

A “Zero-Dimensional Hybrid” tin(IV) chloride from a Sn-C bond cleavage: Synthesis, Infrared and X-ray single-Crystal molecular characterization

Mouhamadou Birame Diop*, Modou Sarr*, Sérigne Cissé*, Libasse Diop*,
Allen G. Oliver**, Mehmet Akkurt***

*(Inorganic and Analytical Chemistry Laboratory, Department of Chemistry, Faculty of Science and Technology, Cheikh Anta Diop University, Dakar, Senegal
Corresponding Email: mouhamadoubdio@gmail.com

** (Department of Chemistry and Biochemistry, University of Notre Dame, 246, Nieuwland, Science Hall, Notre Dame, IN 46557-5670, USA)

*** (Erciyes University, Faculty of Sciences, Department of Physics, 38039 Kayseri, Turkey)

ABSTRACT

The compound $[(C_4H_7N_2)_2][SnCl_6]$ (**1**), was isolated from slow solvent evaporation by reacting in acetonitrile one equivalent of an acidic salt, 2-methylimidazolium hydrogen sulfate, with one equivalent of $SnBuCl_3$. An in situ debutylation occurred during the complex formation process. In the structure, the Sn centre in the dianion, bonded to six chloride ligands, adopts an almost perfect octahedral arrangement. Van der Waals forces connect cations and anions giving rise to a discrete structure.

Keywords – Infrared, 2-methylimidazolium, Sn-C cleavage, tin(IV), X-ray single-crystal.

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I. INTRODUCTION

There are numerous different structures containing $[SnX_6]^{2-}$ (X= Cl, Br, I) dianion compared to those involving 2-methylimidazolium cation which are more scarce. Inorganic-organic hybrid and organotin (IV) materials, a widely studied class of compounds, are still arousing many interests with magnetic, electronic transport, optical, optical photoluminescence... physical properties [1-4]. Optical properties were also found in organotin family compound [5]. An inorganic-organic hybrid salt has recently been prepared, and used to catalyze the reactions enabling the isolation of pyrimido [4,5-b]-quinoline and pyrimido[4,5-d]pyrimidine derivatives [6]. Organotin compounds are the orientation of several groups because of applications found in catalysis [7, 8], their biological activity as potential anticancer [9-16] and their fungicidal activity [17]. The Dakar group has yet reported several papers dealing with chloridotin (IV) and *n*-butyltrichloridostannate (IV) compounds [18, 19]. Sn-C cleavage event follows a S_N2 or a S_E2 reaction and may occur within an organotin compound in the presence of electrophile-nucleophile entities [20]. Several works evidence Sn-C bond cleavage event, however those involving Sn-*n*Bu are most scarce

compared to Sn-Ph [21-23]. The aim of this work was to obtain a new organotin molecule or, after debutylation, a chloridotin molecule with *n*-butyltrichloridostannate (IV) as starting material interacting with 2-methyl-1H-imidazol-3-ium hydrogen sulfate. Surprisingly, in the isolated complex, the hydrogen sulfate anion do not appear even if a debutylation occurred, giving rise to the hexachloridotin (IV) compound whose X-ray single crystal molecular characterization and infrared analysis are carried out and reported herein.

II. EXPERIMENTAL

2.1 GENERAL

Chemicals were purchased from Sigma-Aldrich (Germany) and were used without any further purification. The infrared spectrum was recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate™ ATR device. Elemental analyses were performed at the «Institut de Chimie Moléculaire, Université de Bourgogne Franche-Comté, Dijon, France».

2.2 SYNTHESIS

n-butyl trichloridostannate (97%), $SnBuCl_3$ (m = 596 mg; 2.05 mmol), was preliminarily dissolved in 45 mL of slightly hydrated acetonitrile.

An equimolar amount of 2-methylimidazolium hydrogen sulfate ($m = 370$ mg; 2.05 mmol), preliminarily collected as highly hygroscopic colorless crystals, was then added. After some minutes, a clear solution was obtained. The clear mixture was stirred around two hours at room temperature under a not controlled atmosphere. Colorless crystals suitable for a single-crystal X-ray diffraction study were obtained after some days of slow solvent evaporation at room temperature and were characterized as **1**.

2.3 CRYSTAL STRUCTURE DETERMINATION

X-ray crystallographic data for compound **1** were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 293$ (2) K. Data were measured using φ and ω scans of 0.5° [MoK α radiation ($\lambda = 0.71073$ Å)] using a collection strategy to obtain a hemisphere of unique data determined by the program Apex2. Cell parameters were retrieved and refined using the SAINT software. Data were corrected for absorption and polarization effects and analyzed for space group determination using SADABS [24]. The structure was solved by intrinsic phasing methods and expanded routinely using the ShelXS [25]

structure solution program and refined by Least Squares using ShelXL [26].

Programs used for the representation of the molecular and crystal structure: Platon [27], and Olex2 [25].

The N-bound H atoms were located in difference Fourier maps. Their positions were fixed and their temperature factors were refined as riding with $U_{iso}(H) = 1.2U_{eq}(N)$. All the C-bound H atoms were placed in calculated positions with $C-H = 0.93 - 0.96$ Å and refined as riding with $U_{iso}(H) = 1.5U_{eq}(C\text{-methyl})$ and $1.2U_{eq}(C\text{-aromatic})$. Reflections (1 1 0), (3 2 6), (5 4 4), (3 0 9), (1 9 5), (5 2 8) and (1 2 4) were omitted owing to bad agreement.

CCDC **1866051** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1: Crystal data and structure refinement for compound **1**

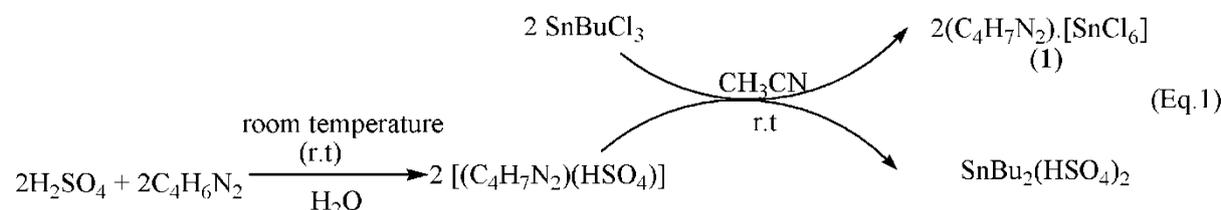
Parameters	Compound 1
Chemical formula	$2(C_4H_7N_2)^+.(SnCl_6)^{2-}$
Formula weight	497.62
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pnmm$
Unit cell dimensions	$a = 7.7403(16)$ Å $\alpha = 90^\circ$ $b = 15.852(3)$ Å $\beta = 90^\circ$ $c = 7.1611(14)$ Å $\gamma = 90^\circ$
Volume	$878.7(3)$ Å ³
Z	2
Density (calculated)	1.881 g.cm ⁻³
Absorption coefficient (μ)	2.357 mm ⁻¹
F(000)	484
Crystal color, habit	colourless, block
Crystal size	$0.11 \times 0.10 \times 0.08$ mm ³
θ range for data collection	3.121 to 28.279°
Index ranges	$-10 \leq h \leq 8$, $-19 \leq k \leq 21$, $-9 \leq l \leq 9$
Reflections collected	10125
Independent reflections	1166 [$R_{int} = 0.0741$]
Completeness to $\theta = 25.242^\circ$	100.0 %
Absorption correction	Multi-scan
Max. and min. transmission	0.7463 and 0.2738

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1166 / 0 / 56
Goodness-of-fit on F ²	1.146
Final R indices [I>2σ(I)]	R ₁ = 0.0455, wR ₂ = 0.0965
R indices (all data)	R ₁ = 0.0555, wR ₂ = 0.0907
Extinction coefficient	n/a
Largest diff. peak and hole	0.847 and -1.528 e ⁻ .Å ⁻³

III. RESULTS AND DISCUSSION

3.1 SYNTHESIS

Compound **1** was isolated from a two-step procedure. Aqueous solutions of sulfuric acid (H₂SO₄) and 2-methylimidazole (C₄H₆N₂) were first mixed together at room temperature leading to the formation of [(C₄H₇N₂)]₂[H₂SO₄]₂ collected as highly hygroscopic colorless crystals (Eq. 1). Various



3.2 FT-IR SPECTROSCOPY

Crystals of **1** were investigated by FT-IR spectroscopy in ATR mode. FT-IR data evidence absorption bands which can be assigned to ammonium cations (N–H, N–C, C–H, C=C and C=N bonds). In the past, several works with FT-IR imidazolium vibration bands investigation have previously been reported [29-38]. Thus, the band located at 1589 cm⁻¹ is assigned to C=C stretching vibrations. The band located at 1522 cm⁻¹ and 1463 cm⁻¹ are attributed to N–H and C–H bending vibrations, whereas those at 1119 cm⁻¹ and 1292 cm⁻¹ correspond to C–N stretching vibrations of the imidazolium. A band is noticed at 1089 cm⁻¹, corresponding to C–N deformation vibrations. The rocking CH₃ vibrations present about 1000-1181 cm⁻¹ are partially overlapped by some imidazolium ring vibrations. The very strong bands observed at 744 cm⁻¹ and 669 cm⁻¹ are assigned to the imidazolium out of plane ring vibrations. The presence of the 2-methylimidazolium cation is also confirmed by the absorptions observed at 3201 cm⁻¹ and 3126 cm⁻¹, assigned to N–H stretching vibrations, while the absorption at 2937 cm⁻¹ is attributed to C–H stretching vibrations in the imidazolium ring. We notice the absence of ν₁, ν₃ and ν₄ of the sulfate anion.

Moreover, the formula of the compound **1**, [(C₄H₇N₂)₂SnCl₆], is in accordance with the elemental analyses [% calculated (% found)]- C: 19.31 (19.13), H: 2.84 (2.85), N: 11.26 (11.29)-;

ammonium hydrogen sulfates were isolated and structurally characterized in the literature. To a solution of SnBuCl₃ in acetonitrile was added an equimolar amount of 2-methylimidazolium hydrogen sulfate, [(C₄H₇N₂)]₂[H₂SO₄]. Single crystals grew from the limpid solution and were characterized as the inorganic-organic hybrid complex **1**, [(C₄H₇N₂)₂SnCl₆].

these results corroborate the presence of both [SnCl₆]²⁻ complex-anion and 2-methylimidazolium cation.

3.3 CRYSTAL AND MOLECULAR STRUCTURE

It seems worthy to outline the Sn-C bond cleavage occurring in its obtention. This cleavage can presumably be explained considering a transfer of n-butyl alkyl and chloride ligands from a Sn centre to another, between two SnBuCl₃ molecules, leading to the formation of the complex [SnBu₂]²⁺. [SnCl₆]²⁻ which then react with 2-methylimidazolium hydrogen sulfate giving rise to the inorganic-organic hybrid complex (**1**). In the past, many structures with a Sn–C bond cleavage were isolated in the case of phenyl groups [21-23] as well as in the case of n-butyl groups [21]. The asymmetric unit of namely bis(2-methylimidazolium) hexachloridostannate(IV), [(C₄H₇N₂)₂SnCl₆] (**1**), is comprised of one cation and half of the inorganic dianion about a centre of inversion. The Sn(IV) centre is bonded to six chloride ligands, giving rise to an octahedral arrangement around the tin atom. The Sn–Cl1 and Sn–Cl2 distance values (see Table 2) in the hexachloridostannate(IV) dianion are comparable to those reported by several research groups [39-44], the longer Sn–Cl length being the apical one. The C1–N1 and C1–N2 distance values (Table 2) within the cations are in accordance with a π delocalization around C1 atom [45]. A representation showing the delocalization within the 2-methylimidazolium

cation is proposed in Fig. 1. The *cis* Cl–Sn–Cl and the *trans* Cl–Sn–Cl angle values are also in accordance with those found in the literature [39-44]. The geometric parameters within the $[\text{SnCl}_6]^{2-}$ dianion indicate an almost regular octahedron around Sn centre (Fig. 2 and Table 2). Van der Waals forces are the main interactions between cations and anions within the lattice. The packing diagram of the complex **1** is depicted in Fig. 3.

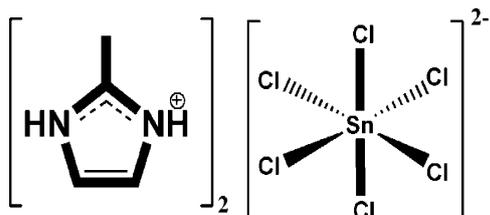


Figure 1: Molecular representation of compound **1** showing the π delocalization within the imidazolium ring.

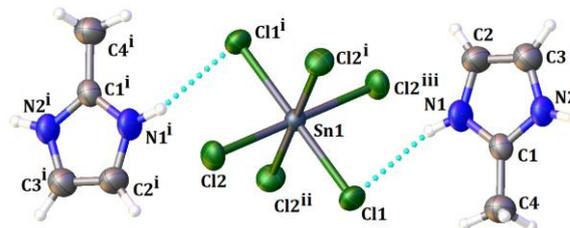


Figure 2: View of the molecular structure of the title complex, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

<i>D</i> – <i>H</i> ··· <i>A</i>	<i>D</i> – <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> – <i>H</i> ··· <i>A</i>
N1–H1N···Cl1	0.85	2.48	3.303 (7)	165

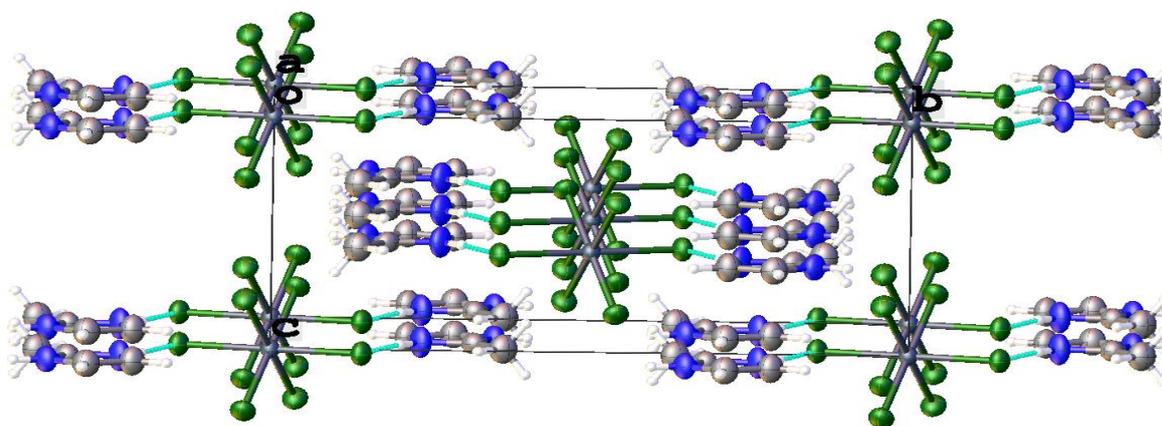


Figure 3: Crystal packing of complex **1** along the *a*-axis. Displacement ellipsoids are drawn at the 50% probability level.

Table 2 Selected geometric parameters (Å, °) for **1** (Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y, -z+1$; (iii) $-x+1, -y+1, z$).

Atom—Atom	Distance	Atom—Atom	Distance
Sn1—Cl2 ⁱ	2.4200 (12)	N1—C1	1.323 (9)
Sn1—Cl2 ⁱⁱ	2.4200 (12)	N1—C2	1.372 (11)
Sn1—Cl2 ⁱⁱⁱ	2.4200 (12)	N2—C1	1.320 (9)
Sn1—Cl2	2.4201 (12)	N2—C3	1.353 (10)
Sn1—Cl1	2.4490 (16)	C2—C3	1.315 (11)
Sn1—Cl1 ⁱ	2.4491 (16)		
Atom-Atom-Atom	Angle value	Atom-Atom-Atom	Angle value
Cl2 ⁱ —Sn1—Cl2 ⁱⁱ	89.71 (7)	Cl2 ⁱ —Sn1—Cl1 ⁱ	90.01 (4)
Cl2 ⁱ —Sn1—Cl2 ⁱⁱⁱ	90.29 (7)	Cl2 ⁱⁱ —Sn1—Cl1 ⁱ	89.99 (4)
Cl2 ⁱⁱ —Sn1—Cl2 ⁱⁱⁱ	180.0	Cl2 ⁱⁱⁱ —Sn1—Cl1 ⁱ	90.01 (4)
Cl2 ⁱ —Sn1—Cl2	180.0	Cl2—Sn1—Cl1 ⁱ	89.99 (4)
Cl2 ⁱⁱ —Sn1—Cl2	90.29 (7)	Cl1—Sn1—Cl1 ⁱ	180.0
Cl2 ⁱⁱⁱ —Sn1—Cl2	89.71 (7)	C1—N1—C2	110.8 (6)
Cl2 ⁱ —Sn1—Cl1	89.99 (4)	C1—N2—C3	110.2 (6)
Cl2 ⁱⁱ —Sn1—Cl1	90.01 (4)	N2—C1—N1	105.4 (7)
Cl2 ⁱⁱⁱ —Sn1—Cl1	89.99 (4)	C3—C2—N1	105.5 (7)
Cl2—Sn1—Cl1	90.01 (4)	C2—C3—N2	108.1 (8)

IV. CONCLUSION

The reaction between *n*-butyltrichloridostannate, SnBuCl₃ and the product obtained by partially neutralizing sulfuric acid with 2-methylimidazole, [C₄H₇N₂][HSO₄] was studied, leading to the isolation as single-crystals of a new zero dimensional hybrid, 2-methylimidazolium chloridostannate complex, 2(C₄H₇N₂)[SnCl₆] (**1**). The 2-methylimidazolium cations and the inorganic anions, mainly interact *via* van der Waals forces leading to a discrete structure. The characterization of **1** was done by infrared, elemental analyses and X-ray single crystal analysis.

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