

Potassium oxoantimonate(V), $K_3[SbO_4]$

Christian Hirschle, Jürgen Rosstauscher and Caroline Röhr*

Institut für Anorganische und Analytische Chemie, Universität Freiburg,
Albertstraße 21, D-79104 Freiburg, Germany
Correspondence e-mail: caroline@ruby.chemie.uni-freiburg.de

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The oxoantimonate $K_3[SbO_4]$ crystallizes in the monoclinic space group $P2/c$ with the $Na_3[BiO_4]$ structure type. The structure contains chains of $[SbO_6]$ octahedra connected *via* common edges. All K and Sb atoms lie on twofold axes, *i.e.* $0, y, \frac{1}{4}$ or $\frac{1}{2}, y, \frac{1}{4}$.

Comment

In the crystal structures of the known alkali metal (*A*) antimonates(V), $[SbO_6]$ octahedra form the important structural building blocks. In compounds with a low alkali metal content, these octahedra are connected *via* common edges to form complex three-dimensional channel structures ($A = K$: Hong, 1974; $A = Rb$ or Cs : Hirschle *et al.*, 2001). A similar structural chemistry is exhibited by compounds of the formula AMO_3 , which are known for nearly all alkali metals and which display the ilmenite or the defect pyrochlore structure. In the series of alkali-metal-rich antimonates A_3SbO_4 , only the first ($A = Li$: Skakle *et al.*, 1996) and the last ($A = Cs$: Hirschle & Röhr, 2000) members have been characterized by single-crystal data. Hoppe and co-workers (Schwedes & Hoppe, 1972) inferred from indexed powder patterns that Na_3SbO_4 is isotopic with the Li compound, and unindexed powder patterns by Duquenois (Duquenois, 1974; Josien & Duquenois, 1980) indicate an isotopic relationship between the Rb and Cs compounds. Whereas the crystal structures of the Li (and Na) phases show chains of edge-sharing $[SbO_6]$ octahedra, the Cs (and Rb) compounds are characterized by isolated $[SbO_4]^{3-}$ tetrahedra. The title compound is thus at the boundary between two structure families, which makes it a likely candidate for polytypic behaviour.

$K_3[SbO_4]$ crystallizes in the monoclinic space group $P2/c$ with the $Na_3[BiO_4]$ (Schwedes & Hoppe, 1972) structure type. In the crystal structure, $[SbO_2O_{4/2}]^{3-}$ octahedra are connected *via* two *trans*-oriented edges to form chains running parallel to the crystallographic *c* axis (Fig. 1); the Sb atoms are located on the twofold axis at $\frac{1}{2}, y, \frac{1}{4}$.

The two terminal Sb—O bond lengths are 1.949 (6) Å (Sb—O1), whereas the bridging Sb—O bonds (Sb—O2) are

significantly longer, at 2.047 (6) and 2.091 (6) Å. The O—Sb—O bond angles in the octahedra vary from 78.4 (3) to 95.7 (2)°.

The three crystallographically independent K^+ cations all lie on twofold axes $\{K1: \frac{1}{2}, y, \frac{1}{4} [2(f)]; K2 \text{ and } K3: 0, y, \frac{1}{4} [2(e)]\}$ and are also located at the centres of the O-octahedra [K—O 2.266 (6)–2.657 (7) Å]. The structure can thus be alternatively described as a cubic close-packed arrangement of O^{2-} ions, with the K^+ and Sb^{5+} cations located in all the octahedral holes, *i.e.* an order variant of the NaCl structure.

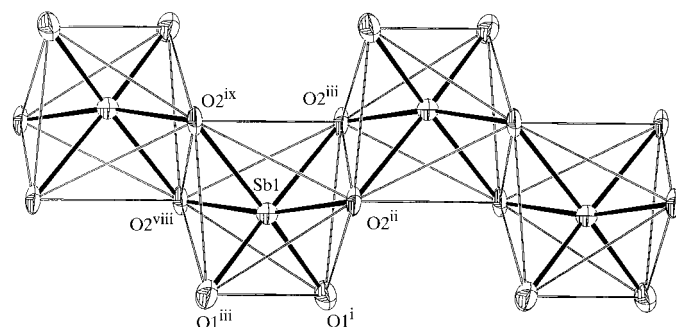


Figure 1
A view of the chain of $[SbO_6]$ octahedra in $K_3[SbO_4]$ shown with 75% probability displacement ellipsoids. Symmetry codes are as given in Table 1.

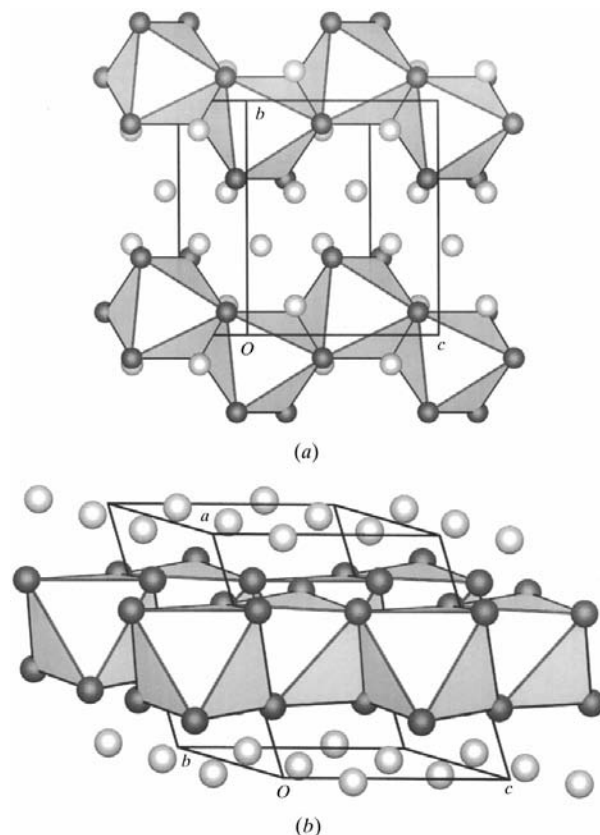


Figure 2
Views of the unit cell of $K_3[SbO_4]$ in two orientations, (a) view perpendicular to the *bc* plane and (b) a perspective view. Light-grey spheres denote K atoms, light-grey octahedra denote $[SbO_6]$ and dark-grey spheres denote O atoms.

Whereas the corresponding Li (Skakle *et al.*, 1996) and Na (Schwedde & Hoppe, 1972) compounds are isotopic with the title compound, Cs₃[SbO₄] (Hirschle & Röhr, 2000) and Rb₃[SbO₄] (only characterized *via* indexed powder patterns) form structures with isolated [SbO₄]³⁻ tetrahedra and significantly shorter Sb—O bond distances. The main differences between the two structure families are also easily seen in the Raman spectra of Cs₃[SbO₄] and the title compound (Fig. 3).

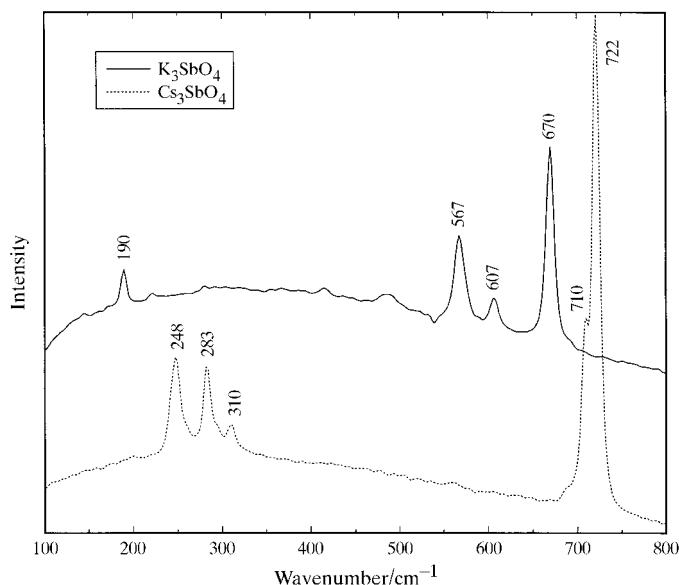


Figure 3
The Raman spectra of K₃[SbO₄] and Cs₃[SbO₄].

In the Cs compound, the totally symmetric stretching mode of the slightly distorted [SbO₄] tetrahedra gives rise to strong bands at 710 and 722 cm⁻¹ (Sb—O 1.78–1.89 Å). In the spectrum of K₃[SbO₄], the Sb—O stretching modes are shifted towards smaller wavenumbers: the band at 670 cm⁻¹ can be assigned to the terminal Sb—O stretching mode [Sb—O1 1.949 (6) Å], while the two bands at 607 and 567 cm⁻¹ result from the two longer bridging Sb—O2 bonds.

Experimental

Single crystals of K₃[SbO₄] were obtained from stoichiometric mixtures of K (223.7 mg, 5.72 mmol), KO₂ (293.7 mg, 4.12 mmol) and Sb₂O₃ (482.6 mg, 1.65 mmol). The samples were heated to 975 K in corundum crucibles under an argon atmosphere, and then cooled to 575 K at a rate of 5 K h⁻¹ and to room temperature at a rate of 15 K h⁻¹. The X-ray powder patterns of the reaction products can be indexed on the basis of the reported single-crystal data, but show additional weak reflections that cannot be assigned to any known phase. The colourless hygroscopic crystals of the title compound were handled in a dry box and mounted in capillaries filled with dry oil. Room-temperature Raman spectra of single crystals of K₃[SbO₄] and Cs₃[SbO₄], sealed in Lindemann capillaries, were recorded with a Raman microscope attached to an FT spectrometer (Bruker IFS-66V).

Crystal data

K₃[SbO₄]
M_r = 303.05
 Monoclinic, *P*2/*c*
a = 5.7971 (12) Å
b = 6.5933 (14) Å
c = 5.4179 (12) Å
 β = 109.394 (4)°
V = 195.33 (7) Å³
Z = 2
D_x = 5.153 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 907 reflections
 θ = 3.1–28.3°
 μ = 10.14 mm⁻¹
T = 293 (2) K
 Irregular, colourless
 0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
T_{min} = 0.192, *T_{max}* = 0.363
 1160 measured reflections
 468 independent reflections
 422 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{max} = 28.3°
h = -6 → 7
k = -8 → 7
l = -7 → 6

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.122
S = 1.24
 468 reflections
 40 parameters
w = 1/[σ²(*F_o*²) + (0.0848*P*)² + 0.0284*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 3.32 e Å⁻³
 Δρ_{min} = -2.83 e Å⁻³
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.128 (16)

Table 1

Selected geometric parameters (Å, °).

Sb1—O1 ⁱ	1.949 (6)	O1—K3 ^v	2.266 (6)
Sb1—O2 ⁱⁱ	2.047 (6)	O1—K3	2.585 (7)
Sb1—O2 ⁱⁱⁱ	2.091 (6)	O2—K1	2.370 (6)
O1—K1	2.387 (6)	O2—K2 ^{vi}	2.355 (6)
O1—K1 ^{iv}	2.355 (6)	O2—K2	2.561 (6)
O1—K2	2.279 (6)	O2—K3 ^{vii}	2.657 (7)
O1 ⁱ —Sb1—O1 ^{iv}	93.8 (3)	O1 ^{iv} —Sb1—O2 ⁱⁱⁱ	170.2 (2)
O1 ⁱ —Sb1—O2 ⁱⁱ	95.7 (2)	O2 ⁱⁱ —Sb1—O2 ⁱⁱⁱ	78.4 (3)
O1 ^{iv} —Sb1—O2 ⁱⁱ	92.3 (2)	O2 ^{viii} —Sb1—O2 ⁱⁱⁱ	93.1 (2)
O2 ⁱⁱ —Sb1—O2 ^{viii}	168.3 (3)	O2 ⁱⁱⁱ —Sb1—O2 ^{ix}	87.6 (3)
O1 ⁱ —Sb1—O2 ⁱⁱⁱ	90.1 (3)		

Symmetry codes: (i) *x*, 1 - *y*, *z* - ½; (ii) 1 - *x*, 1 - *y*, -*z*; (iii) *x*, 1 + *y*, *z*; (iv) 1 - *x*, 1 - *y*, 1 - *z*; (v) -*x*, 1 - *y*, 1 - *z*; (vi) -*x*, -*y*, -*z*; (vii) -*x*, 1 - *y*, -*z*; (viii) *x*, 1 - *y*, ½ + *z*; (ix) 1 - *x*, 1 + *y*, ½ - *z*.

Because of the slightly higher values of the atomic displacement parameters of the K atoms, the site occupancies of the three positions were refined for testing purposes, converging on the ideal value of 0.5 to within experimental error. The maximum difference peak of 3.32 e Å⁻³ lies 0.83 Å from Sb1 and may be attributed to residual absorption errors.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1968) and *DRAWxtl* (Finger & Kroeker, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1475). Services for accessing these data are described at the back of the journal.

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