Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

BING-1: a tin–oxalate–sodium–fluoride framework, $Na_4Sn_4(C_2O_4)_3F_6$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.034
wR factor = 0.087
Data-to-parameter ratio = 18.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

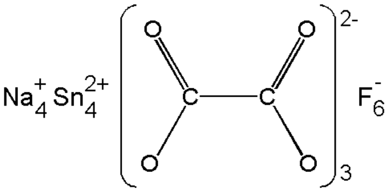
Received 30 January 2001
Accepted 2 February 2001
Online 19 February 2001

BING-1 [tetrasodium tetratin tris(oxalate) hexafluoride] was synthesized solvothermally at 423 K and crystallized in the triclinic system, with the $P\overline{1}$ space group. The asymmetric unit consists of two types of tin(II) centres, connected by oxalate groups. The Sn atoms are also bonded to fluoride ions, which bond the tin oxalate layers together *via* interlayer Na atoms, to define a three-dimensional framework.

Comment

We are currently focusing on the solvothermal synthesis of layered and open-framework materials based on lower Group 14 metals. In particular, we are interested in non-traditional templating agents for the formation of anionic and cationic germanates and stannates. In the course of our work on the Sn–HF–H_2O–pyridine system, where the latter is the non-aqueous solvent, we have discovered a series of new meta-stable three-dimensional and lower dimensionality materials. We denote our structures as BING-*n*, where BING denotes State University of New York (SUNY) at Binghamton, and *n* denotes structure type.

Our structure, (I), is related to the series of tin oxalates recently reported by Cheetham and co-workers (Ayyappan *et al.*, 1998; Natarajan *et al.*, 1999). The latter are layered, where octahedral Sn atoms are three-connected in the plane of the layer by oxalate groups. The anionic layers are separated and charge-balanced by electrostatically bonded organic ammonium groups.



(I)

In the current work, we used a predominantly non-aqueous environment, where a small amount of water and hydrogen fluoride (50% aqueous) was added to a pyridine solvent. Sodium tetrafluoroborate, which is known to act as a mineralizer, was also added to the synthesis mixture. Sodium and fluoride combined with tin oxalate to create the BING-1 three-dimensional framework (Fig. 1). The key feature of BING-1, which enables the formation of a framework, is the pentacoordinate Na1 and heptacoordinate Na2 atoms, which covalently bond to the F and O atoms of the layers, and link the layers along the c axis.

DOI: 101107/S1600536801002409

There are two crystallographically unique tin centres, which are bonded to fluorines and O atoms on one side of the atoms (Fig. 2). The other side of the tin centres are in close proximity to other tins, and appear as bonds in Fig. 1. The distances, however, are on the order of 3.6 to 3.8 Å (Table 2), which is longer than those in metallic tin. The residual electron-density Fourier difference map could not resolve the nature of the tin–tin interaction.

Both Sn1 and Sn2 are four-coordinate with respect to fluorine and oxygen. Sn1 bonds to F1 and F2, as well as O1 and O2 of the C1—C1 oxalate group; the latter links the Sn1 to another Sn1. Sn2 bonds to one fluorine and three O atoms (Table 1). Two of these O atoms, O3 and O5, belong to one side of the C2—C3 oxalate group (torsion angles, Table 1). The third oxygen, O4, bonds to another oxalate group on the other side of Sn2, to define a tin oxalate chain that propagates along the *a* axis. The last oxgyen of the C2—C3 oxalate group, O6, bonds to two Na atoms [O6—Na1 2.419 (3) Å and O6—Na2 2.443 (3) Å]. The C—C distance of the oxalate groups [C1—C1 1.559 (8) Å and C2—C3 1.552 (5) Å] compares well with other metal oxalate structures (Belaj *et al.*, 2000).

Experimental

The reaction mixture consisted of pyridine, H_2O, HF, $NaBF_4$ and $Sn(C_2O_4)$ in a molar ratio of 20:4:1:1:1. The pH of the starting mixture was aproximately 5.8. Solvothermal synthesis was conducted in a 23 ml capacity Teflon-lined Parr autoclave, at 423 K for 5 d. The BING-1 crystals were colourless plates and were manually separated for single crystal X-ray analysis. Small black crystals were also present in the product as a minor side-product. The latter was identified, also by single-crystal X-ray analysis, as tin(II) oxide.

Crystal data

$Na_4Sn_4(C_2O_4)_3F_6$
$M_r = 944.78$
Triclinic, $P\bar{1}$
$a = 6.0283$ (4) Å
$b = 8.7916$ (6) Å
$c = 9.1191$ (6) Å
$\alpha = 69.486$ (1)°
$\beta = 81.508$ (1)°
$\gamma = 83.017$ (1)°
$V = 446.41$ (5) Å^3
$Z = 1$
$D_x = 3.514$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4605 reflections
$\theta = 4.8$–61.0°
$\mu = 5.75$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.15 × 0.10 × 0.08 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.465$, $T_{\max} = 0.631$
7096 measured reflections
2686 independent reflections
2253 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 30.6$°
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 12$
Intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 0.99$
2686 reflections
145 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.07$ e Å^{-3}
$\Delta\rho_{\min} = -1.48$ e Å^{-3}

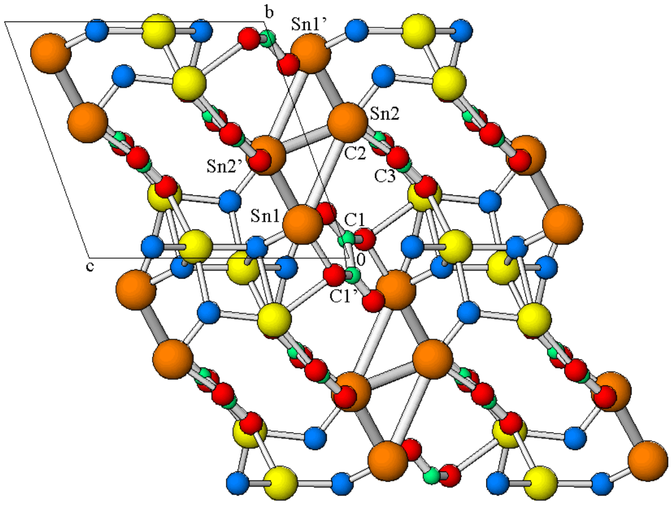


Figure 1
The crystallographic *a* projection of BING-1 highlights the tin oxalate fluoride layers, and the oxalate linkage of the tin centres (colour scheme: orange – Sn, yellow – Na, blue – F, green – C and red – O).

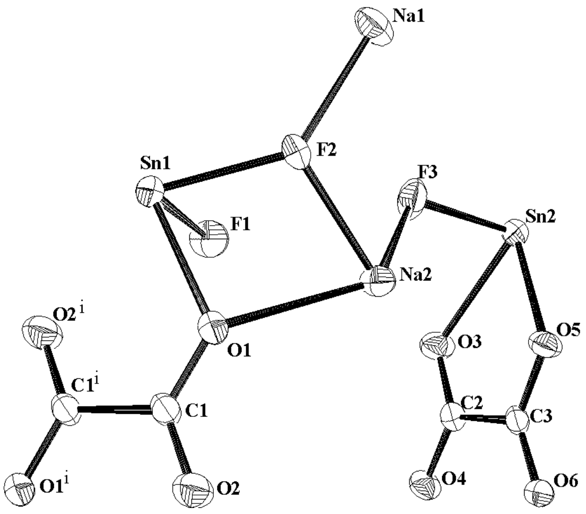


Figure 2
Displacement ellipsoids and labelling scheme for BING-1, shown at 50% probability levels. [Symmetry code: (i) 1 − *x*, −*y*, −*z*.]

Table 1
Selected geometric parameters (Å, °).

Na1—F2	2.190 (3)	Sn1—O2$^{\rm v}$	2.518 (3)
Na1—F1$^{\rm i}$	2.243 (3)	Sn2—F3	2.045 (3)
Na1—F1$^{\rm ii}$	2.257 (3)	Sn2—O5	2.206 (3)
Na1—O6$^{\rm iii}$	2.419 (3)	Sn2—O3	2.299 (3)
Na1—F3$^{\rm ii}$	2.446 (3)	Sn2—O4$^{\rm i}$	2.443 (3)
Na2—F2	2.260 (3)	C1—O2	1.231 (5)
Na2—F3	2.313 (3)	C1—O1	1.265 (5)
Na2—O4$^{\rm iv}$	2.386 (4)	C1—C1$^{\rm v}$	1.559 (8)
Na2—O6$^{\rm iv}$	2.443 (3)	C2—O4	1.249 (5)
Na2—O5$^{\rm iii}$	2.467 (3)	C2—O3	1.252 (5)
Sn1—F1	2.039 (3)	C2—C3	1.552 (5)
Sn1—F2	2.095 (2)	C3—O6	1.221 (5)
Sn1—O1	2.209 (3)	C3—O5	1.279 (5)
O1—C1—C1$^{\rm v}$—O2$^{\rm v}$	−0.3 (6)	O4—C2—C3—O6	2.1 (6)
O3—C2—C3—O5	2.1 (6)		

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, -y, -1-z$; (iii) $-x, 1-y, -1-z$; (iv) $1-x, 1-y, -1-z$; (v) $1-x, -y, -z$.

Table 2
Selected contact distances (Å).

Sn1···Sn2^{i}	3.6304 (5)	Sn2···Sn2^{iii}	3.8563 (5)
Sn1···Sn2^{ii}	3.8637 (5)		

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

We thank the Donors of The Petroleum Research Fund, Grant #36101–G5, in partial support of this research.

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