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Na$_2$NbO$_2$AsO$_4$, a new niobium mono-arsenate

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Abstract

The two-dimensional framework of disodium dioxoniobium arsenate is built up from infinite [NbO$_6$] chains extending along the *c* axis, linked together by AsO$_4$ tetrahedra. Each AsO$_4$ tetrahedron is bonded to three different NbO$_6$ octahedra, two of which belong to the same chain. The Na$^+$ cations are located between the covalent [NbAsO$_6$]$^{2-}$ layers in hexagonal channels. The structure is compared with those of *MM'*XO$_6$ (*M* = K, Tl; *M'* = Sb, Nb; *X* = P, As) and NaVOAsO$_4$.

Comment

In the course of our investigation of the Na$_2$O–Nb$_2$O$_5$–As$_2$O$_5$ system, in a search for open framework structures, we have reported previously the tunnel compound Na$_3$NbO(AsO$_4$)$_2$ (Hizaoui *et al.*, 1999). The present report deals with a new compound found in the same system, *i.e.* Na$_2$NbO$_2$AsO$_4$. Dioxoniobium disodium arsenate has a layer structure, built up from chains of *trans*-corner-sharing NbO$_6$ octahedra with alternating short and long Nb—O bonds; Nb—O5 = 1.882 (2) Å and Nb—O5^i = 2.012 (2) Å [symmetry code: (i) *x*, 1 − *y*, ½ + *z*]. These infinite chains are interconnected laterally in the (100) plane by AsO$_4$ tetrahedra (Fig. 1). Each AsO$_4$ tetrahedron bridges two successive NbO$_6$ octahedra of the same chain by sharing O2 and O3 atoms, and bridges a third NbO$_6$ octahedron of an adjacent chain through O4. The free O-atom apices, O1 and O6, point alternately up and down the layers. This arrangement of polyhedra delimits distorted hexagonal windows connecting the interlayer spaces. In two suc-

cessive layers related by the 2$_1$ axis, the windows form tunnels parallel to the [101] and [$\bar{1}$01] directions, where the Na3$^+$ cations reside (Fig. 2). The Na1$^+$ and Na2$^+$ cations are located in the interlayer space. The NbO$_6$ octahedra are slightly distorted, as in many niobium(V) arsenates; the Nb—O bond lengths range from 1.765 (2) to 2.210 (2) Å [average 2.050 (2) Å]. The AsO$_4$ tetrahedron is almost regular, with As—O distances ranging from 1.652 (2) to 1.705 (2) Å and O—As—O angles ranging from 108.2 (1) to 113.5 (1)°. As is usual in most condensed arsenate ions, the unshared O atom, O1, forms a shorter bond than the other three O atoms. The bond-valence sums (Brown & Altermatt, 1985) for the Nb^V and As^V atoms of 5.042 and 4.984, respectively, are in good agreement with their formal oxidation states. The Na$_2$NbO$_2$AsO$_4$ structure exhibits a relationship with K$_2$SbPO$_6$ (Lachgar *et al.*, 1986), K$_2$SbAsO$_6$ (Botto & Garcia, 1989) and NaVOAsO$_4$ (Haddad *et al.*, 1992). Indeed, one can pass from the structure of K$_2$SbPO$_6$ (one-dimensional) to that of Na$_2$NbO$_2$AsO$_4$ (two-dimensional) by separating one of the two O atoms of the edge shared between successive SbO$_6$ octahedra and forming an Sb—O—P bridge with neighbouring chains. The structure of NaVOAsO$_4$ (three-dimensional) can be derived from that of Na$_2$NbO$_2$AsO$_4$ (two-dimensional) by forming mixed Nb—O—As bridges between successive layers; the O1 apex is shared with the O6 apex, leading to the elimination of one O atom. Electrical neutrality requires the removal of two Na$^+$ cations from the interlayer space. Comparison with the analogous compound Tl$_2$NbPO$_6$ (Fakhfak *et al.*, 1993) shows that Na$_2$NbO$_2$AsO$_4$ and Tl$_2$NbPO$_6$ are both two-dimensional compounds; the two structures differ in the type of connection between the polyhedra.
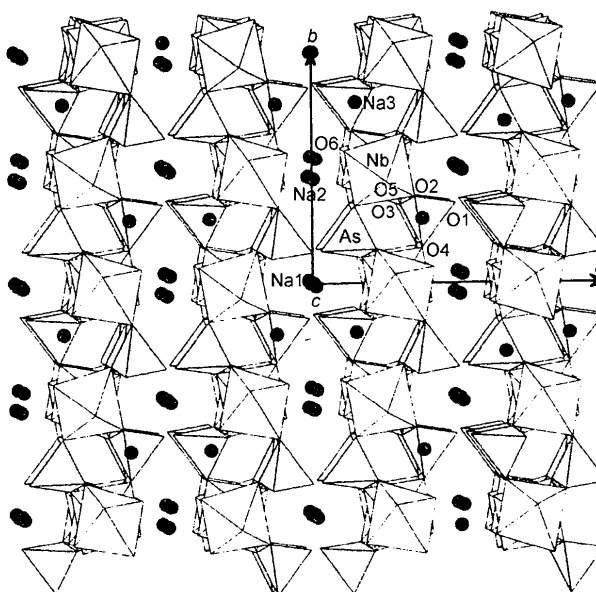

Fig. 1. *DIAMOND* (Bergerhoff, 1996) view along the *c* axis of the crystal structure of Na$_2$NbO$_2$AsO$_4$.
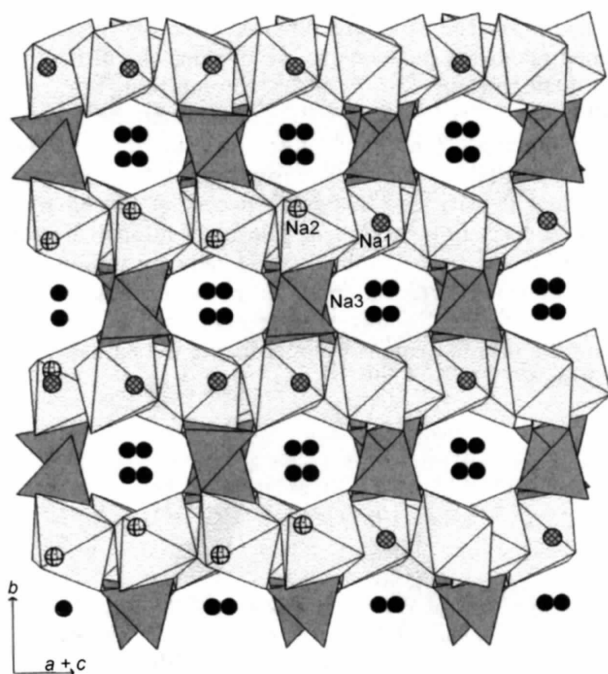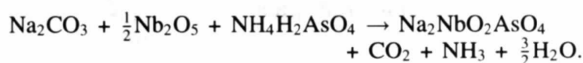
Fig. 2. View of the title compound along [$\bar{1}$10] showing the tunnel where the Na3$^+$ cations are located.

Experimental

The title compound was synthesized from stoichiometric quantities of Na_2CO_3, Nb_2O_5 and $NH_4H_2AsO_4$ according to the following reaction scheme:

$$Na_2CO_3 + \tfrac{1}{2}Nb_2O_5 + NH_4H_2AsO_4 \rightarrow Na_2NbO_2AsO_4 + CO_2 + NH_3 + \tfrac{3}{2}H_2O.$$

The mixture was heated in a porcelain crucible in air and the temperature was increased slowly (10 K h^{-1}) from 523 to 673 K, held at this temperature for 12 h in order to eliminate CO_2, NH_3 and H_2O, heated at 973 K for 72 h after which the furnace was cooled (10 K h^{-1}) to 573 K and turned off to allow the mixture to cool to ambient temperature. The product was obtained as a white crystalline powder.

Crystal data

$Na_2NbO_2AsO_4$	Mo $K\alpha$ radiation
$M_r = 309.81$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 14.5930\,(3)$ Å	$\theta = 10–14°$
$b = 10.8010\,(2)$ Å	$\mu = 8.324$ mm^{-1}
$c = 7.3090\,(2)$ Å	$T = 293\,(2)$ K
$\beta = 108.35\,(2)°$	Prism
$V = 1093.46\,(4)$ Å^3	$0.020 \times 0.018 \times 0.015$ mm
$Z = 8$	Colourless
$D_x = 3.764$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1126 reflections with $I > 2\sigma(I)$

$\omega/2\theta$ scans	$R_{int} = 0.033$
Absorption correction:	$\theta_{max} = 26.99°$
ψ scan (North *et al.*, 1968)	$h = -17 \rightarrow 18$
	$k = 0 \rightarrow 13$
$T_{min} = 0.814$, $T_{max} = 0.883$	$l = -9 \rightarrow 0$
1296 measured reflections	1 standard reflection
1199 independent reflections	frequency: 120 min
	intensity decay: 0.7%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.969$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.021$	$\Delta\rho_{min} = -1.053$ e Å^{-3}
$wR(F^2) = 0.057$	Extinction correction:
$S = 1.192$	*SHELXL*93
1199 reflections	Extinction coefficient:
93 parameters	0.0097 (3)
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 4.7476P]$ where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from *International Tables for Crystallography* (Vol. C)
$(\Delta/\sigma)_{max} = 0.001$	

Table 1. *Selected bond lengths (Å)*

Nb1—O6	1.765 (2)	Na1—O3^v	2.549 (3)
Nb1—O5	1.882 (2)	Na1—O3	2.549 (3)
Nb1—O5^i	2.012 (2)	Na2—O1^{vi}	2.304 (3)
Nb1—O4^{ii}	2.037 (2)	Na2—O6	2.346 (3)
Nb1—O2	2.125 (2)	Na2—O5^{vii}	2.405 (3)
Nb1—O2^i	2.210 (2)	Na2—O3^{viii}	2.433 (3)
As1—O1	1.651 (2)	Na2—O2^{ix}	2.591 (3)
As1—O3	1.687 (2)	Na2—O2	2.657 (3)
As1—O4	1.701 (2)	Na3—O6	2.333 (2)
As1—O2	1.706 (2)	Na3—O6^x	2.333 (2)
Na1—O1^{iii}	2.355 (3)	Na3—O4^{viii}	2.545 (3)
Na1—O1^{iv}	2.355 (3)	Na3—O4^{vi}	2.545 (3)
Na1—O1^v	2.486 (3)	Na3—O6^{xi}	2.668 (3)
Na1—O1	2.486 (3)	Na3—O6^{iv}	2.668 (3)

Symmetry codes: (i) $x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $1 - x, 1 - y, -z$; (iv) $x, 1 - y, z - \frac{1}{2}$; (v) $1 - x, y, -\frac{1}{2} - z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (viii) $\frac{3}{2} - x, \frac{1}{2} - y, -z$; (ix) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; (x) $2 - x, y, \frac{1}{2} - z$; (xi) $2 - x, 1 - y, 1 - z$.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992; Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *SHELXL*93.

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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.
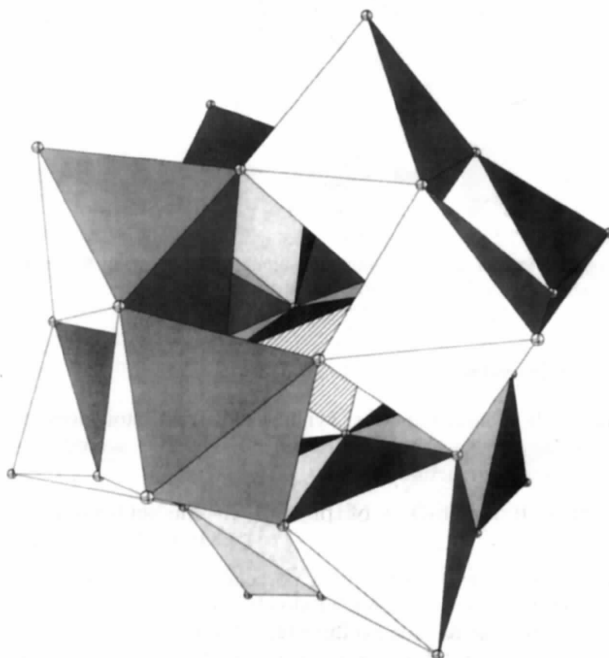
Heteropoly blue $Rb_{4.4}[H_{0.6}V_{0.6}Mo_{12}O_{40}]\cdot 14H_2O$

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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.