

Alkaline metal oxoantimonates(III),
 $A_3[\text{SbO}_3]$ ($A = \text{K}$ or Cs)

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The two title trialkaline trioxoantimonates(III), tripotassium trioxoantimonate(III), $\text{K}_3[\text{SbO}_3]$, (I), and tricaesium trioxoantimonate(III), $\text{Cs}_3[\text{SbO}_3]$, (II), crystallize in the cubic $\text{Na}_3[\text{AsS}_3]$ structure type in space group $P2_13$. The structures show discrete Ψ -tetrahedral $[\text{SbO}_3]^{3-}$ anions with C_{3v} point-group symmetry. The Sb—O distances are 1.923 (4) Å in (I) and 1.928 (2) Å in (II), and the O—Sb—O bond angles are 99.5 (2)° in (I) and 100.4 (1)° in (II).

Comment

The oxoantimonates(III), $A\text{SbO}_2$ [$A = \text{K}$, Rb (Hirschle & Röhr, 2000) or Cs (Hirschle & Röhr, 1998)], are isotypic with the corresponding bismuthates ($A = \text{K}$, Rb or Cs ; Zoche & Jansen, 1998) and contain, in accordance with the lone pair on $\text{Sb}^{\text{III}}/\text{Bi}^{\text{III}}$, the group V atoms coordinated by four O atoms in a Ψ -trigonal-bipyramidal geometry. In the compounds $A_4[\text{Sb}_2\text{O}_5]$ ($A = \text{K}$, Rb or Cs ; Hirschle & Röhr, 2000), two $[\text{SbO}_3]$ Ψ -tetrahedra are connected *via* an oxygen ligand to form $[\text{O}_2\text{Sb}-\text{O}-\text{SbO}_2]^{4-}$ ‘butterfly’ anions. In contrast, $\text{K}_4[\text{Bi}_2\text{O}_5]$ (Zoche *et al.*, 1998) contains $[\text{Bi}_4\text{O}_{10}]^{8-}$ anions, with Bi in both Ψ -trigonal-bipyramidal and Ψ -tetrahedral coordination by oxygen. The bismuthates $A_3[\text{BiO}_3]$, with Ψ -tetrahedral anions as characteristic building blocks, are known for the whole series of alkaline metals A . The isotypic sodium (Stöver & Hoppe, 1980) and potassium (Zoche & Jansen, 1997*b*) compounds can be described as defect NaCl variants, $[\text{A}_3\text{Bi}][\text{O}_3]$, *i.e.* the cations A and Bi form a face-centred cubic sublattice (Cu₃Al type). In the rubidium (Zoche & Jansen, 1997*b*) and caesium (Zoche & Jansen, 1997*a*) phases, the cations are arranged in a body-centred cubic sublattice (Fe₃Al type). For the corresponding oxoantimonate series $A_3[\text{SbO}_3]$, only the sodium compound has been described in the literature to date (Stöver & Hoppe, 1980) and is isotypic with the Na and K bismuthates mentioned above. We present here the structures of two further oxoantimonates, *viz.* $\text{K}_3[\text{SbO}_3]$, (I), and $\text{Cs}_3[\text{SbO}_3]$, (II).

The isotypic compounds (I) and (II) crystallize in the cubic space group $P2_13$ with the $\text{Na}_3[\text{AsS}_3]$ structure type (Palazzi, 1976), and are thus isotypic with the Rb and Cs oxobis-

muthates and most alkaline metal thio- and selenoarsenates, -antimonates and -bismuthates. $\text{Rb}_3[\text{SbO}_3]$ forms the same structure type, with a lattice constant (refined from X-ray powder data) of 8.9523 (6) Å.

The crystal structures of (I) and (II) contain $[\text{SbO}_3]^{3-}$ anions with crystallographic C_{3v} point-group symmetry and nearly equal Sb—O distances for the two compounds; the O—Sb—O bond angles are also very similar. The bond lengths are

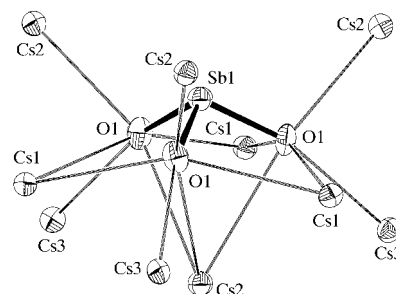


Figure 1
Molecular view of the $[\text{SbO}_3]^{3-}$ Ψ -tetrahedron together with the coordinating Cs cations in (II) (75% probability ellipsoids).

thus slightly longer than those observed in the sodium phase (Sb—O = 1.890 Å).

The oxygen ligands are octahedrally coordinated by one Sb atom and five A cations (Fig. 1). The oxoantimonate ions form a face-centred cubic arrangement (Fig. 2), in which the alkaline metal cations occupy all tetrahedral and octahedral

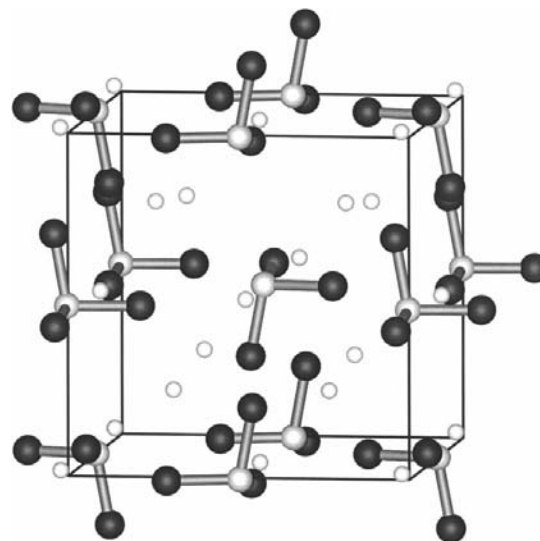


Figure 2
A view of the unit cell of the $A_3[\text{SbO}_3]$ compounds (small light grey balls represent K or Cs and dark grey balls represent O atoms)

interstices. In an alternative description of the structure according to the concept of O’Keeffe & Hyde (1985), the A and Sb atoms form a 3:1 superstructure of a body-centred cubic lattice, the Fe₃Al structure type. Whereas the corresponding K_3Sb phase (Emmerling & Röhr, 2001) crystallizes with a superstructure of the hexagonal Cu₃P type, the direct analogy of the metal-atom arrangement in the intermetallic phase and the oxide is observed for Cs_3Sb (Emmerling & Röhr, 2001) and (II). The unit-cell volumes are also comparable [762.8 (1) Å³ in (II) and 763.7 (1) Å³ in Cs_3Sb].

Experimental

Crystals of (I) were grown from a mixture containing KO₂ (Fluka AG, 99.0%), K (Alkali-Metallhandel GmbH Bonn, 98.0%) and Sb powder (Sigma-Aldrich, 99.8%) in a molar ratio of 0.5:1.5:2. The mixture was heated to 973 K and then cooled to 573 K at a rate of 5 K h⁻¹. The furnace was then turned off. For (II), CsO₂ (803 mg, 4.87 mmol) was reacted with powdered Sb (198 mg, 1.62 mmol) in a corundum crucible under an argon atmosphere. The mixture was heated to 973 K over a period of 3.5 h and then cooled to room temperature at a rate of 5 K h⁻¹. The X-ray powder pattern of the sample [Stadi P diffractometer with linear PSD (position sensitive detector); Stoe & Cie, Darmstadt] could be indexed with the single-crystal data of (II) and showed weak reflections of Cs₃[SbO₄] and elemental Sb. Both title compounds formed hygroscopic colourless crystals, which were handled in a dry box under argon and prepared in capillaries filled with dried oil.

Compound (I)

Crystal data

K ₃ [SbO ₃]	Cell parameters from 25 reflections
<i>M_r</i> = 287.05	$\theta = 3.8\text{--}29.3^\circ$
Cubic, <i>P</i> 2 ₁ 3	$\mu = 6.77\text{ mm}^{-1}$
<i>a</i> = 8.352 (5) Å	<i>T</i> = 293 (2) K
<i>V</i> = 582.7 (5) Å ³	Prism, colourless
<i>Z</i> = 4	0.1 × 0.1 × 0.1 mm
<i>D_x</i> = 3.272 Mg m ⁻³	
Mo <i>K</i> α radiation	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.090
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.4^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = 0 → 10
<i>T</i> _{min} = 0.497, <i>T</i> _{max} = 0.508	<i>k</i> = -10 → 10
1510 measured reflections	<i>l</i> = -10 → 0
266 independent reflections (plus 189 Friedel-related reflections)	3 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on <i>F</i> ²	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{\text{max}} = 0.72\text{ e \AA}^{-3}$
$wR(F^2) = 0.054$	$\Delta\rho_{\text{min}} = -1.03\text{ e \AA}^{-3}$
<i>S</i> = 1.04	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
455 reflections	Extinction coefficient: 0.0025 (9)
20 parameters	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = -0.03 (11)

Table 1

Selected geometric parameters (Å, °) for (I).

Sb—O1 (× 3)	1.923 (4)	K2—O1 (× 3)	2.734 (4)
K1—O1 (× 3)	2.758 (5)	K2—O1 (× 3)	2.961 (5)
K1—O1 (× 3)	2.922 (5)	K3—O1 (× 3)	2.659 (4)
O1—Sb—O1	99.50 (15)		

Compound (II)

Crystal data

Cs ₃ [SbO ₃]	Cell parameters from 25 reflections
<i>M_r</i> = 568.48	$\theta = 2.3\text{--}32.8^\circ$
Cubic, <i>P</i> 2 ₁ 3	$\mu = 17.65\text{ mm}^{-1}$
<i>a</i> = 9.1369 (10) Å	<i>T</i> = 293 (2) K
<i>V</i> = 762.78 (14) Å ³	Prism, colourless
<i>Z</i> = 4	0.11 × 0.08 × 0.06 mm
<i>D_x</i> = 4.950 Mg m ⁻³	
Mo <i>K</i> α radiation	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.063
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.4^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = -11 → 11
<i>T</i> _{min} = 0.197, <i>T</i> _{max} = 0.347	<i>k</i> = -11 → 11
3665 measured reflections	<i>l</i> = 0 → 11
346 independent reflections (plus 240 Friedel-related reflections)	3 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on <i>F</i> ²	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.014$	$\Delta\rho_{\text{max}} = 0.68\text{ e \AA}^{-3}$
$wR(F^2) = 0.036$	$\Delta\rho_{\text{min}} = -0.59\text{ e \AA}^{-3}$
<i>S</i> = 1.07	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
750 reflections	Extinction coefficient: 0.00079 (8)
23 parameters	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + 0.2365P]$ where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = 0.06 (6)

Table 2

Selected geometric parameters (Å, °) for (II).

Cs1—O1 (× 3)	3.077 (2)	Cs2—O1 (× 3)	3.245 (3)
Cs1—O1 (× 3)	3.191 (3)	Cs3—O1 (× 3)	2.888 (2)
Cs2—O1 (× 3)	3.044 (3)	Sb1—O1 (× 3)	1.928 (2)
O1—Sb1—O1	100.43 (9)		

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1968) and *DRAWxtl* (Finger & Kroeker, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1326). Services for accessing these data are described at the back of the journal.

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