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Hydrothermal synthesis and structure of the first tin(II) squarate $Sn_2O(C_4O_4)(H_2O)$—comparison with $Sn_2[Sn_2O_2F_4]$

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Abstract

A tin(II) squarate $Sn_2O(C_4O_4)(H_2O)$ was synthesized by hydrothermal technique. It crystallizes in the monoclinic system, space group $C2/m$ (no. 12) with lattice parameters $a = 12.7380(9)$ Å, $b = 7.9000(3)$ Å, $c = 8.3490(5)$ Å, $\beta = 121.975(3)^\circ$, $V = 712.69(7)$ Å^3, $Z = 4$. The crystal structure determined with an $R = 0.042$ factor, consists of $[(Sn_4O_{10})(H_2O)_2]$ units connected from one another in the [101] and [010] directions via squarate groups to form layers separated by Sn(II) lone pairs. This compound presents the same remarkable structural arrangement as observed in the tin-oxo-fluoride $Sn_2[Sn_2O_2F_4]$ inorganic compound with Sn(II) lone pairs $E(1)$ and $E(2)$ concentrated in large rectangular-shape tunnels running along [001] direction.

Keywords: Tin(II)-squarate; Hydrothermal synthesis; X-ray diffraction; Crystal structure

1. Introduction

The search for open-framework inorganic materials is a very active field in materials chemistry in view of their practical applications as catalysts, molecular sieves, ion-exchangers, etc. A large number of phases have been discovered so far, some of which are reported in extensive review papers [1,2]. Prominent examples are aluminosilicates and transition-metal phosphates.

Hydrothermal synthesis has proven to be the best method, if one excepts solvothermal reactions, to synthesize new open frameworks. If many hybrid organic–inorganic materials based on transition metals have been obtained, there is however very few reports on syntheses involving lone-pair elements such as, for example, Sn(II), In(I) or As(III). Novel open-frameworks tin(II) phosphates and tin(II) oxalates have been reported [3–6].

If one takes into account that, as already demonstrated by Andersson et al. [7] and developed by Galy et al. [8], the effective volume of the lone pair, denoted E, is approximately the same as the volume of an O^{2-} ion, such lone-pair elements could play also the role of structure-directing agents (template effect). Considering, as mentioned above, that Sn(II)-based open networks have been obtained with rigid bidentate ligands such as oxalate, we considered using the monocyclic oxocarbon anion : the squarate ligand $C_4O_4^{2-}$. This latter is able to act as a fourfold monodentate as in the case of $M(C_4O_4)(H_2O)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) [9,10]. Worth to mention is that only one paper referred to a tin squarate but in this case a binuclear tin(IV)-squarate species was isolated [11].

Here we report our attempt to obtain new phases by reacting tin(II) chloride in presence of the squarate dianion and ethylene diamine. The synthesis and structure of a new tin(II) squarate phase is presented and compared with the one of an inorganic tin(II)-oxo-fluoride in which the same peculiar arrangement of tin lone pairs is observed.

2. Experimental

$Sn_2O(C_4O_4)(H_2O)$ was synthesized by hydrothermal synthesis starting from a mixture of $SnCl_2$, $2H_2O$, squaric acid $H_2C_4O_4$, ethylene diamine and H_2O in the molar ratio 1/4/4/200. The home made Teflon lined sealed pressure bombs were heated at 150°C for 96 h under autogeneous pressure and then cooled down to

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room temperature. The pH before and after the treatment was found, respectively, to be 3.4 and 2.4. The resulting mixture contained gold color single crystals admixed with a yellow powder. Increasing the temperature above 180°C resulted in the formation of Casserite-type SnO_2.

Table 1
Crystallographic data for $Sn_2O(C_4O_4)(H_2O)$

Crystal data	
System	Monoclinic
Space group	$C2/m$
a (Å)	12.7380(9)
b (Å)	7.9000(3)
c (Å)	8.3490(5)
β (deg)	121.975(3)
V (Å^3)	712.69(7)
Z	4
Formula weight	383.44
$\rho_{calc.}$ (g/cm^3)	3.574
$\mu_{MoK\alpha}$ (cm^{-1})	69.99
Dimension (mm)	$0.08 \times 0.10 \times 0.13$
Color	Gold aspect
Experimental details	
Temperature (°C)	293.2
Wavelength (Mo$K\alpha$)	0.71069
Max. Bragg angle (deg)	30°
Collected reflections	1929
Data/restraints/parameters	1104/0/61
$R = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum F_o$ %	4.18
$R_w = [\sum w(\lvert F_o^2 - F_c^2 \rvert)^2 / \sum w(F_o^2)^2]^{1/2}$ %	10.79
Goodness of fit on F^2	1.116
Weighting scheme/2 terms Chebychev	0.0752/0.4546
Large difference peak and hole (e Å^3)	3.58/−2.92 at 0.8 Å of Sn1

A suitable crystal for single crystal X-ray diffraction study was isolated under an optical microscope. Data were collected on an Enraf–Nonius four circle diffractometer equipped with a KAPPA-CCD detector. The cell parameters were determined from the collection of ten frames using the program Collect [12]. SIR92 [13] was used to solve the structure by direct methods and refinements were performed using SHEXL-96 [14]. The tin, carbon and oxygen atoms were located first and the remaining hydrogen atom was found by Fourier difference. This atom was introduced in the refinement

Table 3
Bond lengths, interatomic distances (Å) and angles (deg) in $Sn_2O(C_4O_4)(H_2O)$

Sn1–O1 (× 2)	2.433(3)	C1–O1	1.254(5)
Sn1–O3	2.297(5)	C2–O2	1.253(6)
Sn1–O4	2.067(4)	C1–C1^{v}	1.463(8)
Sn2–O4 (× 2)	2.117(3)	C1–C2	1.474(6)
Sn2–O2^{iii} (× 2)	2.534(3)	C2–C2^{v}	1.465(9)
Sn1–Sn2 (× 2)	3.761(5)	O3–H1	0.950(3)
Sn2–Sn2^{ii}	3.321(4)		
O3–Sn1–O4	91.46(17)	Sn2–O4–Sn2^{ii}	103.35(17)
O1–Sn1–O4 (× 2)	80.10(8)	Sn1–O4–Sn2	128.01(9)
O1–Sn1–O3 (× 2)	79.82(7)	O1–C1–C1^{v}	133.4(2)
O1–Sn1–O1^{ii}	151.07(15)	O1–C1–C2	136.5(4)
O2^{iii}–Sn2–O2^{iv}	178.77(15)	O2–C2–C2^{v}	136.0(3)
O2^{iii}–Sn2–O4 (× 2)	88.17(14)	O2–C2–C1	134.0(5)
O2^{iv}–Sn2–O4 (× 2)	90.87(14)	C1^{v}–C1–C2	90.0(3)
O4–Sn2–O4^{i}	76.65(18)	C2^{v}–C2–C1	90.0(3)

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

Table 2
Atomic coordinates and thermal parameters in $Sn_2O(C_4O_4)(H_2O)$

Atom	x	y	z	U_{eq} (Å^2)
Sn1	0.19563(4)	0	0.84429(5)	0.0171(2)
Sn2	1/2	0.21021(5)	0	0.0165(2)
O1	0.2265(3)	0.2982(4)	0.8083(4)	0.0239(7)
O2	0.0772(4)	0.2932(4)	0.3490(5)	0.0259(8)
O3	0.1524(5)	0	0.5400(7)	0.0263(11)
O4	0.3839(4)	0	0.9522(6)	0.0183(8)
C1	0.1844(4)	0.4074(5)	0.6798(5)	0.0149(8)
C2	0.1170(4)	0.4073(6)	0.4718(6)	0.0167(8)
H	0.1136	0.0960	0.4619	0.05

Anisotropic temperature factors

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn1	0.0136(3)	0.0183(3)	0.0146(3)	0	0.0041(2)	0
Sn2	0.0172(3)	0.0104(3)	0.0155(3)	0	0.0043(2)	0
O1	0.0314(17)	0.0148(15)	0.0140(14)	0.0034(11)	0.0043(13)	0.0000(13)
O2	0.039(2)	0.0188(18)	0.0124(15)	−0.0024(12)	0.0081(15)	−0.0019(14)
O3	0.035(3)	0.023(3)	0.016(2)	0	0.010(2)	0
O4	0.018(2)	0.0105(19)	0.020(2)	0	0.0056(17)	0
C1	0.0151(18)	0.011(2)	0.0125(18)	0.0006(13)	0.0035(15)	0.0013(14)
C2	0.018(2)	0.013(2)	0.0118(18)	0.0001(15)	0.0030(15)	0.0009(16)

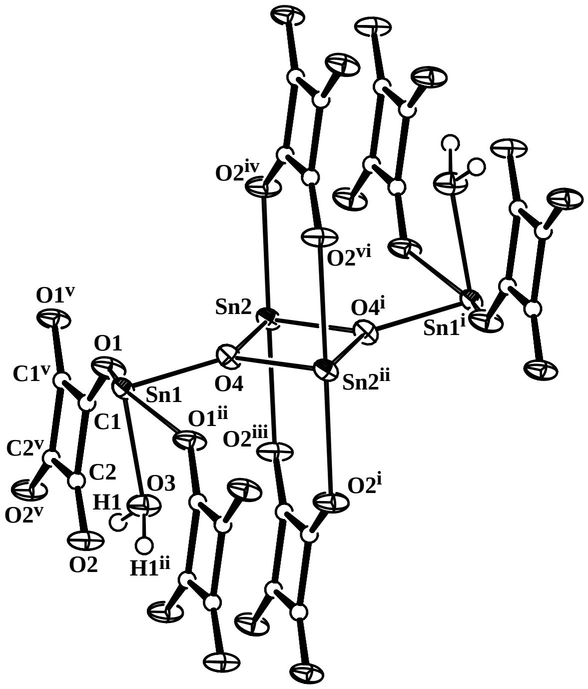

Fig. 1. Ortep representation of the coordination environment around the Sn atoms in $Sn_2O(C_4O_4)(H_2O)$. The tetranuclear Sn clusters are clearly evidenced (tin(II) lone pairs are not represented for clarity).

but it was not refined (O–H distance close to 0.95 Å). An absorption correction was applied using the program SORTAV [15]. The set of physical and crystallographic characteristics as well as the experiment conditions are listed in Table 1. The atomic coordinates and anisotropic thermal parameters are listed in Table 2. Selected bond lengths and angles are given in Table 3.

3. Results

As depicted in Fig. 1, the structure of $Sn_2O(C_4O_4)(H_2O)$ is formed of tin(II) tetranuclear species isolated from one another by squarate groups. Both independent Sn atoms, Sn1 and Sn2, exhibit the typical one-sided coordination towards oxygens due to the stereoactivity of their ns^2 lone pairs. Sn2 atoms present a $[SnO_4E]$ trigonal bipyramid coordination with Sn–O4 = Sn–O4^{i} = 2.117(3) Å bonds and the lone pair E located in the equatorial plane—the atoms O2^{iii} and O2^{iv} of the squarate group distant of 2.534(3) Å located at the apices completing the coordination polyhedron. It is worth noting that two Sn2 trigonal bipyramid share the edge O4–O4^{i} to form a very symmetrical entity of formula $[Sn_2O_6E_2]$ with a mirror plane and a center of

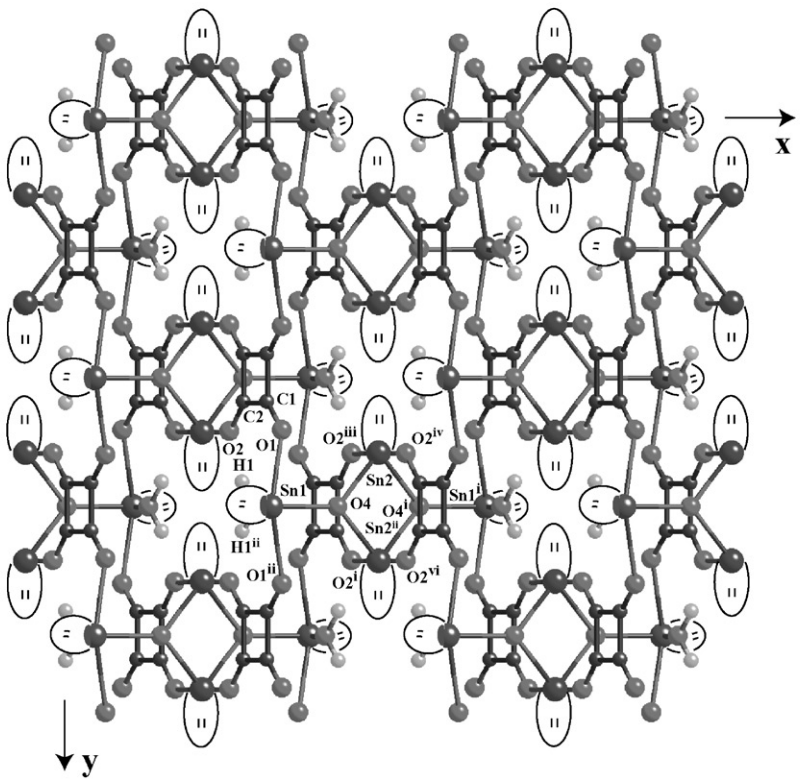

Fig. 2. Ball and stick representation of $Sn_2O(C_4O_4)(H_2O)$ structure projected onto the (001) plane with atom labels. Tin(II) lone pairs are schematically represented.

symmetry which relate the equivalent halves of this tetranuclear species. Such entity is connected in its equatorial plane via the oxygen atoms O4 and O4^{i} to the second independent tin atoms, i.e. Sn1 and Sn1^{i}. The entity $[Sn_2O_6E_2]$ with its Sn2 in $CN = 4 + 1$ shows an unusual high value of 179° of Oapic-Sn2-Oapic angle (generally around 160–170°) due to the bidentate bonding with the very rigid squarate group; the equatorial angle is squeezed to 77° owing to lone-pair bond-pair repulsion.

This Sn1 atom ensures the bridge between two successive $[Sn_2O_6E_2]$ groups along [010] via oxygens O1 and O1^{ii}; the bond Sn1–O3 with the water molecule completes its fourfold coordination. If one takes into account the Sn1 lone pair $E1$, such polyhedron is distorted towards square pyramid coordination—the angle O1–Sn1–O1^{ii} is equal to 151.07(15) Å.

The squarate ligand is very regular (angles C–C–C equal to 90°) and flat with characteristic C–C and C–O bonds of 1.463–1.474 and 1.254 Å, respectively. It presents a remarkable feature. Two of them actually cap via the oxygen atoms O2 the $[Sn_2O_6E_2]$ entities whereas four others are connected via O1 to Sn1 polyhedra. They are parallel (stacked along the same [001] direction) and ensure the linkage between the different tetranuclear tin species. That forms zigzag ribbons running along the [010] direction, see Fig. 2. One can also notice that channels perpendicular to the (001) plane are created in which are located Sn1 and Sn2 lone pairs. A projection of the structure onto the (010) plane indicates that it is formed of layers running along the [102] direction (Fig. 3). Sn1 lone pairs $E1$ point toward the space available between the layers.

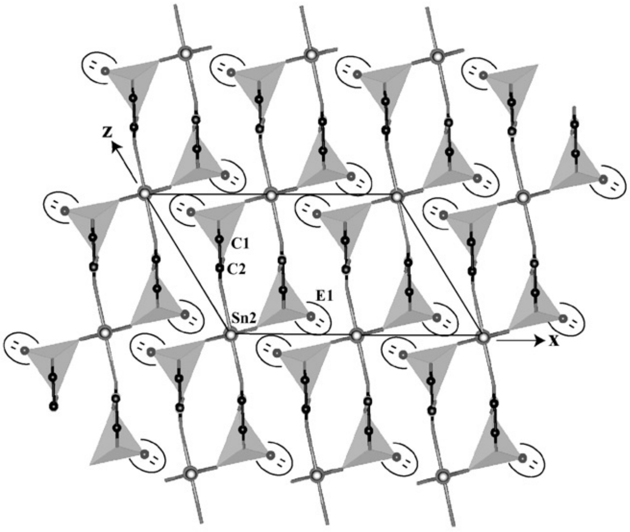

Fig. 3. Ball and stick representation of $Sn_2O(C_4O_4)(H_2O)$ structure projected onto the (010) plane. The coordination polyhedron around Sn1 is represented with E depicted as small black sphere with a lob. The layered character of this structure is clearly observed.

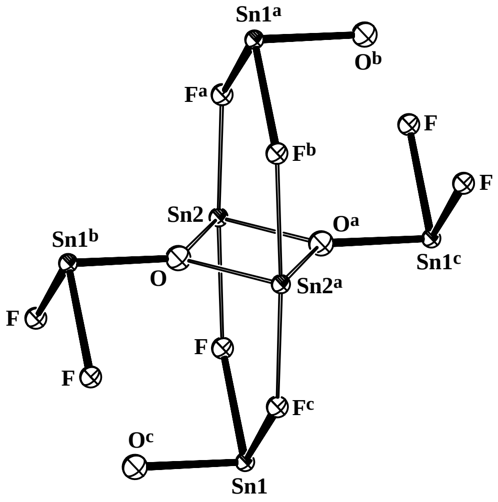

Fig. 4. Ortep representation of the coordination scheme around tin atoms in $Sn_2[Sn_2O_2F_4]$ (structural data from Ref. [16]).

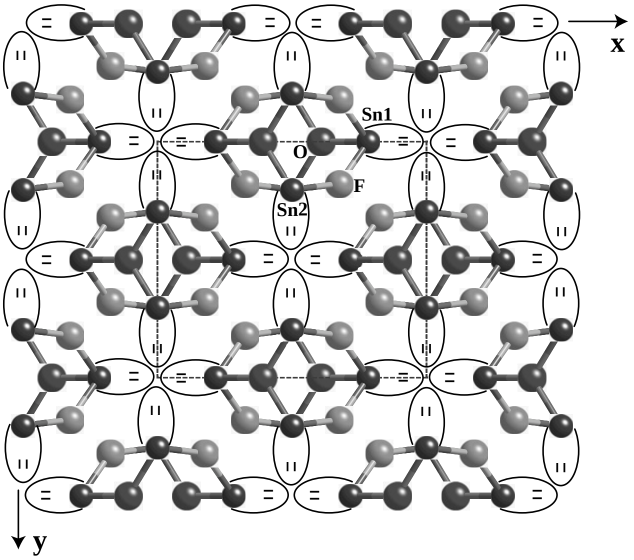

Fig. 5. Projection of $Sn_2[Sn_2O_2F_4]$ onto the (001) plane.

At this point a comparison can be made with $Sn_2[Sn_2O_2F_4]$ [16]. As can be seen in Fig. 4, this latter structure is formed of very similar tin(II) entities with the same type of very symmetrical tin oxo-fluoride $[Sn_2O_2F_4E_2]$ group, capped this time by Sn1 atoms in tetrahedral coordination. Note that the equatorial angle of Sn2, i.e. O–Sn2–O is equal to 77°, a close value as in our compound, while the axial angle F–Sn2–F = 170° is clearly smaller, the angle F–Sn1–F being less rigid than those of the squarate group. Further similarity is evidenced in Fig. 5, where channels are also observed on the projection of the structure onto the (001) plane. Here again, tin(II) lone-pairs E are facing each other to form highly negatively charged tunnels which surround or isolate infinite chains of $(Sn(2)_2O_2F_4)Sn(1)_2)_n$ formula. This structure is rather one dimensional and the cohesion of the network seems to be only ensured by lone pair–lone pair interaction.

In conclusion, the synthesis and structural characterization of the first tin(II) squarate formed of tetranuclear tin complexes have been performed. Very important structural similarities with a tin(II)-oxo-fluoride compound have been evidenced with, in particular, the structure-directing role of tin(II) lone pairs. Then it would be interesting to investigate in a more general way systems based on lone pair elements in the presence of organic species. New open frameworks are the goal to achieve.

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