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BING-2: a layered tin–oxalate potassium fluoride, $KSn(C_2O_4)F$

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The title compound, $KSn(C_2O_4)F$, is a two-dimensional material related to our previously reported three-dimensional framework, $Na_4Sn_4(C_2O_4)_3F_6$. Both are alkali-metal tin–oxalate materials, but here the compound is layered and has potassium in place of sodium. The material was synthesized solvothermally at 423 K and crystallized in the monoclinic space group $P2_1/c$. The structure consists of potassium fluoride layers in the *bc* plane, which are sandwiched on both sides by tin–oxalate chains that extend along the *c* axis.

Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.004 Å
R factor = 0.025
wR factor = 0.059
Data-to-parameter ratio = 20.5

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

Comment

We are interested in group 14 metal-based extended materials for a variety of potential applications, particularly ion exchange and sensors. Our methods involve both commonly used, as well as non-traditional, templating agents. We have discovered a series of new materials, which we denote BING-*n*, where BING denotes State University of New York (SUNY) at Binghamton, and *n* denotes the structure type. These materials can be clusters (Oliver *et al.*, 2001) or extended in one [BING-4, $Sn(C_2O_4)(C_5H_5N)$; Oliver *et al.*, 2001], two (BING-3, $SnO_3PC_6H_5$; Oliver *et al.*, 2001) or three [BING-1, $Na_4Sn_4(C_2O_4)_3F_6$; Salami *et al.*, 2001] dimensions. Here, we report the crystal structure of BING-2, a layered tin–oxalate potassium fluoride material.

Two layered tin–oxalates have been reported recently by Cheetham and co-workers (Ayyappan *et al.*, 1998; Natarajan *et al.*, 1999). The tin centres are octahedral and possess three oxalate groups that bridge to neighbouring Sn atoms in the

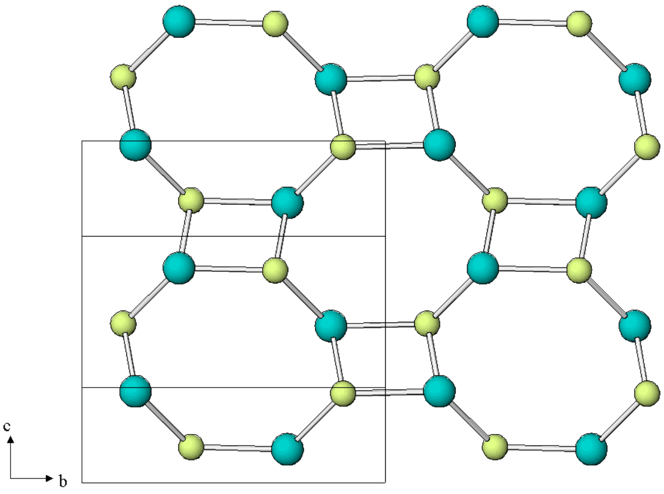

Figure 1
The crystallographic *a*-projection of the central potassium fluoride in one BING-2 layer (colour scheme: K – light blue and F – yellow).

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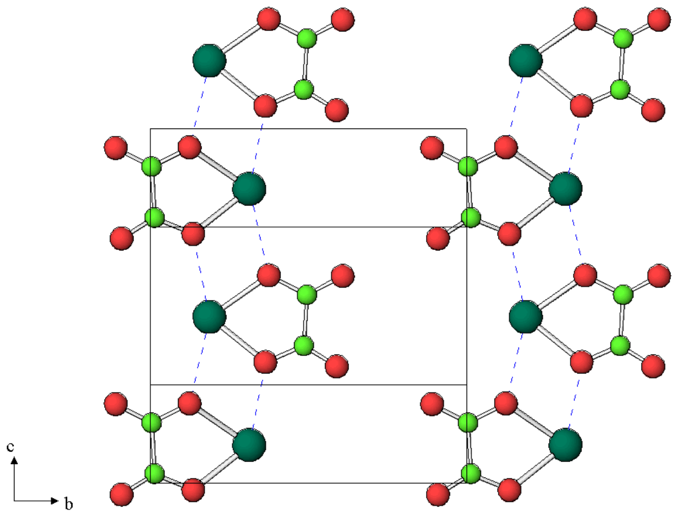

Figure 2
The same projection as Fig. 1, but showing one tin–oxalate layer, highlighting the tin–oxalate chains that propagate along the *c*-axis (colour scheme: Sn – dark green, O – red and C – light green).

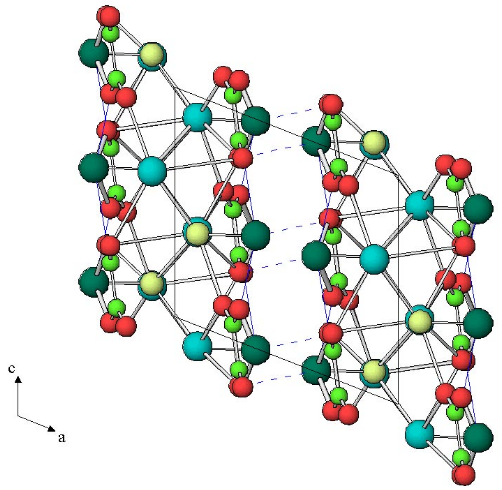

Figure 3
The crystallographic *b*-projection of BING-2, indicating the manner in which the tin–oxalate and potassium fluoride layers connect along the *a* axis.

layer. Traditional cationic organic ammonium templating agents were used to produce these materials, and reside in the interlayer region.

One of the thrusts of our studies is the exclusion of traditional templating agents from the synthesis mixture, and the use instead of other possible building blocks or templating agents. BING-2 was isolated from a predominantly non-aqueous pyridine solvent, to which tin oxalate, hydrogen fluoride (50% aqueous) and potassium tetrafluoroborate were added. Potassium and fluoride in this case became a building-block for the resultant product, and combined with tin oxalate to create the BING-2 structure (Fig. 1).

The layer of BING-2 is a sandwich structure, with two tin–oxalate sheets that connect to a central potassium fluoride layer. The latter is buckled and shown in Fig. 1. This buckling allows the KF layer to bond to the two surrounding Sn–oxalate layers, which are made up of discrete tin–oxalate chains that propagate along the *c* axis (one such layer is shown in Fig. 2). The Sn centers are chelated to one oxalate group, and connect to two neighbouring oxalate groups in the chain through longer contact distances (shown by the broken lines, Fig. 2). The O atoms on the other side of the oxalate groups connect to potassium centers of the potassium fluoride layer. The BING-2 layer is therefore a triple layer (Fig. 3).

The asymmetric unit is relatively simple, containing only one type of each atom in the formula unit (Fig. 4). The oxalate group in BING-2 is not planar (Table 1). This is the first time that we have seen this feature in any of our published BING-*n* structures (Salami *et al.*, 2001), those of others (Ayyappan *et al.*, 1998; Natarajan *et al.*, 1999), or an unpublished one-dimensional tin–oxalate structure (BING-4; Oliver *et al.*, 2001). This non-planarity may allow the formation of a three-dimensional tin–oxalate open framework. We are currently studying other combinations of tin–oxalate and various structure directing agents, in order to isolate inorganic materials capable of our target application of both anion and cation exchange.

Experimental

The reaction mixture consisted of pyridine, H_2O, HF, KBF_4 and $Sn(C_2O_4)$ in a molar ratio of 20:4:1:1:1. Solvothermal synthesis was conducted in a 23 ml capacity Teflon-lined Parr autoclave, at 423 K for 5 d. The BING-3 crystals were colourless plates, and were manually separated for single-crystal X-ray analysis.

Crystal data

$[Sn(C_2O_4)]KF$
$M_r = 264.81$
Monoclinic, $P2_1/c$
$a = 8.0692\ (5)$ Å
$b = 9.5398\ (6)$ Å
$c = 7.7245\ (4)$ Å
$\beta = 111.600\ (1)^\circ$
$V = 552.86\ (6)$ Å^3
$Z = 4$
$D_x = 3.181$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 4624 reflections
$\theta = 5$–63°
$\mu = 5.33$ mm^{-1}
$T = 273\ (2)$ K
Plate, colorless
$0.11 \times 0.10 \times 0.04$ mm

Data collection

CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.658$, $T_{\max} = 0.808$
10 746 measured reflections
1685 independent reflections
1443 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 30.5^\circ$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -11 \rightarrow 11$
Intensity decay: −0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.059$
$S = 1.06$
1685 reflections
82 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.1128P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.75$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—F1	2.0122 (19)	K1—O4^{iv}	2.746 (2)
Sn1—O1	2.234 (2)	K1—O2^{iv}	2.823 (2)
Sn1—O3	2.239 (2)	O1—C1	1.290 (3)
Sn1—O3^{i}	2.608 (2)	O2—C1	1.216 (3)
Sn1—O1^{ii}	2.714 (2)	O3—C2	1.281 (3)
Sn1—O2^{iii}	3.288 (2)	O4—C2	1.217 (3)
K1—F1	2.6461 (19)	C1—C2	1.555 (4)
F1—Sn1—O1	90.50 (9)	O1—Sn1—O3	71.68 (7)
F1—Sn1—O3	85.28 (9)		
O1—C1—C2—O3	−11.0 (4)	O2—C1—C2—O3	169.5 (3)
O1—C1—C2—O4	169.3 (3)	O2—C1—C2—O4	−10.1 (4)

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iii) $2-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$.

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.

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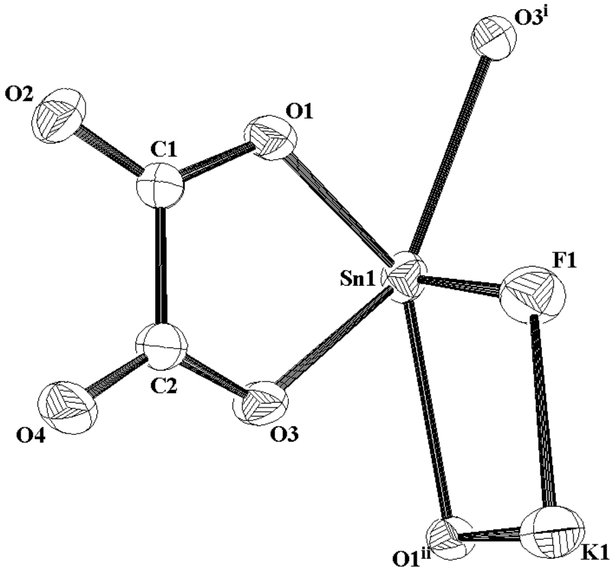

Figure 4
Displacement ellipsoids and labelling scheme for BING-2, with ellipsoids shown at 50% probability levels.

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