

NEW ORGANOTIN (IV) FORMIATO ADDUCTS. SYNTHESIS AND SPECTROSCOPIC STUDIES

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Abstract: Five new formiato complexes have been synthesized and studied by spectroscopic methods. The structures, when the cations are involved through hydrogen bonds, are supramolecular. The anion behaves as a monocoordinating ligand. The existence of tetrahedral $\text{SnBu}_2(\text{HCO}_2)_2$ has been evidenced in this work.

Keywords: *formiato complexes, IR, Mössbauer, monocoordinating ligand, supramolecular structures, tetrahedral $\text{SnBu}_2(\text{HCO}_2)_2$*

INTRODUCTION

The various applications found for some molecules of organotin (IV) family explain the seek of new compounds belonging to this group, carried out by several researchers [1 – 8]. Our group has yet published several papers dealing with [9 – 14].

In the framework of our research work on the coordination ability of oxyanions within organotin (IV) family, we report here the study of the interactions between formic acid salts with dicyclohexylammonium as adverse cation and SnR_2Cl_2 ($\text{R} = \text{Ph}, \text{Bu}$) which have yielded five new formiato adducts. Infrared, Raman and Mössbauer studies have been carried out; then structures were suggested on the basis of spectroscopic data.

EXPERIMENTAL

The formic acid salt $\text{Cy}_2\text{NH}_2\text{HCO}_2$ has been obtained on mixing HCO_2H acid with dicyclohexylamine both in methanol in 1/1 ratio. The obtained precipitate, stirred no less than two hours, has been filtered and dried under P_2O_5 .

When the formic acid salt are mixed with SnR_2Cl_2 ($\text{R} = \text{Ph}, \text{Bu}$) both in MeOH, a white powder is obtained after a slow solvent evaporation. The analytical data reported below, allow suggesting the following formulae (Table 1).

Table 1. Suggested formulae for the synthesized compounds

Comp.	% C		% H		% N		Suggested formulae
	C.	F.	C.	F.	C.	F.	
A	47.48	46.63	8.16	8.27	2.64	2.37	$\text{Cy}_2\text{NH}_2\text{HCO}_2 \cdot \text{SnBu}_2\text{Cl}_2$
B	59.71	59.30	8.35	8.38	4.10	3.98	$3\text{Cy}_2\text{NH}_2\text{HCO}_2 \cdot \text{SnPh}_2\text{Cl}_2$
C	51.22	51.30	8.67	8.72	3.26	3.36	$3\text{Cy}_2\text{NH}_2\text{HCO}_2 \cdot 2\text{SnBu}_2\text{Cl}_2$
D	45.37	45.26	7.50	7.69	1.60	1.63	$\text{Cy}_2\text{NH}_2\text{HCO}_2 \cdot 2\text{SnBu}_2(\text{HCO}_2)_2$
E	55.77	55.66	9.30	9.23	4.01	3.99	$\text{Cy}_2\text{NH}_2\text{HCO}_2 \cdot 2\text{SnBu}_2(\text{HCO}_2)_2 \cdot 4\text{Cy}_2\text{NH}_2\text{Cl}$

C. – calculated; F. – found

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

A: νCO_2 : 1594s, 1406s, 1545s, 1347s; δCO_2 : 716s; $\nu_{\text{as}}\text{SnC}_2$: 695s; $\nu_{\text{s}}\text{SnC}_2$: 594m;

B: νCO_2 : 1681s, 1560m; δCO_2 : 725sh;

C: νCO_2 : 1600vs, 1580m; $\nu_{\text{s}}\text{SnC}_2$: 595m;

D: νCO_2 : 1606s, 1580sh; $\nu_{\text{as}}\text{SnC}_2$: 676m; $\nu_{\text{s}}\text{SnC}_2$: 620s;

E: νCO_2 : 1640 vs, 1580s, 1500s; δCO_2 : 730m; $\nu_{\text{s}}\text{SnC}_2$: 620s

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

A: $\text{QS}_1 = 3.43$, $\text{QS}_2 = 2.91$; $\text{IS}_1 = 1.38$, $\text{IS}_2 = 1.34$; Γ : 0.94; 0.94; Area [%]: 50%; 50%;

B: $\text{QS} = 2.03$; $\text{IS} = 0.85$; Γ : 0.96; Area [%]: 100;

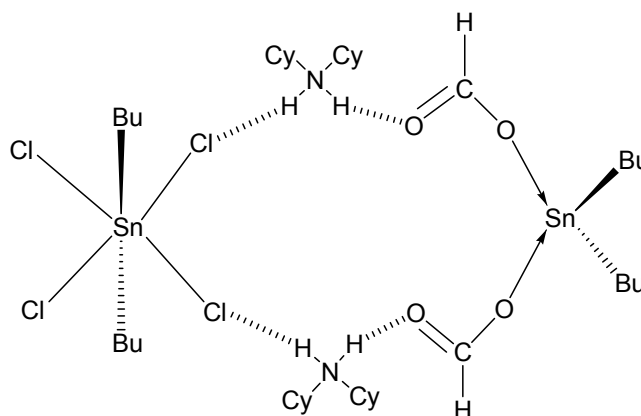
C: $\text{QS} = 3.31$; $\text{IS} = 1.39$; Γ : 0.92; Area [%]: 100;

D: $\text{QS} = 2.71$; $\text{IS} = 1.14$; Γ : 0.94; Area [%]: 100;

E: $\text{QS} = 2.63$; $\text{IS} = 1.17$; Γ : 1.09; Area [%]: 100.

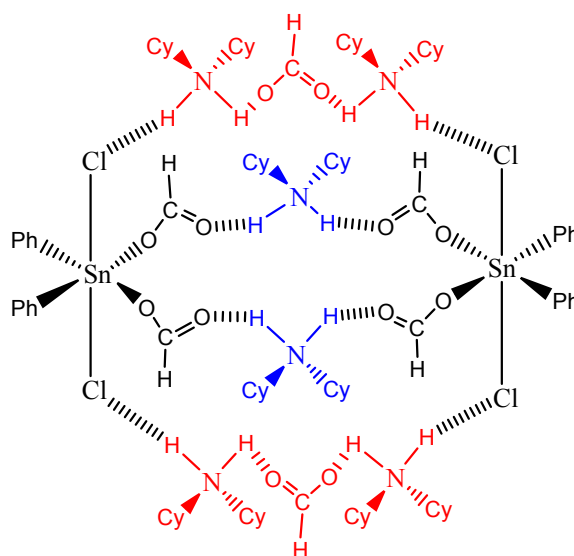
RESULTS AND DISCUSSION

The values of the quadrupole splitting of **A** are consistent with the presence of two types of tin (IV) in the ratio 1/1: one SnBu_2 residue is in a *trans* octahedrally coordinated environment, the other one being tetrahedral according to Platt and al [15, 16]. This allow to suggest an ionic structure containing $[\text{SnBu}_2\text{Cl}_4]^{2-}$ - *trans* coordinated SnBu_2 residue - and $\text{SnBu}_2(\text{HCO}_2)_2$ - tetrahedral environment -, the two entities being linked by hydrogen bonds responsible of absorption on the IR spectrum around 2850 cm^{-1} (Scheme 1).



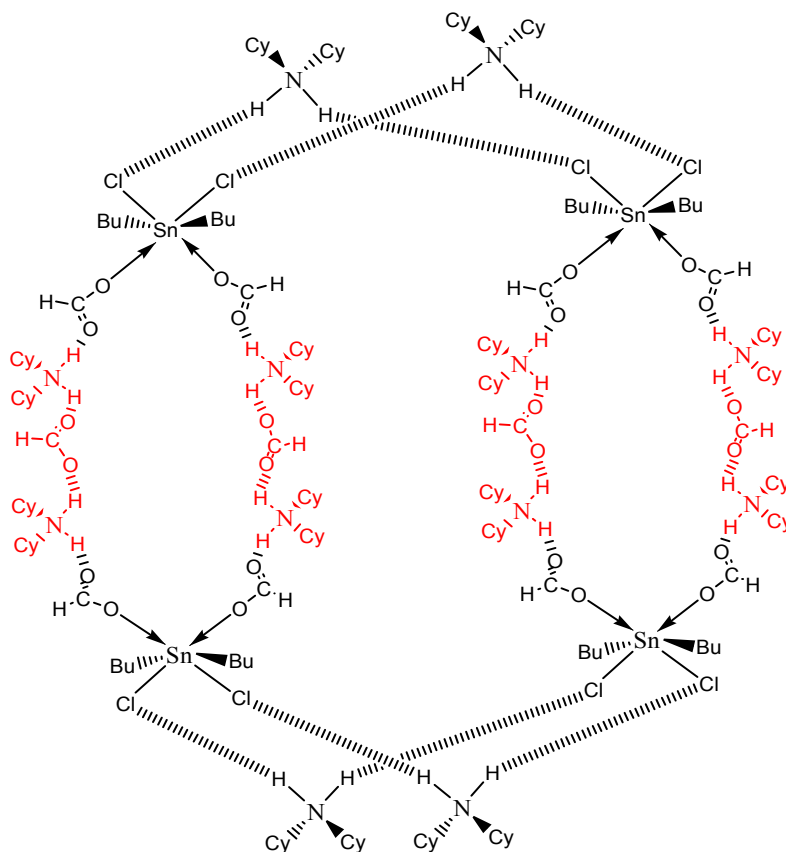
Scheme 1.

The value 2.03 mm.s^{-1} of the quadrupole splitting of the complex **B** is consistent with octahedrally *cis* coordinated SnPh_2 residues according to Platt *et al.* [15, 16] and allows to suggest a dimeric structure built from to monomeric $[\text{SnPh}_2\text{Cl}_2(\text{O}_2\text{CH})_2]^{2-}$ entities linked by dicyclohexylammonium ions, reinforced by “cation-anion-cation” hydrogen bonded strings bridging the chlorine atoms in axial positions (Scheme 2).



Scheme 2.

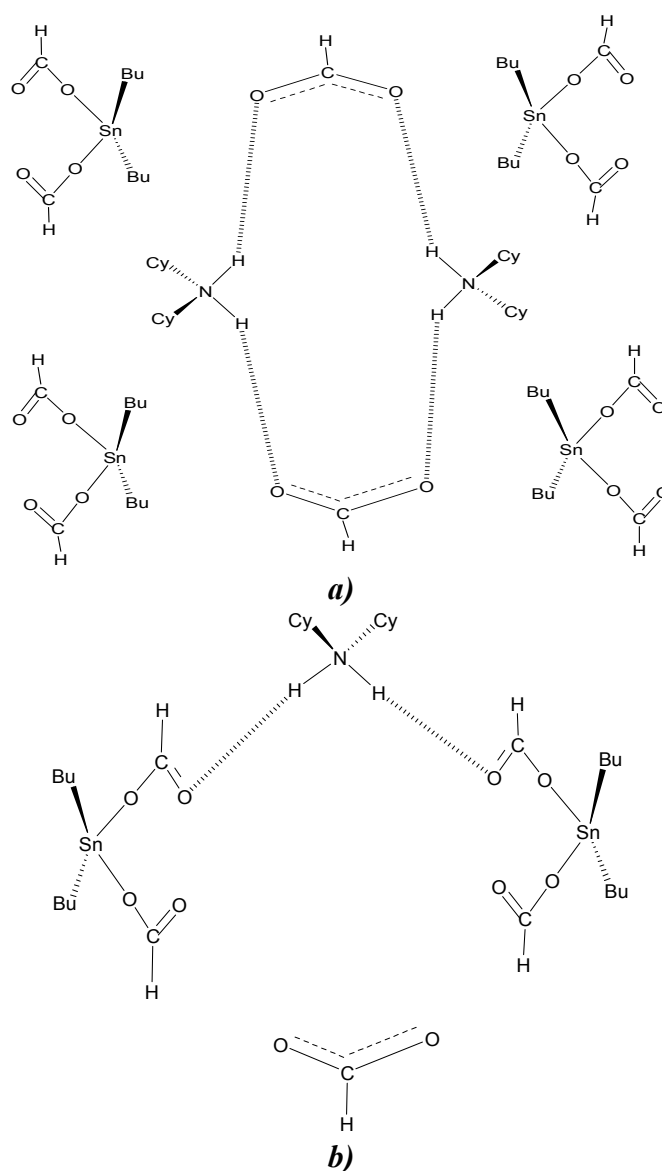
For the complex **C**, the IR and the Raman spectra shows respectively a medium band and a strong line in 595 cm^{-1} assigned to $\nu_s\text{SnBu}_2$. The Mössbauer spectrum indicates only one type of tin (IV) with a quadrupole splitting value of 3.31 mm.s^{-1} consistent with a dissymmetrical *trans* octahedral environment - $[\text{SnBu}_2\text{Cl}_2(\text{HCO}_2)_2]^{2-}$ - according to Platt *et al.* [15, 16]. The suggesting structure is a dimer of dimer with “cation-formiato-cation” hydrogen bonded strings and cations only bridging Cl atoms (Scheme 3).



Scheme 3.

The IR and Raman spectra of the complex **D** shows respectively a strong band and line both at 595 cm^{-1} assigned to $\nu_s\text{SnBu}_2$. The 2.71 mm.s^{-1} value of the quadrupole splitting allows suggesting a tetrahedral environment around the tin centre according to Platt *et al.* [15, 16]. The suggested structure is dimeric with a pair of anions connected by Cy_2NH_2^+ through hydrogen bonds, the four tetrahedral $\text{SnBu}_2(\text{HCO}_2)_2$ molecules being lattice ones or linked very weakly to the oxygen atoms of the hydrogen bonded pair (Schemes 4a and 4b).

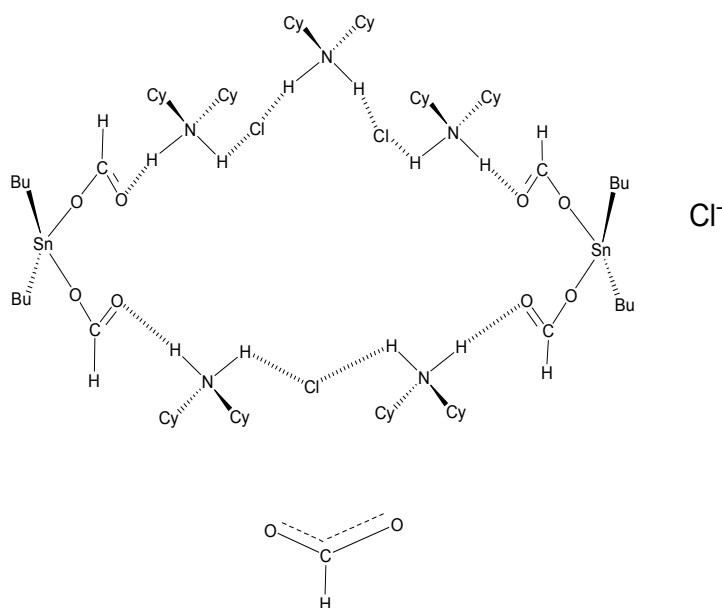
The IR spectrum of the complex **E** show a medium band around 595 cm^{-1} assigned to $\nu_s\text{SnBu}_2$ and allows to suggest a non linear SnBu_2 residue. The Mössbauer spectrum indicates essentially one type of tin IV with the value of quadrupole splitting 2.63 mm.s^{-1} consistent with tetrahedral environment around the tin atom according to Platt *et al.* [15, 16]. The compound **E** derives from compound **D** on adding four $\text{Cy}_2\text{NH}_2\text{Cl}$.

**Scheme 4.**

Therefore the suggested structure can be built from the structure of **D** on connecting the free oxygen atoms by $\text{NH}_2 \dots \text{Cl} \dots \text{NH}_2$ bridges (Scheme 5). The remaining chloride ions cannot be connected to the tin centres because of the value of the quadrupole splitting. They can be considered as adverse anions interacting electrostatically with the polynuclear entity.

CONCLUSION

All the formiato adducts in this work have discrete monomeric or dimeric structure. The formiate is involved through hydrogen bonds with the cation Cy_2NH_2^+ giving macromolecules. The environments of the tin centre are *trans* or *cis* octahedral, tetrahedral. The key role of the cations is noteworthy.



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