Haddad, A., Jouini, T. & Piffard, Y. (1992). *Eur. J. Solid State Inorg. Chem.* **29**, 57–63.

Hizaoui, K., Jouini, N. & Jouini, T. (1999). *J. Solid State Chem.* **144**, 53–61.

Lachgar, A., Deniard-Courant, S. & Piffard, Y. (1986). *J. Solid State Chem.* **63**, 409–413.

Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

al. (1993). The structure reported here has better defined alkali-ion positions as we avoided the difficulties in distinguishing Na^+ from O^{2-} by replacing Na^+ with Rb^+. The formal oxidation state of V cannot be deduced with certainty from these diffraction data. We have chosen a partially occupied V position, as a large negative residual density ($-4.09\,e\,Å^{-3}$) occurs at the $8c$ position if V is fully occupied. The conventional R value is decreased from 0.058 to 0.054 only by refining the V occupancy. Furthermore, both the largest positive and negative residual densities were decreased to less than half the original values by introducing the partial V occupancy.
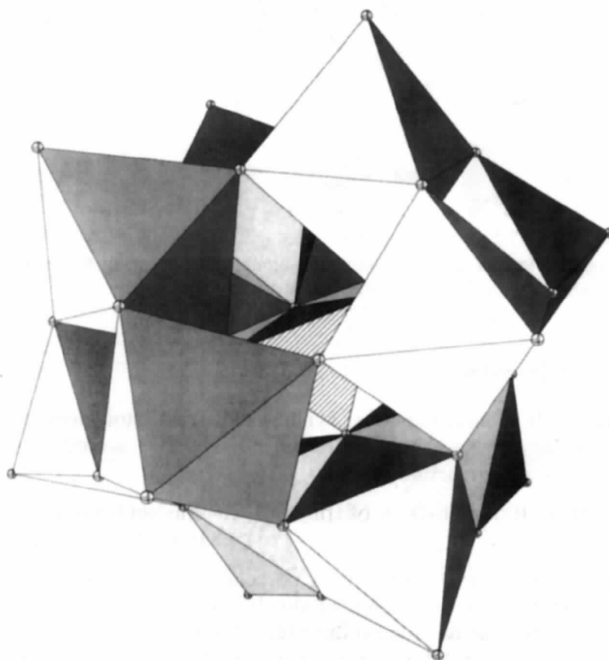
Heteropoly blue $Rb_{4.4}[H_{0.6}V_{0.6}Mo_{12}O_{40}]\cdot 14H_2O$

CESAR PAY GÓMEZ[a] AND LARS ERIKSSON[b]

[a]*Division of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, and* [b]*Division of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden. E-mail: cesar@inorg.su.se*

Abstract

The structure of rubidium tetracontaoxo(hydro)(dodecamolybdo)vanadate tetradecahydrate, $Rb_{4.4}[H_{0.6}V_{0.6}Mo_{12}O_{40}]\cdot 14H_2O$, has been determined by single-crystal X-ray diffraction. The structure is built up of heteropolyoxy anions with the general formula $XM_{12}O_{40}$ ($X = V^V$; $M = Mo^{VI}$ or V^{IV}) that conform with the Keggin family of structures. These anions are separated by rows of Rb^+ ions with interpenetrating water molecules. The structure is closely related to that of $Na_3[VMo_{12}O_{40}]\cdot 19H_2O$ reported previously, the main differences being the higher alkali content, the presence of a small amount of V^{IV} in the structure and the partial occupancy of V^V in the tetrahedral polyoxy anion sites of the title compound.

Comment

The present study is part of a project aimed at synthesizing large-cavity polyoxometalates. One of the main goals is to investigate the possibilities of condensing small molecule moieties into larger clusters. The title compound, $Rb_{4.4}[H_{0.6}V_{0.6}Mo_{12}O_{40}]\cdot 14H_2O$, is built up of heteropolyoxy anions (Figs. 1 and 2) with the general formula $XM_{12}O_{40}$, where $X = V^V$ and $M = Mo^{VI}$ or V^{IV}, thus conforming to the Keggin-type family of structures (Keggin, 1933). A pseudo-isomorphous sodium-containing compound has been reported by Zhang *et*

Fig. 1. A polyhedral representation of the α-Keggin cluster of the title compound. The central tetrahedron is shown with hatched lines.

The presence of reduced species such as Mo^V and V^{IV} in the M sites of the $XM_{12}O_{40}$ α-Keggin cluster has been observed frequently. This is the case in, for example, $K_6(V_2,Mo_{10})VO_{40}\cdot 13H_2O$ (Björnberg & Hedman, 1980), which is closely related to the title compound. $K_6(V_2,Mo_{10})VO_{40}\cdot 13H_2O$ is built up of α-Keggin clusters with interpenetrating K^+ ions and water molecules. The M sites of the $XM_{12}O_{40}$ Keggin clusters are inhabited by Mo^{VI}, V^{IV} and V^V. In contrast to the title compound, $K_6(V_2,Mo_{10})VO_{40}\cdot 13H_2O$ belongs to the cubic space group $P\bar{4}3m$, with $a = 10.6124\,(5)$ Å. In comparing $K_6(V_2,Mo_{10})VO_{40}\cdot 13H_2O$ with $Rb_{4.4}[H_{0.6}V_{0.6}Mo_{12}O_{40}]\cdot 14H_2O$, we see that every other cluster in the unit cell of the title compound is rotated 90° along all three directions parallel to the main cell axes, giving rise to the doubling of the a cell parameter and the F-centring of the lattice.
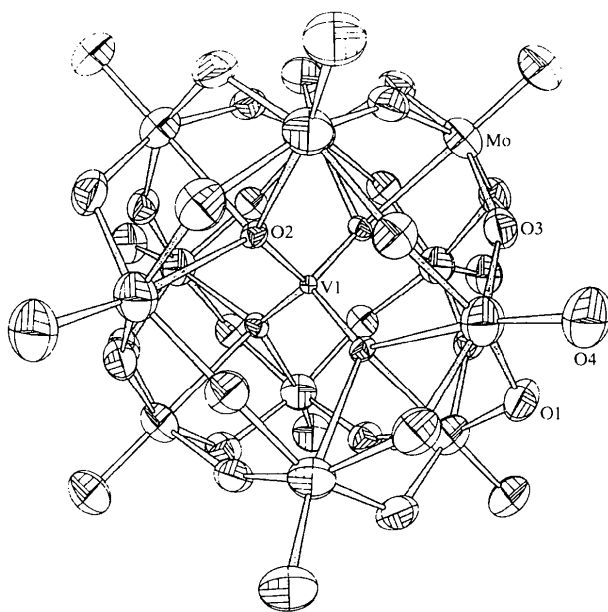
Fig. 2. Displacement ellipsoid plot of the α-Keggin cluster of the title compound. Ellipsoids are shown at the 70% probability level.

The charge misbalance created by the vacancies at the tetrahedral V^V sites is believed to be compensated for by protonation of oxygen on some of the clusters. This has been observed earlier in, for example, the related compound $Rb_4H_8[H_2W_{12}O_{40}]\cdot18H_2O$ (Jeannin et al., 1980). However, no H atoms could be located in the residual density maps, although ^1H NMR measurements confirm the presence of protons in the sample after dehydration under an oxygen atmosphere at 573 K. Thermogravimetric analyses and IR spectra confirm that no water of crystallization remains in the sample after heating to 573 K. Due to the black colour of the sample, it may be assumed that V is in a mixed valence state. An attempt to insert V^{IV} at the Mo position was made, but the occupancy of V was not significantly different from zero. However, it is still possible that a certain amount of V^{IV} is present in the octahedral sites, too small to be refined yet sufficient to cause the dark colour. The small amount of V^{IV} is balanced by the introduction of V^V vacancies.

An attempt was made to synthesize the crystals electrolytically. This yielded dark cubic crystals growing explicitly on the negative electrode, implying that they are indeed a reduced species. Powder photographs of this sample revealed the presence of the title compound and another, as yet unreported, phase of cubic nature and amber colour (work in progress). Transparent needles also precipitated from the bulk solution (work in progress). A separate sample was prepared for the magnetic susceptibility measurement and for powder refinement of the cell parameter of the title compound. The susceptibility measurement indicates the presence of a paramagnetic species. Hydrogen peroxide is believed to

act as a reducing agent (Dean, 1961). The heteropolyoxy anions are separated by rows of Rb^+ ions, with interpenetrating water molecules.

Experimental

Solutions of MoO_3, Rb_2CO_3 and V_2O_5 were mixed to give a molar ratio of 40% Mo, 35% Rb and 25% V. The powders of MoO_3 and Rb_2CO_3 were carefully mixed and ground, and the mixture was dissolved in boiling water. The V_2O_5 was added to a substantial amount of boiling water and H_2O_2 was added until all V_2O_5 was completely dissolved. The two prepared solutions were then mixed together; the resulting solution will be referred to as A. An equal volume (to that of A) of 35 vol% H_2O_2 was then added. Finally, the solution was partly evaporated by boiling to one tenth of the original volume and left to evaporate at room temperature. In this final stage, the solution had acquired a dark yellow colour. An amorphous yellow precipitate was formed, whereby the remaining solution gradually shifted to a green–black colour. Finally, black cubic crystals were formed from the dark solution. The yellow precipitate was highly soluble in water and a single phase sample of black crystals could be obtained after washing the sample. The electrolysis was carried out using two gold electrodes dipped into a concentrated solution of A; the applied tension throughout the experiment was equal to 2.00 V. The magnetic susceptibility measurements were made on a Lakeshore 7000 weak field AC susceptometer. The ^1H NMR experiment was performed in a 5 mm tube on a Varian Mercury-400 FT spectrometer using 25 mg of sample in 0.7 ml D_2O at 298 K.

Crystal data

$Rb_{4.4}[H_{0.6}V_{0.6}Mo_{12}O_{40}]\cdot$	Mo $K\alpha$ radiation
$14H_2O$	$\lambda = 0.71073$ Å
$M_r = 2464.72$	Cell parameters from 989
Cubic	reflections
$Fm\bar{3}m$	$\theta = 2.58-25.70°$
$a = 22.294\,(2)$ Å	$\mu = 6.64$ mm^{-1}
$V = 11\,080.1\,(19)$ Å^3	$T = 293\,(2)$ K
$Z = 8$	Cubic prism
$D_x = 2.955$ Mg m^{-3}	$0.18 \times 0.17 \times 0.15$ mm
D_m not measured	Black

Data collection

Stoe IPDS diffractometer	479 reflections with
Area-detector scans	$I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.056$
numerical (XRED; Stoe,	$\theta_{max} = 25.77°$
1997)	$h = -19 \rightarrow 15$
$T_{min} = 0.295$, $T_{max} = 0.362$	$k = -13 \rightarrow 19$
6882 measured reflections	$l = 2 \rightarrow 27$
591 independent reflections	Intensity decay: <1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$\Delta\rho_{max} = 1.733$ e Å^{-3}
$wR(F^2) = 0.186$	$\Delta\rho_{min} = -0.845$ e Å^{-3}
$S = 1.154$	Extinction correction: none

591 reflections
50 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.1209P)^2 + 188.5222P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
V1†	1/4	1/4	1/4	0.006 (3)
Mo	0.13794 (3)	0.24552 (4)	0.13794 (3)	0.0313 (6)
O1	0.0989 (3)	0.1830 (2)	0.1830 (2)	0.0278 (16)
O2	0.2100 (2)	0.2100 (2)	0.2100 (2)	0.012 (2)
O3	0.1169 (3)	0.3009 (2)	0.1991 (2)	0.0244 (15)
O4	0.0860 (2)	0.2591 (3)	0.0860 (2)	0.0372 (18)
Rb1‡	0	0.2061 (3)	0	0.0678 (19)
Rb2§	0.1498 (2)	0.8502 (2)	1/2	0.065 (2)
Rb3¶	0	0	0	0.070
Rb4††	0	1/2	0	0.070
OW1‡‡	0.2427 (5)	0.2573 (5)	0	0.016 (4)
OW2	0	0.1271 (5)	0.1271 (5)	0.068 (4)
OW3	0	0.3366 (18)	0	0.138 (12)
OW4§§	0.0735 (13)	0.4265 (13)	0.0735 (13)	0.15 (3)

† Site occupancy = 0.62 (3).   ‡ Site occupancy = 0.698 (12).   § Site occupancy = 0.363 (9).   ¶ Site occupancy = 0.11 (2).   †† Site occupancy = 0.07 (2).   ‡‡ Site occupancy = 0.50.   §§ Site occupancy = 0.74 (8).

All metal atoms and the O atoms in the Keggin-type cluster were refined with anisotropic displacement parameters using a 'rigid-bond' restraint to U_{ij} of two bonded atoms (Rollett, 1970), implemented as the *DELU* instruction in *SHELXL97* (Sheldrick, 1997). All water O atoms were refined isotropically. OW1 was originally located at the 24d position but was split to a half-occupied 48h position. OW2 and OW3 are fully occupied, while the occupancy of OW4 decreased significantly during the refinement. Rb3 and Rb4 are located in large voids at 4a and 4b. The isotropic displacement parameters U_{iso} of Rb3 and Rb4 were fixed to 0.07 and the occupancy was refined for both atoms. The largest residual densities are located at 1.9 Å from Rb4 and 0.5 Å from OW1.

Data collection: *EXPOSE* (Stoe, 1997). Cell refinement: *PIRUM* (Version 930101; Werner, 1969). Data reduction: *IN-TEGRATE* (Stoe, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *DIAMOND* (Bergerhoff, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1070). Services for accessing these data are described at the back of the journal.

References

Bergerhoff, G. (1996). *DIAMOND. Visual Crystal Structure Information System.* Gerhard-Domagk-Straße 1, 53121 Bonn, Germany.

Björnberg, A. & Hedman, B. (1980). *Acta Cryst.* B36, 1018–1022.
Dean, G. A. (1961). *Can. J. Chem.* 39, 1174–1183.
Jeannin, Y., Launay, J. P. & Seid Sedjadi, M. A. (1980). *Inorg. Chem.* 19, 2933–2935.
Keggin, J. F. (1933). *Nature,* 132, 351.
Rollett, J. S. (1970). *Crystallographic Computing,* edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 167–181. Copenhagen: Munksgaard.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Stoe & Cie (1997). *X-RED* (Version 1.09), *EXPOSE* (Version 2.87) and *INTEGRATE* (Version 2.87). Stoe IPDS, Darmstadt, Germany.
Werner, P.-E. (1969). *Ark. Kemi.* 31, 513–516.
Zhang, S. W., Huang, G. Q., Wei, Y. G., Shao, M. C. & Tang, Y. Q. (1993). *Acta Cryst.* C49, 1446–1448.

Ba3TaAs3O displaying the distorted tetrahedral TaAs3O6− anion

Gaëlle Derrien, Laure Monconduit, Monique Tillard and Claude Belin

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, ESA 5072 CC15, Université de Montpellier II, Sciences et Techniques du Languedoc, 2 Place Eugène Bataillon, 34095 Montpellier CEDEX 5, France. E-mail: mtillard@univ-montp2.fr

Abstract

The orthorhombic cell of tribarium tantalum arsenate, Ba_3TaAs_3O, contains pseudo-tetrahedral $TaAs_3O^{6-}$ anions surrounded by Ba^{2+} cations. This forms a three-dimensional network of interconnected trigonal prisms. The compound is isostructural with Ba_3NbAs_3O and Eu_3TaAs_3O.

Comment

The quaternary phase Ba_3TaAs_3O (orthorhombic *Pnma*) is isostructural with the compounds Ba_3NbAs_3O (Monconduit *et al.*, 1999) and Eu_3TaAs_3O (Wang *et al.*, 1980). The unit cell contains four $TaAs_3O^{6-}$ anions stacked above each other along **b**, with their Ta—O bonds parallel to the *a* axis. The As atoms, with surrounding Ba atoms, form the base of a pseudo-trigonal prism centered by the Ta—O bond. The anionic $TaAs_3O^{6-}$ unit, with 32 valence electrons, is isoelectronic with more or less distorted tetrahedral ML_4^{q-} an-