

$K_6[Mo_6V_2O_{26}] \cdot 4H_2O$

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(V-O) = 0.003\text{ \AA}$

R factor = 0.024

w R factor = 0.065

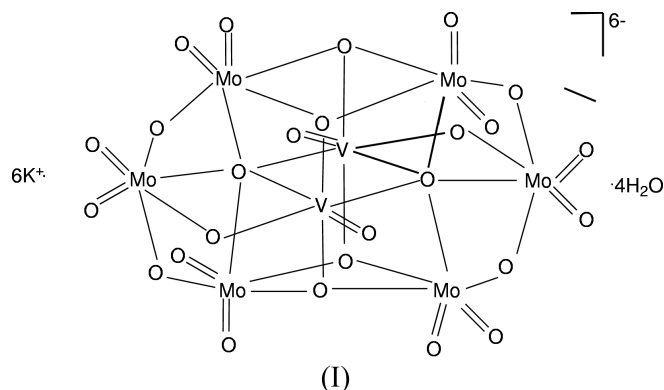
Data-to-parameter ratio = 27.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The new polyoxomolybdovanadate, hexapotassium hexamolybdodivanadate tetrahydrate, $K_6[Mo_6V_2O_{26}] \cdot 4H_2O$, has been isolated from a solution of potassium molybdate and ammonium vanadate. The polyoxoanion, with crystallographically imposed $2/m$ symmetry, is built up of six MoO_6 and two VO_6 edge-sharing distorted octahedra.

Comment

$K_6[Mo_6V_2O_{26}] \cdot 4H_2O$, (I), has been isolated from a solution of potassium molybdate and ammonium vanadate at $pH = 5.90$. The crystal structure is built up of $[Mo_6V_2O_{26}]^{6-}$ anions joined together in a three-dimensional framework by electrostatic $K^+ \cdots O$ linkages, as well as by hydrogen bonds.



The polyoxoanion, which is isostructural with the β -octamolybdate $[Mo_8O_{26}]^{4-}$ anion (Lindquist, 1959) and with the β -hexamolybdodivanadate $[Mo_6V_2O_{26}]^{6-}$ anion found in the mixed potassium sodium salt $K_5Na[Mo_6V_2O_{26}] \cdot 4H_2O$ (Nenner, 1985), is composed of six MoO_6 and two VO_6 edge-sharing distorted octahedra, and has crystallographically imposed $2/m$ symmetry. Mo and V atoms are differently coordinated by the oxo ligands: Mo1 is coordinated by two terminal O_b , three double-bridging O_b , and one five-bridging O_{5b} atoms; Mo2 by two terminal O_b , one double-bridging O_b , two triple-bridging O_{3b} , and one five-bridging O_{5b} ; and V1 by one terminal O_b , one double-bridging O_b , two triple-bridging O_{3b} and two five-bridging O_{5b} atoms. However, the metal-to-oxygen distances show the usual distribution: two short bonds, two bonds of medium length and two long bonds. The potassium ion K1, situated in special position $(c) \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ of space group $C2/m$, occupies the same site as the sodium ion in the structure of the mixed salt $K_5Na[Mo_6V_2O_{26}] \cdot 4H_2O$. However, whereas the sodium cation is surrounded by six terminal O atoms from two polyoxoanions, with $Na^+ \cdots O$ distances ranging

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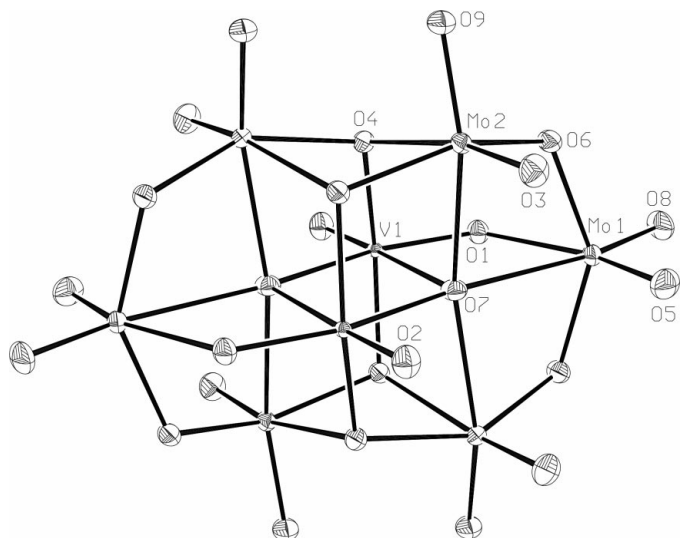


Figure 1
The structure of the $[\text{Mo}_6\text{V}_2\text{O}_{26}]^{6-}$ anion found in the title compound.

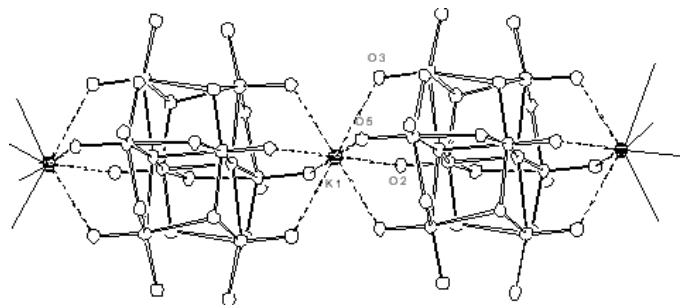


Figure 2
Part of the packing, showing the coordination of the K1 ion, viewed in the direction [001].

from 2.40 to 2.57 Å, the K1 cation is surrounded by eight terminal O atoms, with $\text{K1}\cdots\text{O}$ distances ranging from 2.600 (2) to 2.925 (2) Å. In this way, chains of polyoxoanions parallel to the [001] direction are formed in both structures. A bond-strength calculation (Brown & Altermatt, 1985) shows that the bond-valence sum around K1 is 1.69, much larger than 1.0, the theoretical value for the K ion, thus indicating that the structure cannot expand in the [001] direction to provide the ideal space required by K. The analogous value, calculated for the Na ion in the structure of the mixed sodium potassium salt (Nenner, 1985), is 0.92. The remaining two cations, K2 and K3, are located at the same positions as two symmetry-independent potassium ions in the structure of $\text{K}_5\text{Na}[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$. The cation K2, situated in a general position, is irregularly surrounded by nine O atoms, seven from the polyoxoanions and two from water molecules, $\text{K2}\cdots\text{O}$ distances vary from 2.796 (2) to 3.0692 (17) Å. The cation K3, located in the special position $(b) 0, \frac{1}{2}, 0$, is surrounded by eight O atoms from four polyanions, with $\text{K3}\cdots\text{O}$ distances ranging from 2.8604 (16) to 3.236 (3) Å, forming layers of polyoxoanions parallel to the (201) plane. The bond-valence sums around cations K2 and K3 are 0.95 and 0.73, respectively. The

molybdovanadate anions are additionally interconnected by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds realised through water molecules. One of the H atoms, H2, is involved in a three-centred hydrogen bond between water molecules and two terminal O atoms from the polyoxoanion.

Experimental

A mixture of K_2MoO_4 (0.8 g) and NH_4VO_3 (0.12 g) was dissolved in water (15 ml) and heated under reflux for 2 h. The suspension was filtered off and the pH was adjusted to 5.9 by adding 2M HCl (5 ml). The clear yellow solution was left at room temperature. After standing for 14 d, yellow crystals were filtered off and dried *in vacuo*.

Crystal data

$\text{K}_6[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$	$D_x = 3.417 \text{ Mg m}^{-3}$
$M_r = 1400.18$	Mo $K\alpha$ radiation
Monoclinic, $C2/m$	Cell parameters from 3364 reflections
$a = 14.717$ (3) Å	$\theta = 2.4\text{--}36.3^\circ$
$b = 12.813$ (3) Å	$\mu = 4.36 \text{ mm}^{-1}$
$c = 9.251$ (2) Å	$T = 293$ (2) K
$\beta = 128.73$ (3)°	Prism, yellow
$V = 1360.9$ (8) Å ³	$0.16 \times 0.15 \times 0.13 \text{ mm}$
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.013$
$2^\circ \varphi$ and ω scans	$\theta_{\text{max}} = 36.3^\circ$
Absorption correction: none	$h = -24 \rightarrow 24$
6362 measured reflections	$k = -21 \rightarrow 20$
3364 independent reflections	$l = -15 \rightarrow 15$
3267 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 8.9089P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.09$	$\Delta\rho_{\text{max}} = 1.53 \text{ e \AA}^{-3}$
3364 reflections	$\Delta\rho_{\text{min}} = -1.88 \text{ e \AA}^{-3}$
123 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.00280 (13)

Table 1

Selected geometric parameters (Å).

Mo1—O8	1.708 (2)	Mo2—O7	2.2658 (6)
Mo1—O5	1.738 (2)	Mo2—O4	2.3050 (14)
Mo1—O6 ⁱ	1.9198 (14)	V1—O2	1.625 (2)
Mo1—O6	1.9198 (14)	V1—O1	1.723 (2)
Mo1—O1	2.196 (2)	V1—O4	1.9202 (14)
Mo1—O7	2.435 (2)	V1—O4 ⁱ	1.9202 (14)
Mo2—O9	1.7172 (15)	V1—O7 ⁱⁱⁱ	2.107 (2)
Mo2—O3	1.7235 (15)	V1—O7	2.371 (2)
Mo2—O6	1.9090 (16)	V1—Mo2 ⁱⁱⁱ	3.1305 (9)
Mo2—O4 ⁱⁱ	1.9530 (17)	V1—Mo2 ⁱⁱ	3.1305 (9)

Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, -z$; (iii) $-x, -y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{OW}-\text{H1}\cdots\text{O1}$	0.94 (4)	1.87 (4)	2.779 (2)	162 (4)
$\text{OW}-\text{H2}\cdots\text{O9}^{\text{iv}}$	1.02 (6)	2.20 (7)	2.908 (2)	125 (5)
$\text{OW}-\text{H2}\cdots\text{O8}^{\text{v}}$	1.02 (6)	2.23 (6)	3.040 (3)	136 (5)

Symmetry codes: (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (v) $1 - x, -y, 1 - z$.

The maximum and minimum electron-density peaks were located 0.25 Å from V1 and 0.41 Å from K2, respectively.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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