

Multicomponent Polyanions.

27. Crystal Structure and Electron Spin Resonance Spectrum of $K_6(V_2,Mo_{10})VO_{40} \cdot 13H_2O$, a New 'One-Electron Heteropoly Blue'

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Abstract

$K_6(V_2,Mo_{10})VO_{40} \cdot 13H_2O$ is cubic, space group $P\bar{4}3m$, with $a = 10.6124(5)$ Å, $Z = 1$. Refinement resulted in a final R of 0.061, based on 545 counter reflexions. The structure contains $(V_2,Mo_{10})VO_{40}^{6-}$ anions linked together by K^+ ions and water molecules. The heteropolyanion has the well known Keggin structure (α isomer). The 12 metal atoms in the cage of the anion comprise 10 Mo atoms and 2 V atoms in a random distribution. The $M-M$ ($M = Mo$ or V) distances between MO_6 octahedra in the anion are 3.49 Å. The distance $V-M$ from the central atom is 3.49 Å. $M-O$ distances are 1.62, 1.82 or 2.01 and 2.35 Å for O atoms coordinated to one, two and three M atoms respectively. There is rotational disorder in the structure, with the anion distributed between two positions interrelated by a 90° rotation. Results from the ESR investigations indicate that the true formula of the anion, which can be described as a 'one-electron heteropoly blue', should be written $(V^{IV},V^V,Mo_{10}^{VI})-V^VO_{40}^{6-}$.

Introduction

This study originated as part of a project aimed at determining the formation constants and the nature of the complexes present in aqueous solutions containing Mo^{VI} and V^V (Pettersson, 1979). The interpretation of data from potentiometric titrations is difficult in this system due to the formation of several polynuclear complexes. Crystallization experiments yielded a number of different compounds containing discrete molybdovanadate anions, among them the previously described $K_8Mo_4V_8O_{36} \cdot 12H_2O$ and $Na_6Mo_6V_2O_{26} \cdot (H_2O)_{16}$ (Björnberg, 1979*a,b*).

In solutions containing P^V or Si^{IV} as well as Mo and V, Keggin-type anions are readily formed (Weakley, 1974). Owing to the similarity in behaviour between P^V and V^V in aqueous solution, a Keggin anion with V^V as the central atom was considered as a species likely to be found in the solutions investigated. Initially, how-

ever, all crystalline phases obtained in several experiments contained one of the two anions mentioned above or the structurally determined $Mo_8V_5O_{70}^{7-}$ anion (Björnberg, 1980). This anion has the formula of a possible Keggin anion, but the structure is quite different.

The phase $K_6(V_2,Mo_{10})VO_{40} \cdot 13H_2O$ appeared in a solution that had been left standing for a few months, and its black or darkish-brown colour, as opposed to the yellow colour of all the other molybdovanadates produced, clearly suggested this phase to contain a reduced species with Mo or V in a mixed-valence state, thus belonging to the class of compounds known as 'heteropoly blues'. The ability to form reduced compounds is well known among hetero- and isopolyoxyanions containing V, Mo or W if they have structures containing metal atoms that are coordinated to one terminal O atom (Pope, 1972). Among the several types of such structures known, most studies of heteropoly blues have been performed on anions with the $XM_{12}O_{40}$ (Keggin, 1934) or $X_2M_{18}O_{62}$ structures (Dawson, 1953; Matsumoto & Sasaki, 1975). M in these anions can be either Mo or W (with X mostly being Si^{IV} or P^V) but quite often a number of M atoms are substituted by V or Cr. There also exist hydrolysed forms of these anions, $PW_{11}O_{39}^{19-}$ and $P_2W_{17}O_{61}^{19-}$ (Souhay & Tézé, 1969), which are capable of forming blues upon reduction.

Polyanions forming blues through the reduction of V are less common. However, the well known $V_{10}O_{28}^{6-}$ anion has been shown to be reducible (Ostrowsky, 1964), and recently Evans & Konnerth (1978) determined the structure of the mineral sherwoodite, which they formulated $Ca_{4.5}(AlV_{12}V_2^{IV}O_{40}) \cdot 28H_2O$. The greenish-black colour of the crystals supports the conclusion that V is in a mixed-valence state.

In all heteropoly blues investigated so far, the reduced metal ion has been octahedrally coordinated. In no case has a reduction of a tetrahedrally coordinated central atom been observed.

The present study concerns the phase $K_6(V_2,Mo_{10})VO_{40} \cdot 13H_2O$, a compound which is unreported in earlier literature.

Experimental

Crystal preparation, analyses and data

Crystals are formed from the solution prepared for the synthesis of $K_8Mo_4V_8O_{36} \cdot 12H_2O$ (Björnberg, 1979a). If the solution with the first-formed crystals is left standing in a sealed beaker, the crystals transform into an amorphous yellow phase and dark-brown cube-shaped crystals, which are sparingly soluble in water, appear on the yellow precipitate. The crystals are relatively stable in air, but decay rapidly upon X-ray exposure during which they were therefore enclosed, together with part of the mother liquor, in a sealed capillary of Lindemann glass. The synthesis gives a very low yield, and, since it is difficult to separate the dark-brown crystals from the yellow precipitate, only 16 mg of pure substance could be obtained for analysis. The results of the analyses, performed with a Jones reductor, were: Mo 42.8 and V 9.2 wt%; calculated: Mo 43.2 and V 6.9 wt% (Caven, 1962).

From Weissenberg and precession photographs the crystals were found to be cubic with $m\bar{3}m$ symmetry. There are no systematic extinctions, which leaves a choice between three different space groups, $P432$, $Pm\bar{3}m$ and $P43m$, of which the last was chosen, the choice being confirmed by the success of the refinements. The unit-cell length was refined by least-squares methods from powder photographs taken with a Guinier-Hägg camera and $Cu K\alpha_1$ radiation ($\lambda = 1.54051$ Å) with Si as internal standard ($a[Si] = 5.43054$ Å, 298 K). Attempts were made to determine the density of the crystals by flotation in a diiodomethane-chloroform solution, but the density was found to be strongly dependent on the crystal size, the larger crystals being lighter, probably due to water inclusions. The smallest crystal possible to use practically was found to have a density of 2.98 Mg m^{-3} . Crystal data are given in Table 1.

Data collection and reduction

A crystal $0.31 \times 0.23 \times 0.17$ mm was chosen for the X-ray data collection, which was made on a Syntex R3 automatic four-circle diffractometer with graphite-monochromatized $Mo K\alpha$ radiation ($\lambda = 0.71069$ Å). The $\theta/2\theta$ scan method was used, and the 2θ scan speed

was allowed to vary between 0.75 and 6° min^{-1} depending on the intensity of the measured reflexion. 1063 independent reflexions were collected in the region $(\sin \theta/\lambda) < 1.00$ Å $^{-1}$. The background was measured for half the scan time at each side of the interval. 545 reflexions with $F_o^2 \geq 4\sigma(F_o^2)$ were considered observed and were used in the calculations. An empirical absorption correction, based on the measurement of 18 reflexions with various $\sin \theta/\lambda$ values, each reflexion with 36 points taken by a full rotation around the diffraction vector in steps of 10° , was applied [$\mu(Mo K\alpha) = 3.627$ mm $^{-1}$] and the transmission factor varied between 0.721 and 1.000.

The recording of ESR spectra

ESR spectra were recorded with a polycrystalline sample at 77 K with a Varian V-4502-11 X-band spectrometer. The microwave frequency was determined with DPPH as reference.

The sample was mounted in a quartz tube which was placed in an immersion Dewar with the tube axis perpendicular to the magnetic-field direction.

Structure determination and refinement

The Mo/V atom position was located from a Patterson synthesis, and routine heavy-atom methods gave the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with isotropic temperature factors gave an R of 0.117, which decreased to 0.061 when anisotropic temperature factors were applied. A difference synthesis calculated at this stage showed a large peak (≈ 7.5 e Å $^{-3}$) at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. When the anion O atoms of both rotational positions of the anion were included, with parameters interlocked (*i.e.* inverted coordinates and identical thermal parameters) to maintain the same number of refined parameters, R dropped to 0.055. In this refinement, however, e.s.d.'s of a number of positional parameters would not refine to definite values. Consequently, only one of the rotations was included in the final refinement, which converged with $R = 0.061$ ($R_w = 0.063$), with $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, and $R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}}{[\sum w(|F_o| - |F_c|)^2]}$ was minimized.

In the final cycle the parameter shifts, save those of three thermal parameters, were $< 0.5\sigma$. 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). The computer programs used were those supplied with the Syntex R3 crystallographic system, and the final calculations were made with programs described by Antti (1976). Computations were performed with the DG Nova 3 computer at the Department of Inorganic

Table 1. Crystal data for $K_6(V_2, Mo_{10})VO_{40} \cdot 13H_2O$

Cubic, space group $P43m$	
$a = 10.6124$ (5) Å	$D_x = 3.085$ Mg m^{-3}
$Z = 1$	$\mu(Mo K\alpha) = 3.627$ mm $^{-1}$
$M_r = 2220.95$	
$V = 1195.20$ Å 3	

Table 2. *The fractional atomic coordinates ($\times 10^4$, for Mo/V $\times 10^5$) with their e.s.d.'s in parentheses*

Coordinates are given for one rotational position only; coordinates for the other are obtained by taking $\bar{x}, \bar{y}, \bar{z}$ for those given.

	x	y	z
Mo/V	26736 (8)	26736 (8)	49981 (40)
V	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O(1)	5895 (10)	5895 (10)	5895 (10)
O(2)	3928 (8)	3928 (8)	2214 (12)
O(3)	3604 (8)	3604 (8)	8201 (10)
O(4)	1599 (7)	1599 (7)	5093 (38)
K(1)	0	$\frac{1}{2}$	$\frac{1}{2}$
K(2)	3661 (10)	0	0
Aq(1)	2229 (14)	2229 (14)	57 (35)
Aq(2)	0	0	0

Table 3. *Bond distances (Å) and angles (°) in $K_6(V_2, Mo_{10})VO_{40} \cdot 13H_2O$*

Mo/V—O(1)	2.350 (10)	Mo/V—Mo/V	3.494 (6) (edge-shared)
—O(2)	1.816 (4)	Mo/V—Mo/V	3.489 (6) (corner-shared)
—O(3)	2.009 (6)	Mo/V—V	3.491 (1)
—O(4)	1.617 (11)		
O(1)—O(2)	2.902 (11)	O(1)—Mo/V—O(2)	87.3 (5)
O(1)—O(3)	2.56 (2)	O(1)—Mo/V—O(3)	71.5 (4)
O(2)—O(2)	2.57 (2)	O(1)—Mo/V—O(4)	153 (2)
O(2)—O(3)	2.678 (12)	O(2)—Mo/V—O(2)	90.2 (4)
O(2)—O(4)	2.84 (2)	O(2)—Mo/V—O(3)	88.7 (5)
O(3)—O(3)	2.71 (2)	O(2)—Mo/V—O(4)	111.5 (10)
O(3)—O(4)	2.55 (2)	O(3)—Mo/V—O(3)	84.8 (6)
V—O(1)	1.64 (2)	O(3)—Mo/V—O(4)	88.6 (11)
O(1)—O(1)	2.69 (2)		
K(1)—O(2)	2.848 (12)	K(2)—O(4)	2.74 (2)
K(1)—O(3)	2.834 (11)	K(2)—O(4)	2.84 (2)
		K(2)—Aq(1)	2.812 (7)
Aq(1)—O(3)	2.85 (3)		

Chemistry, University of Umeå, and with the CD Cyber 172 computer at the University of Umeå. Final atomic positional parameters are given in Table 2.*

Description and discussion of the structure

The structure consists of $(V_2, Mo_{10})VO_{40}^{6-}$ anions which are joined in a three-dimensional framework by K^+ ions and water molecules. Since the space group does not contain any pure fourfold rotation axis, there are two possible orientations of the anion. The structure can be equally well refined with either orientation. This disorder is the probable reason behind the comparably high final R . The only other Keggin structure with a V atom at the centre which has been solved, $K_7V_5W_8-$

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35009 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$O_{40} \cdot 12H_2O$ (Nishikawa, Kobayashi & Sasaki, 1975), is isostructural with $K_6(V_2, Mo_{10})VO_{40} \cdot 13H_2O$.

Bond distances and angles are given in Table 3.

The $(V_2, Mo_{10})VO_{40}$ group

The unit cell contains one $(V_2, Mo_{10})VO_{40}^{6-}$ polyanion (Figs. 1, 2) with a VO_4 tetrahedron at the centre. In this anion three MO_6 ($M = Mo$ or V) octahedra link together by sharing edges to form an M_3O_{13} unit. The O atom common to these three octahedra is also coordinated to the central V atom. The four M_3O_{13} groups are connected to each other by sharing corners. The $M-M$ distance within the M_3O_{13} unit is 3.494 (6) Å and the distance between M atoms of different M_3O_{13} units is 3.489 (6) Å. The apparent equivalence of these distances is most certainly caused by the rotational disorder. In ordered Keggin structures the corresponding values are of the order of 3.40 and 3.70 Å respectively (Strandberg, 1977). The $M-V$ distance is also very similar to the $M-M$ distances: 3.491 (1) Å.

The MO_6 octahedra

Since the central atom of these octahedra is either Mo^{VI} , V^{IV} or V^V , comparison of bond distances with those found in other structures is difficult. $M-O$ distances to O atoms shared between two or three M atoms resemble very much those found in all-Mo Keggin anions. The $M-O$ terminal distance

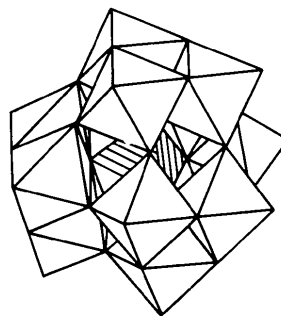


Fig. 1. The $(V_2, Mo_{10})VO_{40}^{6-}$ anion drawn with idealized polyhedra.

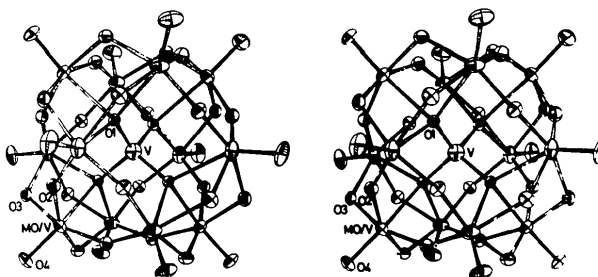


Fig. 2. A stereoscopic drawing of the $(V_2, Mo_{10})VO_{40}^{6-}$ anion. The thermal ellipsoids are scaled to enclose 50% probability (Johnson, 1976).

Table 4. Mo—O and X—O average bond distances (Å) in some $X\text{Mo}_{12}\text{O}_{40}^{4-}$ anions

The anions compared are $\text{PMo}_{12}\text{O}_{40}^{3-}$ (Strandberg, 1975), $\text{GeMo}_{12}\text{O}_{40}^{4-}$ (Strandberg, 1977), $\text{SiMo}_{12}\text{O}_{40}^{4-}$ (Ichida, 1979) and the present structure. The notation for the O atoms has been chosen to agree with that used elsewhere in this paper.

	X = P	X = Si	X = V	X = Ge
X—O(1)	1.54	1.63	1.64	1.73
Mo—O(1)	2.43	2.23	2.35*	2.29
Mo—O(2)	1.92	1.85	1.82*	1.82
Mo—O(3)	1.92	1.99	2.01*	2.04
Mo—O(4)	1.68	1.69	1.62*	1.69

* Mo = Mo/V.

[1.617 (11) Å] is very short for a Mo—O bond, but the value of this distance is probably affected by the positional uncertainty of O(4) caused by the rotational disorder of the crystal. 1.617 Å is on the short side even when the fact that this is a weighted average of one $\text{V}^{\text{IV}}\text{—O}$, one $\text{V}^{\text{V}}\text{—O}$ and ten $\text{Mo}^{\text{VI}}\text{—O}$ bonds is taken into account. In structures containing V^{IV} the V—O terminal bonds are usually near 1.58 Å, this being attributed to the presence of VO^{2+} ions in the structure (Tachez, Théobald, Watson & Mercier, 1979). $\text{V}^{\text{V}}\text{—O}$ terminal bonds are usually about 1.61 Å (Evans, 1966).

Table 4 gives a comparison between metal—oxygen bond distances in Keggin anions with Mo in the cage and various central tetrahedral atoms. The systematic difference in Mo—O distances that can be detected [the Mo—O(1) distance increases with decreasing size of the central tetrahedron] indicates that the shape of the Mo—O cage is approximately the same regardless of which central atom is present. An interesting feature is the equal lengths of the Mo—O(2) and Mo—O(3) bonds in the P^{V} compound. In the other structures the O atoms of the larger central tetrahedra apparently force the O(3) atoms away from the Mo atom.

The VO_4 tetrahedron

Owing to space-group symmetry, the VO_4 tetrahedron is perfectly regular with a V—O distance of 1.64 (2) Å and an O—O edge length of 2.68 (2) Å. The thermal parameters of O(1) are even lower than for the other O atoms, indicating that the regularity of the tetrahedron is real and not a result of rotational disorder of the anion. This seems very reasonable, since the VO_4^{3-} anion in a water solution (or at least in $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$, which very much resembles a water solution; Tillmanns & Baur, 1971) is very nearly regular. There are numerous examples where VO_4 tetrahedra have two short (~1.65 Å) and two long (~1.80 Å) V—O bonds, but this always seems to be in connexion with the sharing of two of the corners with

other metal atoms (Evans, 1966). In the Keggin structure all four corners of the tetrahedron again have equivalent surroundings.

The potassium ions and water molecules

Of the six K^+ ions in the unit cell, three [K(1)] are in the threefold site 3(c) ($0, \frac{1}{2}, \frac{1}{2}$). The remaining three [K(2)] occupy one half of the sixfold site 6(f) ($x, 0, 0$) with equal probability. (The ratio between the respective peak heights in the Fourier synthesis was 2:1, which was confirmed by refinements.) The K(2) atoms, along with the water molecules, are situated in channels running along the unit-cell edges. At their narrowest point [$\frac{1}{2}, 0, 0$, between four O(4) atoms] these channels have an approximate diameter of 2.4 Å, which is slightly too narrow to allow the passage of a K^+ ion. Both K^+ ions coordinate eight O atoms or water molecules: K(1) is surrounded by four O(2) and four O(3) atoms at distances of 2.848 (12) and 2.834 (12) Å respectively, forming a distorted square antiprism, and K(2) is situated in a more regular square antiprism created by four O(4) atoms at distances of 2.75 (2) and 2.84 (2) Å and by four Aq(1) molecules at a distance of 2.812 (7) Å.

The water molecules are not very tightly bonded in the structure. The only significant hydrogen bond seems to be Aq(1)···O(3) with an O···O distance of 2.85 (3) Å. The other H atom of Aq(1) could possibly be engaged in a weak bifurcated hydrogen bond to two other Aq(1) atoms at an O···O distance of 3.26 (6) Å. Aq(2), whose H atoms must be disordered, has no nearer neighbour than the twelve Aq(1) atoms at 3.35 (2) Å.

Results of the ESR measurements

The first derivative spectrum recorded at 77 K is shown in Fig. 3. For comparison the spectra of reduced $\text{H}_5\text{Mo}_{10}\text{V}_2\text{PO}_{40}$ (Otake, Komiyama & Otaki, 1973) and vanadyl(IV) tropolonate (Stewart & Porte, 1972) are included. From the similarity of the three spectra it is evident that the paramagnetic atom is the same in all three compounds, *i.e.* V^{IV} . The redox potentials of the two redox pairs $\text{V}^{\text{V}}\text{—V}^{\text{IV}}$ and $\text{Mo}^{\text{VI}}\text{—Mo}^{\text{V}}$, 999.6 mV and 530 mV respectively, also indicate that V^{V} should be the more easily reducible species (Hart & Partington, 1940; Höltje & Geyer, 1941).

The sharp signal at half the magnetic field strength, which is shown in the spectrum of the presently described compound, is probably caused by a triplet with the odd electrons of neighbouring anions interacting. There is also the possibility of a disproportionation of electrons between anions in the crystal, creating 'two-electron blues', in which such a triplet state could be found.

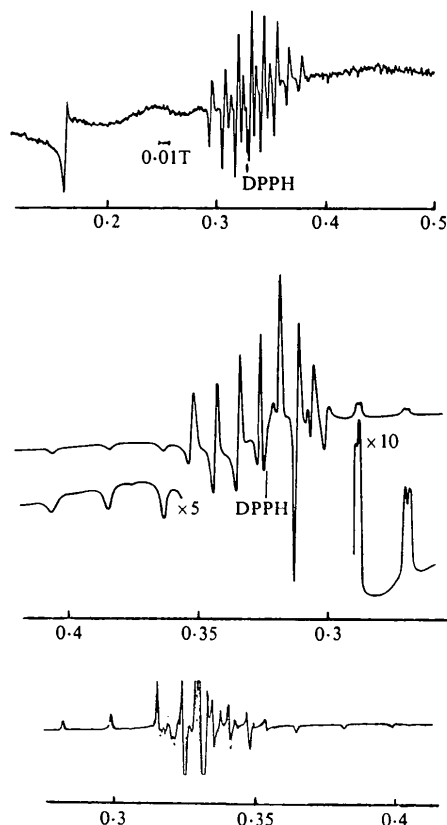


Fig. 3. ESR spectra of (top to bottom) $K_6(V_2, Mo_{10})VO_{40} \cdot 13H_2O$, reduced $H_3Mo_{10}V_2PO_{40}$ and vanadyl(IV) tropolonate. The magnetic field strength (T) is shown below each spectrum.

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