

Three Selenate New Organotin (IV) and Magnesium Chloride Adducts: Synthesis and Spectroscopic Study

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Abstract: By allowing H_2SeO_4 , Cy_2NH , CyNH_2 or Bz_2NH to react respectively with SnPh_3Cl (in methanol), SnPh_2Cl_2 (in water + methanol) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (in methanol) in specific ratios, the studied complexes are obtained. The suggested structures are discrete and polymer, the environment of the tin center being trans trigonal bipyramidal (compound 1), tetrahedral (compound 2) and octahedral (compound 3), the anions behaving as a bidentate selenate.

Key words: Bidentate, discrete structures, SnPh_3Cl , SnPh_2Cl_2 or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ react, selenate, infinite chain hydrogen bonds, monochelating monodentate, trigonal bipyramidal or tetrahedral environments, C_{2v} symmetry, magnesium.

1. Introduction

Many applications (medicine, industry, agriculture, pharmaceutical ...) have been found in organotin (IV) family [1, 2]. Many research groups have been focusing on synthesizing new molecules belonging to this family for both structural aspects and biological tests [3-7]. Our group has yet synthesized hundreds and hundreds of new molecules that were reported in many papers [8-15]. We present here the study of the interactions between H_2SeO_4 , Cy_2NH and SnPh_3Cl in methanol (compound 1); H_2SeO_4 , CyNH_2 and SnPh_2Cl_2 in water + methanol (compound 2); H_2SeO_4 , Bz_2NH and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in methanol (compound 3) which have yielded the studied complexes. Spectroscopies studies have been carried out and the structures were suggested based on the spectroscopic data.

2. Experimental

The compound 1 is obtained by a methanolic (MeOH) solution of H_2SeO_4 , Cy_2NH and SnPh_3Cl in 1/2/2 ratio, the compound 2 is obtained by a (water+methanolic) solution of H_2SeO_4 , CyNH_2 and SnPh_2Cl_2 in 1/2/1 ratio

and the compound 3 is obtained by a methanolic solution of H_2SeO_4 , Bz_2NH and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 1/2/1 ratio. All the mixtures were given after 2 h of ambient temperature, then filtered before being submitted to a slow solvent evaporation white powder for both compounds. The analytical data allow suggesting the following formulae (Table 1).

The elemental analyses have been obtained from the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France. The ^{119}Sn NM 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 (Infrared) spectra of the compounds were recorded at room temperature using an FTIR (Fourier Transform Infrared Spectrometer) 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 4,500 to 400 cm^{-1}) in the form of suspension of powders in Nujol or crushed dry. The UV-visible spectra have been obtained from the spectrometer at the University Cheikh Anta Diop Dakar.

Table 1 Suggested formulae of synthesized compounds and the elemental analyses.

Compound	Chemical formulae	Elemental analyses (%)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
1	SeO ₄ (SnPh ₃) ₂ ·2MeOH	50.39	50.32	4.22	4.32	0.00	0.00
2	(CyNH ₃) ₂ [(SeO ₄) ₂ SnPh ₂]	37.97	37.95	5.07	5.24	3.69	3.67
3	(Bz ₂ NH ₂) ₂ [SeO ₄ MgCl ₂ (H ₂ O) ₂]	34.42	34.16	5.54	5.66	5.73	5.94

3. Results and Discussion

Let us consider the IR, ¹¹⁹Sn NMR (Nuclear Magnetic Resonance) and UV-visible data. IR (cm⁻¹): - for 1: ν(CH₃) = 2,940(br); ν(OH) = 3,100(br); δ (NH) = 1,591(s);

δ (OH) = 1,337(m); ν_{as}(SeO₄²⁻) = 894(vs), 851(s), 849(s); ν(SnPh₃) = 721(vs), 692(vs); ν(Sn-O) = 587(vs)

- for 2: ν(NH) = 2,889(br); δ (NH) = 1,455(s); ν_{as}(SeO₄²⁻) = 877(s), 850(w), 829(s); ν(Ph) = 755-702(vs); ν(Sn-O) = 536(vs)

- for 3: ν(NH) = 2,930(br); ν(OH) = 3,342(br); δ (NH) = 1,598(m); δ (OH) = 1,385(s); ν_{as}(SeO₄²⁻) = 893(s), 860(vs), 849(s); ν(Mg-O) = 596(m) ¹¹⁹Sn NMR (ppm): for 1: δ = -220

UV-visible (nm): for 1: λ_{max} = 295 ; for 2: λ_{max} = 296; for 3: λ_{max} = 259; 296.

3.1 SeO₄(SnPh₃)₂·2MeOH (1)

While considering the IR (Fig. 4) of the SeO₄(SnPh₃)₂·2MeOH derivative, the breakup of T₂ into several bands 894, 851, and 849 cm⁻¹ in the valence zone of selenate shows the presence of a selenate ion with non-T_d symmetry, it has C_{2v} symmetry. The doublet at 721 and 692 cm⁻¹ is assigned to the phenyl group of the SnPh₃ residue and the band at 588 cm⁻¹ corresponding to the Sn-O [16] vibration. On the ¹¹⁹Sn NMR spectrum (Fig. 6), the only signal at -220 ppm indicates the presence of a single type of pentacoordinated tin in the structure. The only strong absorption at 295 nm (Fig. 5) attributed to n→π* transitions, reflects the mesomeric effect observed on the free oxygen doublets of selenate. We propose a discrete structure (Fig. 1) with a bidentate selenate bridging the SnPh₃ residues, each of which is coordinated by a methanol molecule, the

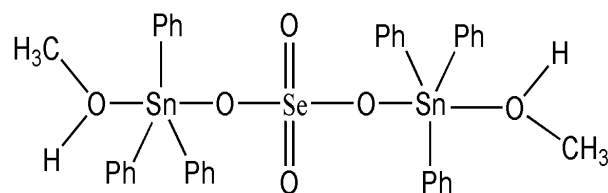
environment around the tin center being trans trigonal bipyramidal.

3.2 (CyNH₃)₂[(SeO₄)₂SnPh₂] (2)

The broad absorption spreading from 2,800 cm⁻¹ to 2,900 cm⁻¹ (Fig. 7) indicates the existence of hydrogen bonds in the compound 2. The breakup of T₂ into several bands 894, 851, and 849 cm⁻¹ in the valence zone of selenate shows the presence of a selenate ion with non-T_d symmetry, it has C_{2v} symmetry. The two bands at 752 and 702 cm⁻¹ are assigned to the phenyl groups of the SnPh₂ residue. The ν_{as}(SnPh₂) band appears weak at 536 cm⁻¹ in agreement with a linear SnPh₂ residue. The only strong absorption at 295 nm (Fig. 8) assigned to n→π* transitions, reflects the mesomeric effect observed on the free oxygen doublets of selenate. The suggested polymer structure contains an anion bidentate a SnPh₂ linear and by cations through NH...O hydrogen bond, finally infinite chain (Fig. 2).

3.3 (Bz₂NH₂)₂[SeO₄MgCl₂(H₂O)₂] (3)

On the infrared spectrum (Fig. 9), the broad band centered at 2,930 cm⁻¹ confirms the presence of hydrogen bonds via the Bz₂NH₂⁺ cation and that at 3,342 cm⁻¹ confirms the presence of water molecules. At low frequency the average band at 596 cm⁻¹ confirms the presence of Mg—O bond [16]. The splitting of T₂

**Fig. 1** Proposed structure for the compound 1.

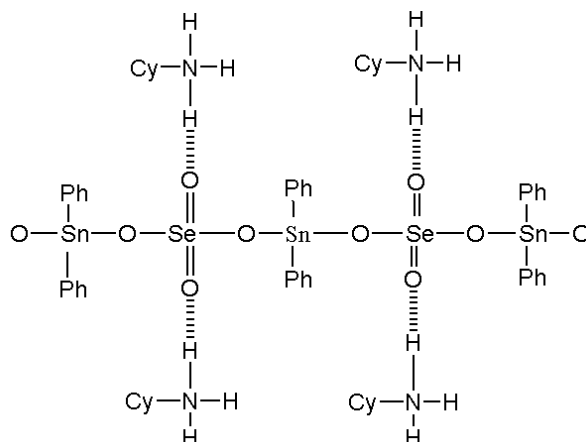


Fig. 2 Proposed structure for the compound 2.

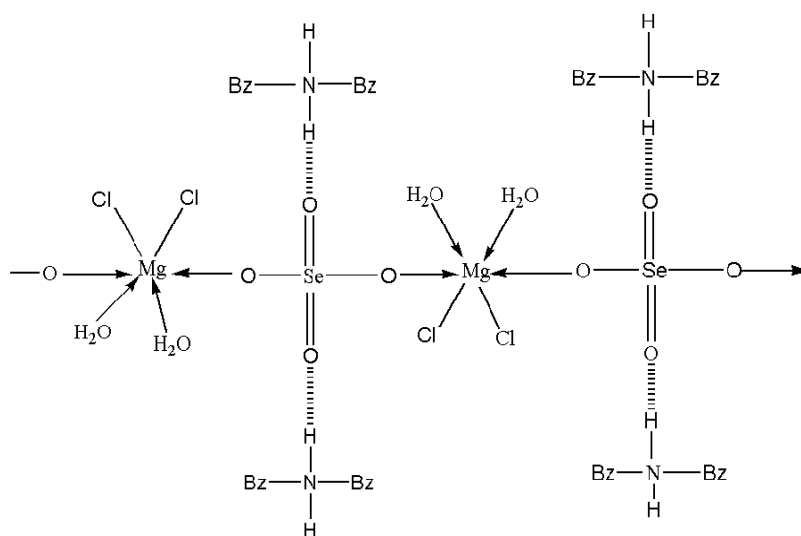


Fig. 3 Proposed structure for the compound 3.

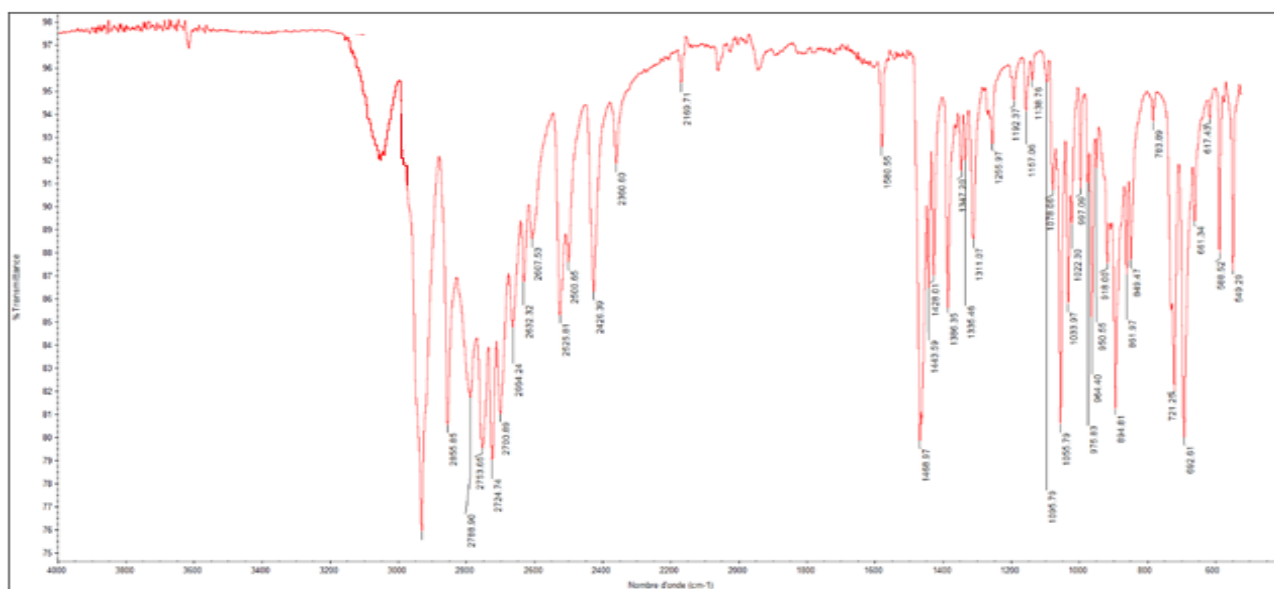


Fig. 4 IR spectrum compound 1.

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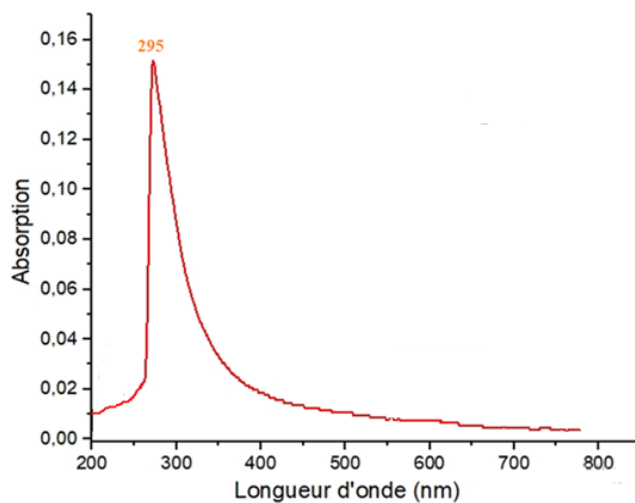


Fig. 5 UV-visible spectrum compound 1.

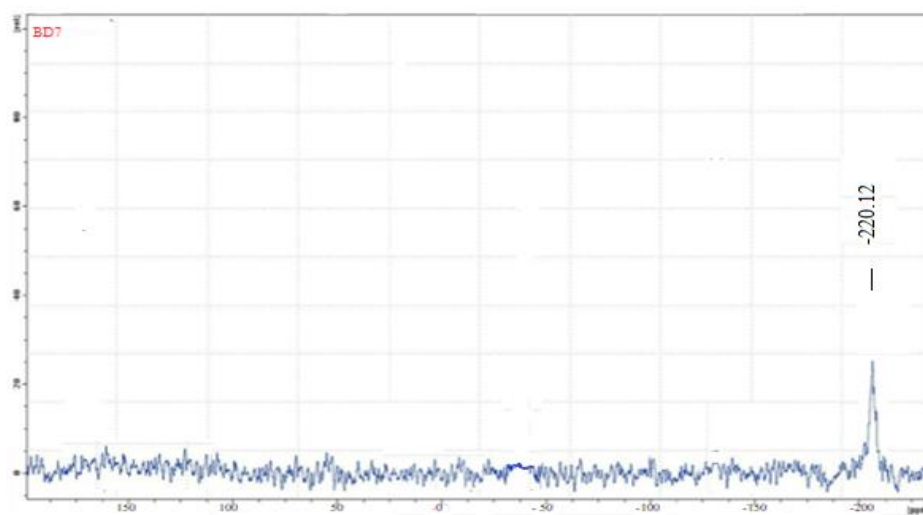


Fig. 6 ^{119}Sn NMR spectrum compound 1.

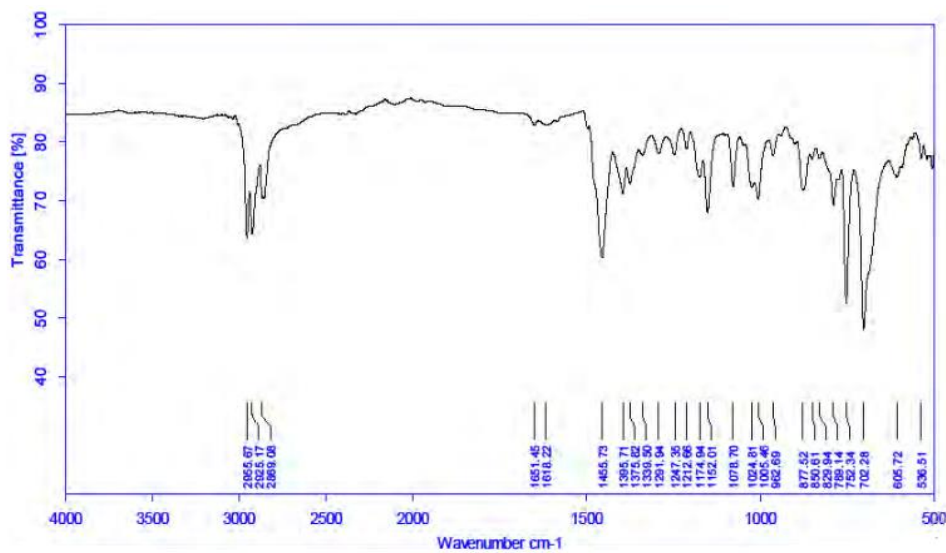


Fig. 7 IR spectrum compound 2.

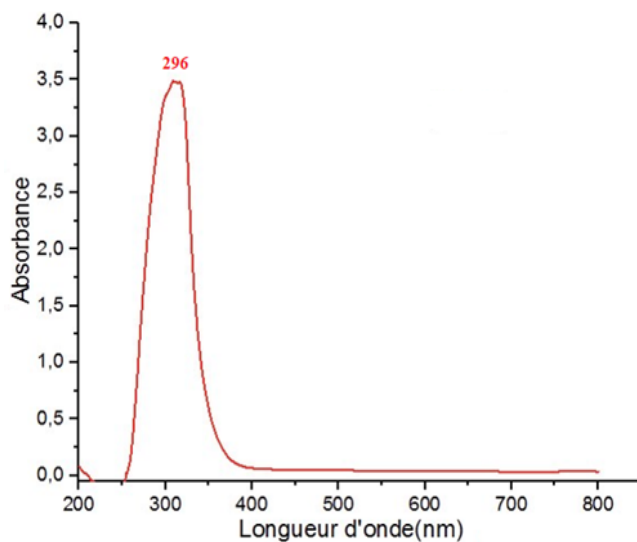


Fig. 8 UV-visible spectrum compound 2.

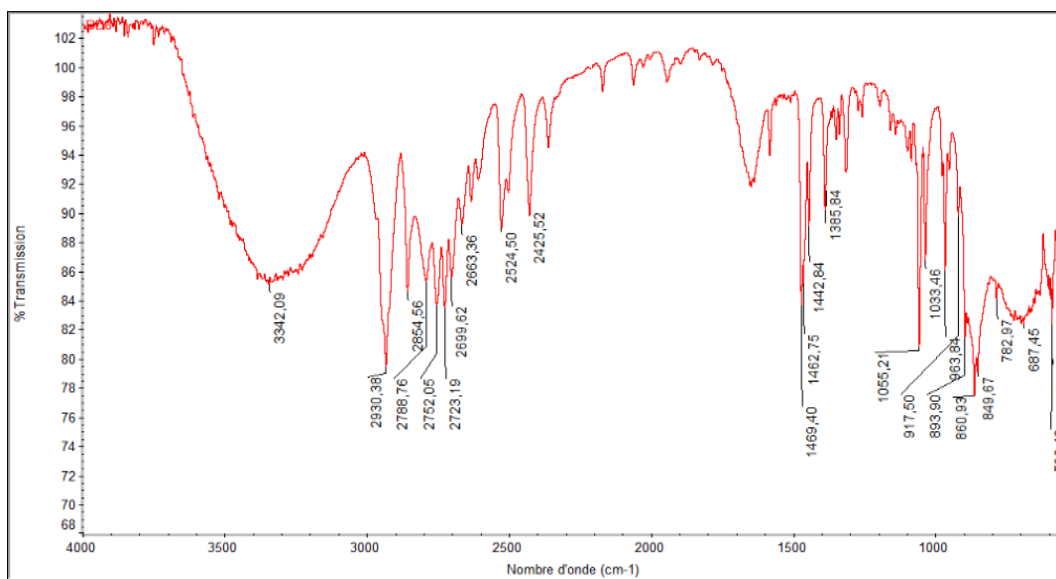


Fig. 9 IR spectrum compound 3.

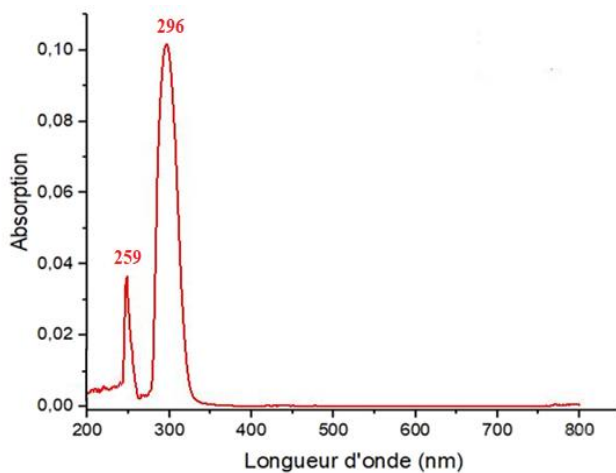


Fig. 10 UV-visible spectrum compound 3.

into several bands in the valence zone of the selenate ion shows that it is not of Td symmetry. The bands at 893, 860 and 849 cm⁻¹ show that the selenate has C_{2v} symmetry. However, these two bands which appear at 259 nm and 296 nm on the UV-visible spectrum (Fig. 10) of the compound, can only be attributed respectively to the $\pi \rightarrow \pi^*$ transitions present in the aromatic ring of the benzyl group and to the $n \rightarrow \pi^*$ transitions. Based on the non-bonding electron pairs present on the oxygen atoms of the selenate anion, we propose an infinite chain structure (Fig. 3) with a bidentate selenate and the environment around the magnesium is octahedral. The selenate oxygens occupy the axial positions and the water molecules the equatorial positions.

4. Conclusion

The studied adducts have discrete and polymer structures with bidentate anion, the cations being involved in hydrogen bonding in the compound. The environment around the tin center is tetrahedral (compound 2), trans trigonal bipyramidal compound (1) and the magnesium center is octahedral (compound 3). For compound 2 and 3 the cation may interact via hydrogen bonds leading to a supramolecular architecture. For the compound 1, the methanol molecule is coordinated to the tin (IV) atom.

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Conflicts of Interest

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

List of Notations

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

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