be monoclinic. Systematic extinctions hkl , $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$ showed the space group to be either *Cc* or *C2/c*; the latter was chosen due to the existence of special-position peaks in the Patterson synthesis and later success of the refinements.

The cell parameters were measured with an Enraf-Nonius CAD-4 four-circle diffractometer at the Department of Inorganic Chemistry, University of Uppsala. The parameters were determined by least squares from the setting angles for 25 reflexions. The density was determined by flotation in a bromoform/carbon tetrachloride solution. Complete crystal data are given in Table 1.

Data collection and reduction

A crystal 0.15 × 0.28 × 0.20 mm was mounted and rotated about z , which was approximately parallel to

Table 1. *Crystal data for* K₈Mo₄V₈O₃₆·12H₂O

Monoclinic, space group *C2/c*

$a = 23.255 (2) \text{ \AA}^*$	FW	= 1896.28
$b = 11.708 (1)$	D_x	= 2.746 Mg m ⁻³
$c = 18.453 (8)$	D_m	= 2.744 (3)
$\beta = 114.11 (2)^\circ$	$\mu(\text{Mo } K\alpha)$	= 3.378 mm ⁻¹
$Z = 4$		

* Throughout this paper, numbers given in parentheses denote the e.s.d.'s and refer to the last decimal place.

the 0.20 mm edge. Intensities were collected at 298 K with a Philips Paired linear diffractometer and Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) monochromatized with graphite. 11 483 reflexions were scanned in the layers $hk0$ – $hk29$ and within $(\sin \theta)/\lambda \leq 0.84 \text{ \AA}^{-1}$. The measurements were made with a scan speed of 1° min^{-1} and a background time of 40 s at the beginning and end of the interval.

Reflexions with a relative statistical error (Antti, 1973) $\Delta I_o/I_o > 0.5$ were omitted leaving 6901 reflexions. The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied ($\mu = 3.378 \text{ mm}^{-1}$) with a $4 \times 6 \times 8$ Gaussian grid; the transmission factor varied between 0.506 and 0.865.

Structure determination and refinement

The structure was solved by the heavy-atom method. Since the temperature factor of Aq(6) was anomalously high, this atom was removed, and a following difference synthesis showed two peaks with heights corresponding to an electron density of about 4 e \AA^{-3} close to the former Aq(6) position. This atom was therefore assumed to be distributed between two positions, Aq(6a) and Aq(6b). A refinement of the occupation factors gave 0.55 (3) and 0.45 (3) for the *a* and *b* positions respectively.

Refinements converged with $R = 0.055$ ($R_w = 0.073$), $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, and with $\sum w(|F_o| - |F_c|)^2$ as the function minimized. In the last cycle the parameter shifts were $< 0.6\sigma$. Since the program could refine only 140 parameters simultaneously, the 319 parameters had to be refined in three sets for each cycle. Mo $^{3+}$, V $^{3+}$, O $^-$ (anion O atoms), O and K $^+$ 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). A weighting scheme according to Cruickshank (1965) was applied, $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ with $a = 100$, $c = 0$ and $d = 10^{-5}$.

The final difference synthesis showed no anomalies and the highest peaks were about 1.0 e \AA^{-3} . The final atomic coordinates with their e.s.d.'s are given in Table 2.*

Description and discussion of the structure

The structure is built from Mo $_4$ V $_8$ O $_{36}^{8-}$ anions mutually arranged as shown in Fig. 1. The anions are connected

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34502 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. The fractional atomic coordinates ($\times 10^4$, for Mo and V $\times 10^5$)

The numbers of the anion O atom designation denote the metal atom(s) to which each oxygen is coordinated.

	x	y	z
Mo(1)	48282 (2)	26470 (4)	60226 (2)
Mo(2)	33993 (2)	42019 (4)	30335 (3)
V(3)	36977 (4)	43367 (8)	50308 (5)
V(4)	36013 (4)	19131 (8)	41575 (5)
V(5)	39215 (4)	66121 (8)	40567 (5)
V(6)	51414 (4)	41429 (7)	43335 (5)
O(1)	4514 (2)	2616 (4)	6731 (2)
O'(1)	4962 (2)	1236 (4)	5888 (3)
O(15)	5637 (2)	3183 (4)	6614 (2)
O(134)	3994 (2)	2732 (3)	5077 (2)
O(136)	4557 (2)	4435 (3)	5806 (2)
O(156)	5236 (2)	3138 (3)	5156 (2)
O(2)	3801 (3)	4484 (5)	2444 (3)
O'(2)	2643 (3)	4033 (5)	2380 (3)
O(24)	3630 (2)	2643 (4)	3292 (3)
O(25)	3327 (2)	5804 (4)	3318 (2)
O(234)	3185 (2)	4055 (4)	4072 (2)
O(2356)	4383 (2)	4538 (4)	4117 (3)
O(3)	3270 (2)	4310 (4)	5544 (3)
O(356)	3845 (2)	5880 (4)	4926 (2)
O(4)	2887 (2)	1543 (5)	4057 (3)
O'(4)	4005 (3)	747 (4)	4256 (3)
O(5)	3605 (2)	7834 (4)	4042 (3)
O(6)	5143 (2)	3376 (4)	3608 (3)
K(1)	5362 (1)	999 (2)	4578 (1)
K(2)	0	194 (2)	$\frac{1}{4}$
K(3)	0	4504 (3)	$\frac{1}{4}$
K(4)	1621 (1)	2056 (2)	3084 (1)
K(5)	2306 (1)	4219 (3)	745 (2)
Aq(1)	1273 (4)	4208 (6)	2360 (4)
Aq(2)	2026 (3)	3634 (7)	4283 (4)
Aq(3)	2949 (4)	1206 (9)	1889 (6)
Aq(4)	4509 (5)	1428 (10)	2829 (9)
Aq(5)	3797 (8)	472 (11)	1019 (10)
Aq(6a)	3414 (8)	2981 (16)	1005 (12)
Aq(6b)	3119 (14)	2681 (20)	484 (17)

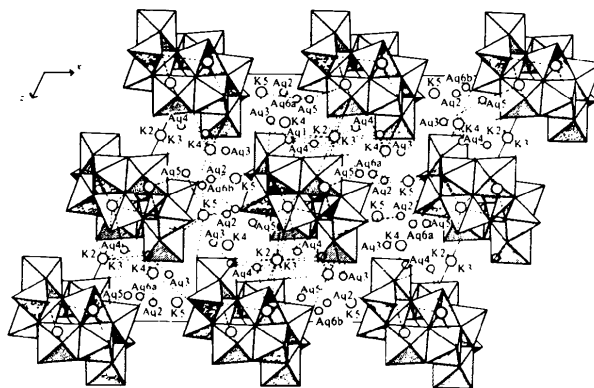


Fig. 1. The K–O and hydrogen bonds in the structure projected along *y*. For clarity the complete set of bonds is drawn for only one or two of each atom type.

by hydrogen bonds and by K^+ ions to form layers parallel to the yz plane. Around $x \approx \frac{1}{4}$ the layers contain mainly K^+ ions and water molecules resulting in a very good (100) cleavage plane. The shortest O—O distance between O atoms in adjacent anions is 2.814 (9) Å [O(1)—O(1)] which implies that the anions are packed quite close together.

The $Mo_4V_8O_{36}^{8-}$ anion

As can be seen from Figs. 2 and 3, this anion consists of twelve edge-sharing polyhedra related in pairs by an inversion center. The central part is an approximately planar ring of six octahedra, two of which are Mo-centered [Mo(1)] and the remaining four V-centered [V(3), V(5)]. The ring is capped on either side by a V-centered [V(6)] pyramid. Above and below the plane of the six-membered ring there is an additional MoO_6 octahedron [Mo(2)] sharing an edge each with the V(3) and V(5) octahedra, while the remaining two V atoms [V(4)] are found in trigonal bipyramids sharing edges with the V(3) and Mo(2) octahedra. The MoO_6 octahedra have no O atoms in common. Metal—metal distances within the anion are given in Table 3. The shortest V—V distances are 3.011 (2) [V(5)—V(6)] and 3.041 (1) Å [V(3)—V(6)]. Both of these are distances from an octahedral to a square-pyramidal V atom, and are comparable in

length with the shortest V—V distance in the $V_{10}O_{28}^{6-}$ anion (Evans, 1966) which is 3.05 Å. The longest V—V edge-sharing distance in the anion is between the two octahedrally coordinated V(3) and V(5) atoms, 3.371 (1) Å. The Mo—V edge-sharing distances vary between 3.094 (1) [Mo(1)—V(5)] and 3.464 (2) Å [Mo(2)—V(3)].

The MoO_6 octahedra

As is usually the case with Mo^{VI} in octahedral coordination, the octahedra are rather distorted. The Mo—O distances are shortest for terminal O atoms, varying between 1.689 (6) and 1.740 (4) Å. For bridging O atoms bonded to two metal atoms, the Mo—O distance is between 1.856 (4) and 1.973 (4) Å, while for O atoms shared between three metal atoms it varies between 2.012 (4) and 2.241 (4) Å. The longest Mo—O distance is from Mo(2) to the four-coordinated O(2356), 2.376 (4) Å. The angles also show a marked difference from ideal octahedra, with O—Mo—O for O atoms in *cis* positions between 71.9 (2) and 104.2 (3)°, and for those in *trans* positions between 151.5 (2) and 169.6 (2)°.

These values are in good agreement with those found in other Mo-containing heteropoly complexes (Strandberg, 1974).

The vanadium—oxygen coordination

Unlike the MoO_6 octahedra, the V coordination polyhedra are of less-common types. V(3) and V(5) have distorted octahedral coordination, the main distortion being created by an extremely long V—O distance to the four-coordinated O(2356) [V(3)—O(2356) 2.761 (4), V(5)—O(2356) 2.638 (4) Å]. Especially for V(3) this distance is on the limit of making the six-coordination uncertain, but since Mo(2)—O(2356) is noticeably longer than the other Mo—O distances, it seems probable that O(2356) is subjected to interactions from V(3) and V(5). Otherwise the V(3) and V(5) octahedra show normal V—O distances, each having only one terminal O atom at V—O distances of 1.629 (5) and 1.605 (5) Å respectively (Evans, 1966).

The coordination of V(6) represents an intermediate between five- and six-coordination. It can be described as a square pyramid with V—O distances between 1.612 (5) and 2.190 (4) Å. The description of the polyhedron as a square pyramid is not unambiguous, since it could almost equally well be described as a trigonal bipyramid [with O(156) and O(136) as top and bottom corners] (Björnberg & Hedman, 1977). The main reason for describing it as a square pyramid is that O(2356) is situated at a V—O distance of 3.032 (5) Å directly below the bottom of the pyramid, V(6) thus approaching six-coordination. This distance, being longer than the shortest V—V distance, is probably too

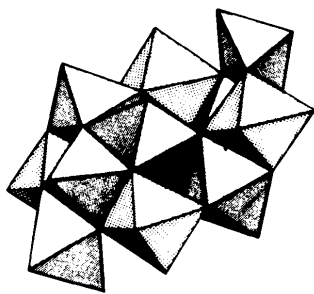


Fig. 2. The $Mo_4V_8O_{36}^{8-}$ anion. The MoO_6 octahedra are those with the lighter shading.

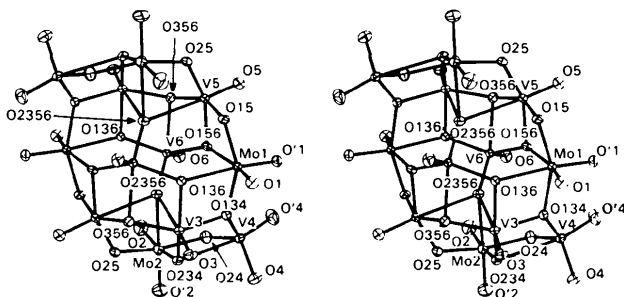


Fig. 3. A stereoscopic view of the $Mo_4V_8O_{36}^{8-}$ anion. The thermal ellipsoids are scaled to enclose 50% probability (ORTEP II; Johnson, 1976).

Table 3. Distances (Å) and angles (°) in the $\text{Mo}_4\text{V}_8\text{O}_{36}^{8-}$ anion

	O(1)	O'(1)	O(15)	O(134)	O(136)	O(156)
Mo(1)–	1.740 (4)	1.717 (4)	1.856 (4)	2.012 (4)	2.176 (4)	2.241 (4)
O(1)–		2.728 (6)	2.787 (6)	2.789 (6)	2.757 (6)	
O(156)–		2.808 (6)	2.462 (5)	2.870 (6)	2.789 (5)	
O'(1)–			2.781 (6)	2.760 (6)		
O(136)–			2.759 (5)	2.462 (6)		
O(1)–Mo(1)–		104.1 (2)	101.6 (2)	95.8 (2)	88.8 (2)	166.3 (2)
O(156)–Mo(1)–		89.4 (2)	73.2 (2)	84.7 (2)	78.3 (1)	
O'(1)–Mo(1)–			102.1 (2)	95.2 (2)	162.7 (2)	
O(136)–Mo(1)–			86.0 (2)	71.9 (2)		
	O(2)	O'(2)	O(24)	O(25)	O(234)	O(2356)
Mo(2)–	1.731 (6)	1.689 (6)	1.907 (5)	1.973 (4)	2.176 (4)	2.376 (4)
O(2)–		2.699 (8)	2.786 (7)	2.767 (7)		2.821 (7)
O(234)–		2.851 (7)	2.663 (6)	2.572 (6)		2.810 (6)
O(25)–		2.752 (7)				2.728 (6)
O(24)–		2.756 (7)				2.851 (6)
O(2)–Mo(2)–		104.2 (3)	99.9 (2)	96.4 (2)	161.0 (2)	85.2 (2)
O(234)–Mo(2)–		94.2 (2)	81.2 (2)	76.4 (2)		76.1 (2)
O(25)–Mo(2)–		97.1 (2)	152.7 (2)			77.1 (2)
O(24)–Mo(2)–		99.9 (2)				82.7 (2)
	O(3)	O(234)	O(356)	O(136)	O(134)	O(2356)
V(3)–	1.629 (5)	1.713 (4)	1.864 (4)	1.929 (4)	1.991 (4)	2.761 (4)
O(3)–		2.658 (6)	2.777 (6)	2.834 (6)	2.859 (6)	
O(2356)–		2.810 (6)	2.790 (6)	2.694 (6)	3.120 (6)	
O(134)–		2.555 (6)		2.462 (6)		
O(356)–		2.725 (6)		2.459 (6)		
O(3)–V(3)–		105.3 (2)	105.1 (2)	105.3 (2)	103.9 (2)	175.7 (2)
O(2356)–V(3)–		73.6 (2)	71.2 (2)	76.5 (2)	80.3 (2)	
O(134)–V(3)–		86.9 (2)	147.6 (2)	77.8 (2)		
O(356)–V(3)–		99.2 (2)		80.8 (2)		
	O(4)	O'(4)	O(24)	O(134)	O(234)	
V(4)–	1.651 (5)	1.625 (6)	1.836 (5)	1.836 (4)	2.670 (4)	
O(4)–		2.642 (8)	2.936 (7)	2.855 (7)	3.018 (7)	
O'(4)–			2.754 (7)	2.781 (7)		
O(134)–			3.050 (6)		2.555 (6)	
O(234)–			2.663 (6)			
O(4)–V(4)–		107.5 (3)	114.6 (2)	109.8 (3)	85.2 (2)	
O'(4)–V(4)–			105.3 (2)	106.8 (2)	167.2 (2)	
O(24)–V(4)–				112.3 (2)	69.7 (2)	
O(134)–V(4)–					66.1 (2)	
	O(5)	O(25)	O(356)	O(15)	O(156)	O(2356)
V(5)–	1.605 (5)	1.769 (4)	1.890 (4)	1.919 (4)	1.927 (4)	2.638 (4)
O(5)–		2.674 (6)	2.731 (6)	2.783 (6)	2.739 (6)	
O(2356)–		2.728 (6)	2.790 (6)	2.982 (6)	2.681 (6)	
O(25)–			2.710 (6)	2.643 (6)		
O(156)–			2.487 (6)	2.462 (6)		
O(5)–V(5)–		104.8 (2)	102.5 (2)	104.0 (2)	101.3 (2)	175.8 (2)
O(2356)–V(5)–		73.5 (2)	74.0 (2)	80.0 (2)	80.6 (2)	
O(25)–V(5)–			95.5 (2)	91.5 (2)	153.8 (2)	
O(156)–V(5)–			81.3 (2)	79.6 (2)		
	O(6)	O(2356)	O(156)	O(136)	O(356)	O(2356)
V(6)–	1.612 (5)	1.707 (4)	1.861 (4)	1.865 (4)	2.190 (4)	3.032 (5)
O(6)–		2.686 (6)	2.789 (6)	2.758 (6)	2.901 (6)	
O(2356)–			2.681 (6)	2.694 (6)	2.790 (6)	
O(156)–				2.789 (5)	2.487 (6)	
O(136)–					2.459 (6)	
O(6)–V(6)–		108.0 (2)	106.6 (2)	104.7 (2)	98.3 (2)	
O(2356)–V(6)–			97.3 (2)	97.8 (2)	153.7 (2)	
O(156)–V(6)–				138.7 (2)	75.2 (2)	
O(136)–V(6)–					74.2 (2)	

Table 3 (*cont.*)

	Mo(2)	V(3)	V(4)	V(5)	V(6)
Mo(1)–	5.270 (1)	3.201 (1)	3.564 (2)	3.094 (1)	3.894 (2)
Mo(2)–		3.464 (2)	3.303 (1)	3.336 (1)	5.041 (2)
V(3)–			3.226 (1)	3.371 (1)	3.041 (1)
V(4)–				5.565 (1)	4.336 (1)
V(5)–					3.011 (2)

long for any perceptible bond interaction. This coordination figure is frequently encountered in V^V oxo compounds (Evans, 1960) and a wide range of V–O distances to the sixth O atom has been found, from <2.15 Å, making the coordination decidedly octahedral, up to >3.5 Å.

V(4) is coordinated to five O atoms in a trigonal-bipyramidal arrangement. As for V(3) and V(5) there is an extremely long V–O distance [V(4)–O(234), 2.670 (4) Å]. The remaining four O atoms are in the normal range for an edge-sharing VO₄ tetrahedron, with two V–O bonds close to 1.65 Å and two close to 1.85 Å and angles not too far from the tetrahedral angle. As for V(3) and V(5) it seems highly probable, however, that O(234) really is coordinated to V(4), since Mo(2)–O(234), 2.176 (4) Å, is abnormally long for an O atom shared only between two metal atoms. Also a VO₄ tetrahedron attached only to two O atoms seems unlikely.

Since the Mo₄V₈O₃₆⁸⁻ anion does not contain any obvious subunits, the mechanism behind its formation is not easily explained. The deep-orange color of the molybdovanadate solution, both before and after acidification, indicates the formation of decavanadate complexes (Schwarzenbach & Geier, 1963), but to determine what species take part in the reactions forming the Mo₄V₈O₃₆⁸⁻ anion remains a task of some difficulty.

The potassium ions and water molecules

There are five crystallographically independent K⁺ ions, K(1)–K(5). They are all coordinating between eight and ten O atoms from either the anions or the water molecules. These O–K⁺–O bonds seem to be the most important forces in the crystal-structure framework, since O...H–O–H...O hydrogen bonds between two different anions are found only for the Aq(2) and Aq(3) water molecules (with O–O distances <3.0 Å). Aq(6), when in the *a* position, is also engaged in weak hydrogen bonding between adjacent anions, with Aq(6a)–O(356) 2.895 (19) and Aq(6a)–O(2) 3.000 (20) Å.

The anions are packed to form layers parallel to the *yz* plane (Fig. 1). There are comparatively few bonds between these layers. Except for the Aq(2) and Aq(3) hydrogen bonds, only O–K⁺–O bonds across K(4) and K(5) hold the layers together.

K–O and hydrogen-bond distances are given in Tables 4 and 5, and a representation of the hydrogen bonds between layers is given in Fig. 1. As can be seen from the table, K–O bonds tend to be shorter for water O atoms than for anion O atoms.

The disordered water molecule

Aq(6) is disordered over two positions with occupancy factors 0.55 (3) and 0.45 (3) for positions *a* and *b* respectively. The reason for this is probably the possibility of weak hydrogen-bond formation in both positions. Since Aq(6*b*)–Aq(6*b*) is the strongest of these bonds with an O–O distance of 2.73 (6) Å, it is highly probable that the *a* and *b* positions occur in pairs, the members of which, in the *b* position, are situated opposite each other across the *x* ≈ ±¼ layers.

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Table 4. K–O distances (Å) <3.5 Å

The superscripts refer to the following symmetry operations:

None, (0)	<i>x</i> , <i>y</i> , <i>z</i>	(vi)	–½ + <i>x</i> , ½ – <i>y</i> , –½ + <i>z</i>
(i)	1 – <i>x</i> , – <i>y</i> , 1 – <i>z</i>	(vii)	½ – <i>x</i> , ½ – <i>y</i> , 1 – <i>z</i>
(ii)	1 – <i>x</i> , <i>y</i> , ½ – <i>z</i>	(viii)	–½ + <i>x</i> , ½ + <i>y</i> , <i>z</i>
(iii)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>	(ix)	½ – <i>x</i> , ½ + <i>y</i> , ½ – <i>z</i>
(iv)	–½ + <i>x</i> , –½ + <i>y</i> , <i>z</i>	(x)	– <i>x</i> , <i>y</i> , ½ – <i>z</i>
(v)	½ – <i>x</i> , –½ + <i>y</i> , ½ – <i>z</i>	(xi)	<i>x</i> , 1 – <i>y</i> , –½ + <i>z</i>
		(xii)	½ – <i>x</i> , ½ – <i>y</i> , – <i>z</i> .
K(1)–Aq(5 ^{ll})	2.679 (17)	K(2)–O(2 ^{lv,v})	2.870 (6)
K(1)–O'(1 ^l)	2.762 (5)	K(2)–O(6 ^{lv,v})	2.875 (5)
K(1)–O(156)	2.785 (5)	K(2)–O(136 ^{vi,vii})	2.897 (4)
K(1)–O'(4 ^l)	2.896 (6)	K(2)–O(1 ^{vi,vii})	2.925 (5)
K(1)–O'(1)	2.936 (5)	K(2)–O(15 ^{vi,vii})	3.233 (4)
K(1)–O'(4)	2.978 (7)		
K(1)–O(5 ^{lll})	3.020 (5)	K(3)–Aq(4 ^{viii,ix})	2.704 (12)
K(1)–Aq(4)	3.062 (14)	K(3)–O(1 ^{vi,vii})	2.853 (5)
K(1)–O(6)	3.235 (5)	K(3)–O'(1 ^{vi,vii})	3.065 (5)
		K(3)–Aq(1 ^{0,x})	3.095 (8)
		K(3)–Aq(5 ^{viii,ix})	3.215 (16)
K(4)–Aq(2)	2.738 (8)	K(5)–Aq(6 <i>b</i>)	2.791 (27)
K(4)–O(15 ^{vl})	2.758 (4)	K(5)–O'(2)	2.798 (7)
K(4)–Aq(1)	2.811 (7)	K(5)–O(4 ^{lx})	2.807 (6)
K(4)–O(4)	2.817 (5)	K(5)–O(5 ^y)	2.819 (6)
K(4)–O(1 ^{vl})	2.823 (5)	K(5)–Aq(6 <i>a</i>)	2.821 (17)
K(4)–O(3 ^{vl})	2.917 (5)	K(5)–O(3 ^{xl})	2.968 (6)
K(4)–O(25 ^{lx})	3.019 (5)	K(5)–Aq(6 <i>b</i> ^{xll})	3.039 (26)
K(4)–O(2 ^y)	3.194 (6)	K(5)–Aq(5 ^{xll})	3.238 (17)

Table 5. Assumed hydrogen-bond distances (Å)
<math> < 3.15 \text{ \AA}</math>

The superscripts refer to the following symmetry operations:

(i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	(iv) $1 - x, y, \frac{1}{2} - z$
(ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$	(v) $x, 1 - y, -\frac{1}{2} + z$
(iii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$	(vi) $\frac{1}{2} - x, \frac{1}{2} - y, -z$
Aq(1)–Aq(3 ⁱ) 2.935 (12)	Aq(5)–Aq(2 ⁱⁱⁱ) 2.781 (16)
Aq(1)–Aq(4 ⁱ) 3.110 (14)	Aq(5)–Aq(6b) 2.979 (28)
Aq(2)–O(234) 2.917 (7)	Aq(5)–Aq(6a) 3.067 (23)
Aq(2)–O(3) 2.985 (8)	Aq(5)–Aq(3) 3.129 (19)
Aq(2)–O(4 ⁱⁱ) 2.994 (9)	Aq(6a)–O(356 ^v) 2.895 (19)
Aq(3)–O(25 ⁱⁱⁱ) 2.870 (9)	Aq(6a)–O(2) 3.000 (20)
Aq(3)–O(24) 2.949 (11)	Aq(6a)–Aq(3) 3.097 (21)
Aq(4)–O(6) 2.777 (13)	Aq(6b)–Aq(6b ^{vi}) 2.730 (58)
Aq(4)–O(24) 2.892 (13)	Aq(6b)–O(356 ^v) 2.857 (27)
Aq(4)–Aq(4 ^{iv}) 2.991 (24)	

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Multicomponent Polyanions.

26. The Crystal Structure of $\text{Na}_6\text{Mo}_6\text{V}_2\text{O}_{26}(\text{H}_2\text{O})_{16}$, a Compound Containing Sodium-Coordinated Hexamolybdodivanadate Anions

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Abstract

$\text{Na}_6\text{Mo}_6\text{V}_2\text{O}_{26}(\text{H}_2\text{O})_{16}$ is triclinic, $P\bar{1}$, with $a = 10.176$ (2), $b = 10.416$ (4), $c = 10.292$ (2) Å, $\alpha = 113.19$ (2), $\beta = 95.54$ (2), $\gamma = 101.73$ (2)°, $Z = 1$. The structure was refined to a final R of 0.036 based on 5936 independent reflexions. The structure is built up from $\text{Mo}_6\text{V}_2\text{O}_{26}^{6-}$ anions which are linked together by Na^+ ions and water molecules in a three-dimensional framework. The anions consist of a flat ring of six edge-sharing MoO_6 octahedra with one VO_4 tetrahedron on

each side capping the hole in the center of the ring. The short Mo–Mo distances are 3.27–3.28 Å and V–Mo distances are 3.71–3.77 Å. The Mo–O distances vary with the number of metal atoms coordinated to each O atom, the average distances being 1.71, 1.91 and 2.35 Å for one-, two- and three-coordinated O atoms respectively. The V–O distances are 1.640 (3) Å for the terminal O atom and 1.78 Å for O atoms shared with Mo.