

**SYNTHESIS AND SPECTROSCOPIC STUDIES OF
(Cy₂NH₂)₂C₂O₄·2SnMe₂Cl₂, (Me₄N)₂C₂O₄·2SnMe₂Cl₂ AND
(Cy₂NH₂)₂C₂O₄·2SnMe₂(C₂O₄)₂(Cy₂NH₂)₂**

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Abstract: Three new oxalato organotin IV adducts and complex have been synthesized, their infrared and Mössbauer studies carried out. In the three compounds the coordination number of tin IV is 6, the SnMe₂ residue being linear, the oxalate anion behaving as a bichelating or a monocoordinating ligand. The structures, suggested from spectroscopic data, are all discrete. The key role of the non symmetrical cation Cy₂NH₂⁺ involved in NH---O and NH---Cl hydrogen bonds is noteworthy.

Key words: *tin IV, adducts, complex, trans octahedrally coordinated SnMe₂ residue, hydrogen bonds*

INTRODUCTION

In the seek of new organotin IV compounds because of the various applications discovered for complexes and derivatives containing SnMe_2 residue several papers have been reported by various groups [1 – 4]. The X ray structure of $\text{SnMe}_2(\text{C}_2\text{O}_4)_2(\text{Cy}_2\text{NH}_2)_2\cdot\text{H}_2\text{O}$ has been reported by Ng [5]: it consists of two monochelating oxalate anions, the water molecule being coordinated to the tin centre which is seven coordinated. In our group, we had yet reported various papers on organotin chemistry dealing with the coordinating ability of oxyanions [6 – 9] and have initiated here the study of the interactions between $(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ or $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and SnMe_2Cl_2 which have yielded two new oxalato SnMe_2Cl_2 adducts and a dinuclear oxalato SnMe_2 residue containing complex. Their infrared and Mössbauer studies have been carried out and structures suggested on the basis of spectroscopic data.

EXPERIMENTAL

The infrared spectra were recorded at the University of Cheikh Anta Diop Dakar (Senegal) by means of a BX FT-IR type or at the University of Padova (Italy) using a PE 580 or a Bruker FTIR spectrometer, the sample being as Nujol mulls, using CsI or polyethylene windows. Mossbauer spectra were obtained as described previously [10]. Infrared data are given in cm^{-1} (abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak), (vw) very weak). Mössbauer parameters are given in $\text{mm}\cdot\text{s}^{-1}$ (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height). The elemental analyses performed by the CNRS “Service Central d’Analyses” Vernaison-France, the laboratory of Microanalysis – University of Padova – Italy or the Microanalysis Centre – University of Bath – UK are reported in table 1.

Syntheses of salts and complexes

$(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ($\text{Cy} = \text{C}_6\text{H}_{11}$)

The complete neutralization of a water solution containing 1.82 g (10 mmol) of Cy_2NH_2 (Aldrich) with an aqueous solution containing 0.63 g (5 mmol) of $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (Aldrich) gives a white precipitate stirred no less than two hours, filtered and dried at 65°C . Analytical data - % calculated (% found) - C = 68.99 (69.02), H = 10.69 (10.59), N = 6.19 (6.20).

$(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ has been obtained on mixing a water solution of Me_4NOH (20%) with oxalic acid in 2/1 ratio; the white powder collected after solvent evaporation is recrystallized in EtOH. Analytical data - % calculated (% found) - C = 44.10 (44.02), H = 10.36 (10.50), N = 10.29 (10.15).

When $(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ in MeOH is mixed with SnMe_2Cl_2 (Aldrich) in absolute ethanol in 1/2 ratio, a white precipitate is obtained.

The mixture of ethanolic solutions of $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ with SnMe_2Cl_2 in 1/2 ratio gives a white precipitate.

When $(\text{Cy}_2\text{NH})_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and SnMe_2Cl_2 in 95% hydrated ethanol are mixed in 2/1 ratio a white powder is obtained after a slow solvent evaporation.

All the precipitates have been stirred no less than two hours and washed with hot ethanol.

Table 1. Results of the elemental analyses [% cal (% found)]

Complexes	% C	% H	% N	% Cl	% Sn
A $(\text{Cy}_2\text{NH})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2\text{Cl}_2$	40.17 (40.22)	6.85 (6.82)	3.14 (3.07)	15.92 (16.00)	26.61 (26.50)
B $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2\text{Cl}_2$	24.91 (24.87)	5.12 (5.33)	3.96 (4.14)	21.02 (20.49)	35.14 (35.31)
C $(\text{Cy}_2\text{NH})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2(\text{C}_2\text{O}_4)_2(\text{Cy}_2\text{NH})_2$	57.6 (57.35)	9.01 (8.81)	4.37 (4.58)	traces	-

RESULTS AND DISCUSSION

In tables 2 and 3 are respectively summarized the assignments of the main bands of the complexes and their Mössbauer parameters.

Table 2. Attribution of the main bands

Complexes	vas COO^-	vs COO^-	δ COO^-	vas SnC_2	vs SnC_2
A $(\text{Cy}_2\text{NH})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2\text{Cl}_2$	1637s	1313m 1271m	785s	587m	-
B $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2\text{Cl}_2$	1637vs	1346m 1305s	800vs	575m	-
C $(\text{Cy}_2\text{NH})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2(\text{C}_2\text{O}_4)_2(\text{Cy}_2\text{NH})_2$	1637s	1313m 1271m	785s	587m	515vw

Very strong: vs; strong: s; medium: m; very weak: vw

Table 3. Mössbauer parameters

Complexes	δ (mm.s^{-1})	ΔE (mm.s^{-1})	Γ (mm.s^{-1})	A
A $(\text{Cy}_2\text{NH})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2\text{Cl}_2$	1.37	4.52	1.07	100
B $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2\text{Cl}_2$	1.58	4.36	0.90	100
C $(\text{Cy}_2\text{NH})_2\text{C}_2\text{O}_4 \cdot 2\text{SnMe}_2(\text{C}_2\text{O}_4)_2(\text{Cy}_2\text{NH})_2$	1.64	4.19	0.93	100

The absence of vsSnC_2 expected around 515 cm^{-1} on the spectra of **A** and **B**, its appearance as a very weak band on the spectrum of **C** and the high values of the quadrupole splitting allow to conclude to the presence of linear SnMe_2 residues according to Group Theory [11] and Bancroft and Platt [12]. For the compound **A** a dimeric cage structure with two bichelating oxalate anions is suggested, the cations ensuring the cohesion of the two dinuclear complex ions (Figure 1a, 1b). For compound **B** the structure is monomeric (Figure 2).

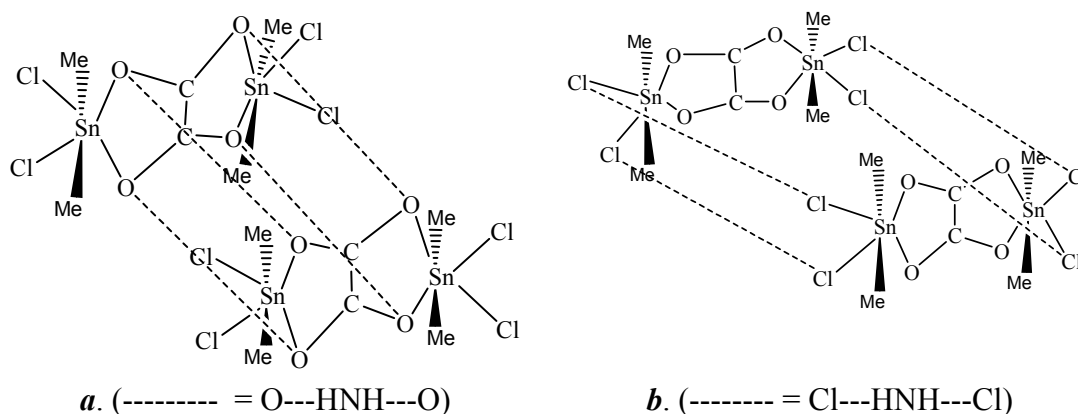


Figure 1. Suggested structures for compound A

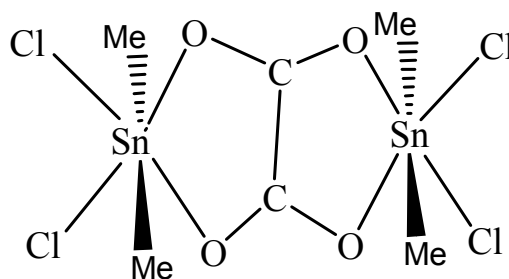


Figure 2. Suggested structure for compound B

NB: The bichelating oxalate and the chlorine atoms are in the same plan while the methyl groups are perpendicular to that plan.

The compound **C** can be considered as the compound **A** in which the chloride ions have been replaced by $[C_2O_4Cy_2NH_2]^-$ groups; the suggested structure contains a central bichelating oxalate and four monocoordinating external anions linked by the cations through $NH\cdots O$ hydrogen bonds. We can consider the oxalate pair of anions linked by the cation in chair, boat or almost planar conformations (Figure 3a, 3b). (We have not drawn the almost planar conformation).

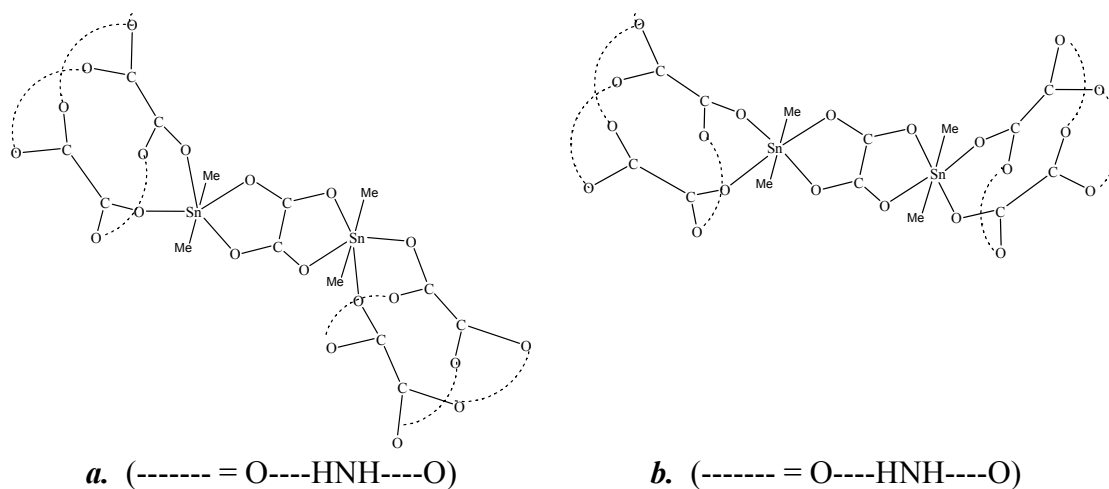


Figure 3. Suggested structure for compound C

The complex **C** can be considered as a $\frac{1}{2}$ adduct between $(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4$ and $\text{SnMe}_2(\text{C}_2\text{O}_4)_2(\text{Cy}_2\text{NH}_2)_2$; the monochelating oxalate anion within $\text{SnMe}_2(\text{C}_2\text{O}_4)_2(\text{Cy}_2\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ moving from chelation to monocoordination during the addition process.

The wide and strong absorption in the IR spectra of **A** and **C** centered around 2900 cm^{-1} is due to $\text{NH}\cdots\text{Cl}$ and $\text{NH}\cdots\text{O}$ bonds present in the two structures.

CONCLUSION

We have seen that the cation plays an important role in the formation of adducts and complex. The cations, through hydrogen bonds ensure the dimerization or the cohesion of the structure. The oxalate anion is a bichelating or a monocoordinating ligand.

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