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Synthesis and Spectroscopic Characterization of Some New Oxalato SnPh_2X ($\text{X} = \text{Cl}, \text{Ncs}, \text{Ncse}$) Containing Derivatives and Adduct

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ABSTRACT

Six new oxalato chlorodiorganostannic derivatives and adduct have been synthesized, their infrared and Mössbauer studies carried out. Polymeric structures have been suggested, the oxalate behaving as a monochelating or a bichelating donor. R_2NH_2^+ cations, when involved, lead to supramolecular structures.

Keywords: oxalato, chlorodiorganotin (IV) group, spectroscopy, infrared, Mössbauer, polymeric structures, mono- and bichelating oxalate, supramolecular structures.

INTRODUCTION

The relatively high antitumor activity of SnR_2 - containing derivatives and complexes have been emphasized by several authors including recent reviews /1 – 5/; it is what explains all the interest of research workers for organostannic compounds. Among these organostannic complexes and derivatives, those containing SnPh_2Cl fragment are in good place /6-14/.

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Within the framework of our research work since several years in this field /15-21/, we have initiated in this work the study of the interactions between symmetrical and non-symmetrical quaternary ammonium salts of oxalic acid with SnPh_2Cl_2 , seeking for new organotin IV compounds, and have isolated six new partially substituted oxalato SnPh_2Cl residue containing compounds, infrared and Mössbauer studies of which have been carried out and structures suggested on the basis of the spectroscopic data.

EXPERIMENTAL

L₁ : (isoBu)₂NH₂HC₂O₄

The mixture of an aqueous solution containing 1.95 g (15 mmol) of (isoBu)₂NH and 1.90 g (15 mmol) of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ gives a white precipitate stirred no less than two hours, filtered and dried at 65°. Analytical data calculated (found): %C = 54.77(55.00), %H = 9.55(9.39), %N = 6.39(6.45).

L₂ : (Cy₂NH₂)₂C₂O₄ (Cy = C₆H₁₁)

The mixture of an ethanolic solution containing 1.82 g (10mmol) of Cy_2NH with an aqueous solution containing 0.63 g (5mmol) of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ gives a white precipitate stirred no less than two hours, filtered and dried at 65°. Analytical data calculated (found): %C = 68.99(67.02), %H = 10.69(10.59), %N = 6.19(6.20)

L₃ : (Me₄N)₂C₂O₄ .2H₂O; L₄ : (Et₄N)₂C₂O₄ .4H₂O

The salts **L₃** and **L₄** were obtained by neutralizing oxalic acid with Me_4NOH and Et_4NOH as 20% water solutions.;the obtained solutions are submitted to solvent evaporation at 65°; a white powder is collected, recrystallized in EtOH and dried under P_2O_5 . Analytical data- calculated (found): **L₃**: %C = 43.78(44.02), %H = 11.02(10.50), %N = 10.21(10.15); **L₄**: %C = 51.40(51.17), %H = 11.50(11.60), %N= 6.66(6.75)

The mixture of ethanolic solutions of **L₁**, **L₂**, **L₃** and **L₄** with an ethanolic solution of SnPh_2Cl_2 gives a white precipitate(C, D, E, F) stirred no less than two hours and washed with hot ethanol; when solutions(A, B) result from mixing $\text{Et}_4\text{NC}_2\text{O}_4\text{SnPh}_2\text{Cl}$ in acetonitrile with KSCN or KSeCN in MeOH, a white powder is obtained after a slow solvent evaporation.

The elemental analyses performed by 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 below. %calculated(%found) **Et₄NC₂O₄SnPh₂SCN (A)**: C=50.29(49.99), H=5.51(5.50), N=5.10(5.13), Sn=21.61(21.44); **Et₄NC₂O₄SnPh₂SeCN (B)**: C=46.34(46.22), H=5.07(4.96), N=4.70(4.65) Sn=19.91(20.10); **Me₄NC₂O₄SnPh₂Cl.3H₂O (C)**: C=41.21 (41.89), H=5.38 (5.15), N=2.67 (2.17); **Et₄NC₂O₄SnPh₂Cl (D)**: C=50.17, (50.17) H=5.74 (5.70), N=2.66 (2.66), Cl=6.73(6.46);;

$C_2O_4(SnPh_2Cl)_2$ (E): C=44.31(44.12), H=2.86(2.76), Sn=33.69(33.55), Cl=10.06(9.96);
 $Cy_2NH_2C_2O_4SnPh_2Cl.SnPh_2Cl_2.2H_2O$ (F) : C=47.61 (47.57), H=5.05(5.05), N=1.46(1.46)

The infrared spectra were recorded at the University of Cheikh Anta Diop Dakar and at the University College of Saint-Boniface (Winnipeg-Canada) by means of a BX FT-IR type, at the University of Padova (Italy) with a PE 580 or a Bruker FTIR spectrometer, the sample being as Nujol mulls using CsI or polyethylene windows. Mössbauer spectra were obtained as described previously /22/

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 mms^{-1} (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height).

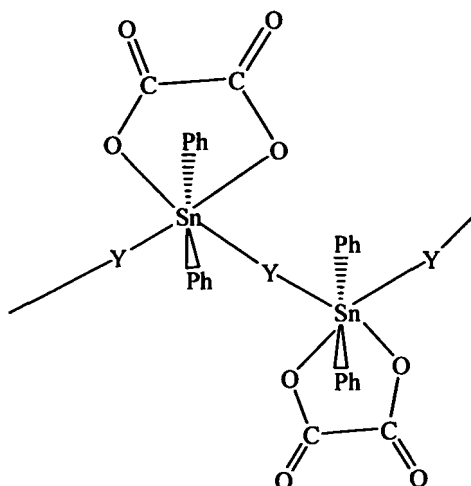
All the chemicals were from Aldrich or Merck Companies and used without any further purification.

RESULTS AND DISCUSSION

Let us consider the ir and Mossbauer data of the studied compounds: $\nu_{as}COO$ -(1659vw, 1617vs); $\nu_{s}COO$ -(1308m, 1268w), δ COO 793m, $\nu_{as}SnC_2$ 300m for (A); $\nu_{as}COO$ -(1660s1618vs), $\nu_{s}COO$ -1313w, δ COO 794m, $\nu_{as}SnC_2$ 300m for (B); $\nu_{as}COO$ -1625vs, $\nu_{s}COO$ -(1310m,1275m), δ COO 791s for (C); $\nu_{as}COO$ -1608vs, $\nu_{s}COO$ -(1251m,1261m), δ COO 812w for (D); $\nu_{as}COO$ - 1617vs; $\nu_{s}COO$ -(1314m, 1353m), δ COO 798m, $\nu_{as}SnC_2$ 490m for (E); $\nu_{as}COO$ -1614s, $\nu_{s}COO$ -1311m, δ COO 799s, $\nu_{as}SnC_2$ 691m; $\delta=1.43mms^{-1}$, $QS=4.02 mms^{-1}$, $\Gamma=0.98 mms^{-1}$, $A=100$ for (A); $\delta=1.42 mms^{-1}$, $QS=4.06 mms^{-1}$, $\Gamma=0.95 mms^{-1}$, $A=100$ for (B); $\delta=1.13 mms^{-1}$, $QS=3.87 mms^{-1}$, $\Gamma=0.98 mms^{-1}$, $A=100$ for (C); $\delta=1.30 mms^{-1}$, $QS=3.76 mms^{-1}$, $\Gamma=0.80 mms^{-1}$, $A=100$ for (D); $\delta=1.35 mms^{-1}$, $QS=4.34 mms^{-1}$, $\Gamma=0.99 mms^{-1}$, $A=100$ for (E); $\delta=1.35 mms^{-1}$, $QS=4.29 mms^{-1}$, $\Gamma=0.87 mms^{-1}$, $A=100$

The infrared spectra of these four complexes (A-D) exhibit the presence of a non-centrosymmetrical oxalate because of the presence of more than two bands in the stretching vibrations region; the quadrupole splitting values of (A), (B), (C) and (D) (Q.S = 4.02 (A), 4.06 (B), 3.87 (C) and 3.76 mms^{-1} (D)) are in agreement with a trans octahedral environment around the tin centre according to Bancroft and Platt /23/. In $(Me_4N)_2C_2O_4.2SnPh_2Cl_2$ we had reported $QS = 3.69 mms^{-1}$ /22/.

We suggest for (A), (B), (C) and (D) an infinite chain structure with bridging chlorides (Scheme 1). The interactions between the infinite chain and the cations are of electrostatic type.

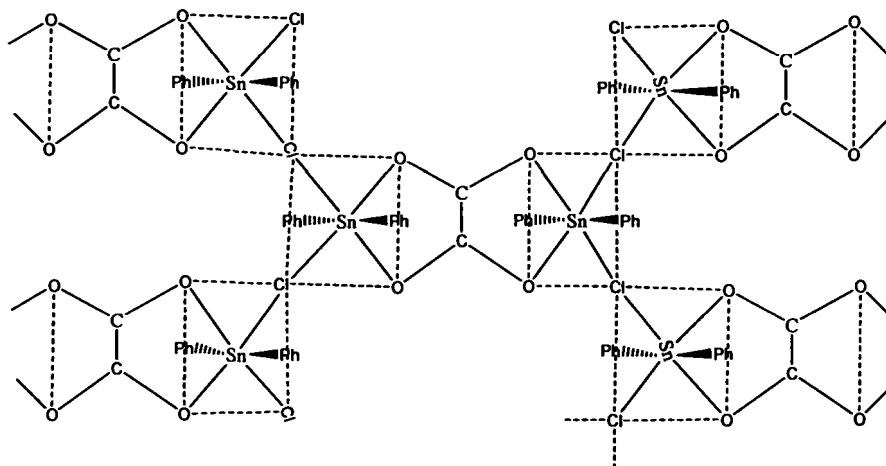


Scheme 1 (Y= Cl, NCS, NCSe)

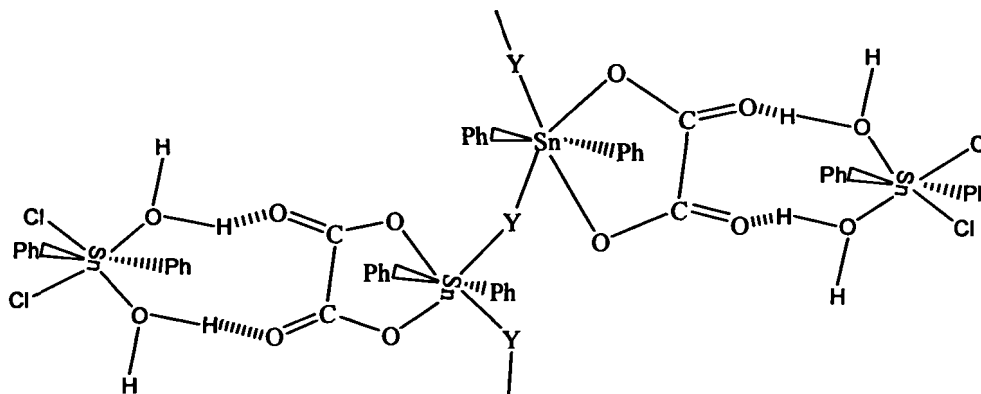
$C_2O_4(SnPh_2Cl)_2$ (E); $Cy_2NH_2C_2O_4SnPh_2Cl.SnPh_2Cl_2.2H_2O$ (F)

The values of the quadrupole splitting of these two compounds as above are consistent with the presence of trans octahedrally coordinated $SnPh_2$ groups and allow to suggest for (E) a layered structure with a bichelating oxalate (Scheme 2).

The compound (F) $Cy_2NH_2C_2O_4SnPh_2Cl.SnPh_2Cl_2.2H_2O$ can be considered as an adduct of $Cy_2NH_2C_2O_4SnPh_2Cl$ with the cis coordinated adduct $SnPh_2Cl_2.2H_2O$ through $OH\cdots O$ bonds involving the free oxygen atoms of the oxalate anion. The suggested structure derives from the structure reported on Scheme 1 on binding the cis coordinated $SnPh_2Cl_2.2H_2O$ adduct to the chain (Scheme 3). The same environment of $SnPh_2Cl_2O_2$ framework-the $SnPh_2$ residue has $D_{\infty h}$ symmetry- explains the similarity of the two tin (IV) centres in Mössbauer spectroscopy. The cation, when involved through $NH\cdots Cl$ hydrogen bonds lead to supramolecular architecture



Scheme 2



Scheme 3

CONCLUSION

In the partially substituted complexes studied in this work, the oxalate anion behaves as a mono- or a bichelating ligand, the suggested structures being of infinite type (chains or layered), the chloride, SCN^- or SCN^- anions moieties ensuring the connection between tin centres. Non-symmetrical cations, when involved through hydrogen bonds, lead to supramolecular structures. The environment around the tin is in all cases trans octahedral.

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