SYNTHESIS AND INFRARED STUDY OF SOME PHENYLPHOSPHONATE, DIPHENYLPHOSPHINATE AND ACETATOPHOSPHONATE NEW ORGANOTIN (IV) DERIVATIVES AND ADDUCTS

MODOU SARR*[1], AMINATA DIASSE-SARR[1], LIBASSE DIOP[1]

[1]*Université Cheikh Anta Diop, Faculté des Sciences et Techniques, Département de Chimie, Laboratoire de Chimie Minérale et Analytique, Dakar, Sénégal*

Abstract: Three organotin (IV) derivatives $PhPO_3HSnBu_2Cl$, $SnBu_2Ph_2PO_2Cl\cdot 3/2H_2O$, $Sn(PhPO_3)Cl_2\cdot 2H_2O$ obtained on allowing $PhPO_3H_2$ or propylammonium $PhPO_3H$ to react with $SnBu_2Cl_2$, $SnCl_2\cdot 2H_2O$ and two adducts $[(C_6H_5CH_2)_2NH_2]_3O_2C(CH_2)_2PO_3\cdot 3SnPh_3Cl$, $[CyNH_3(HO_2POCH_2\text{-}N(CH_2CO_2H)_2]_2\cdot 3SnCl_4.2H_2O\cdot NH_4Cl$ obtained on allowing $(C_6H_5CH_2)NH_2)_3O_2C(CH_2)_2PO_3$ or $[CyNH_3(HO_2POCH_2\text{-}N(CH_2\ CO_2H)_2]_2$ and $SnPh_3Cl$ or $SnCl_2\cdot 2H_2O$ to react in ethanolic media have been characterized by elemental analyses, infrared and Mossbauer techniques. The suggested structures, while considering the anionic counterpart, are discrete, dimeric, double and triple metallic components or of infinite chain types, the anion behaving as a monochelating, a bichelating or a bidentate ligand. In OH containing structures, when extra hydrogen bonds are considered, supramolecular architectures may be obtained.

Keywords: bidentate, bichelating, hydrogen bonds, monochelating, $PhPO_3H^-$, $Ph_2PO_2^-$, $[O_2C\ (CH_2)_2\ PO_3]^{3-}[(HO_2POCH_2\text{-}N(CH_2CO_2H)_2]^-$, infrared and Mossbauer techniques, supramolecular architectures

1. INTRODUCTION

The organotin (IV) compounds are known for several applications in the industrial field (antifouling paints, wood preservatives) and also as drugs against cancer [1, 2], that explains the focus of several research teams in the attempt to obtain new molecules of this family [3-5]. In the dynamic of our research activity, we have yet published many papers dealing with organotin chemistry [6-10]. In this paper we have initiated the study of the interactions between $PhPO_3H_2$, propylammonium $PhPO_3H$, $[(C_6H_5CH_2)_2NH_2]_3O_2C(CH_2)_2PO_3$ or $[(CyNH_3)(HO_2POCH_2\text{-}N(CH_2CO_2H)_2]_2$ and $SnBu_2Cl_2$, $SnCl_2\cdot 2H_2O$ or $SnPh_3Cl$ which has yielded five new compounds. Infrared and Mossbauer studies were carried out and structures were suggested on the basis of the spectroscopic data.

2. MATERIALS AND METHODS

On allowing $PhPO_3H_2$ to react with $SnBu_2Cl_2$, or $SnCl_2\cdot 2H_2O$ in 1:1 ratio, propylammonium $PhPO_3H$ with $SnBu_2Cl_2$ in 1:2 ratio, $[(C_6H_5CH_2)_2NH_2]_3O_2C(CH_2)_2PO_3$ with $SnPh_3Cl$ or $[CyNH_3(HO_2POCH_2\text{-}N(CH_2CO_2H)_2]_2$ with $SnCl_2\cdot 2H_2O$ respectively in ethanol 1:2 or 1:3, white powders have been obtained after a slow solvent evaporation. The analytical data calculated(found) have allowed to suggest the following formulae:

- [**A**]: $PhPO_3HSnBu_2Cl$; % C = 39.52 (39.74), % H = 5.69 (5.58);

---

* Corresponding author: modousarr4@gmail.com

- [**B**]: $Sn(PhPO_3)Cl_2\cdot 2H_2O$; % C = 18.88 (18.75), % H = 2.38 (2.33);
- [**C**]: $SnBu_2Ph_2PO_2Cl\cdot 3/2H_2O$; % C = 46.86 (46.98), % H = 6.05 (5.99);
- [**D**]: $[(C_6H_5CH_2)_2NH_2]_3O_2C(CH_2)_2PO_3H\cdot 3SnPh_3Cl$: % C = 62.51 (62.62), % H = 5.14 (5.18), % N = 2.21 (2.18);
- [**E**]: $[(CyNH_3)(HOPOCH_2\text{-}N(CH_2CO_2H)_2]_2\cdot 3SnCl_4\cdot 2H_2O\cdot NH_4Cl$: % C = 16.95 (16.80), % H = 3.29 (3.24), % N = 4.70 (4.68).

The infrared spectra were recorded using a spectrometer Nicolet 6700 FT-IR, the sample being as Nujol mulls using CsI windows. The Mossbauer spectra were obtained as reported in [11]. Infrared data are given in cm^{-1} (abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak, d (doublet)). Mossbauer parameters are given in mms^{-1} (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, r = full width at half-height). All the chemicals were purchased from ALDRICH Company-Germany-and used as such.

3. RESULTS AND DISCUSSION

Let us consider the main infrared data of the studied derivatives and adducts:

- **[A]:** ν (PO_3) 1129 (s), 1066 (s), 1015 (w), 996 (w), νas ($SnBu_2$) 691 (s);
- **[B]:** ν (PO_3) 1140 (m), 1034 (s), 1009 (s), 991 (s);
- **[C]:** ν (PO_3) 1132 (m), 1097 (s), 1073 (m), νas ($SnBu_2$), 692 (s), νs ($SnBu_2$), 617 (w);
- **[D]:** ν (NH_3) 3043 (broad), 2991 (broad), 2931 (broad), νas COO^-1644 (m), 1573 (m), νs COO^- 1430 (vs), ν (PO_3), 1079 (broad), ν ($SnPh_3$), 1000 (t), 700 (d);
- **[E]:** ν (NH_3) 2937 (broad), 2860 (broad), νas COO^- 1654 (broad), 1500 (m), 1447 (m), νs COO^-1354 (s), 1280 (w), ν (PO_3) 1068, 1015 (broad).

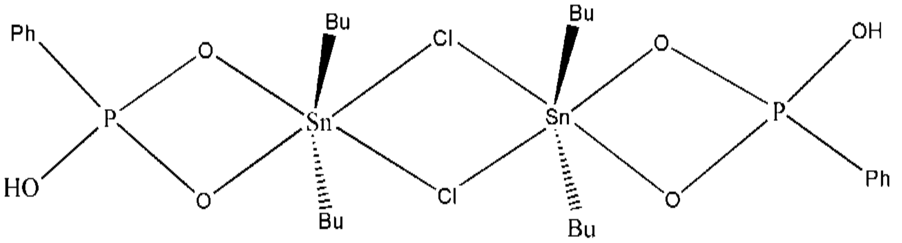
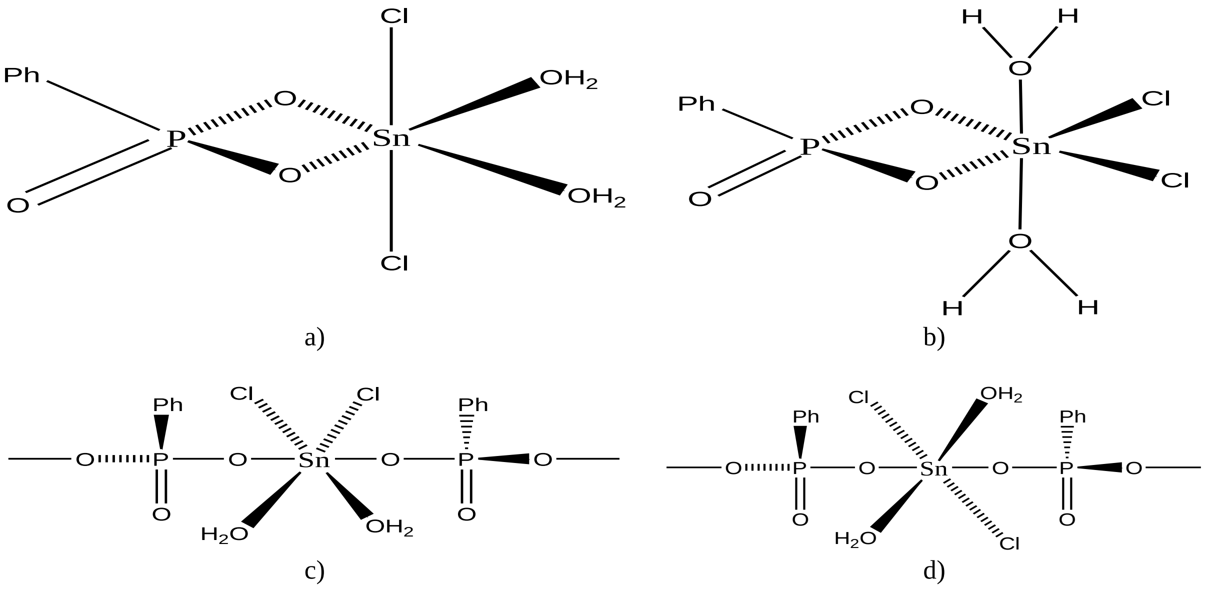


Fig. 1. Proposed structure for compound A.



a) b)

c) d)

Fig. 2. Proposed structure for compound B.

The value of the quadrupole splitting of compound **A** indicates the presence of a *trans* octahedrally coordinated $SnBu_2$ group according to Parish and Platt [12]: the suggested structure is discrete with a monochelating anion (Figure 1).

In compound **B** the value of the quadrupole splitting is consistent with both *cis* or *trans* octahedrally coordinated $SnCl_2$ framework.

The suggested structures are reported in Figures 2a, 2b (discrete ones) with the anion behaving as a monochelating ligand or on Figures 2c and 2d (infinite chain structures) with a bidentate anion. The environment around the tin center in all cases is octahedral.

For $SnBu_2Ph_2PO_2Cl{\cdot}3/2H_2O$ while considering a dimerization followed by a rearrangement **C** can be written as: $[SnBu_2Cl_2]\ SnBu_2(Ph_2PO_2)_2{\cdot}3H_2O$.

The values of the quadrupole splitting allow to suppose the presence of both a *trans* octahedrally coordinated $SnBu_2$ residue and a second $SnBu_2$ residue in a trigonal bipyramidal environment according to Parish and Platt [12]. A two metallic components structure may be suggested:
–a first metallic component is $SnBu_2(Ph_2PO_2)_2$ which contains bridging anions and a *trans* octahedral environment around the tin centre leading to an infinite chain ($4.46 mm{\cdot}s^{-1}$);
- a second metallic component $H_2O{\cdot}SnBu_2Cl_2$ contains a Sn centre in a bipyramidal trigonal environment ($3.16 mm{\cdot}s^{-1}$).

These two metallic components may connect *via* hydrogen bonds to give the structure (Figure 3) (the 2 extra water molecules are considered as lattice).

The discrete suggested structure of compound **[D]** is reported on Figure 4.

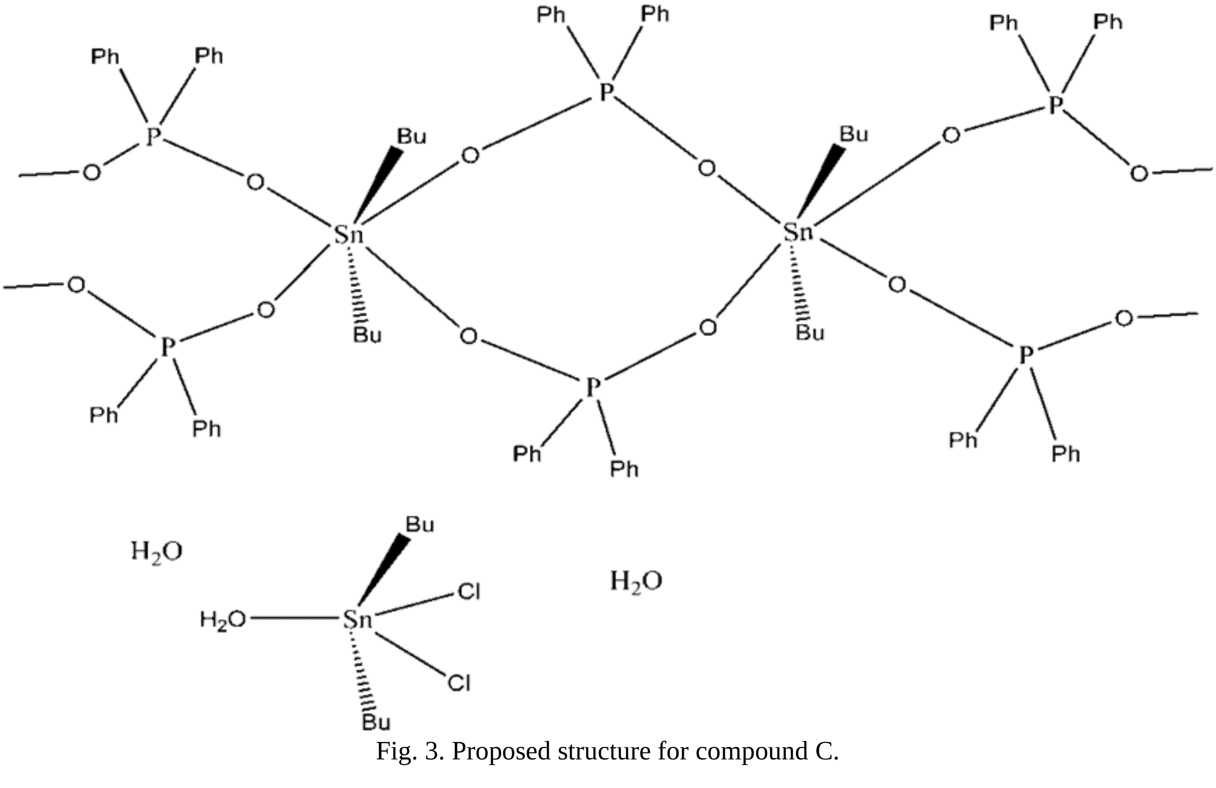


Fig. 3. Proposed structure for compound C.

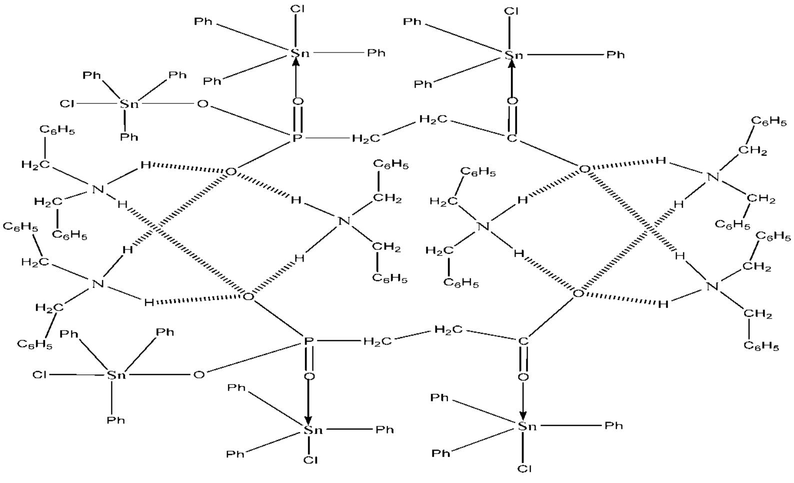
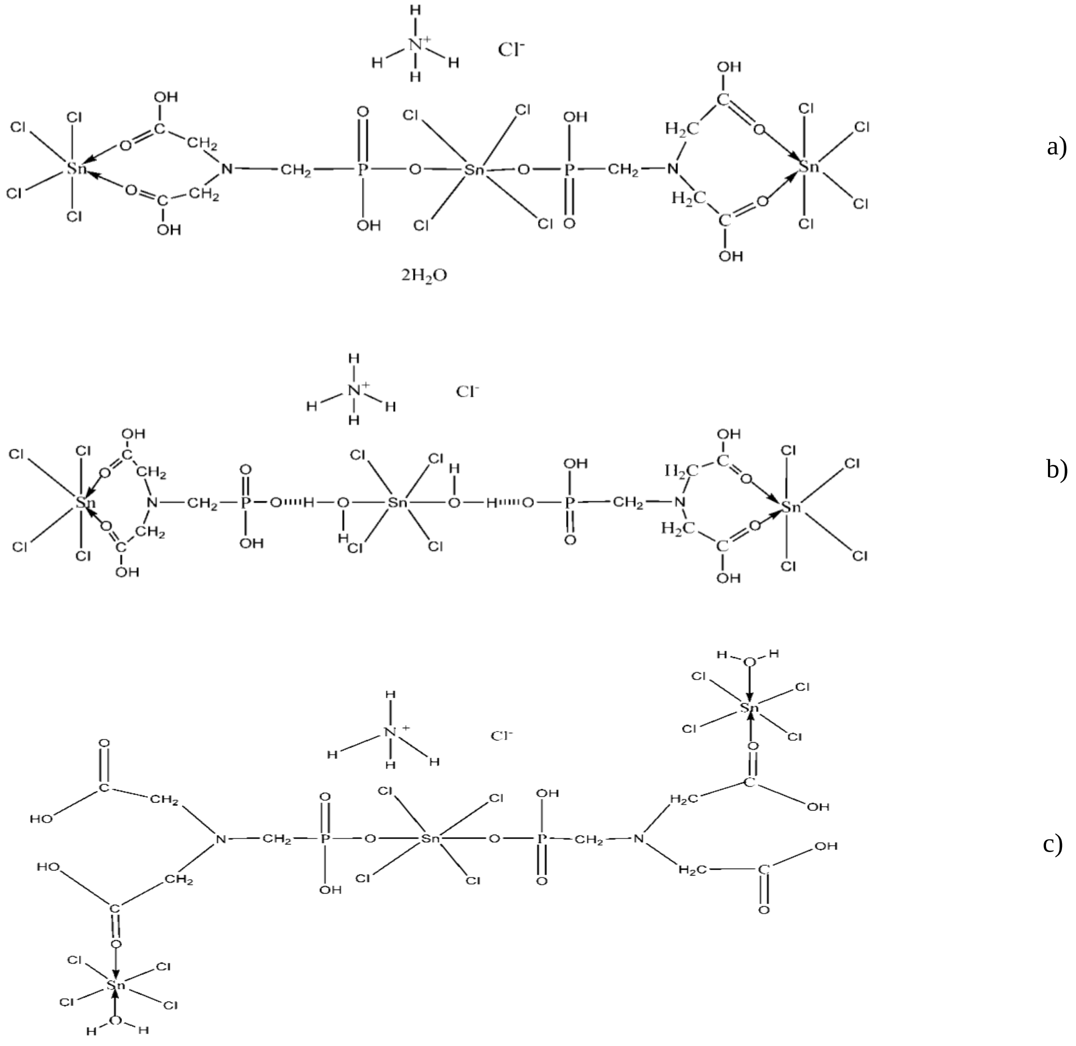
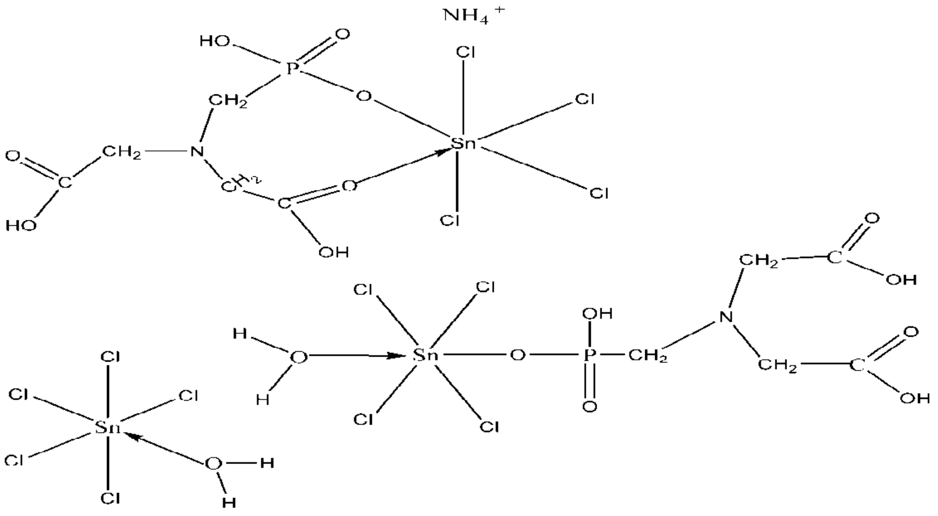


Fig. 4. Proposed structure for compound D.

Considering the adduct $[(C_6H_5CH_2)_2NH_2]_3O_2C(CH_2)_2PO_3H \cdot 3SnPh_3Cl$ [**D**], we know that many $SnPh_3Cl$ adducts with oxygens atoms containing ligands are O monocoordinated [13]. In the complex anion $[O_2C(CH_2)_2PO_3H.3SnPh_3Cl]^{3-}$, three of its five oxygen atoms monocoordinate a $SnPh_3Cl$ molecule.





d)

Fig. 5. Proposed structure for the compound E.

The anion is tridentate, the environment around the tin center being *trans* trigonal bipyramidal. The cations ensure the dimerization.

The compound $(CyNH_3)(HOPOCH_2\text{-}N(CH_2CO_2H)_2]_2{\cdot}3SnCl_4{\cdot}2H_2O$ NH_4Cl [**E**] contains three $SnCl_4$ molecules which are generally present in a $SnCl_4O_2$ octahedral arrangement. This allows for the compound compound [**E**] to suggest the four structures reported on Figures 5 (a, b, c, d) - NH_4Cl is lattice in the three first structures while being coordinated through the chloride to $SnCl_4$ in the structure 5d.

Three first structures of compound [E] are discrete **(**Figure 5a-c) while the last one **(**Figure 5d) is a three metallic component one. The anion behaves as:
- a monochelating and monodentate ligand in the first structure and last structure;
- a monochelating and hydrogen bond involved ligand in the second structure;
- a bridging bidentate ligand in the third structure.

In these structures when the cations are involved in hydrogen bonds a supramolecular architecture may be obtained.

4. CONCLUSION

The five adducts studied have discrete, dimeric, two or three metallic components or infinite chain type structures, the anion behaving as a monodentate, bidentate, tridentate, mono-or bichelating ligand. The environments of the tin (IV) centres are trigonal bipyramidal or octahedral. In free OH or NH containing structures, when extra hydrogen bonds are considered, supramolecular architectures may be obtained.

ACKNOWLEDGEMENTS

We thank Professor Patrick Rosa and Dr. Sergiu Calancea (ICMCB, Bordeaux University-France) for equipment support.

REFERENCES

[1] Evans, C.J., Karpel, S., Organotin compounds in modern technology, Journal of Organometallic Chemistry Library, 16, Elsevier Science Ltd., Amsterdam, 1985, p.178-215.
[2] Gielen, M., Organotin compounds: from kinetics to stereochemistry and antitumour activities, Applied Organomettalic Chemistry, vol. 19, no. 4, 2005, p. 440–450.

[3] Dutrecq, A., Willem, R., Biesemans, M., Boualam, M., Meriem, A., Gielen, M., Toxicity of a series of tri- and di organotin(IV) compounds against phytogenic fungal and bacterial strains, Main Group Metal Chemistry, vol. 15, no. 6, 1992, p. 285–291.

[4] Alvarez Boo, P., Casas, J.S., Couce, M.D., Farto, R., Fernandez- Moreira, V., Freijanes, E., Sordo, J., Vazquez-Lopez, E., Synthesis, characterization and antibacterial activity of some new triphenyltin(IV) sulfanylcarboxylates: Crystal structure of $[(SnPh_3)_2(p\text{-}mpspa)]$, $[(SnPh_3)_2(cpa)]$ and $[(SnPh_3)_2(tspa)(DMSO)]$, Journal of Organometallic Chemistry, vol. 691, no. 1-2, 2006, p. 45-52.

[5] Kapoor, R.N., Guillory, P., Schulte, L., Cernvantes-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, vol. 19, 2005, p. 510-517.

[6] Diallo, W., Okio, K.Y.A., Diop, C.A.K., Diop, L., Diop, L.A., Russo, U., New selenito residues containing complexes and adducts: Synthesis and spectroscopic studies, Main Group Metal Chemistry, vol. 32, no. 2, 2009, p. 93-99.

[7] Boye, M. S., Diasse-Sarr, A., Lebraud, E., Guionneau, P., Bis(1,1-dimethylguanidinium) tetraaquadimethyltin(IV) bis(sulfate), ActaCrystallographica, vol. E68, 2012, p. 70.

[8] Gueye, N., Diop, L., Molloy, K.C., Kociok-Köhn, G., Dibenzylazanium (oxalato-κ2O,O')triphenylstannate (IV), Acta Crystallographica, vol. E68, 2012, p. 854-855.

[9] Okio, K.Y.A., Diop, L., Russo, U., Ionic structure in $SnX_4(Cy_2NH)_4$ (X=Cl, Br): spectroscopic studies, Main Group Metal Chemistry, vol. 33, no. 6, 2010, p. 133-135.

[10]De Barros, D., Diop, L., Mathieu, B., $MeNHWO_4SnPh_3X$ (X = Cl, Br), $R_4NWO_4SnPh_3$(R = Me, Et) and $(Snbu_3)_2WO_4$: Synthesis and spectroscopic, studies, Main Group Metal Chemistry, vol. 33, no. 1-2, 2010, p. 91-95.

[11]Diallo, W., Diop, L., Russo, U., Wattiaux, A., New sulphato organotin (IV) derivates and adducts: Synthesis and spectroscopic studies, Main Group Metal Chemistry, vol. 32, no. 4, 2009, p. 219-227.

[12] Parish, R.V., Platt, R.H., Studies in mossbauer, Part II: The structure of organotin halide and a test of the point- charge model, Inorganic Chemistry Acta, vol. 4, 1970, p. 65-72.

[13] Kane, H.Q., Okio, K.Y.A., Diop, L., Mathieu, B., $Et_4NC_2O_4SnPh_3 \cdot 2SnPh_3Cl$ and $Cy_2NH_2C_2O_4\,SnPh_3 \cdot 2Sn\,Ph_3Cl$: Synthesis and spectroscopic characterization, Main Group Metal Chemistry, vol. 32, no. 4, 2009, p. 229-233.