

# Some Salicylato New Organotin (IV) and Copper Chloride Adducts and Derivative: Synthesis and Spectroscopic Study

## Boucar Diouf\*, Waly Diallo, Bocar Traoré, Mamadou Sidibé

Département de Chimie Laboratoire de Chimie Minérale et Analytique, Faculté des Sciences et Techniques, Université Cheikh Anta Diop de Dakar, Dakar, Sénégal Email: \*boucaramasiga18@gmail.com

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## Abstract

Three new salicylate complexes and derivatives have been synthesized and studied by infrared, <sup>119</sup>Sn NMR and UV-visible spectroscopies. The suggested structures for the two compounds are discrete with NH-O and NH-Cl hydrogen bonds. The salicylate oxyanion is monochelating for the first salicylate compound with an octahedral tin (IV) centre and monodentate for the second salicylate compound, the environments around the tin centre being tetrahedral. For the cooper complex, the salicylate ligand is monochelating and the environments around the copper atom centre are tetrahedral.

## **Keywords**

Discrete Structures, Hydrogen Bonds, Monochelating Monodentate, Octahedral or Tetrahedral Environments

# **1. Introduction**

Several papers about carboxylate compounds have yet been published because of their coordinating ability [1]-[5]. For widening the data on coordinating ability of carboxylate summarized by Hathaway [6]. We have been, in this work, a MeOH or EtOH solution methylamine (MeNH<sub>2</sub>) with salicylic acid and SnPh<sub>3</sub>Cl or SnCl<sub>4</sub> or CuCl<sub>2</sub>·2H<sub>2</sub>O in a specific ratio. In this paper, we have initiated the study of the interactions between HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, MeNH<sub>2</sub>, SnPh<sub>3</sub>Cl or SnCl<sub>4</sub> or CuCl<sub>2</sub>·2H<sub>2</sub>O which has yielded three new complexes. These compounds have been studied using Infrared, <sup>119</sup>Sn NMR and UV-visible techniques and structures suggested on the basis of spectroscopic data.

## 2. Materials and Methods

The compound **1** is obtained by a methanolic solution of MeNH<sub>2</sub> with salicylic acid and SnPh<sub>3</sub>Cl in 2/2/1 ratio. The compounds **2** and **3** were obtained by mixing in ethanolic solution of MeNH<sub>2</sub> with salicylic acid and SnCl<sub>4</sub> (2) or CuCl<sub>2</sub>·2H<sub>2</sub>O (3) in the ratio 1/1/1. All the mixtures gave limpid solution after three hours of reflux at 60°C and have been submitted to a slow solvent evaporation. The analytical data allow to suggest the following formulae (Table 1).

Table 1.	Suggested	formulae o	f svr	nthesized	com	oounds	and	the	elemental	analy	vses.
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		Elemental analyses (%)							
Compound	Chemical formulae	(	С		н	N			
		calc.	found	calc.	found	calc.	found		
1	[HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> (SnPh <sub>3</sub> )]	61.64	61.78	4.14	4.26	0.00	0.00		
2	$(MeNH_3)[OHC_6H_4CO_2(SnCl_4)]$	18.85	18.94	2.18	2.16	2.75	2.56		
3	$(MeNH_3)[OHC_6H_4CO_2(CuCl_2)]\cdot 2H_2O$	28.54	28.48	3.59	3.56	4.16	4.20		

The elemental analyses have been obtained from the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France. The <sup>119</sup>Sn NMR spectra were performed at the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France using a Bruker Avance 400 MHz Spectrometer with a low sensitivity band. The IR spectra of the compounds were recorded at room temperature using an FTIR spectrometer at the University Cheikh Anta Diop Dakar and at the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France (over a range from 4500 to 400 cm<sup>-1</sup>) in the form of suspension of powders in Nujol or crushed dry. The UV-visible have been obtained from the spectrometer at the University Cheikh Anta Diop Dakar.

### 3. Results and Discussion

Let us consider the IR, <sup>119</sup>Sn NMR and UV-visible data.

*IR* (cm<sup>-1</sup>): 1:  $\nu$  (OH) = 3250 (br);  $\nu_{as}$  (COO<sup>-</sup>) = 1651 (m), 1585 (m);  $\nu_{s}$  (COO<sup>-</sup>) = 1472 (s), 1383 (vs);  $\delta$  (COO<sup>-</sup>) = 865 (w), 852 (m);  $\nu_{as}$  (SnPh<sub>3</sub>) = 727 (vs), 692 (vs) 2:  $\nu$  (NH) = 2935 (br);  $\nu$  (OH) = 3213 (br);  $\delta$  (NH) = 1524 (vs);  $\nu_{as}$  (COO<sup>-</sup>) = 1651 (m), 1585 (m);  $\nu_{s}$  (COO<sup>-</sup>) = 1472 (s), 1383 (vs);  $\delta$  (COO<sup>-</sup>) = 893 (s), 851 (s);  $\nu$  (Sn-O) = 587 (m) 3:  $\nu$  (NH) = 2935 (br);  $\nu$  (OH) = 3229 (br);  $\delta$  (NH) = 1440 (s);  $\nu_{as}$ (COO<sup>-</sup>) = 1652 (s), 1481 (s);  $\nu_{s}$  (COO<sup>-</sup>) = 1463 (m), 1384 (m);  $\delta$  (COO<sup>-</sup>) = 887 (s), 851 (m);  $\nu$  (Sn-O) = 603 (m) *IISn NMR* (CDCl<sub>3</sub>, ppm): 1:  $\delta$  = -110.21 (s).

*UV-visible* (nm): 1:  $\lambda_{max} = 298$  (s)

**2:**  $\lambda_{\text{max}} = 296$  (s)

From these spectroscopic data, we suggest:

 $[HOC_6H_4CO_2(SnPh_3)] (1)$ 

While considering the IR of the [HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>(SnPh<sub>3</sub>)] derivative, the doublet

at 727 and 692 cm<sup>-1</sup> attributed to phenyl vibrations confirming the presence of the SnPh<sub>3</sub> residue. Several carboxylate bands appear, including the one at 1462 cm<sup>-1</sup> strong confirms its presence. The broad band centered at 3350 cm<sup>-1</sup> is attributed to the  $\nu$  (OH) vibration. Through these IR data, the suggested structure is discret with the salicylate ligand is monochelating and the environment around the tin centre being tetrahedral (**Figure 1**).



Figure 1. Proposed structure for the compound 1.

On the <sup>119</sup>Sn NMR spectrum, the only signal at -110 ppm indicates the presence of a single type of tetracoordinated tin in the structure. This value is characteristic of a tin atom with a tetrahedral environment as reported in the literature [7]. The only strong absorption at 298 nm attributed to  $\pi \rightarrow \pi^*$  transitions based on the aromatic double bonds of the salicylate.

 $(MeNH_3)[OHC_6H_4CO_2(SnCl_4)]$  (2)

The IR spectrum of the complex (MeNH<sub>3</sub>)[OHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>(SnCl<sub>4</sub>)] shows several bands in the valence zone of the carboxylate, including the one at 1481 cm<sup>-1</sup> which appears strong, confirming its presence. The existence of hydrogen bonds in compound **2** is explained by the presence of the broad band centered at 2935 cm<sup>-1</sup> and the average one at 587 cm<sup>-1</sup> to the Sn-O vibration [8]. Through these IR data, a discret structure reported in **Figure 2** with a tin centre in an octahedral environment is suggested, the salicylate behaving as a monochelating ligand [9]. When the cation is involved through NH...Cl hydrogen bonds a supramolecular architecture may be obtained.



Figure 2. Proposed structure for the compound 2.

#### $(MeNH_3)[OHC_6H_4CO_2(CuCl_2)]\cdot 2H_2O$ (3)

While considering the IR of the (MeNH<sub>3</sub>)[OHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>(CuCl<sub>2</sub>)]·2H<sub>2</sub>O derivative, we note several bands in the valence zone of the carboxylate including the one at 1481 cm<sup>-1</sup>, which appears strong confirms its presence. The broad band centered at 2935 cm<sup>-1</sup> is due to the presence of hydrogen bonds and the medium band at 603 cm<sup>-1</sup> to the Cu-O vibration [9].

For **3** the suggested structures are discrete (**Figure 3**), the environment around the copper centre being tetrahedral and the salicylate behaving as a monochelating ligand. When the cation is involved through NH...Cl hydrogen bonds a supramolecular architecture may be obtained [10]. Water molecules are in a network.



Figure 3. Proposed structure for the compound 3.

For compound **3** the cation may interact via hydrogen bonds leading to a supramolecular architecture. For the compound **2**, OH groups may also be involved in intermolecular hydrogen bonds leading to a supramolecular architecture.

## 4. Conclusion

The Three Adducts studied have discrete structures, with the anion behaving as a monodentate or monochelating ligand. The environments of the tin (IV) centres are trigonal bipyramidal or octahedral. In free OH or NH...Cl containing structures, when extra hydrogen bonds are considered, supramolecular architectures may be obtained. The environment around the tin centre is octahedral or tetrahedral and the environment around the copper centre is tetrahedral. When extra intermolecular hydrogen bonds are considered supramolecular architectures may be obtained.

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# **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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## **List of Notations**

IR abbreviations: Br (Broad); VS (Very Strong); S (Strong); M (Medium), W (Weak)