

NEW ORGANOTIN (IV) HETEROPOLYNUCLEAR COMPLEXES CONTAINING $[\text{SnPh}_2\text{Cl}_2\text{X}]^-$ (X = Cl, Br): SYNTHESIS AND SPECTROSCOPIC STUDIES

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Abstract: Four $[\text{SnPh}_2\text{Cl}_2\text{X}]^-$ (X = Cl, Br) containing complexes with metal complexes adverse cations have been synthesized and studied by infrared and Mössbauer spectroscopy. The suggested structures are ionic, $\text{SnPh}_2\text{Cl}_2\text{X}^-$ as mononuclear, a binuclear or a trinuclear anion being in electrostatic interactions with the metal complex cation.

Keywords: *mono-, bi-, trinuclear $[\text{SnPh}_2\text{Cl}_2\text{X}]^-$, infrared, Mössbauer, discrete structures*

INTRODUCTION

The biological activity and industrial applications of SnPh_2 residue containing compounds have been outlined by several authors [1 – 5]. In a recent study Garcia-Seijo *et al.* [6] have transferred the chloride ion on SnPh_2Cl_2 from Pd and Pt chloro complexes and have obtained mixed metal complexes containing $\text{SnPh}_2\text{Cl}_3^-$ and $\text{SnPh}_2\text{Cl}_4^{2-}$ complex-anions. Our group, in the organotin (IV) field has yet published several papers [7 – 12]. We have initiated here, for widening the organotin (IV) family, the study of the interactions between ethylenediamine complexes of MX_2 ($\text{M} = \text{Zn}, \text{Cu}, \text{Co}$; $\text{X} = \text{Cl}, \text{Br}$) and SnPh_2Cl_2 for obtaining mixed new tin – transition metal new $[\text{SnR}_2\text{Cl}_3]^-$ containing complexes. This study has yielded four new compounds, infrared and Mössbauer studies of which have been carried out and structures suggested on the basis of spectroscopic data.

EXPERIMENTAL

A solution is obtained on mixing ethylenediamine (en) with CuCl_2 and SnPh_2Cl_2 as ethanolic solutions in ratio 3 : 1 : 2, which gives a powder when a slow solvent evaporation is allowed. The other (en) complexes were obtained as precipitates on mixing MX_2 ($\text{M} = \text{Cu}, \text{Co}, \text{Zn}$; $\text{X} = \text{Cl}, \text{Br}$) in ethanol with (en) in ethanol in the ratio 1 : 3 respectively. When these ethylenediamine complexes in hot EtOH were mixed with SnPh_2Cl_2 in the ratio 1 : 2, a powder is obtained after a slow solvent evaporation. The analytical data reported below allow suggesting the following formulae, presented in Table 1.

Table 1. Suggested formulae for **A – D** compounds, based on elemental analyses

Compound	Formulae	Color	Chemical composition (% by weight)					
			C		H		N	
			Calc.	Found	Calc.	Found	Calc.	Found
A	$\text{Cu(en)}_2\text{Cl}_2 \cdot 2\text{SnPh}_2\text{Cl}_2$	green	35.69	36.30	3.85	4.40	5.95	6.22
B	$\text{Cu(en)}_2\text{Br}_2 \cdot 2\text{SnPh}_2\text{Cl}_2$	green	32.60	31.30	3.52	3.40	5.43	5.58
C	$\text{Zn(en)}_2\text{Cl}_2 \cdot 2\text{SnPh}_2\text{Cl}_2$	white	35.62	36.00	3.84	4.10	5.93	5.72
D	$\text{Co(en)}_2\text{Cl}_2 \cdot 3\text{SnPh}_2\text{Cl}_2$	orange	37.49	38.09	3.62	4.55	4.37	4.42

The IR spectra were recorded at Cheikh Anta Diop University – Dakar, Sénégal, using a Bruker FTIR spectrometer, the samples being as Nujol mulls using KBr optical windows. The Mössbauer spectra were obtained at the University of Rouen, France, as yet reported [13]. The elemental analyses have been performed by the "Laboratoire de Mesures Physiques", Montpellier 2 University, France. The infrared data are given in cm^{-1} and the Mössbauer ones in $\text{mm} \cdot \text{s}^{-1}$. Infrared abbreviations: s (strong), m (medium). Mössbauer abbreviations: (IS = Isomer Shift, QS = Quadrupole Splitting, Γ = Width at Half Height, A = Area). All the chemicals were from Aldrich and used without any further purification.

RESULTS AND DISCUSSION

Let us consider the infrared data dealing with NH_2 group and Mössbauer data of **A-D**:

A: $\nu(\text{NH}_2) = 3585 \text{ s}, 3298 \text{ s}, 3232 \text{ s}$; $\delta\text{NH}_2 = 1601 \text{ m}$; $\rho\text{NH}_2 = 1044 \text{ s}$; $\omega\text{NH}_2 = 816 \text{ m}$;

B: $\nu(\text{NH}_2) = 3585 \text{ s}, 3297 \text{ s}, 3229 \text{ s}$; $\delta\text{NH}_2 = 1571 \text{ m}$; $\rho\text{NH}_2 = 1045 \text{ s}$; $\omega\text{NH}_2 = 816 \text{ m}$;

C: $\nu(\text{NH}_2) = 3586 \text{ s}, 3296 \text{ s}, 3230 \text{ s}$; $\delta\text{NH}_2 = 1601 \text{ m}$; $\rho\text{NH}_2 = 1033 \text{ s}$; $\omega\text{NH}_2 = 818 \text{ m}$;

D: $\nu(\text{NH}_2) = 3295 \text{ s}, 3230 \text{ s}$; $\delta\text{NH}_2 = 1571 \text{ s}$; $\rho\text{NH}_2 = 1061 \text{ s}$; $\omega\text{NH}_2 = 791 \text{ m}$;

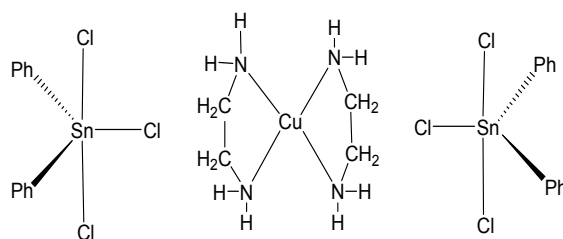
A: $\text{IS} = 1.07$; $\text{QS} = 2.63$; $\Gamma = 1.1$; $\text{A}\% = 100$;

B: $\text{IS} = 1.09$; $\text{QS} = 2.60$; $\Gamma = 0.99$; $\text{A}\% = 100$;

C: $\text{IS} = 0.99$; $\text{QS} = 2.17$; $\Gamma = 1.11$; $\text{A}\% = 100$ (1 doublet);

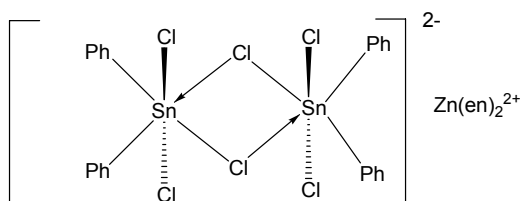
D: $\text{IS} = 1.25/1.28$; $\text{QS} = 2.43/3.32$; $\Gamma = 0.94$; $\text{A}\% = 35/65$;

The values of the quadrupole splitting of **A** ($2.63 \text{ mm}\cdot\text{s}^{-1}$) and **B** ($2.60 \text{ mm}\cdot\text{s}^{-1}$) are similar to the value found for $[\text{Pd}(\text{triphos})\text{Cl}][\text{SnPh}_2\text{Cl}_3]^-$ – $2.67 \text{ mm}\cdot\text{s}^{-1}$ and allow to suggest a trigonal bipyramidal environment around the tin centre as found from the X-ray structure determination of Garcia-Seijo *et al.* [6]: the structure is reported on Scheme 1 (the presence of a wide absorption on the infrared spectrum around 2900 cm^{-1} indicates $\text{NH}\cdots\text{Cl}$ hydrogen bonds)

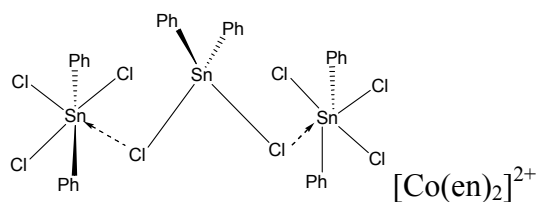


Scheme 1.

The value of the quadrupole splitting of the complex **C** is consistent with a *cis* octahedrally coordinated SnPh_2 residue according to Platt *et al.* [14, 15], allowing to suggest the dimeric structure reported on Scheme 2.



Scheme 2.



Scheme 3.

The complex **D** contains two types of tin centre, one *trans* octahedral (Sn_1 , $\text{QS} = 3.34 \text{ mm}\cdot\text{s}^{-1}$), the other being tetrahedral (Sn_2 , $\text{QS} = 2.43 \text{ mm}\cdot\text{s}^{-1}$) in the ratio $\text{Sn}_1/\text{Sn}_2 = 2$. The suggested structure is built on linking two $[\text{SnPh}_2\text{Cl}_3]^-$ complex-anions monocoordinated by the central SnPh_2Cl_2 molecule. The environment around the external tin (IV) centres is then dissymmetrically octahedral. A similar trinuclear complex-anion $[\text{Sn}_3\text{Me}_6\text{Cl}_8]^{2-}$ has yet been reported by Shimizu *et al.* [16]. The

suggested structure is reported on Scheme 3 – the Lewis basicity of SnPh_2Cl_2 towards $[\text{SnPh}_2\text{Cl}_3]^-$ complex-anions is noteworthy; the enhancement of the quadrupole splitting of $[\text{SnPh}_2\text{Cl}_3]^-$ compared to its value in **A** indicates coordination.

CONCLUSION

The polyheteronuclear complexes studied have all ionic structures and contain mononuclear $[\text{SnPh}_2\text{Cl}_3]^-$, dimeric $[\text{SnPh}_2\text{Cl}_3]_2^{2-}$, trinuclear $[\text{SnPh}_2\text{Cl}_2.(\text{SnPh}_2\text{Cl}_3)_2]^{2-}$, the adverse cation being $[\text{M}(\text{en})_2]^{2+}$, the environment around the tin centre being octahedral, tetrahedral or trigonal bipyramidal. Interactions between the complex-cation and the anionic components through $\text{NH}\dots\text{Cl}$ hydrogen bonds in all the compounds can be outlined.

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