INORGANIC COMPOUNDS

K₄Sb₂O₃ containing the Sb₂O₃⁴⁻ anion

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Abstract

The title compound, tetrapotassium diantimony trioxide, $K_4Sb_2O_3$, crystallizes in the hexagonal space group $P6_3mc$. The structure consists of stacking of trigonal-pyramidal $Sb_2O_3^{4-}$ anions along the c axis. The Sb—Sb bond length of 2.803 (3) Å corresponds to a metal–metal single bond, while very short Sb—O bond lengths of 1.74 (2) Å are characteristic of double bonds. Raman spectroscopy and *ab initio* molecular-orbital calculations confirm this bonding description.

Comment

The structure of $K_4Sb_2O_3$ has been determined in the non-centrosymmetric space group $P6_3mc$ (No. 186). The compound contains the anionic $Sb_2O_3^{4-}$ unit which, with 32 valence electrons, is isoelectronic with more or less distorted tetrahedral ML_4^{5-} anions such as $InTe_4^{5-}$ (Sportouch *et al.*, 1994), ClO_4^-, PO_4^{3-}, SO_4^{2-} and $S_2O_3^{2-}$.

In the present structure, the $Sb_2O_3^{4-}$ anion displays C_{3v} symmetry. It can be described formally as a central Sb^{5+} cation ligated by one Sb^{3-} and three O^{2-} anions, but this does not provide any indication of the bonding scheme within the anion. The Sb—Sb distance of 2.803 (3) Å is characteristic of a single metal–metal bond and agrees well with Pauling's single-bond distance (Pauling, 1947, 1949). The K···Sb2 distances range from 3.46 (6) to 3.83 (1) Å, and the shortest K···O contacts are between 2.48 (2) and 3.10 (1) Å. The Sb—O distance of 1.74 (2) Å is significantly shorter than those observed in other compounds [1.987 Å in $BaBi_{0.5}Sb_{0.5}O_3$ (Fu *et al.*, 1997) and 1.940–2.028 Å in $Ba_2Ce_{0.75}SbO_6$ (Ijdo & Helmholdt, 1993)] and deviates greatly from the sum of Pauling's single-bond radii.

In the Raman spectrum recorded at room temperature, the very sharp principal line observed at 812 cm⁻¹ is assigned to the symmetric ν_s(Sb═O) stretching vibration. ν_s(Te═O) is found at nearly the same frequency

(837 cm⁻¹) in the $(F_4Te═O)^{2-}$ anion (Milne & Moffett, 1973). The Sb═O double-bond length of 1.74 (2) Å compares well with the Xe═O distance of 1.73 Å in XeO_4 (McDowell & Asprey, 1972), and the double-bond nature can also be seen with reference to other double-bond lengths: N═O of 1.26 Å in $HNO_3 \cdot H_2O$ (Delaplane *et al.*, 1975), P═O of 1.43 Å in $F_3P═O$ (Moritani *et al.*, 1971) and As═O of 1.63 Å in $(C_6H_5)_3As═O$ (Shao *et al.*, 1982). Molecular-orbital *ab initio* [DFT (density functional theory) at the B3PW91 level] calculations have been performed and overlap populations were obtained from a Mulliken population analysis. The overlap population between atoms i and j is the sum of the off-diagonal S_{ij} and S_{ji} (of equal magnitude) components of the overlap matrix over the basis functions. Calculated overlap populations of 0.536 for Sb—O and 0.226 for Sb—Sb should be in the same ratio as corresponding bond orders, *i.e.* single bond for Sb—Sb and double-bond character for Sb═O.
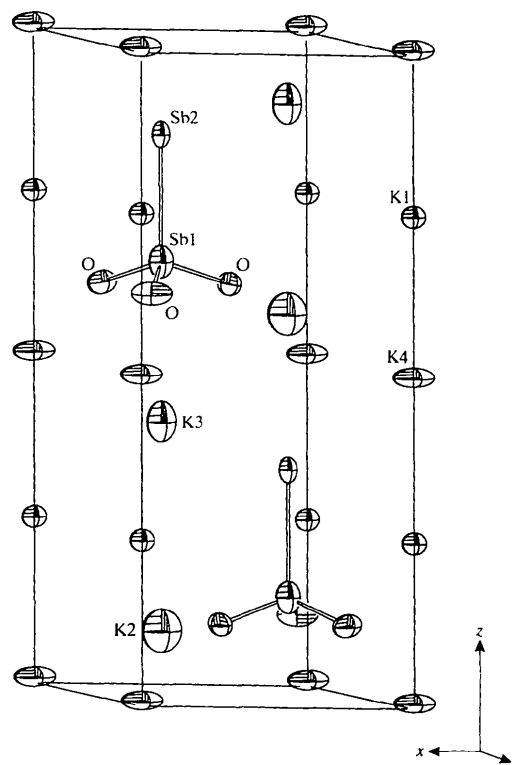

Fig. 1. Representation of the unit cell of $K_4Sb_2O_3$, showing 50% probability displacement ellipsoids.

Experimental

$K_4Sb_2O_3$ was obtained as a side product during the synthesis of $Ba_2K_2NbOSb_3$, which is isostructural with Ba_3NbOAs_3

(Monconduit *et al.*, 1999), from potassium metal (Merck), barium peroxide (Ba_2O, Merck, analytical grade), niobium and antimony powders (Fluka, purissimum). The weld-sealed niobium reactor was heated at 1373 K for 12 h and then allowed to cool to room temperature at a rate of 40 K h^{-1}. Elemental analyses (SEM) of flat crystals confirmed the presence of potassium and antimony, in an approximate 2:1 ratio, and the absence of barium and niobium. The air-sensitive crystals were inserted in Lindemann glass capillaries for X-ray data collection and Raman spectroscopic analysis.

Crystal data

$K_4Sb_2O_3$
$M_r = 447.90$
Trigonal
$P6_3mc$
$a = 6.142\,(1)$ Å
$c = 14.395\,(2)$ Å
$V = 470.3\,(1)$ Å^3
$Z = 2$
$D_x = 3.163$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7-15°$
$\mu = 7.458$ mm^{-1}
$T = 295\,(2)$ K
Wedge
$0.20 \times 0.09 \times 0.06$ mm
Dark grey

Data collection

Nonius CAD-4 diffractometer
$\omega-\frac{1}{3}\theta$ scans
Absorption correction: numerical (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.51$, $T_{max} = 0.65$
1070 measured reflections
302 independent reflections

211 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$
$\theta_{max} = 29.98°$
$h = 0 \rightarrow 8$
$k = -8 \rightarrow 0$
$l = 0 \rightarrow 20$
3 standard reflections every 100 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.126$
$S = 1.133$
302 reflections
24 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$

$\Delta\rho_{max} = 2.203$ e Å^{-3}
$\Delta\rho_{min} = -1.601$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.0 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^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}
Sb1	1/3	2/3	0.8421	0.0357 (14)
Sb2	2/3	1/3	0.1474 (2)	0.0217 (8)
K1	0	0	0.747 (2)	0.0264 (13)
K2	2/3	1/3	0.907 (3)	0.078 (11)
K3	1/3	2/3	0.086 (2)	0.054 (6)
K4	0	0	0.491 (2)	0.060 (3)
O	0.1778 (15)	0.356 (3)	0.8793 (9)	0.041 (4)

Table 2. *Selected geometric parameters (Å, °)*

Sb1—O^i	1.739 (16)	Sb1—Sb2^{ii}	2.803 (3)
O^{iii}—Sb1—O	111.0 (4)	O—Sb1—Sb2^{ii}	107.9 (5)

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

The symmetry and crystallographic space group were initially determined by oscillation and Weissenberg techniques. The best diffracting crystal was used for accurate determination of the cell parameters and data collection. The room-temperature Raman spectrum of a single crystal sealed in a Lindemann capillary was recorded with a LABRAM–Dilor spectrometer. An He–Ne laser (632.817 nm, 20 mW) was focused on the sample using a BX40 microscope (magnification × 50). Owing to the irregular shape of the crystal, absorption correction by a numerical procedure (*SHELX*76; Sheldrick, 1976) is not optimal and leads to an R_{int} value of only 0.0914 for all reflections [or 0.0743 for reflections with $I > 2\sigma(I)$]. This may account for the somewhat surprising anisotropic displacement parameters of the K atoms. However, these problems may have resulted from refinement in an inappropriate space group. The structure was therefore refined in the non-centrosymmetric trigonal space group $P31c$, in which Sb atoms occupy two independent sites ($\frac{1}{3},\frac{2}{3},z$) with multiplicity 2. Since distribution of antimony and potassium is very close to centrosymmetry, attempts to refine the structure in centrosymmetric space groups $P6_3/mmc$ and $P\bar{3}1c$ lead to disordered positions for O atoms, as does refinement in the non-centrosymmetric $P\bar{6}2c$ space group. Refinement was also performed in other (lower symmetry) hexagonal and trigonal space groups ignoring extinction conditions ($hh2\bar{h}l$ and/or $00l$), for example, $P6_3$, $P3m1$ and $P3$. All refinements led to the same behaviour for K atoms. The structure was also refined in the orthorhombic subgroup $Cmc2_1$ and in the less symmetrical $C222_1$ group. All these refinement attempts make us confident that the structure described in the $P6_3mc$ space group is correct. Furthermore, site occupations for alkali metals refine slightly above the normal site factor (but within s.u. limits). This excludes any atomic defection or replacement by an Na atom (very improbable). With the exception of one peak of 2.2 e Å^{-3} located in the vicinity (0.06 Å) of the K1 atom, residual densities on the final difference Fourier map are less than 1.04 e Å^{-3}. *Ab initio* molecular-orbital calculations were performed using the *GAUSSIAN*94 program (Frisch *et al.*, 1995) with DFT models at the B3PW91 level. All computations were carried out on a PentiumII 266 computer.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976).

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The lamellar double-hydroxide (LDH) compound with composition $3CaO \cdot Al_2O_3 \cdot Ca(NO_3)_2 \cdot 10H_2O$

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Abstract

The title compound, tetracalcium dialuminum dodecahydroxide dinitrate tetrahydrate, of composition $3CaO \cdot Al_2O_3 \cdot Ca(NO_3)_2 \cdot 10H_2O$, is a layered compound constituted by positively charged $[Ca_4Al_2(OH)_{12}]^{2+}$ main layers and negatively charged $[2NO_3 \cdot 4H_2O]^{2-}$ interlayers. It crystallizes in the trigonal $P\bar{3}c1$ space group. The interlayer part of the structure is strongly disordered.

The Al^{3+} and Ca^{2+} ions are six- and seven-oxygen-coordinated, respectively. Half of the water molecules and nitrate groups assume statistically the seventh coordination position of the calcium ions. Thus, half the water molecules are considered as bonded water and half as free or slightly bonded. The planar NO_3^- groups are bonded and perpendicular to the main layers. Nitrate groups are on disordered positions close to the [001] axis and free water molecules fill the interlayer space, also in a disordered manner. This is interpreted as a dynamic disorder resulting from free rotation of the nitrate group around the [001] axis, and this interpretation is compatible with Raman microspectroscopy results realised on the same specimen used for this study.

Comment

The title compound, $3CaO \cdot Al_2O_3 \cdot Ca(NO_3)_2 \cdot 10H_2O$, and several of the many related basic salts called AFm phases are important because they occur on hydration of cements. They form positively charged brucite-like $[Ca_2(Al,Fe)(OH)_6]^+$ layers and negatively charged $[X_z \cdot nH_2O]^-$ interlayers to assume electroneutrality; X is a monovalent anion $[OH^-, Cl^-, NO_3^-, Al(OH)_4^-]$ with $z = 1$ or a bivalent anion (CO_3^{2-}, SO_4^{2-}) with $z = \frac{1}{2}$, where n can vary depending on the humidity, the temperature and the nature of the inserted anion. A structural model for these AFm phases has been proposed but not refined (Ahmed & Taylor, 1967). At present, structures based on single-crystal data have been determined for the monosulfate $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ (Allmann, 1977) and the chloride $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ (Terzis et al., 1987). Recently, the equivalent carbonated compound $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ was studied. Two modifications of this phase were resolved. The first is totally ordered (François et al., 1998), whereas the interlayer region of the second presents a statistical disorder between one carbonate group and three water molecules (Renaudin et al., 1999).

The chemical composition of the compound $3CaO \cdot Al_2O_3 \cdot Ca(NO_3)_2 \cdot 10H_2O$, commonly named binitroaluminate, was checked by a thermogravimetric experiment, taking into account the indications given by Ahmed et al. (1968) on its thermal decomposition. The studied compound crystallizes in the centrosymmetric trigonal space group $P\bar{3}c1$. Hexagonal parameters are consistent with those previously indicated (Kuzel, 1970). The structure contains nine crystallographic non-H atom sites. There is one $3CaO \cdot Al_2O_3 \cdot Ca(NO_3)_2 \cdot 10H_2O$ formula unit per lattice. Selected interatomic distances are reported in Table 2. The main layers of the structure defined by Al, Ca and O sites are completely ordered, while the interlayers, filled by water molecules ($OW1$ and $OW2$) and nitrate groups ($ON1$, N, $ON2$ and $ON3$), are disordered, as seen by occupancy factors inferior to the unity and elevated displacement parameters.