

SYNTHESIS AND INFRARED STUDY OF SOME SULFATO TRIORGANOTIN DERIVATIVES AND ADDUCTS

Daouda Ndoeye, Libasse Diop*

*Université Cheikh Anta Diop, Faculté des Sciences et Techniques,
Département de Chimie, Laboratoire de Chimie Minérale et Analytique
(LACHIMIA), Dakar, Sénégal*

*Corresponding author: dlibasse@gmail.com

Received: March, 19, 2014

Accepted: July, 18, 2014

Abstract: On allowing ethylenediammonium sulfate or $\text{Me}_4\text{NSO}_4\text{H}$ to react with SnPh_3Cl or SnBu_2Cl_2 in ethanolic media in specific ratios the three sulfato complexes were obtained and their infrared study carried out. The molecular structures of these compounds have been proposed on the basis of the infrared data. Discrete structures are suggested: the sulfate anion is tetradentate in two of them and monodentate in the other, the tin center being in a trigonal bipyramidal environment in all the structures. When the ethylenediammonium ion is involved through hydrogen bonds, dimeric structures may be obtained.

Keywords: *coordinating sulfate, dimeric structures, infrared, planar SnR_3 residue ($R = \text{Ph}, \text{Bu}$)*

INTRODUCTION

The organotin (IV) molecules are known as wood preservatives, anti-fouling paints, drugs, etc. [1 – 7]. This is why several groups including our [8 – 10] have been focusing in the synthesis of new compounds of this family. In this paper we have initiated the study of the interactions between ethylenediammonium sulfate (enH_2SO_4) or $\text{Me}_4\text{NSO}_4\text{H}$ and SnPh_3Cl or SnBu_2Cl_2 which have yielded the three complexes, infrared studies of which have been carried out, then structures suggested on the basis of infrared data.

MATERIALS AND METHODS

When ethanolic solutions containing 0.174 g (0.45 mmol) of SnPh_3Cl and 0.071 g (0.45 mmol) of enH_2SO_4 are mixed a clear solution is obtained, stirred for two hours and submitted to a slow solvent evaporation, a white powder is collected. The analytical data - % calculated (% found) **C**: 43.70 (43.92); **H**: 4.71 (4.69); **N**: 5.10 (5.22) - have allowed to suggest $\text{enH}_2\text{SO}_4 \cdot \text{SnPh}_3\text{Cl} \cdot 1/3\text{H}_2\text{O}$ (**A**) as formula.

When ethanolic solutions containing 0.096 g (0.25 mmol) of SnPh_3Cl and 0.086 g (0.50 mmol) of $\text{Me}_4\text{NSO}_4\text{H}$ are mixed the clear solution obtained is stirred for two hours and submitted to a slow solvent evaporation, a white powder is collected. The analytical data - % calculated (% found) **C**: 51.40 (51.16); **H**: 4.64 (4.21); **N**: 1.50 (1.79) - have allowed to suggest $(\text{Me}_4\text{N})_2\text{SO}_4 \cdot 4\text{SnPh}_3\text{Cl} \cdot \text{H}_2\text{O} \cdot 1/4\text{SnCl}_4$ (**B**) as formula.

When ethanolic solutions containing 0.091 g (0.30 mmol) of SnBu_2Cl_2 and 0.047 g (0.30 mmol) of enH_2SO_4 are mixed the clear solution obtained is stirred for two hours and submitted to a slow solvent evaporation, a white powder is collected. The analytical data - % calculated (% found) **C**: 40.63 (40.50); **H**: 8.18 (7.31); **N**: 1.90 (1.79) - have allowed to suggest $\text{enH}_2\text{SO}_4 \cdot 4\text{SnBu}_3\text{Cl} \cdot \text{H}_2\text{O}$ (**C**) as formula.

The elemental analyses were performed by the Microanalyses Laboratory of the Department of Chemistry, University of Bath (UK). The infrared spectra were recorded by FTIR-Nicolet (4000-400 cm^{-1}) spectrometers at the University of Addis Ababa (Ethiopia) and Dakar University (Senegal), the sample being as Nujol mulls, using CsI windows. Infrared data are given in cm^{-1} [IR abbreviations: (br) broad, (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak, (vw) very weak].

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

RESULTS AND DISCUSSION

Let us consider the infrared data (cm^{-1}):

- for **A**: $\nu_3(\text{SO}_4) = 1123$ s; $\nu_1(\text{SO}_4) = 995$ sh; $\nu_4(\text{SO}_4) = 662$ sh; $\nu(\text{Ph}) = 695$ s, 728 s; $\nu(\text{NH}_2) = 2900$ br;
- for **B**: $\nu_3(\text{SO}_4) = 1074$ s; $\nu_4(\text{SO}_4) = 613$ vs; $\nu(\text{Ph}) = 695$ s, 728 s;
- for **C**: $\nu_3(\text{SO}_4) = 1107$ vs; $\nu_1(\text{SO}_4) = 991$ sh; $\nu_4(\text{SO}_4) = 593$ m; $\nu_2(\text{SO}_4) = 485$ vw; $\nu_s(\text{SnBu}_3) = 621$ m; $\nu(\text{NH}_2) = 2900$ br.

Characterization of $\text{enH}_2\text{SO}_4 \cdot \text{SnPh}_3\text{Cl} \cdot 1/3\text{H}_2\text{O}$ (A)

The broad band centered at 2900 cm^{-1} indicates the existence of hydrogen bonds. The absence of $\nu_1(\text{SO}_4)$ band and the presence of $\nu_3(\text{SO}_4)$ as one band indicate that the SO_4^{2-} anion has a T_d symmetry according to the Theory Group [11].

On the basis of these infrared data, the structure suggested is a dinuclear dimer in which the tin atoms are trans-coordinated in a trigonal bipyramidal environment. In each monomer, the SO_4^{2-} anion is monodentate and coordinates the SnPh_3Cl molecule, the two $[\text{SO}_4\text{SnPh}_3\text{Cl}]^{2-}$ anionic components being then linked by $\text{NH} \cdots \text{O}$ hydrogen bonds. The free protons of ethylenediammonium cations and oxygen atoms of the sulfate anions may interact through hydrogen bonds thus giving a supramolecular architecture (Figure 1).

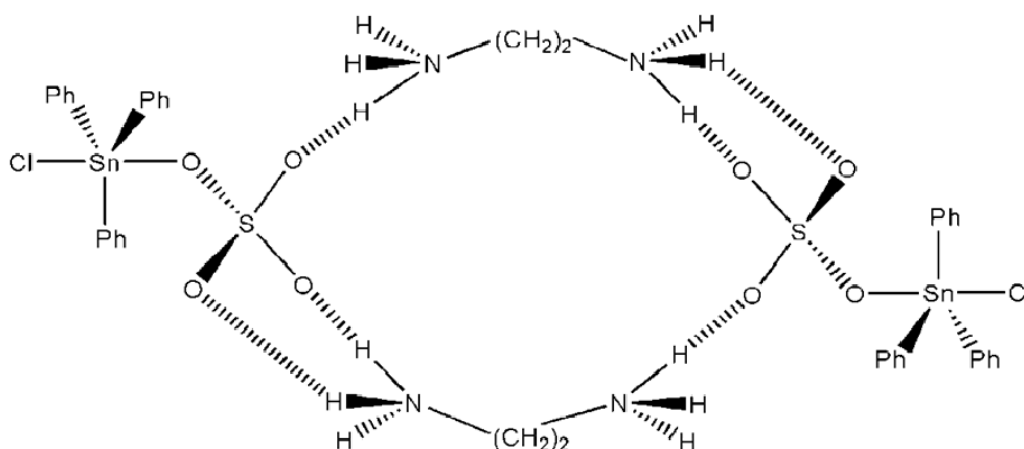


Figure 1. The proposed structure for the compound **A**

Characterization of $(\text{Me}_4\text{N})_2\text{SO}_4 \cdot 4\text{SnPh}_3\text{Cl} \cdot \text{H}_2\text{O} \cdot 1/4\text{SnCl}_4$ (B)

The appearance of both $\nu_3(\text{SO}_4)$ and $\nu_4(\text{SO}_4)$ as one band and the absence of $\nu_1(\text{SO}_4)$ and $\nu_2(\text{SO}_4)$ bands allow to justify the T_d symmetry according to the Theory Group applied to the SO_4^{2-} anion [11].

The proposed structure is discrete and consists of a central sulfate anion tetra-coordinated to four SnPh_3Cl molecules conferring thus to SnC_3 skeletons a planar geometry (Figure 2).

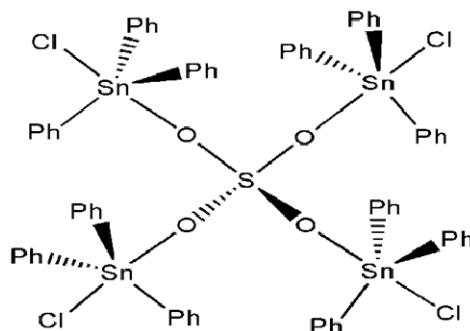


Figure 2. The proposed structure for the compound **B**

Characterization of $\text{enH}_2\text{SO}_4 \cdot 4\text{SnBu}_3\text{Cl} \cdot \text{H}_2\text{O}$ (C)

It seems worthy to outline the alkylation of the SnBu_2 group into a SnBu_3 residue in this compound. The appearance of $\nu_1(\text{SO}_4)$ band as shoulder and the very weak $\nu_2(\text{SO}_4)$ band indicate that the SO_4^{2-} has T_d symmetry according to the Theory Group [11]. The appearance of $\nu_s(\text{SnBu}_3)$ as a medium band at 621 cm^{-1} is an indication of a non-planar SnBu_3 residue. The broad band centered at 2900 cm^{-1} proves the existence of hydrogen bonds in the structure.

The proposed structure is a dimer in which each of the two SO_4^{2-} anions is tetra-coordinated to four SnBu_3Cl molecules (Figure 3).

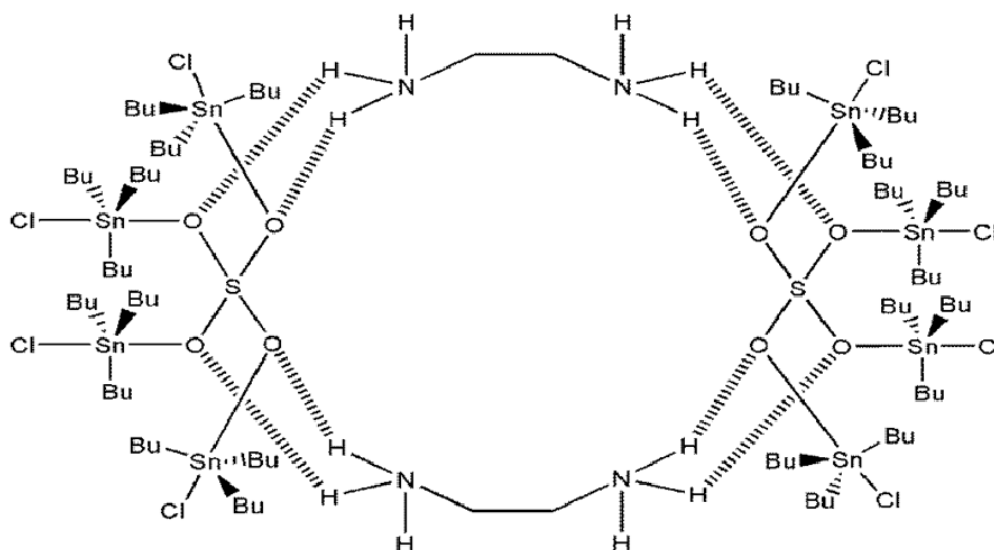


Figure 3. The proposed structure for the compound C

The two tetra-coordinated SO_4^{2-} anions may be linked by hydrogen bonds involving all the oxygen atoms from the SO_4^{2-} anions and the labile hydrogen atoms from the two ethylenediammonium cations.

CONCLUSIONS

The studied adducts have discrete and dimeric structures; the tin centre is in a trigonal bipyramidal environment and the sulfate being monodentate and tetradentate. Hydrogen bonded macromolecules may be obtained because of the presence of cations.

ACKNOWLEDGEMENTS

We thank Professor A. Tidjani (Dakar University, Senegal), Professor M. Redi (Addis Ababa University, Ethiopia) for performing the IR spectra and Professor K.C. Molloy (University of Bath, UK) for performing the elemental analyses.

REFERENCES

1. Evans, J.C, Karpel, S.: *Organotin Compounds in Modern Technology (Journal of Organometallic Chemistry, Library, 16)*, Elsevier Science Ltd., Amsterdam, **1985**;
2. Yin, H.D., Wang, C.H.: Crystallographic report: Crystal and molecular structure of triphenyltin thiazole-2-carboxylate, *Applied Organometallic Chemistry*, **2004**, 18 (8), 411-412;
3. Kapoor, R.N., Guillory, P., Schulte, L., Cervantes-Lee, F., Haiduc, I., Parkanyi, L., Pannell, K.H.: Di(*p*-*tert*-butylphenyl)-*N,N*-di(*iso*-butyl)carbamoylmethylphosphine oxide and its organotin and uranyl adducts: structural and spectroscopic characterization, *Applied Organometallic Chemistry*, **2005**, 19 (4), 510-517;
4. Zhang, W.L., Ma, J.F., Jiang, H.: μ -Isophthalato-bis[triphenyltin-(IV)][$\text{Sn}_2(\text{C}_6\text{H}_5)_6(\text{C}_8\text{H}_4\text{O}_4)$], *Acta Crystallographica Section E: Structure Reports Online*, **2006**, E62 (3), m460-m461;
5. Chandrasekhar, V., Boomishankar, R., Steiner, A., Bickley, J.F.: First example of a hydrogen-bonded three-dimensional pillared structure involving an organotin motif: Synthesis and X-ray crystal structures of $\{[\text{nBu}_2\text{Sn}(\text{H}_2\text{O})_3(\text{L})\text{Sn}(\text{H}_2\text{O})_3\text{nBu}]^{2+}[\text{L}]^{2-}\} \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ and $\{[\text{Ph}_3\text{Sn}(\text{L})\text{Sn}(\text{H}_2\text{O})\text{Ph}_3]_n\} \cdot \text{THF}$ (L = 1,5-Naphthalenedisulfonate), *Organometallics*, **2003**, 22 (17), 3342-3344;
6. Hertrich, T., Merzweiler, K.: $[(\text{Ph}_3\text{Sn})_3\text{VO}_4] \cdot \text{CH}_3\text{CN}$ und $[(\text{Ph}_3\text{Sn})_3\text{VO}_4] \cdot 2 \text{ DMF}$, Triphenylzinnvanadate mit neuartigen Kettenstrukturen, *Zeitschrift für Anorganische und Allgemeine Chemie*, **2006**, 632 (14), 2341-2344;
7. Gielen, M., Tiekink, E.R.T., Bouhdid, A., de Vos, D., Biesemans, D., Verbruggen, I., Willem, R.: Synthesis, characterization and *in-vitro* antitumour activity of dibutyltin carboxylates involving the perfluorophenyl moiety: Crystal structure of the dimeric bis[(4-fluoro- and pentafluorobenzoato)di-*n*-butyltin] oxides, *Applied Organometallic Chemistry*, **1995**, 9 (7), 639-648;
8. Diallo, W., Diassé-Sarr, A., Diop, L., Mahieu, B., Biesemans, M., Willem, R., Kociok-Köhn, G., Molloy, K.C.: X-Ray structure of tetrabutylammonium chlorotrimethyltin hydrogenosulphate: The first cyclic dimer hydrogenosulphato hydrogen bonded adduct, *Scientific Study & Research - Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2009**, 10 (3), 207-212;
9. Diallo, W., Okio, K.Y.A., Diop, C.A.K., Diop, L., Diop, L.A., Russo, U.: New selenito SnPh_3 residue containing complexes and adducts: Synthesis and spectroscopic studies, *Main Group Metal Chemistry* **2009**, 32 (2), 93-100;
10. Kane, H.Q., Okio, K.A., Fall, A., Diop, L., Russo, U., Mahieu, B.: Interactions between $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot \text{SnPh}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and some Lewis acids: Synthesis, IR and Mössbauer studies of new trinuclear dioxalato complexes, *Main Group Metal Chemistry*, **2009**, 32 (5), 263-268;
11. Nakamoto, K.: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edition, John Wiley and Sons, New York, **1997**.