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KMo_5O_{13} and $KNb_{1.76}Sb_{3.24}O_{13}$

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The title compounds, potassium pentamolybdenum oxide, KMo_5O_{13}, and potassium niobate antimonate or potassium niobium antimony oxide (1/1.76/3.24), $KNb_{1.76}Sb_{3.24}O_{13}$, were synthesized by solid-state reactions and are isomorphous in space group *Cmcm*. The structure of the Mo complex has three unique Mo atoms and consists of MoO_6 octahedra sharing edges to form Mo_2O_6 pairs and Mo_3O_9 triplets, which, in turn, form layers by sharing corners. These layers are linked together in the [100] direction, yielding a three-dimensional network similar to that of KSb_5O_{13}. This framework delimits interconnected tunnels, running approximately along the [110] and [$\bar{1}$10] directions, in which K^+ ions are located. In the isomorphous $KNb_{1.76}Sb_{3.24}O_{13}$ structure, one of the Mo sites in KMo_5O_{13} is replaced by Sb and the other two Mo sites have been replaced by Nb/Sb.

Comment

KMo_5O_{13} crystallizes in the orthorhombic space group *Cmcm* and is isotypic with KSb_5O_{13} (Bodenstein *et al.*, 1983). The structure possesses a three-dimensional network, which can be described by the succession of MoO_6 octahedra sharing edges to form [Mo2Mo1Mo2]O_9 triplets. These triplets are associated by sharing O1 corners, yielding zigzag chains running along the [001] direction. These chains are, in turn, associated by sharing axial oxygen corners, with pairs of $Mo3_2O_6$ octahedra sharing edges to form layers parallel to the (100) plane (Fig. 1).

In the [100] direction, these layers are associated with an *ABA* ordering. Each $Mo3_2O_6$ pair of one layer links two [Mo2Mo1Mo2]O_9 triplets of the two neighbouring layers by sharing each of its three equatorial oxygen corners with the axial corners of each triplet.

This arrangement of octahedra generates interconnected tunnels, parallel to the [110] and [$\bar{1}$10] directions, in which the K^+ ions are located (Fig. 2).

In the structure of KMo_5O_{13}, all Mo—O bond distances are similar to those customarily encountered with Mo^V and O. However, we note the existence of longer bond distances for Mo1—O4, Mo2—O4 and Mo3—O4 (Table 1) that can be explained by the sharing of atom O4 with the three Mo atoms (Mo1, Mo2 and Mo3). This makes the interaction between the metal atoms and the O atom weaker. The K^+ ions are coordinated by seven O atoms.

The crystal structure of $KNb_{1.76}Sb_{3.24}O_{13}$ is isomorphous with that of KMo_5O_{13} (Table 2). The characteristic feature of

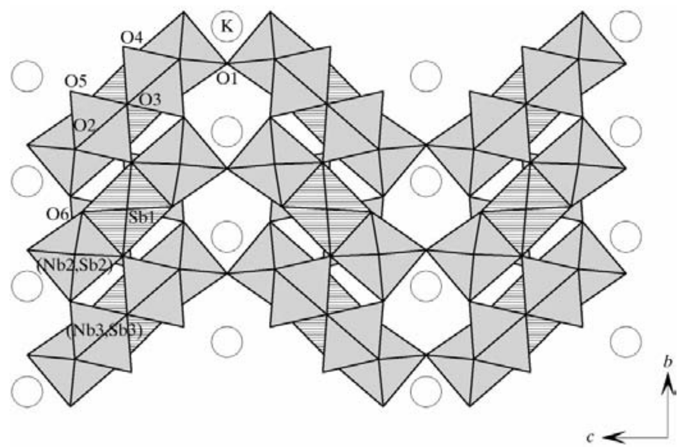

Figure 1
A layer of the $KNb_{1.76}Sb_{3.24}O_{13}$ structure (similar to the KMo_5O_{13} structure), viewed along the [100] direction. The $Sb1O_6$ octahedra ($Mo1O_6$ octahedra in the KMo_5O_{13} structure) are hatched, and the (Nb2,Sb2)O_6 (Mo2 in KMo_5O_{13}) and (Nb3,Sb3)O_6 (Mo3 in KMo_5O_{13}) octahedra are grey. Open circles denote K atoms.

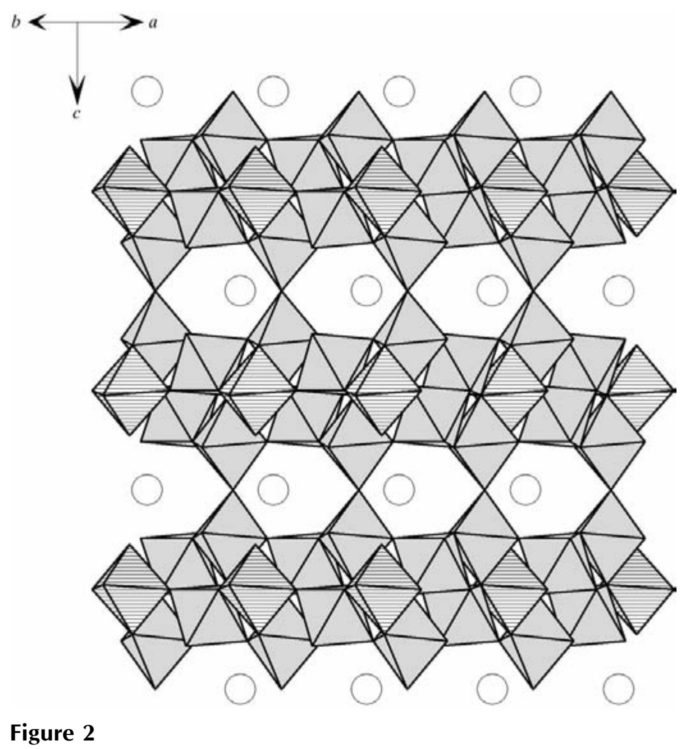

Figure 2
A projection of the structures of $KNb_{1.76}Sb_{3.24}O_{13}$ (similar to the KMo_5O_{13} structure) along the [110] direction, showing the tunnels. The shading key is the same as for Fig. 1.

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this structure is the double occupancy of sites 2 and 3 by Sb and Nb atoms; the occupancies of the Sb and Nb atoms in both sites are 0.56 and 0.44, respectively.

For both compounds, atom O2 lies on a general position, atom O3 lies on a twofold axis, K and O1 have *mm* symmetry, Mo1 and Sb1 have 2/*m* symmetry and all other atoms have *m* symmetry.

Experimental

Single crystals of KMo_5O_{13} were prepared from a mixture of K_2CO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and H_3BO_3, in a molar ratio of 5:1:5. The mixture was ground, heated in a platinum crucible at 1073 K for 40 h and then cooled to room temperature at a rate of 0.1 K min^{-1}. Colourless plates were extracted from the boron glass using hot water. Qualitative analysis of the sample by electron microscope probe revealed it to contain K and Mo.

Transparent and colourless single crystals of $KNb_{1.76}Sb_{3.24}O_{13}$ were prepared from a mixture of K_2CO_3, Sb_2O_3 and Nb_2O_5, in a molar ratio of 5:2:2. The powder was ground and homogenized with boric acid (H_3BO_3) as a flux, then heated in a porcelain crucible in air to 1273 K. This temperature was maintained for 20 h, then the mixture was cooled to 773 K at a rate of 6 K h^{-1} and held at that temperature for 2 h, before being cooled to room temperature at a rate of 30 K h^{-1}. Single crystals were extracted from the boron glass using hot water. Qualitative analysis of the single crystals by electron microscope probe revealed them to contain K, Nb and Sb.

Compound (I)

Crystal data

KMo_5O_{13}	Mo $K\alpha$ radiation
$M_r = 726.79$	Cell parameters from 24 reflections
Orthorhombic, *Cmcm*	$\theta = 9.1$–$14.0°$
$a = 6.6027$ (10) Å	$\mu = 6.62$ mm^{-1}
$b = 8.9552$ (10) Å	$T = 293$ (2) K
$c = 16.844$ (2) Å	Plate, colourless
$V = 996.0$ (2) Å^3	0.09 × 0.07 × 0.02 mm
$Z = 4$	
$D_x = 4.847$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.008$
$\omega/2\theta$ scans	$\theta_{max} = 30.0°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -1 \rightarrow 9$
$T_{min} = 0.601$, $T_{max} = 0.910$	$k = 0 \rightarrow 12$
2790 measured reflections	$l = 0 \rightarrow 23$
812 independent reflections	2 standard reflections frequency: 120 min intensity decay: 0.6%
740 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 28.8946P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.100$	$\Delta\rho_{max} = 1.94$ e Å^{-3}
$S = 1.22$	$\Delta\rho_{min} = -2.48$ e Å^{-3}
812 reflections	Extinction correction: *SHELXL*97
58 parameters	Extinction coefficient: 0.0062 (4)

Table 1
Selected interatomic distances (Å) for (I).

Mo1—Mo2^{i}	3.1198 (7)	Mo2—O6	1.989 (7)
Mo1—O3^{i}	2.054 (8)	Mo3—O2	1.917 (5)
Mo1—O4^{i}	2.026 (7)	Mo3—O3^{iv}	2.073 (5)
Mo1—O6^{i}	1.909 (7)	Mo3—O4	2.046 (8)
Mo2—O1	1.921 (3)	Mo3—O5	1.937 (8)
Mo2—O2^{iii}	1.961 (6)	K—O1^{i}	2.826 (12)
Mo2—O4	2.174 (8)	K—O2^{vi}	2.727 (6)
Mo2—O5^{ii}	1.934 (7)	K—O6^{v}	2.636 (7)

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

Compound (II)

Crystal data

$KNb_{1.76}Sb_{3.24}O_{13}$	Mo $K\alpha$ radiation
$M_r = 804.67$	Cell parameters from 25 reflections
Orthorhombic, *Cmcm*	$\theta = 10.0$–$14.5°$
$a = 6.697$ (1) Å	$\mu = 10.74$ mm^{-1}
$b = 9.027$ (1) Å	$T = 293$ (2) K
$c = 17.047$ (2) Å	Parallelepiped, colourless
$V = 1030.6$ (2) Å^3	0.20 × 0.05 × 0.04 mm
$Z = 4$	
$D_x = 5.186$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	743 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$\theta_{max} = 29.9°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -9 \rightarrow 0$
$T_{min} = 0.567$, $T_{max} = 0.643$	$k = 0 \rightarrow 12$
832 measured reflections	$l = -23 \rightarrow 0$
832 independent reflections	2 standard reflections frequency: 120 min intensity decay: 0.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 3.9495P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.072$	$\Delta\rho_{max} = 1.34$ e Å^{-3}
$S = 1.18$	$\Delta\rho_{min} = -1.53$ e Å^{-3}
832 reflections	Extinction correction: *SHELXL*97
66 parameters	Extinction coefficient: 0.00129 (12)

Table 2
Selected interatomic distances (Å) for (II).

Sb1—O3	2.061 (4)	Sb2—O6	1.98 (2)
Sb1—O4^{i}	2.030 (4)	Nb3—O2^{iv}	1.858 (12)
Sb1—O6	1.924 (4)	Nb3—O3^{v}	2.142 (14)
Nb2—O1	1.89 (6)	Nb3—O4	1.984 (17)
Nb2—O2^{iii}	1.987 (6)	Nb3—O5	2.044 (15)
Nb2—O4	2.22 (6)	Sb3—O2^{iv}	1.921 (8)
Nb2—O5^{ii}	1.89 (4)	Sb3—O3^{v}	2.076 (9)
Nb2—O6	2.02 (4)	Sb3—O4	2.112 (11)
Sb2—O1	1.96 (3)	Sb3—O5	1.900 (11)
Sb2—O2^{iii}	1.980 (3)	K—O1^{i}	2.935 (6)
Sb2—O4	2.14 (3)	K—O2^{vi}	2.810 (3)
Sb2—O5^{ii}	1.92 (2)	K—O6^{i}	2.679 (4)

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

For both compounds, data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement:

CAD-4 *EXPRESS*, plus *WinGX* (Farrugia, 1999) for (I); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1369). Services for accessing these data are described at the back of the journal.

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