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Rubidium stannate(IV), Rb_4SnO_4

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The title compound, tetrarubidium tetraoxatin(IV), crystallizes with the Na_4CoO_4 structure type, showing discrete SnO_4^{4-} anions as main building blocks. The structure is thus isotypic with a series of corresponding compounds A_4MO_4 (A = alkali metal and M = group IV element).

Comment

Rb_4SnO_4 crystallizes in the triclinic space group $P\overline{1}$ and is isotypic with the Na_4CoO_4 structure type (Jansen, 1975). Corresponding alkaline metal oxotetrelates(IV) with the same structure type are the stannates Na_4SnO_4 (Hoppe & Bernet, 1988), K_4SnO_4 (Marchand *et al.*, 1975) and Cs_4SnO_4 (Bernet & Hoppe, 1990), the plumbates of Na, K and Rb (Brandes & Hoppe, 1994; Nowitzki & Hoppe, 1983), the germanates of Na and K (Halwax & Völlenkle, 1985), and Na_4SiO_4 (Baur *et al.*, 1986).

The Sn atoms in Rb_4SnO_4 are coordinated by four O atoms in a slightly distorted tetrahedral environment, with Sn—O distances ranging from 1.93 (1) to 1.977 (9) Å and O—Sn—O angles from 105.1 (4) to 115.1 (4)°. As in all stannates of the types A_4SnO_3 and A_4SnO_4 (A = alkali metal), all the O ligands are coordinated by five alkali metal atoms and one Sn atom in a distorted octahedral geometry (Fig. 1). The Sn—O distances in the title compound are thus comparable with those observed in the stannates(IV) K_4SnO_4 (Sn—O 1.95–1.96 Å) or Cs_4SnO_4 (Sn—O 1.94–1.97 Å) and they differ significantly from those observed in the stannates(II) K_4SnO_3 (Sn—O 2.041–2.052 Å; Röhr, 1995) or Cs_4SnO_3 (Sn—O 2.028–2.049 Å; Röhr & Zönnchen, 1998).

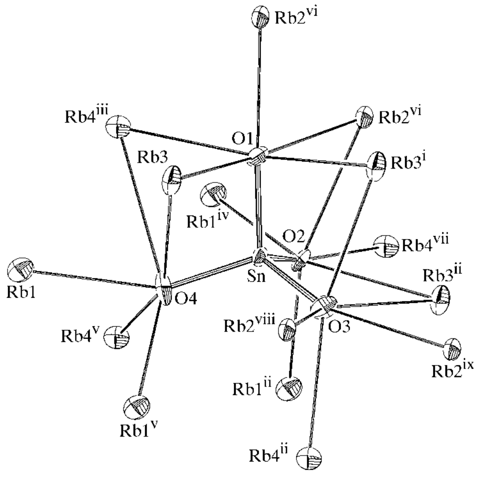

Figure 1
ORTEP (Johnson, 1968) view of the $[SnO_4]^{4-}$ anion in Rb_4SnO_4, together with the coordination spheres of the O atoms. Displacement ellipsoids are shown at the 50% probability level.

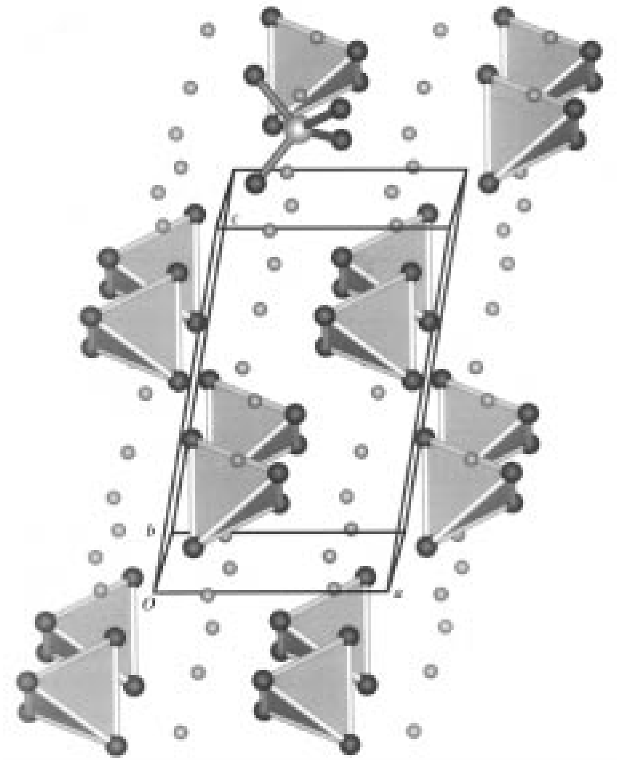

Figure 2
View of the unit cell of the crystal structure of Rb_4SnO_4. Small spheres denote Rb, while tetrahedra denote SnO_4.

A view of the unit cell of Rb_4SnO_4 is given in Fig. 2. The coordination numbers of the Rb cations vary from 4 (Rb1) to 4+1 (Rb4) and 5 (Rb2, Rb3). A similar description of the packing as given for Cs_4PbO_4 (Müller *et al.*, 1991) or Cs_4SnO_3 (Röhr & Zönnchen, 1998) is also possible for Rb_4SnO_4; the Rb

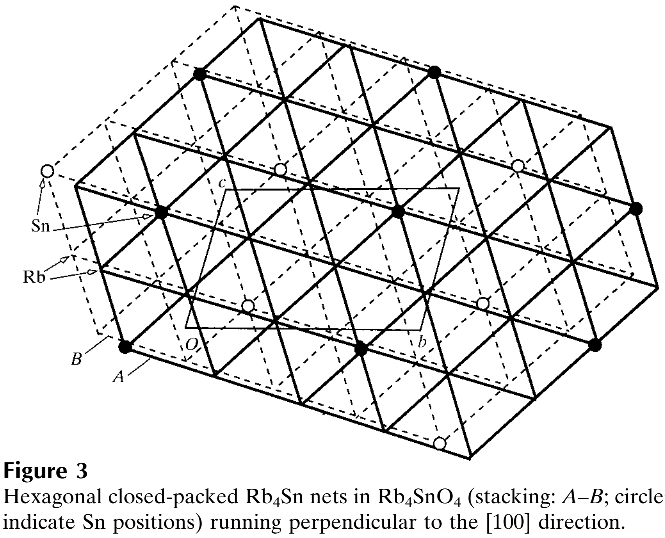

Figure 3
Hexagonal closed-packed Rb_4Sn nets in Rb_4SnO_4 (stacking: *A*–*B*; circles indicate Sn positions) running perpendicular to the [100] direction.

and Sn atoms together form planes of nearly hexagonal close-packed layers running perpendicular to the [100] direction. These layers are stacked in the sequence *A*–*B*, where the stacking is intermediate between the hexagonal closed-packed arrangement and the *α-U* structure type observed for the packing of Cs and Sn in Cs_4SnO_3 (Fig. 3).

The Raman spectrum of Rb_4SnO_4 recorded at room temperature shows four bands that can be assigned to the four normal modes of an ideal tetrahedron XY_4. The totally symmetric stretching mode (ν_1, A_1) is observed at 638 cm^{-1} and the asymmetric stretching mode (ν_3, F_2) is observed as a weak band at 620 cm^{-1}. The symmetric (ν_2, E) and the antisymmetric (ν_4, F_2) bending modes are observed at 188 and 137 cm^{-1}, respectively. This assignment is consistent in the series of MO_4 silicates, germanates and stannates (Nyquist & Kagel, 1997).

Experimental

Single crystals of Rb_4SnO_4 were formed by the reduction of a mixture of RbO_2 and SnO with elemental rubidium. Liquid rubidium (756.9 mg, 8.856 mmol; Maassen, 99%) was reacted with RbO_2 (346.8 mg, 2.952 mmol) and powdered SnO (399.3 mg, 2.965 mmol; ABCR, 99%) in corundum crucibles under an argon atmosphere. The mixtures were heated up to 1000 K within 5 h and cooled to room temperature at a rate of 4 K h^{-1}. The thick honey-yellow hygroscopic crystals of the title compound were handled in a dry-box and prepared in capillaries filled with dried oil. The X-ray powder pattern of the sample could be indexed on the basis of the reported single-crystal data of Rb_4SnO_4 but show additional reflections of Rb_2SnO_2 (Braun & Hoppe, 1982). The room-temperature Raman spectrum of a single crystal sealed in a Lindemann capillary was recorded with a Raman microscope attached to an FT spectrometer (Bruker IFS66V).

Crystal data

Rb_4SnO_4
$M_r = 524.57$
Triclinic, $P\overline{1}$
$a = 6.773$ (2) Å
$b = 6.776$ (3) Å
$c = 10.122$ (3) Å
$\alpha = 71.72$ (3)°
$\beta = 79.48$ (2)°
$\gamma = 66.64$ (2)°
$V = 404.0$ (2) $Å^3$

$Z = 2$
$D_x = 4.312$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.3$–21.4°
$\mu = 27.047$ mm^{-1}
$T = 293$ (2) K
Plate, pale yellow
0.10 × 0.07 × 0.04 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.109$, $T_{max} = 0.339$
1710 measured reflections
1575 independent reflections

$R_{int} = 0.049$
$\theta_{max} = 26°$
$h = 0 \rightarrow 8$
$k = -7 \rightarrow 8$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.150$
$S = 1.101$
1575 reflections
83 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1006P)^2 + 1.5556P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 4.132$ e $Å^{-3}$
$\Delta\rho_{min} = -4.368$ e $Å^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0139 (17)

Table 1
Selected geometric parameters (Å, °).

Sn—O4	1.934 (10)	Rb2—O2	3.024 (9)
Sn—O3	1.959 (9)	Rb3—$O2^{iii}$	2.877 (9)
Sn—O2	1.962 (8)	Rb3—$O1^{vii}$	2.880 (9)
Sn—O1	1.977 (9)	Rb3—O1	2.947 (8)
Rb1—$O4^{i}$	2.758 (11)	Rb3—$O3^{vii}$	3.056 (9)
Rb1—$O2^{ii}$	2.773 (9)	Rb3—$O3^{iii}$	3.063 (9)
Rb1—$O2^{iii}$	2.783 (8)	Rb4—$O4^{i}$	2.858 (11)
Rb1—O4	2.797 (11)	Rb4—$O1^{viii}$	2.873 (9)
Rb2—$O1^{iv}$	2.764 (9)	Rb4—$O3^{iii}$	2.924 (9)
Rb2—O1	2.802 (8)	Rb4—$O2^{ix}$	2.985 (9)
Rb2—$O3^{v}$	2.855 (9)	Rb4—$O4^{viii}$	3.252 (12)
Rb2—$O3^{vi}$	2.932 (10)		
O4—Sn—O3	113.4 (4)	O4—Sn—O1	105.1 (4)
O4—Sn—O2	115.1 (4)	O3—Sn—O1	109.8 (4)
O3—Sn—O2	107.3 (4)	O2—Sn—O1	105.7 (3)

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

$\Delta\rho_{max}$ and $\Delta\rho_{min}$ lie within 0.8 Å of the Sn atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1993); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1968) and *DRAWxtl* (Finger & Kroeker, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1266). Services for accessing these data are described at the back of the journal.

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