

NEW COMPLEX SELENITO AND OXALATO ADDUCTS CONTAINING SnPh_3 AND SnPh_2 RESIDUES: SYNTHESIS AND SPECTROSCOPIC STUDIES

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Abstract: Three new organotin complexes (two selenito and an oxalate one) adducts have been synthesized and studied by infrared and Mössbauer techniques. A discrete structure is suggested with a bi-unidentate selenito oxyanion and *trans* bipyramidal SnPh_3 residue; the oxalato adduct can be seen as an insertion compound between $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ and $[\text{Cu}(\text{En})_3]\text{C}_2\text{O}_4 \cdot 4\text{SnPh}_2\text{C}_2\text{O}_4$. This last compound has a discrete ionic structure with *cis* coordinated SnPh_2 residues.

Keywords: *bi-unidentate selenito oxyanion, discrete structure, IR and Mössbauer techniques, inserted $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$, selenito organotin complexes, trans bipyramidal residue*

INTRODUCTION

The various fields of applications [1 – 5] of the organotin compounds are the reasons why many research groups have been involved in founding new molecules belonging to that family. From our laboratory, many papers dealing with have already been published [6 – 10]. Some selenito compounds of this family have also reported by our group [11]. In this work we report the characterization of three new complexes: $\text{Cu}(\text{En})_2\text{Cl}_2 \cdot \text{SeO}_3(\text{SnPh}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{SeO}_3(\text{SnPh}_3)_2 \cdot 2\text{SC}(\text{NH}_2)_2$ and $\text{Cu}(\text{En})_3\text{C}_2\text{O}_4 \cdot 2\text{C}_2\text{O}_4(\text{SnPh}_3)_2 \cdot 4\text{C}_2\text{O}_4\text{SnPh}_2 \cdot \text{H}_2\text{O}$, infrared and Mössbauer studies of which have been carried out then structures suggested on the basis of spectroscopic data.

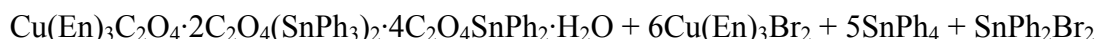
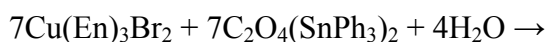
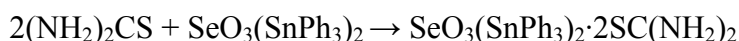
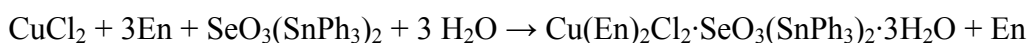
EXPERIMENTAL

On mixing H_2SeO_3 or $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with SnPh_3OH both in EtOH in 1/2 ratio respectively, a precipitate of $\text{SeO}_3(\text{SnPh}_3)_2$ or $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ is obtained [12]. When the selenite derivative is mixed with ethylenediamine (En) and CuCl_2 or thiourea molecule as ethanolic solutions in 1/3/1 or 1/2 ratio respectively, a blue powder (**A**) or a white powder (**B**) are obtained after a slow solvent evaporation. The $\text{Cu}(\text{En})_3\text{Br}_2$ complex is obtained by mixing in EtOH CuBr_2 with ethylenediamine in 1/3 ratio respectively. The obtained precipitate, stirred no less than two hours, has been filtered and dried under P_2O_5 . When the $\text{Cu}(\text{En})_3\text{Br}_2$ complex in hot MeOH is mixed with $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ in EtOH in 1/1 ratio, a blue precipitate (**C**) is obtained, stirred no less than two hours, filtered and dried under P_2O_5 . The analytical data reported below allow suggesting the following formulae (Table 1).

Table 1. Suggested formulae of synthesized compounds

	Suggested formulae	Chemical composition (% mass)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
A	$\text{Cu}(\text{En})_2\text{Cl}_2 \cdot \text{SeO}_3(\text{SnPh}_3)_2 \cdot 3\text{H}_2\text{O}$	42.30	42.40	4.62	4.52	4.93	4.75
B	$\text{SeO}_3(\text{SnPh}_3)_2 \cdot 2\text{SC}(\text{NH}_2)_2$	46.62	46.43	3.88	3.80	5.72	5.60
C	$\text{Cu}(\text{En})_3\text{C}_2\text{O}_4 \cdot 2\text{C}_2\text{O}_4(\text{SnPh}_3)_2 \cdot 4\text{C}_2\text{O}_4\text{SnPh}_2 \cdot \text{H}_2\text{O}$	49.42	49.50	4.04	4.08	2.96	2.86

The equations of the three reactions are:



The infrared data are given in cm^{-1} and the Mössbauer ones in mm^{-1} . Infrared abbreviations (w: weak; m: medium; s: strong; vs: very strong). Mössbauer abbreviations (IS = isomer shift, QS = quadrupole splitting, Γ = width at half height, A = area). The infrared spectra were recorded at the University of Cheikh Anta Diop Dakar by means of a Bruker FT-IR type, the sample being as Nujol mulls using CsI

windows. The ^{119}Sn Mössbauer spectra were measured at the University of Munich, Germany, with a source of $^{119\text{m}}\text{Sn}$ in a matrix of CaSnO_3 . Both the source and the absorber were kept at 4.2 K in a liquid helium bath cryostat. The Mössbauer spectrometer was operated with a sinusoidal velocity waveform, a scintillation detector being used for gamma-ray detection. The isomer shifts are referred to the CaSnO_3 source. The elemental analyses were performed at the Microanalyses Centre of the Faculty of Pharmacy, University of Geneva, Switzerland. All the chemicals were from Aldrich or Merck Companies and used without any further purification.

RESULTS AND DISCUSSION

Let us consider the infrared data in cm^{-1} :

A: νSeO_3 : 676s, νSeO_3 : 745w, ρNH_2 : 1034s;

B: νSeO_3 : 728vs, νSeO_3 : 676vs;

C: νasCO_2 : 1691vs; 1598vs; νCO_2 : 1429vs, 1289vs, δCO_2 : 774s; νNH_2 : 3233s; ωNH_2 : 796s.

and Mossbauer data in mm.s^{-1} :

A: QS = 2.74; IS = 0.98;

B: QS = 2.83; IS = 0.96;

C: QS₁ = 1.90; IS₁ = 1.32; Area 51%; QS₂ = 2.82; IS₂ = 1.25; Area 49%.

The values of the QS of the complex (**A**) and (**B**) show a coordinated SnPh_3L ($\text{L} = \text{Cl}$, $\text{SC}(\text{NH}_2)_2$) (for free SnPh_3Cl QS = 2.55 mm.s^{-1}) and a *trans* coordinated SnPh_3 residue [13, 14] that allows to suggest a discrete structure; the SeO_3^- is bi-unidentate and the environment around the tin (IV) centre being dissymmetrical trigonal bipyramidal (Figures 1 and 2).

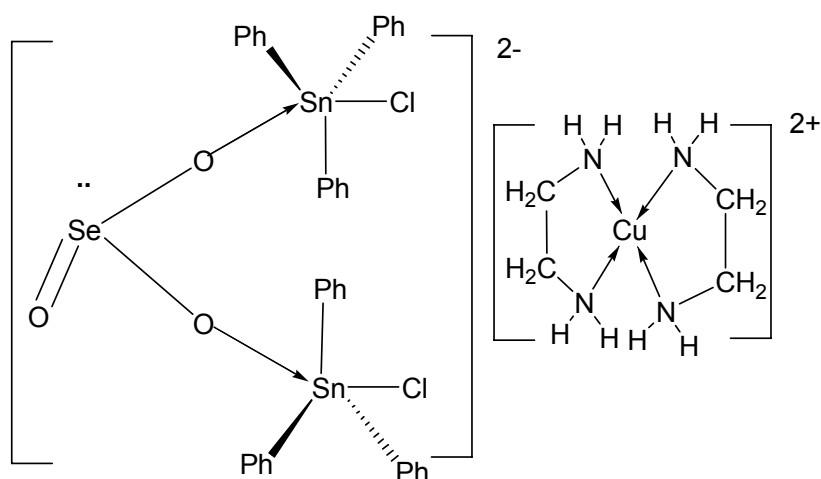


Figure 1. Suggested structure for compound **A**

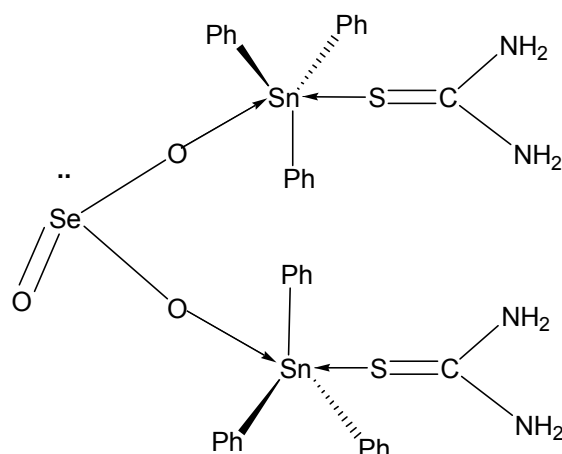


Figure 2. Suggested structure for compound **B**

The IR spectrum of the complex **C** shows two bands in the stretching region of the oxalate allowing suggesting a non centrosymmetrical anion. The IR spectrum of $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ is fully present in the spectrum of **C** with the characteristic doublet at $796/774\text{ cm}^{-1}$. The values of the quadrupole splitting are consistent with the presence of two types of tin (IV) in the ratio 1/1: one SnPh_2 residue is in a *cis* octahedrally coordinated environment ($\text{QS}_1 = 1.90\text{ mm.s}^{-1}$), the other one being tetrahedral ($\text{QS}_2 = 2.82\text{ mm.s}^{-1}$) as in free $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$. The compound **C** can be seen as an insertion compound between $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ and the remaining compound $[\text{Cu}(\text{en})_3]\text{C}_2\text{O}_4 \cdot 4\text{SnPh}_2\text{C}_2\text{O}_4$. This last compound has a discrete ionic structure with *cis* coordinated SnPh_2 residues (Figure 3).

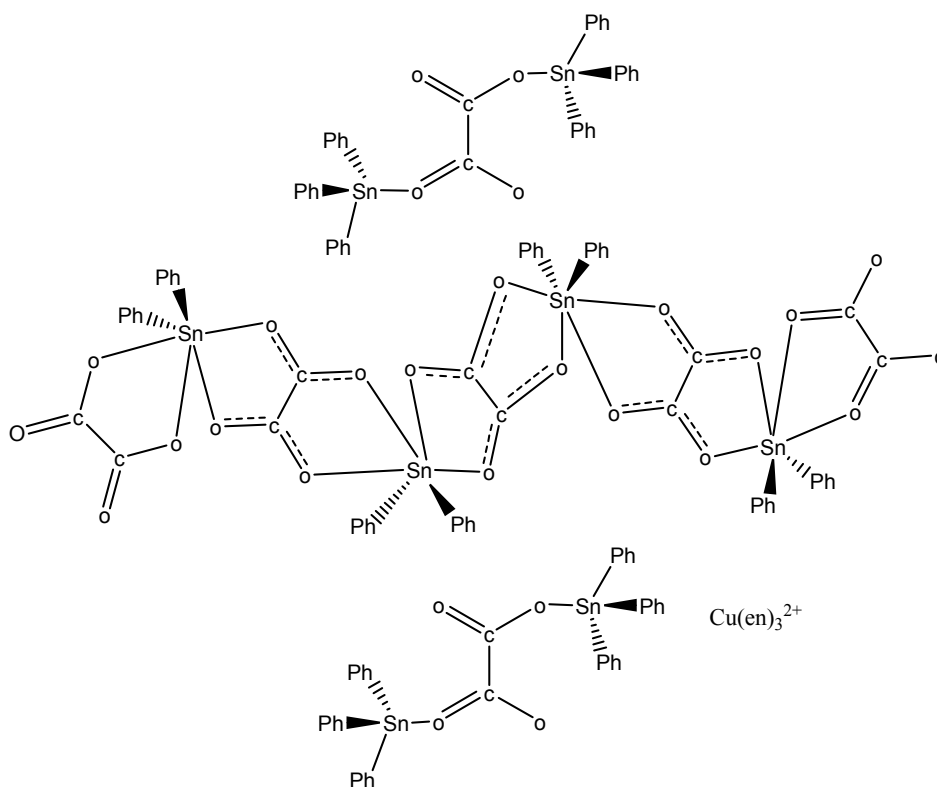


Figure 3. Suggested structure for compound **C**

CONCLUSION

In all the complexes, the structures are discrete, the environment around the tin being *trans* trigonal bipyramidal. The selenite and oxalate anions behave as coordinating ligands (bidentate mono- or bichelating)

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