Synthesis and Spectroscopic Characterization of Some New Oxalato Snph$_2$x (X = Cl, Ncs, Ncse) Containing Derivatives and Adduct

Kochikpa A. Okio[1], Alioune Fall[1], Hayat Qamar-Kane[1], Yaya Sow[1],
Libasse Diop[1*], Lamine A. Diop[2] Umberto Russo[3], A. Wattiaux[4]

[1]Laboratoire de Chimie Minérale et Analytique, Département de chimie,
Faculté des Sciences et Techniques, Université Cheikh Anta Diop – Dakar- SENEGAL
[2]Collège universitaire de Saint-Boniface, Winnipeg, Canada
[3]Dipartimento di Chimica Inorganica Metallorganica ed Analitica, Via Loredan 4,
Università degli studi di Padova, I-35135 Padova, Italy
[4]Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS,
Université de Bordeaux- France

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/.

---

[*] dlibasse@gmail.com

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

L_1 : $(isoBu)_2NH_2HC_2O_4$

The mixture of an aqueous solution containing 1.95 g (15 mmol) of $(isoBu)_2NH$ and 1.90 g (15 mmol) of $H_2C_2O_4.2H_2O$ 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).

L_2 : $(Cy_2NH_2)_2C_2O_4$ ($Cy = C_6H_{11}$)

The mixture of an ethanolic solution containing 1.82 g (10mmol) of Cy_2NH with an aqueous solution containing 0.63 g (5mmol) of $H_2C_2O_4.2H_2O$ 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)

L_3 : $(Me_4N)_2C_2O_4.2H_2O$; L_4 : $(Et_4N)_2C_2O_4.4H_2O$

The salts L_3 and L_4 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): L_3: %C = 43.78(44.02), %H = 11.02(10.50), %N = 10.21(10.15); L_4: %C = 51.40(51.17), %H = 11.50(11.60), %N= 6.66(6.75)

The mixture of ethanolic solutions of L_1, L_2, L_3 and L_4 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 $Et_4NC_2O_4SnPh_2Cl$ 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) **$Et_4NC_2O_4SnPh_2SCN$ (A)**: C=50.29(49.99), H=5.51(5.50), N=5.10(5.13), Sn=21.61(21.44); **$Et_4NC_2O_4SnPh_2SeCN$ (B)**: C=46.34(46.22), H=5.07(4.96), N=4.70(4.65) Sn=19.91(20.10); **$Me_4NC_2O_4SnPh_2Cl.3H_2O$ (C)**: C=41.21 (41.89), H=5.38 (5.15), N=2.67 (2.17); **$Et_4NC_2O_4SnPh_2Cl$ (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).

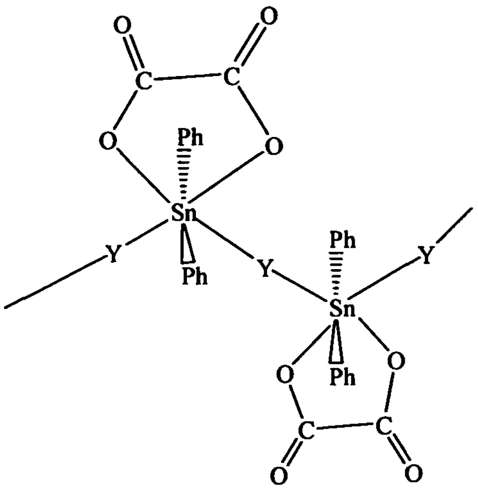
All the chemicals were from Aldrich or Merck Companies and used without any further purification.

RESULTS AND DISCUSSION

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

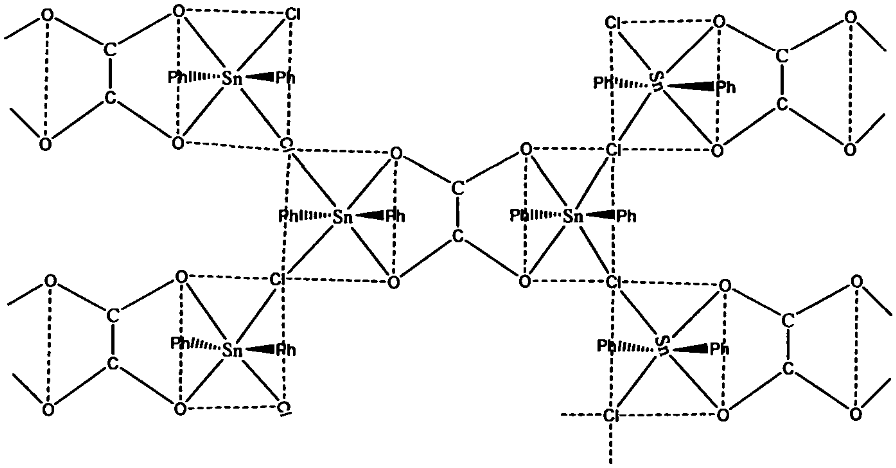


Scheme 1 (Y= Cl, NCS, NCSe)

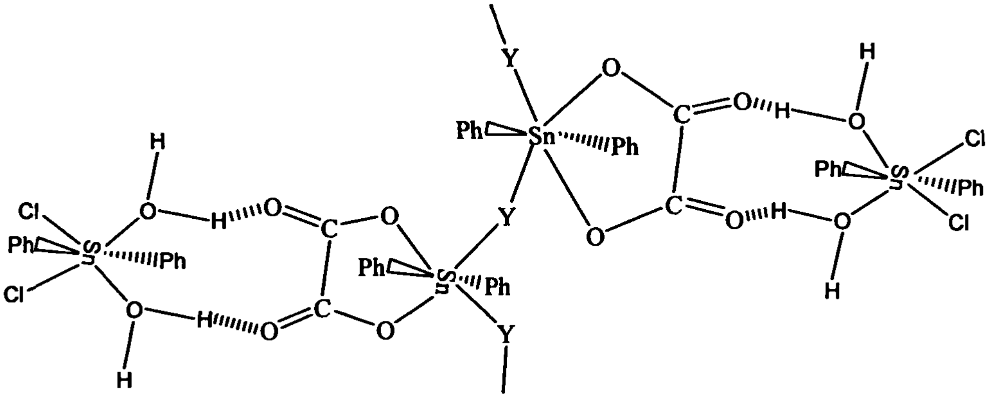
$C_2O_4(SnPh_2Cl)_2$ (E); $Cy_2NH_2C_2O_4SnPh_2Cl.SnPh_2Cl_2.2H_2O$ (F)

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----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∞h symmetry- explains the similarity of the two tin (IV) centres in Mössbauer spectroscopy. The cation, when involved through NH---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.

ACKNOWLEDGEMENTS:

We thank Professors M. Vidali (Univ. of Padova-Italy), K.C. Molloy (Univ. of Bath- UK) for equipment support and elemental analyses, Professor A. Tidjani, (Dakar-Cheikh Anta Diop University-Senegal) for recording some infrared spectra.

REFERENCES

1. L. Pellerito and L. Nagy, *Coord. Chem. Rev*, **224**, 111, (2002)
2. M. Gielen, *Appl. Organomet. Chem.*, **16**, 481, (2002)
3. Chunlin Ma and J. Zhang, *Appl. Organomet. Chem*, **17**, 788, (2003)
4. S. W. Ng, V.G.Kumar Das, J. Holecek, A. Lycka, M. Gielen and M. G.B. Drew, *Appl. Organomet. Chem.*, **11**, 39, (1997)
5. A. Meriem, R. Willem, J. Meunier-Piret, M. Biesemans, B. Mahieu and M. Gielen, *Main Group Metal Chem.*, **13**, (3), 165, (1990)
6. V. Barba, E. Vega, R. Luna, H. Hopfl, I. Beltran and L.S. Zamudio-Rivera, *J. Organomet. Chem.*, **692** ,731, (2007)

7. S. K. Thodupunoori, I.A. Alamudun, F. Cervantes-Lee, F.D. Gomez, Y.P. Carrasco and K.H. Pannell, *J. Organomet. Chem.*, **691**, 1790, (2006)
8. C. Camacho-Camacho, V.M. Jimenez-Perez, J.C.Galvez-Ruiz, A. Flores-Pana and R. Contreras, *J.Organomet.Chem.*, **691**,1590, (2006)
9. Xueqing Song, G. Zhong, Q. Xie and G. Eng, *Inorg. Chem. Commun.*, **8**, 725, (2005)
10. G. Reeske, M. Schurmann, B. Costisella and K. Jurkschat, *Eur.Inorg. Chem.*, **28**, 81, (2005)
12. J. R. Anocona, C. Rivas and G.D.d. Delgado, *J. Coord. Chem.*, **56**, 245, (2003)
13. Chunlin Ma, Junhong Zhang and Rufen Zhang, *Can. J. Chem.*, **81**, 1070, (2003)
14. Liang-Fu Tang, Pei-Juan Zhu and Ji-Tao Wang, *J. Chem. Res.*, **370**, (2002)
15. C.A.K. Diop, H. Qamar, I. Cisse, L. Diop and U. Russo, *Main Group Met. Chem* , **22**,1,13, (1999)
16. M. Lahlou and L. Diop, *Spectrochim.Acta*, **47A**, 12, 1775, (1991)
17. M. Sidibé, M. Lahlou, L Diop and B. Mahieu, *Main Group Met. Chem.*, **21**,(10), 605, (1998)
18. C.A.K.Diop, K.Y.A.Okio, L.Diop and B.Mahieu, *Main Group Met. Chem.*, **23**,9,493, (2000)
19. A.Touré, C.A.K.Diop, L.Diop and B.Mahieu, *Comptes Rendus Chimie Académie des Sciences Paris*, **10**, 493, (2007)
20. A. Diassé-Sarr, L. Diop, M.F.Mahon and K.C.Molloy *Main Group Met. Chem.*, **20**,4, 223, (1997)
21. M.Lahlou and L.Diop, *Spectrochim. Acta.*,**47A**, 12, 1775, (1991)
22. M.Gielen, A,Bouhdid, F.Kayser, M.Biesemans, D.de Vos, B.Mahieu and R.Willem *Appl.Organomet.Chem.*, **9**, 251, (1995)
23. G. M. Bancroft and R. H Platt, *"Mossbauer Spectra of Inorganic Compounds" : Structure and bonding in Advanced Inorganic Chem. and Radio Chem.*, **15**, Ed. by H. T. Emeleus et A. G. Sharpe, Acad. Press, New York, (1972), 112
24. F. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*(1986) 4th.ed., J. Wiley and Sons, New York
25. C. A. K. Diop, L. Diop and A. R. Toscano, *Main Group Met. Chem.* **25**, 5 , 327, (2002)