Interactions between $(Me_4N)_2C_2O_4.SnPh_2C_2O_4.H_2O$ and some Lewis acids: Synthesis, IR and Mössbauer studies of new trinuclear dioxalato complexes

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ABSTRACT

Five new trinuclear dioxalato diphenyltin (IV) adducts with SnR_2Cl_2 (R = Ph, Bu, Me), $CdCl_2$ and $SbCl_3$ have been synthesized. Discrete structures have been suggested on the basis of infrared and Mössbauer data, the oxalate behaving as a bichelating ligand.

Keywords: discrete structure, bichelating oxalate, infrared and Mössbauer data

INTRODUCTION

Many $SnBu_2$-containing derivatives have been reported to be biologically active /1-5/. In the framework of our research in organotin chemistry /6-15/ we have initiated a study of the interactions between $(Me_4N)_2(C_2O_4)_2SnPh_2.H_2O$ with various Lewis acids. This has yielded new trinuclear adducts, infrared and Mössbauer studies of which have been carried out and structures suggested on the basis of spectroscopic data.

EXPERIMENTAL

The infrared spectra were recorded at the University Cheikh Anta Diop (Dakar-Sénégal) by means of a Bruker FT-IR spectrometer, at the University of Padova (Italy) using a PE 580 or a Bruker FTIR

spectrometer, the sample being as Nujol mulls, the windows being CsI or polyethylene; infrared data are given in cm^{-1} (abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak).

Mössbauer spectra were obtained as reported in (16). Details of required Mössbauer parameters are given in mms^{-1}, (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height).
The elemental analyses performed by either the CNRS "Service Central d'Analyses" Vernaison-France , the laboratory of Microanalyses – University of Padova – Italy or the Microanalyses Centre – University of Bath- UK, are reported in Table I.

All chemicals were purchased from Aldrich Company and used without any further purification.

Syntheses

$(Me_4N)_2C_2O_4.2H_2O$ was obtained on mixing an aqueous solution of Me_4NOH (20%) with oxalic acid in 2:1 ratio; the white powder collected after solvent evaporation was recrystallized from EtOH. Analytical data % calculated for $C_{10}H_{28}N_2O_6$ (%found) –C = 44.10(44.02), H = 10.36(10.50), N = 10.29(10.15)
$(Me_4N)_2C_2O_4.SnPh_2C_2O_4.H_2O$ (L_1) was obtained as a white precipitate on mixing ethanolic solutions of $SnPh_2Cl_2$ with $(Me_4N)_2C_2O_4\,2H_2O$ in 1: 2 ratio. Analytical data % calculated for $C_{24}H_{36}O_9N_2Sn$ (%found). C = 48.85(49.07), H = 5.68(5.81), N = 4.38(4.26), Sn = 18.57(18.63)

When ethanolic solutions of L_1 and Lewis acids react in 1:2 ratio, white precipitates are obtained and stirred no less than two hours, filtered and washed with hot ethanol. The elemental analyses summarized in Table I has allowed to suggest the following formulae.

Table I

Analytical data

Complexes	%C	%H	%N	%Cl	%Sn	%M
A	43.82 (44.16)	4.20 (4.18)	2.18 (2.27)	11.05(10.94)	27.72(27.11)	-
B	39.84(40.01)	5.81(5.77)	2.32(2.22)	29.56(29.40)	11.79(11.83)	-
C	32.42(32.27)	4.44(4.50)	2.70(2.81)	34.36(34.50)	13.70(13.66)	-
D	28.47(29.89)	3.47(3.52)	2.65(2.90)	15.14(14.73)	11.54(12.31)	24.57(23.33)
E	28.61(27.29)	3.72(3.22)	3.24(2.65)	20.22(20.18)	12.68(11.24)	22.54(23.07)

M = Cd, Sb

$(Me_4N)_2(C_2O_4)_2SnPh_2.\ 2SnPh_2Cl_2$ (A); $(Me_4N)_2(C_2O_4)_2SnPh_2.\ 2SnBu_2Cl_2$ (B)
$(Me_4N)_2(C_2O_4)_2SnPh_2.\ 2SnMe_2Cl_2$ (C);
$(Me_4N)_2(C_2O_4)_2SnPh_2.\ 2CdCl_2$ (D); $(Me_4N)_2(C_2O_4)_2SnPh_2.\ 2SbCl_3$ (E)

All the compounds are air stable and insoluble in non coordinating solvents

RESULTS AND DISCUSSION

In Tables II and III are respectively reported the frequencies of the main bands of the adducts with assignments and their Mössbauer parameters.

Table II

IR main bands of the adducts

Assignments → **Complexes ↓**	vasCOO-	vsCOO-	δ COO^-	vasSnC_2	vsSnC_2	vSnCl
A	1680vw 1620vs	1350vw 1304s	796s	284s	-	-
B	1687m 1620vs	1348m 1308m	793m	686m	595m	288w
C	1696s 1636vs	1349s 1308s	796vs	668w	-	280w
D	1684vw 1614vs	1309m 1350vw	796s	274s	-	-
E	1631s	1288m	796s	284s	-	-

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

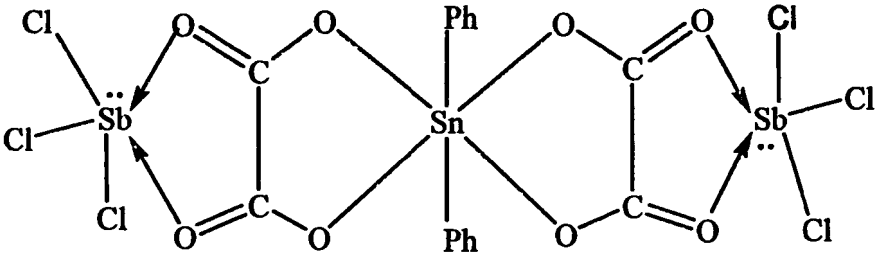
Table III

Mössbauer parameters of the adducts

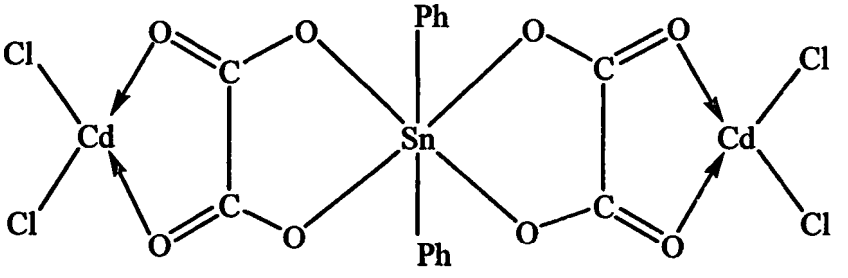
Complexes	δ (mm/s)	ΔE (mm/s)	Γ (mm/s)	A (%)
A	1.38 1.37	4.07 3.49	0.88	35 65
B	1.48 1.40	4.48 3.41	0.96	66 33
C	1.40 1.24	4.61 3.80	0.92	66 33
D	1.61	3.69	0.87	100
E	1.27	3.78	0.86	100

The value of the quadrupole splitting of $(Me_4N)_2C_2O_4.SnPh_2C_2O_4.H_2O$ (1.85 mm / s) is consistent with a cis octahedral coordination of the $SnPh_2$ residue according to Bancroft and Platt/17/. In the case of $(Cy_2NH_2)_2SnPh_2(C_2O_4)_2$, a cis coordinated $SnPh_2$ residue has previously been reported from an X Ray structure determination /18/. However data for D and E show that the tin has switched to a trans geometry-

surely because of steric effects in the cis conformation- leading to discrete structures in which the two oxalate ions bichelate the central tin and Sb or Cd (Scheme Ia and Ib)

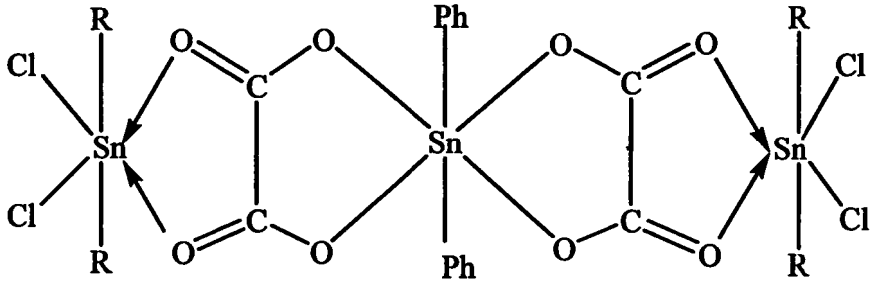


Scheme Ia



Scheme Ib

The tin site in A – C of intensity 1- with a quadrupole splitting higher than 4.00mms^{-1}- is also trans $Ph_2Sn(ox)_2$; the second tin environments in these 3 adducts- with a quadrupole splitting lower than 3.90mms^{-1}- are also trans R_2Sn (coordination number 6). This leads to the structure shown in scheme II.



Scheme II (R = Ph, Me, Bu)

The four oxalate stretching bands of the oxalate in almost all the infrared spectra are consistent with non centrosymmetric oxalate ions due to the asymmetrical bichelation.

All our attempts to obtain monocrystals were unsuccessful.

CONCLUSION

The oxalato trimetallic adducts studied in this work have discrete structures and contain two non symmetrically bichelating oxalate anions, the environment around all tin centres being octahedral, pentagonal around Sb and tetrahedral around Cd.

ACKNOWLEDGEMENTS:

We thank Professors M. Vidali (University of Padova, Italy) and K.C. Molloy (University of Bath, UK) for equipment support, Professor A. Tidjani, Dr M. Diagne and Mr Guèye (Laboratory of Nuclear Physics - Dakar University) for recording some infrared spectra.

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