

Co-crystallization of Oxalate Salts of Monoprotonated Amines with a Double Sn-Ph Bond Cleavage

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Abstract: Two oxalate compounds $[(C_4H_7N_2)_3][Sb(C_2O_4)_3]$ (1) and $[(Et_3NH)][SnPhCl(C_2O_4)_2]$ (2), have been isolated and characterized by single-crystal X-ray diffraction. Compound 1 crystallizes in the monoclinic system, space group $P2_1/c$ with $a=13.3944$ (6) Å, $b=11.3554$ (5) Å, $c=16.3314$ (7) Å, $\beta=107.206$ (1), $V=2372.82$ (18) Å³ and $Z=4$. Compound 2 crystallizes in the monoclinic system, space group $P2_1/n$ with $a=8.6903$ (4) Å, $b=15.3844$ (8) Å, $c=20.3144$ (10) Å, $\beta=100.869$ (2), $V=2667.2$ (2) Å³ and $Z=4$. The complex-anion $[Sb(O_2CCO_2)_3]^{3-}$ of the compound 1 adopts a distorted pentagonal pyramidal arrangement with monochelating oxalates. The asymmetric unit of 1 consists of three 2-methyl-1H-imidazolium cations, $C_4H_7N_2^+$, three oxalate anions, $C_2O_4^{2-}$, and one antimony (III) ion, Sb^{3+} . From a supramolecular point of view, in 1 complex-anions are connected by cations through N-H...O and N-H...O hydrogen bonds involving the two oxalates of the basal plane into sheets which are then connected via the remaining oxalate and cations through N-H...O hydrogen bonds to give rise to a three-dimensional structure. The complex-anion of 2 is comprised of a tin centre linked to a chlorine atom and a phenyl group, and *cis*-chelated by two oxalates in a distorted octahedral fashion. Each triethylammonium cation is connected to the complex-anion through bifurcated N-H...O hydrogen bonds. These interactions lead to a discrete structure. A double Sn-C bond cleavage has occurred during the process of the formation of the compound 2. In both compounds 1 and 2, one cation exhibits some positional disorder.

Keywords: Oxalate, Antimony (III), Tin(IV), 2-Methylimidazolium, Triethylammonium, Sn-C Cleavage, X-ray Crystal Crystallography

1. Introduction

Quaternary ammonium salts are used by countless research groups in co-crystallization and crystal engineering. They play a pivotal role, because of the interesting diversity of supramolecular structures they display. Many groups of researchers are focusing in synthesizing such type of materials which have shown interesting physical properties [1-3]. In these amine salts hydrated or not, the amine can be neutral or protonated, the anionic component being acidic or non-acidic: they are soluble in organic solvents and are used in the study of their interactions with metal halides, acetates and organotin compounds for example to isolate new complexes. The structures of some

fluoro antimony (III) oxalate complexes with alkaline have been published [4-8]. The structures of $K_3Sb(C_2O_4)_3$ and $(NH_4)_3Sb(C_2O_4)_3$ have also been reported [9]. Monoamines are known in their reactions with $SnPh_3Cl$ to impulse Sn-Ph bonds cleavages [10]. Numerous works reporting crystalline structures evidencing the presence of Sn-Ph bonds cleaved from partial to total dearylation have been reported [11]. Organotin compounds display interesting inhibition towards pancreatic cancer cells [12-15], their biological and anticancer activities [16-21], their catalytic application [22], their fungicidal activity [23] has been reported; they are also used in the preparation of some thin-film transistor matrix [24]. Oxalate complexes with interesting properties such as fluorescence, proton conductivity, magnetic and quantum spin

liquid are known [25-29]. For decades, the Dakar group has focused on the synthesis and characterization of organo-and halotin oxalate complexes [30-35]. As a continuation of our contribution in oxalate compounds, dealing with the nature of the counter cation and its involvement in hydrogen bonding, we have initiated in this work the study of the interactions between trifluoro antimony(III) (SbF_3) and bis-(2-methylimidazolium) oxalate and triphenyltin chloride (SnPh_3Cl). Thus, herein are reported the syntheses and X-ray crystal structure characterizations of $[(\text{C}_4\text{H}_7\text{N}_2)_3][\text{Sb}(\text{C}_2\text{O}_4)_3]$ (1) and $[(\text{Et}_3\text{NH})][\text{SnPhCl}(\text{C}_2\text{O}_4)_2]$ (2).

2. Experimental

2.1. General

All reagents were purchased from Sigma-Aldrich (Germany) and were used without any further purification.

2.2. Synthesis of $[(\text{C}_4\text{H}_7\text{N}_2)_3][\text{Sb}(\text{C}_2\text{O}_4)_3]$ (1)

Crystals of bis(2-methylimidazolium) oxalate, $(\text{C}_4\text{H}_7\text{N}_2)_2\text{C}_2\text{O}_4$ (L_1) were obtained on allowing 15 mL aqueous solutions of 2-methylimidazole, $\text{C}_4\text{H}_6\text{N}_2$ [4 mmol (328.4 mg)] and oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [2 mmol (252.2 mg)] to react. When equimolar aqueous solutions of $(\text{C}_4\text{H}_7\text{N}_2)_2\text{C}_2\text{O}_4$ (L_1) [1 mmol (254.2 mg), 15 mL] and SbF_3 [1 mmol (178.7 mg), 10 mL] are mixed, a clear solution is obtained then stirred 2h at room temperature in the open atmosphere. Colorless block-like crystals of the compound tris(2-methylimidazolium) trioxalatoantimonate (III) (1) suitable for a single-crystal X-ray crystallographic analysis were obtained after a few weeks of a slow solvent evaporation at room temperature (300 K).

2.3. Synthesis of $\{[(\text{C}_2\text{H}_5)_3\text{NH}]_2\}[\text{SnPhCl}(\text{C}_2\text{O}_4)_2]$ (2)

Bis(triethylammonium) oxalate, $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{C}_2\text{O}_4$ (L_2) [%calculated (%found)-C: 57.50 (57.10), H: 11.03 (10.87), N: 9.58 (9.53)-] was obtained as a white powder by adding a 15 mL aqueous solution of oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [3.58 mmol (452 mg)] in a 10 mL triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$ one [7.17 mmol (1 mL; 726 mg)]. The compound triethylammonium dioxalatophenylchlorotin (IV) (2) was obtained by reacting 15 mL methanol solutions of

$[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{C}_2\text{O}_4$ (L_2) [0.84 mmol (246 mg)] and triphenyltin chloride, SnPh_3Cl [0.42 mmol (162 mg)]. The colorless resulting mixture was stirred 2h at room temperature in the open atmosphere. Colorless block-like crystals of (2) were obtained after some days of a slow solvent evaporation at room temperature (300 K).

The proposed equations of reactions leading to the isolation of compounds 1 and 2 are shown in Figure 1.

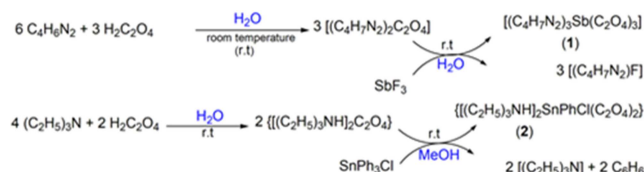


Figure 1. Proposed equation of reactions of the synthesis of compounds 1 and 2.

2.4. X-ray Crystallography

The X-ray crystallographic data for salts 1 and 2 were collected using a Bruker Kappa X8-APEX-II diffractometer operating at $T=120$ (2) K. All data were measured using ϕ and ω scans of 0.5° using $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) using a collection strategy to obtain a hemisphere of unique data determined by Apex3 [36]. Cell parameters were retrieved and refined using the SAINT software [37]. Data reduction was performed using the SAINT software which corrects for Lorentz polarization [37]. Data were corrected for absorption and polarization effects and analyzed for space group determination [38]. The structures were solved by dual-space analysis using SHELXT [39] and the structure refined using least-squares minimization (SHELXL) [40].

Programs used for the representation of the molecular and crystal structures: Platon [41] and Mercury [42]. Crystal data, data collection and structure refinement details for compounds 1 and 2 are summarized in Table 1.

CCDC 1951781 (1) and 1951782 (2) contain the supplementary crystallographic data this paper. Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement of compounds 1 and 2.

Parameters	Compound	
	1	2
Empirical formula	$\text{C}_{18}\text{H}_{21}\text{N}_6\text{O}_{12}\text{Sb}$	$\text{C}_{22}\text{H}_{37}\text{N}_2\text{ClO}_8\text{Sn}$
Formula weight	635.16	611.67
Temperature (K)	120 (2)	120 (2)
Crystal system	Monoclinic	Monoclinic
Space group	$P21/c$	$P21/n$
a, (Å)	13.3944 (6)	8.6903 (4)
a, (°)	90	90
b, (Å)	11.3554 (5)	15.3844 (8)
β, (°)	107.206 (1)	100.869 (2)
c, (Å)	16.3314 (7)	20.3144 (10)
γ, (°)	90	90

Parameters	Compound	
	1	2
Volume (Å ³)	2372.82 (18)	2667.2 (2)
Z	4	4
ρ_{calc} (g/cm ³)	1.778	1.523
μ (mm ⁻¹)	1.239	1.104
$F(000)$	1272	1256
Crystal size (mm ³)	0.24 × 0.12 × 0.08	0.256 × 0.156 × 0.125
Radiation (Å)	MoK α (λ =0.71073)	MoK α (λ =0.71073)
2 θ range for data collection (°)	2.22–28.25°	2.43–28.26°
Index ranges	$-17 \leq h \leq 17$	$-7 \leq h \leq 11$
	$-14 \leq k \leq 15$	$-20 \leq k \leq 20$,
	$-21 \leq l \leq 21$	$-27 \leq l \leq 27$
Reflections collected	45897	56674
Independent reflections	5921 [R_{int} =0.0259]	6644 [R_{int} =0.0226]
Data/restraints/parameters	5921/0/416	6644/0/334
Goodness-of-fit on F^2	1.080	1.078
Final R indexes	R_1 =0.0264,	R_1 =0.0243,
[$I > 2\sigma(I)$]	wR_2 =0.0659	wR_2 =0.0636
Final R indexes [all data]	R_1 =0.0313, wR_2 =0.0683	R_1 =0.0290, wR_2 =0.0615
Largest diff. peak/hole (e Å ⁻³)	1.598/–0.558	1.494/–0.392

$R1 = \sum(|F_o| - |F_c|) / \sum |F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 2.0584P]$ for 1 and $w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 1.1918P]$ for 2 where $P = (F_o^2 + 2F_c^2)/3$; χ^2 goodness of fit = $[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$.

3. Results and Discussion

3.1. Crystal and Molecular Structure of $[(C_4H_7N_2)_3][Sb(C_2O_4)_3]$ (1)

Complex 1, namely 2-methyl-1H-imidazol-3-ium trioxalatoantimonate (III), crystallizes as colorless block-like crystals. There are three 2-methyl-imidazolium cations and one trioxalatoantimonate in the unit cell of the primitive, centrosymmetric, monoclinic space group $P2_1/c$ (Figure 1). The Sb centre, in the $[Sb(O_2CCO_2)_3]^{3-}$ anion, adopts a distorted pentagonal pyramidal geometry. Four oxygen atoms in two of the three oxalate moieties coordinate the Sb centre in the basal plane of the pentagonal pyramid while the remaining oxalate occupies the remaining basal site and the apical position. This leaves an apparently large, vacant coordination hole on one side of the asymmetric coordination sphere. Inspection of close contacts to the Sb centre on this open side reveals no interactions shorter than 3.6 Å, thus the Sb does not form a dimeric pair, or any other conFigureuration, through oxygen contacts and is a discrete anion species. The 2-methyl-imidazolium cation N5/N6 was found to be positional disordered by approximately 180° rotation perpendicular to the plane of the ring. The Sb-O distances (Table 2) are in the range of those yet reported, the shorter being the one involving the O atom located at the apical position of the pyramid [43]. The C-O distances indicate

double and single bond character [34, 44]. The torsion angles show a slightly twisted as well as an almost planar oxalate (Table 2). The sum of the O-Sb-O angles involving O1, O3, O5, O9 and O11 equal to 355.13° evidence an almost planar pentagonal arrangement of the oxygen atoms, the Sb centre being slightly out this plane. The distances C7-N1/C7-N2, C11-N3/C11-N4, C15-N5/C15-N6 and those of N1-C8/N2-C9, N3-C12/N4-C13 and N5-C16/N6-C17 in the imidazolium cation are in accordance with some π -bonding character around C7, C11 and C15. The length values of the C8-C9, C12-C13 and C16-C17 bonds also suggest some π -bonding character for the imidazolium. All the nitrogen H atoms are involved in strong intermolecular hydrogen-bonds with oxalate oxygen atoms (see Figure 2 and Table 3). Due to polarizing effects of the imidazolium cation, the olefinic hydrogen atoms have longer, weaker contacts to oxalate oxygen atoms. The overall packing is a three-dimensional hydrogen-bonded network. The framework is comprised of sheets of imidazolium cations involved in hydrogen-bonds with the oxalate oxygen atoms in the basal plane of the $[Sb(O_2CCO_2)_3]^{3-}$ anion. These sheets are approximately parallel to the $[3\ 0\ -4]$ direction. These sheets are linked through hydrogen bonds *via* the apical bonding oxalate to imidazolium cation N3/N4 (Figure 2). Extra weak C-H...O hydrogen bonds strengthen the hydrogen bond network.

Table 2. Selected geometric parameters (Å, °) for compound 1.

Atom-Atom	Bond length	Atom-Atom	Bond length
Sb1-O7	2.0346 (15)	O9-C5	1.248 (3)
Sb1-O1	2.2229 (14)	N4-C11	1.322 (3)
Sb1-O3	2.2339 (15)	N4-C13	1.371 (3)
Sb1-O5	2.2342 (14)	N5-C15	1.330 (7)
Sb1-O11	2.3486 (16)	N5-C16	1.370 (8)
Sb1-O9	2.4008 (15)	N6-C15	1.321 (7)

Atom-Atom	Bond length	Atom-Atom	Bond length
N1-C7	1.332 (3)	N6-C17	1.377 (7)
N1-C8	1.369 (3)	N6-C15	1.321 (7)
N2-C7	1.327 (3)	N6-C17	1.377 (7)
N2-C9	1.365 (3)	N5A-C15A	1.316 (8)
C7-C10	1.465 (4)	N5A-C16A	1.368 (9)
C8-C9	1.344 (3)	N6A-C15A	1.307 (7)
N3-C11	1.326 (3)	N6A-C17A	1.378 (9)
N3-C12	1.370 (3)	O10-C5	1.237 (3)
O12-C6	1.228 (3)	O11-C6	1.269 (3)
C1-C2	1.545 (3)	C3-C4	1.545 (3)
O1-C1	1.274 (2)	C5-C6	1.539 (3)
O2-C1	1.232 (2)	C11-C14	1.474 (4)
O3-C2	1.274 (2)	C12-C13	1.336 (3)
O4-C2	1.231 (3)	C15-C18	1.471 (7)
O5-C3	1.267 (3)	C15A-C18A	1.474 (8)
O6-C3	1.227 (3)	C16A-C17A	1.348 (8)
O7-C4	1.308 (3)	C16-C17	1.344 (7)
O8-C4	1.206 (3)		
Atom-atom-atom	Angle value	Atom-atom-atom	Angle value
O1-Sb1-O3	71.98 (5)	O1-Sb1-O11	70.61 (5)
O7-Sb1-O5	76.05 (6)	O1-Sb1-O9	135.96 (5)
O1-Sb1-O5	138.33 (5)	O3-Sb1-O9	143.64 (5)
O3-Sb1-O5	72.96 (5)	O5-Sb1-O9	71.28 (5)
O7-Sb1-O11	80.33 (6)	O11-Sb1-O9	68.31 (5)
O2-C1-C2-O4	-2.0 (3)	O1-C1-C2-O3	-1.6 (3)
O6-C3-C4-O8	5.1 (3)	O5-C3-C4-O7	5.3 (3)
O10-C5-C6-O12	5.7 (4)	O9-C5-C6-O11	7.0 (3)

Table 3. Hydrogen-bonds geometry in the crystal of **1** [Symmetry codes: (i) $x, y+1, z$; (ii) $x+1, -y+1/2, z+1/2$; (iii) $-x+1, y+1/2, -z+1/2$; (iv) $-x+2, y+1/2, -z+3/2$; (v) $-x+2, y-1/2, -z+3/2$; (vi) $x, -y+1/2, z-1/2$; (vii) $x-1, -y+1/2, z-1/2$; (viii) $-x+1, y-1/2, -z+1/2$].

D—H...A	D-H	H...A	D...A	D-H...A
N1—H1N...O4	0.80 (3)	2.01 (3)	2.811 (2)	173 (3)
N2—H2N...O11 ⁱ	0.89 (4)	1.99 (4)	2.855 (2)	166 (3)
N2—H2N...O12 ⁱ	0.89 (4)	2.55 (4)	3.225 (3)	134 (3)
N3—H3N...O2	0.85 (3)	1.94 (3)	2.750 (2)	158 (3)
N3—H3N...O4	0.85 (3)	2.46 (3)	3.016 (2)	124 (3)
N4—H4N...O6 ⁱⁱ	0.90 (4)	2.00 (4)	2.786 (3)	145 (3)
N4—H4N...O8 ⁱⁱ	0.90 (4)	2.39 (4)	3.074 (3)	132 (3)
N5—H5N...O10	0.92 (4)	1.83 (4)	2.623 (5)	143 (4)
N6A—H5N...O10	0.90 (4)	1.83 (4)	2.709 (5)	166 (4)
N6—H6N...O10 ⁱⁱⁱ	0.85 (5)	2.18 (5)	2.726 (5)	122 (4)
N6—H6N...O12 ⁱⁱⁱ	0.85 (5)	2.08 (5)	2.850 (5)	150 (5)
N5A—H6N...O10 ⁱⁱⁱ	0.84 (5)	2.18 (5)	2.864 (6)	138 (4)
N5A—H6N...O12 ⁱⁱⁱ	0.84 (5)	2.08 (5)	2.709 (5)	131 (5)
C8—H8...O7 ^{iv}	0.95	2.45	3.200 (3)	136.2
C10—H10A...O3	0.98	2.31	3.273 (3)	169.0
C12—H12...O7 ^{iv}	0.95	2.62	3.334 (3)	132.7
C13—H13...O8 ^{iv}	0.95	2.60	3.320 (3)	132.4
C14—H14C...O6 ^v	0.98	2.50	3.415 (4)	155.2
C16—H16...O9	0.95	2.52	3.107 (6)	120.3
C17—H17...O8 ^{vi}	0.95	2.15	2.967 (5)	142.9
C18—H18A...O4 ^{vii}	0.98	2.59	3.557 (7)	169.3
C18—H18C...O6 ^{viii}	0.98	2.65	3.550 (6)	153.2
C18A—H18E...O9	0.98	2.51	3.414 (6)	153.8

3.2. Crystal and Molecular Structure of $\{[(C_2H_5)_3NH]_2\}[SnPhCl(C_2O_4)_2]$ (**2**)

The asymmetric unit of the primitive, centrosymmetric, monoclinic space group $P2_1/n$ (Figure 3) of the compound (**2**) consists of one $[SnPhCl(C_2O_4)_2]^{2-}$ complex-anion and two

triethylammonium cations in general position. The tin atom is monochelated by two oxalate anions and linked to the phenyl group and the chlorine atom. The environment around the tin centre is octahedral. There are two different cations yet chemically identical in **2**: the first one linked to an oxalate through bifurcated hydrogen bonds

N1-H1N...(O6,O8) and the second one linked to the remaining oxalate through N2-H2...(O2,O4) bifurcated hydrogen bonds (Figure 4 and Table 5). The C-O distances in the carboxylic groups of the complex (2) are comparable to those found in (1) and are in accordance with the presence of double and single C-O bonds [34, 44-48]. As found in 1, the torsion angles show for 2 a slightly twisted oxalate too (Table 4). The oxalate C-C distances in (1) and (2) are similar and are in the range of the published values. The Sn-O distances show a non-symmetrical oxalate chelation. The Sn-Cl and Sn-C length values are similar to reported ones [31, 44, 45, 48]. The apical angle value (O1-Sn-Cl) of 165.00 (4) Å indicates a great distortion in the octahedral arrangement around the tin atom. Complex (2) exhibits some positional disorder involving C17, C19 and C21 atoms in one triethylammonium cation. Inter species hydrogen bonding interactions between the two triethylammonium cations and the $[\text{SnPhCl}(\text{C}_2\text{O}_4)_2]^{2-}$ complex-anion lead to discrete ionic species (Figure 5). It is noteworthy to point out the double Sn-Ph cleavage occurring in the process of obtention of complex (2). In the past several Sn-C bond cleavage involving alkyl and phenyl groups have been encountered by several worldwide research groups [11].

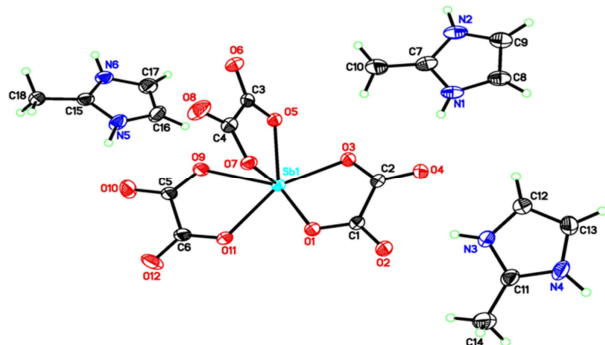


Figure 2. ORTEP view of the full molecular structure of 1 with atom labeling. Only one orientation of the disordered fragments is represented. Displacement ellipsoids are drawn at the 50% probability level.

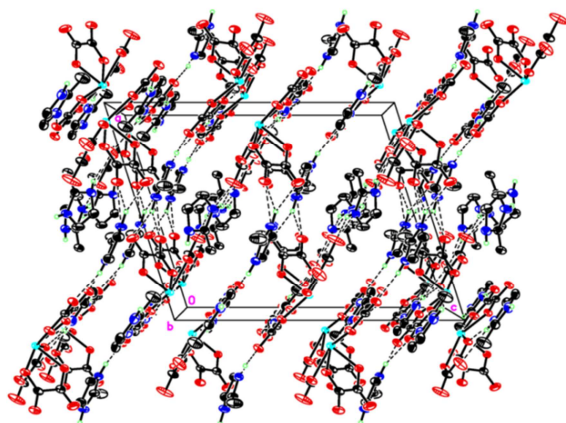


Figure 3. Crystal packing of the compound 1 showing the three-dimensional arrangement through NH...O intermolecular interactions (dashed lines). Displacement ellipsoids are drawn at the 50% probability level.

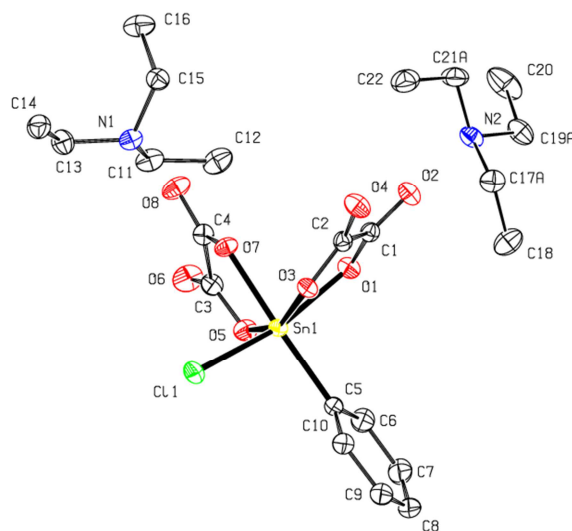


Figure 4. ORTEP view of the molecular structure of 2 with atom labeling. H atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

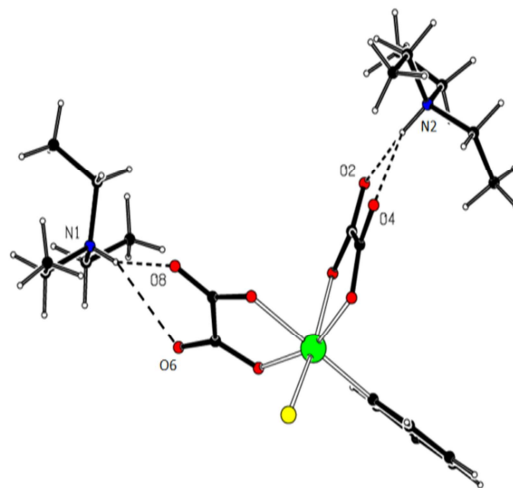


Figure 5. View of 2 showing the inter-species hydrogen bonding interactions. Displacement ellipsoids are drawn at the 30% probability level.

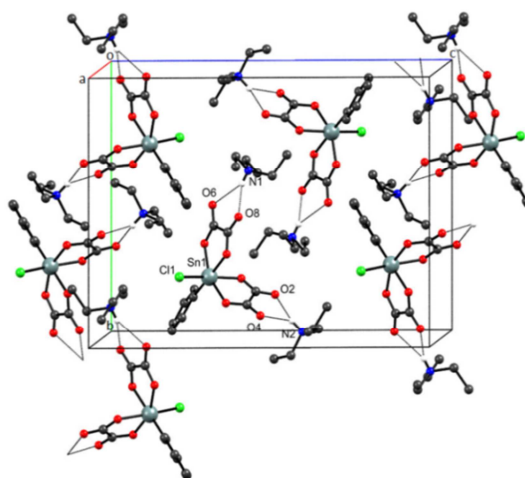


Figure 6. Crystal packing of 2 showing the arrangement within the lattice. Only hydrogen atoms involved in the interactions are shown. Displacement ellipsoids are drawn at the 30% probability level.

Table 4. Selected geometric parameters (*A*, °) for compound 2.

Atom-Atom	Bond length	Atom-Atom	Bond length
Sn1-O3	2.0874 (11)	C7-C8	1.375 (3)
Sn1-O5	2.0897 (11)	C8-C9	1.373 (3)
Sn1-O7	2.1009 (11)	N1-C13	1.495 (2)
Sn1-C5	2.1220 (16)	N1-C11	1.497 (2)
Sn1-O1	2.1341 (12)	N1-C15	1.500 (2)
Sn1-Cl1	2.3893 (5)	C11-C12	1.501 (3)
O1-C1	1.277 (2)	C13-C14	1.504 (3)
O2-C1	1.2155 (19)	C15-C16	1.511 (2)
O3-C2	1.2823 (19)	N2-C17B	1.334 (9)
O4-C2	1.2123 (19)	N2-C21A	1.463 (3)
O5-C3	1.289 (2)	N2-C17A	1.510 (2)
O6-C3	1.207 (2)	N2-C19A	1.519 (3)
O7-C4	1.278 (2)	N2-C19B	1.562 (9)
O8-C4	1.213 (2)	N2-C21B	1.588 (9)
C1-C2	1.551 (2)	C17A-C18	1.478 (3)
C3-C4	1.547 (2)	C17B-C18	1.646 (9)
C5-C10	1.382 (2)	C19A-C20	1.526 (3)
C5-C6	1.392 (2)	C19B-C20	1.615 (9)
C6-C7	1.387 (3)	C21A-C22	1.551 (3)
C21B-C22	1.361 (8)		
Atom-atom-atom	Angle value	Atom-atom-atom	Angle value
O3-Sn1-O5	156.69 (4)	O8-C4-C3	119.81 (15)
O3-Sn1-O7	81.93 (5)	O7-C4-C3	115.48 (14)
O5-Sn1-O7	77.68 (4)	C10-C5-C6	119.01 (16)
O3-Sn1-C5	103.33 (6)	C10-C5-Sn1	120.52 (13)
O5-Sn1-C5	96.00 (5)	C6-C5-Sn1	120.44 (13)
O7-Sn1-C5	172.37 (5)	C7-C6-C5	120.17 (18)
O3-Sn1-O1	77.96 (5)	C8-C7-C6	120.07 (18)
O5-Sn1-O1	88.11 (5)	C9-C8-C7	120.15 (17)
O7-Sn1-O1	82.22 (5)	C8-C9-C10	120.11 (18)
C5-Sn1-O1	93.39 (6)	C5-C10-C9	120.47 (17)
O3-Sn1-Cl1	89.93 (3)	C13-N1-C11	109.10 (13)
O5-Sn1-Cl1	100.24 (4)	C13-N1-C15	113.85 (13)
O7-Sn1-Cl1	87.40 (3)	C11-N1-C15	114.27 (14)
C5-Sn1-Cl1	98.04 (5)	N1-C11-C12	113.73 (15)
O1-Sn1-Cl1	165.00 (4)	N1-C13-C14	113.64 (14)
C1-O1-Sn1	114.31 (11)	N1-C15-C16	113.88 (15)
C2-O3-Sn1	115.08 (10)	C21A-N2-C17A	112.58 (16)
C3-O5-Sn1	116.53 (10)	C21A-N2-C19A	112.05 (16)
C4-O7-Sn1	115.72 (10)	C17A-N2-C19A	109.19 (16)
O2-C1-O1	126.16 (15)	C17B-N2-C19B	117.9 (5)
O2-C1-C2	118.37 (14)	C17B-N2-C21B	113.4 (5)
O1-C1-C2	115.46 (13)	C19B-N2-C21B	102.2 (4)
O4-C2-O3	125.61 (15)	C18-C17A-N2	113.60 (17)
O4-C2-C1	118.86 (14)	N2-C17B-C18	113.7 (6)
O3-C2-C1	115.51 (13)	N2-C19A-C20	111.7 (2)
O6-C3-O5	126.39 (16)	N2-C19B-C20	104.9 (5)
O6-C3-C4	119.36 (15)	N2-C21A-C22	113.11 (18)
O5-C3-C4	114.26 (14)	C22-C21B-N2	116.8 (6)
O8-C4-O7	124.71 (15)		
O2-C1-C2-O4	7.0 (2)	O1-C1-C2-O3	7.2 (2)
O6-C3-C4-O8	-5.1 (3)	O5-C3-C4-O7	-5.5 (2)

Table 5. Hydrogen-bonds geometry in the crystal of 2.

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1N...O6	0.83 (2)	2.679 (19)	3.3176 (19)	134.5 (16)
N1-H1N...O8	0.83 (2)	1.97 (2)	2.7418 (18)	153.9 (18)
N2-H2N...O2	0.93 (2)	2.12 (2)	2.9051 (18)	141.7 (17)
N2-H2N...O4	0.93 (2)	2.19 (2)	2.9313 (19)	136.1 (17)

4. Conclusion

The complexes 1 and 2 are six bonded around the metallic centre; the first is pyramidal pentagonal while the last is octahedral. Two oxalate types are present in compounds 1 and 2: one type whose oxygen atoms involved in coordination are positioned in the basal plane of the pyramidal pentagonal or the octahedron, and another whose one oxygen atom complete the basal positioning, the second oxygen atom being in apical one. Some positional disorders involving one 2-methylimidazolium in 1 and one triethylammonium in 2 are present. Even if the geometrical arrangements and metallic centres are different, the oxalate dianion behaviour is similar in complexes 1 and 2. The interconnections between cations and complex-anions led to a supramolecular 3D-structure for 1 and to a discrete hydrogen bonded species disposed within the lattice for 2.

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