



ISSN NO. 2320-5407

Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/6460
DOI URL: <http://dx.doi.org/10.21474/IJAR01/6460>



RESEARCH ARTICLE

SOME NEW OXALATO AND SULFATO SnR_3 ($\text{R}=\text{Me}, \text{Ph}$) AND $\text{SnR}'_2\text{Cl}$ ($\text{R}'=\text{Ph}, \text{Bu}$) RESIDUES CONTAINING DERIVATIVES AND COMPLEXES: SYNTHESIS, INFRARED, NMR AND MÖSSBAUER STUDIES.

Waly Diallo¹, Assane Touré², Cheikh A. Khadir Diop¹ and Mamadou Sidibe¹.

1. Université Cheikh Anta Diop, Faculté des Sciences et Techniques, Département de Chimie, Laboratoire de Chimie Minérale et Analytique, Dakar, Sénégal.
2. Université Cheikh Anta Diop, Faculté des Sciences et Technologies de l'Éducation et de la Formation (FASTEF), Département de Physique-Chimie.

Manuscript Info

Manuscript History

Received: 11 December 2017
Final Accepted: 13 January 2018
Published: February 2018

Keywords:-

Oxalate and sulfato compounds;
Monochelating and bidentate ligands;
Trans trigonal bipyramidal or octahedral
environment; Supramolecular
architectures,

Abstract

Ten new oxalato and sulfato complexes and derivatives containing SnR_3 or SnR_2 ($\text{R}=\text{Ph}, \text{Me}, \text{Bu}$) have been synthesized and studied by infrared, NMR and Mossbauer spectroscopies. The suggested structures are discrete, infinite or oligomers. The environments around the tin centre are trigonal bipyramidal or octahedral, the oxalate and sulfate anions behave as monochelating and bidentate ligands. When cations are involved, supramolecular architectures are obtained.

Copy Right, IJAR, 2018,. All rights reserved.

Introduction:-

The large field of applications (medicine, agriculture, wood preservation and PVC production) for many organotin (IV) molecules family is the pretext of the focus of several research groups in this field until nowadays (Davis and al., 1982; Davis and al., 1997; Evans, 1985; Xuan, 2016).

The coordination between oxyanions and organotin (IV) compounds has been studied since many years (Sougoule and al., 2015; Basu Baul and al., 2015; Yang and al., 2016).

Several structures in particular oxalate and sulfate adducts and complexes have been isolated (Smith and al., 2017; Grzeskowiak and al., 2017; Rathod and al., 2017; Döring and al., 2017).

In our laboratory, many X ray structures of complexes and derivatives containing oxalate or sulfate anions has been published (Gueye and al., 2014; Diop and al., 2015; Diallo and al., 2015).

1. The structure of bis(cyclohexylammonium) tetrachlorido(oxalato)stannate(IV) anion is a 3D supramolecular structure with a distorted octahedral coordination sphere around the Sn(IV) centre. Cations and anions are linked through $\text{N-H} \cdots \text{O}$ and $\text{N-H} \cdots \text{Cl}$ interactions into a layered arrangement parallel (Sarr and al., 2013).
2. The structure $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Sn}_2(\text{CH}_3)_6\text{Cl}(\text{SO}_4)]$ is a polymer, the two independent Sn(IV) atoms are coordinated in a trigonal-bipyramidal geometry by three methyl groups in the equatorial plane and in the axial positions by either two O atoms of bridging SO_4^{2-} anions or by a Cl atom and one O atom of a bridging SO_4^{2-} anion, respectively (Diop and al., 2013).

Corresponding Author:- Waly Diallo.

Address:- Université Cheikh Anta Diop, Faculté des Sciences et Techniques, Département de Chimie, Laboratoire de Chimie Minérale et Analytique, Dakar, Sénégal.

In the framework of our research on the coordinating ability of oxyanions within organotin (IV) chemistry, we have synthesized and isolated ten new oxalate and sulfate complexes and derivatives. These compounds were characterized by infrared and NMR or Mossbauer spectroscopies and structures have been suggested.

Experimental section:-

H₂C₂O₄ and H₂SO₄ (98%) were purchased from Merck Chemicals, Hohenbrunn bei München, Germany while CyNH₂, Cy₂NH, *n*-Bu₂NH, SnR₃Cl, SnR₂Cl₂ (R=Ph, Me, Bu), were acquired from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used without any further purification.

Infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate™ ATR device (Infrared data are given in cm⁻¹) [IR abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak].

¹¹⁹Sn NMR spectrum was recorded on a Bruker Avance 400 MHz spectrometer with a wide band sensor BBFO. Spectra are reported downfield from Me₄Sn, as the internal standard and chemical shifts (□ □ □ are given in ppm.

¹¹⁹Sn Mössbauer spectra were collected at 80 K as reported in (Gueye and al, 1993).

Elemental analyses were performed at the "Institut de Chimie Moléculaire", University of Burgundy, Dijon-France.

Procedure for synthesis of (CyNH₃)[C₂O₄SnMe₃]:-

An ethanolic solution (25 ml) containing (1.500mmol; 0.148g) of CyNH₂, (1.500mmol; 0.135g) of H₂C₂O₄, (1.500mmol; 0.3g) of SnMe₃Cl was stirred up at room temperature for more than two hours. Slow solvent evaporation gives white a powder after one week (**A**). The white powder thus formed was washed with hot ethanol and dried in.

Spectroscopic data:-

1. IR data (cm⁻¹): ν_{as}COO= (1627vs, 1556vs); ν_sCOO= (1340s, 1298s); ν_{NH₃}= (3070vs, 2925vs, 2853vs); δ_{NH₃}= (1981m); ν_{as}SnC₃= 549m, ν_sSnC₃= 517vw
2. ¹¹⁹Sn NMR data (CDCl₃): δ=-198 ppm

Elemental Analysis:-

for C₁₁H₂₃NO₄Sn-% found (% calculated): C=37.48 (37.53) H=6.37 (6.59) N=4.01 (3.98); yield: 78.21%

Procedure for synthesis of (CyNH₃)[C₂O₄SnPh₂Cl]:-

A methanolic solution (20 ml) containing (0.3g; 3.027 mmol) of CyNH₂, (0.272g; 3.027 mmol) of H₂C₂O₄ and (6.05 mmol; 2.082g) of SnPh₂Cl₂ was stirred up at room temperature for more than two hours. The white precipitate thus formed (**B**) was filtered, washed with hot methanol and dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm⁻¹): ν_{as}COO=(1619vs, 580vs); ν_sCOO=(1297vs, 1270s); ν_{NH₃}= (2931vs-2857vs), δ_{NH₃}=1504s
2. ¹¹⁹Sn NMR data (CDCl₃): δ=-278 ppm

Elemental Analysis:-

for C₂₀H₂₄ClNO₄Sn- % found (% calculated): C=48.21 (48.37) H=4.75 (4.87) N=3.04 (2.82) yield: 35.14%

Procedure for synthesis of (Bu₂NH₂)[C₂O₄SnBu₂Cl]:-

An ethanolic solution (20 ml) containing (0.987mmol; 0.344g) of (Bu₂NH₂)₂C₂O₄ (obtained from an aqueous mixture of Bu₂NH and H₂C₂O₄ in 1 : 1 ratio) and (0.987mmol; 0.3g) of SnBu₂Cl₂ was stirred up at room temperature for more than two hours. Slow solvent evaporation gives white a powder after one week (**C**). The white powder thus formed was washed with hot ethanol and dried in an oven at 60° C.

Spectroscopic data:-

IR data (cm⁻¹): ν_{NH₂}= (2959vs, 2877vs); ν_{as}COO = (1682s, 1606s); ν_{as}SnC₂=636vs; ν_sSnC₂= 583m; ν_sCOO =(1482vs, 1462s),

Elemental Analysis:-

for $C_{18}H_{38}ClNO_4Sn$: % found (%calculated): C=44.36 (44.42) H=8.02 (7.87) N= 2.75 (2.88) ; yield : 71.54%

Procedure for synthesis of $HC_2O_4SnPh_2Cl$:-

An ethanolic solution (20 ml) containing (0.987mmol; 0.284g) of $(CyNH_3)_2C_2O_4$ (obtained from an aqueous mixture of $CyNH_2$ and $H_2C_2O_4$ in 1 : 1 ratio) and of (0.987mmol; 0.339g) $SnPh_2Cl_2$ was stirred up at 60°C for more than two hours. The white precipitate thus formed (**D**) was filtered, washed with hot ethanol and dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : $\nu_{as}COO = (1625vs, 1585vs)$; $\nu_{s}COO = (1360s, 1270s)$; $\nu_{OH} = 3720s$; $\delta_{OH} = 1590s$
2. ^{119}Sn NMR data($CDCl_3$) : $\delta = -277$ ppm;

Elemental Analysis:-

for $C_{14}H_{11}ClO_4Sn$ - % found (% calculated) : C= 42.78 (42.31) H= 2.84 (2.79); yield: 58.47%

Procedure for synthesis of $HC_2O_4SnBu_2Cl$ (E):-

An ethanolic solution (15 ml) containing (0.987mmol; 0.284g) of $(CyNH_3)_2C_2O_4$ (obtained from an aqueous mixture of $CyNH_2$ and $H_2C_2O_4$ in 1 : 1 ratio) and (0.987mmol; 0.3g) of $SnBu_2Cl_2$ was stirred up at 60°C for more than two hours. Slow solvent evaporation gives white a powder after one week (**E**). The white powder thus formed was washed with hot ethanol and dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : $\nu_{as}COO = (1681vs, 1603vs)$; $\nu_{s}COO = (1348s, 1307s)$; $\nu_{OH} = 3432s$; $\delta_{OH} = 1600s$; $\nu_{as}SnC_2 = 645s$; $\nu_{s}SnC_2 = 580m$
2. ^{119}Sn NMR data ($CDCl_3$) : $\delta = -260$ ppm

Elemental Analysis:-

for $C_{10}H_{19}ClO_4Sn$: % found (% calculated) : C=33.39(33.60) H=5.36(5.96) ; yield : 54.65%

Procedure for synthesis of $(CyNH_3)[SO_4SnPh_2Cl]$ (F):-

An ethanolic solution (20 ml) containing (8.723mmol; 0.256g) of $(CyNH_3)_2SO_4$ (obtained from an aqueous mixture of $CyNH_2$ and H_2SO_4 in 1 : 2 ratio) and (8.723mmol; 0.3g) of $SnPh_2Cl_2$ was stirred up at 60°C for more than two hours. The white precipitate thus formed (**F**) was filtered, washed with hot methanol and dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : $\nu_{as}SO_4 = (985s, 1025vs, 1041vs)$; $\nu_{s}SO_4 = (1143s, 1062vs)$; $\nu_{NH_3} (3245, 3035, 2995)L$; $\delta_{NH_3} = 1599m$
2. ^{119}Sn NMR data ($CDCl_3$): $\delta = -183$ ppm

Elemental Analysis:-

for $C_{18}H_{24}ClNO_4SSn$ - % found (% calculated) : C=42.84(42.84) H=4.79(4.79) N=2.78(2.78)

Procedure for synthesis of $(CyNH_3)[SO_4SnPh_3SnPh_3Cl]$ (G):-

An ethanolic solution (20 ml) containing (0.388mmo; 0.115g) of $(CyNH_3)_2SO_4$ (obtained from an aqueous mixture of $CyNH_2$ and H_2SO_4 in 1 : 2 ratio) and (0.777mmol; 0.3g) of $SnPh_3Cl$ was stirred up at 60°C for more than two hours. The white precipitate thus formed (**G**) was filtered, washed with hot methanol and dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : $\nu_{as}SO_4 = (990s, 1035vs, 1052vs)$; $\nu_{s}SO_4 = (1147s, 1061vs)$; $\nu_{NH_3} = (3080, 2996, 2857)L$; $\delta_{NH_3} = 1537m$
2. ^{119}Sn NMR data ($CDCl_3$) : $\delta = -247$ ppm and -260 ppm

Elemental Analysis:-

for $C_{42}H_{44}ClNO_4SSn_2$: % found (% calculated) : C=54.22(54.14) H=4.53(4.76) N=1.55(1.50)

Procedure for synthesis of $(Cy_2NH_2)[SO_4SnMe_3]$ (H):-

A methanolic solution (20 ml) containing (1.500mmol; 0.445g) of $Cy_2NH_2HSO_4 \cdot H_2O$ (—obtained as a powder on neutralizing SO_4H_2 with Cy_2NH in water- in 1 : 1 ratio) and (1.500mmol; 0.3g) of $SnMe_3Cl$ was stirred up at room temperature for more than two hours. Slow solvent evaporation gives white a powder after one week (H). The white powder thus formed was washed with hot methanol and dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : $\nu_{as}SO_4^{2-}$ = (906s-1045s) ; $\nu_sSO_4^{2-}$ = (1100s-1150s), $\nu_{as}SnC_3$ = 520s, ν_sSnC_3 = 505vw ; νNH_2 (3258s, 3055s, 2876s); δNH_2 = 1560m
2. Mössbauer data ($mm \cdot s^{-1}$) : δ = 1.30 QS = 3.67 Γ = 0.91

Elemental Analysis:-

for $C_{15}H_{33}NO_4SSn$: % found (% calculated) : C=39.15 (39.45) H=7.67 (7.03) N=2.90 (3.04); yield: 55.21%

Procedure for synthesis of $(Cy_2NH_2)[SO_4SnPh_3]$ (I):-

A methanolic solution (20 ml) containing (0.815mmol; 0.0242g) of $Cy_2NH_2HSO_4 \cdot H_2O$ (—obtained as a powder on neutralizing SO_4H_2 with Cy_2NH in water in 1 : 1 ratio—) and (0.815mmol; 0.3g) of $SnPh_3OH$ was stirred up at room temperature for more than two hours. The white precipitate thus formed (I) was filtered, washed with hot methanol and dried in an oven at 60° C.

Spectroscopic data:-

IR data (cm^{-1}) : $\nu_{as}SO_4^{2-}$ = (971s, 1035vs) ; $\nu_sSO_4^{2-}$ = (1080vs, 1120vs) ; νNH_2 (3648, 3045, 2856)L; δNH_2 = 1594m

Elemental Analysis:-

for $C_{30}H_{39}NO_4SSn$: % found (% calculated): C= 57.20 (57.34) H= 6.56 (6.26) N= 2.49 (2.23); yield: 45.56%

Procedure for synthesis of $(Cy_2NH_2)_2(HSO_4)_4SnBu_2$ (J):-

A methanolic solution (20 ml) containing (0.987mmol; 0.1788g) of Cy_2NH ; (0.4935mmol; 0.048g) of H_2SO_4 and (0.987mmol; 0.3g) of $SnBu_2Cl_2$ was stirred up at room temperature for more than two hours. Slow solvent evaporation gives white a powder after one week (J). The white powder thus formed was washed with hot ethanol and dried in an oven at 60° C.

Spectroscopic data:-

1. IR(cm^{-1}) : $\nu_{as}SO_4^{2-}$ = (980s-1020vs) ; $\nu_{as}SO_4^{2-}$ = (1070vs-1120vs) $\nu_{as}SnC_2$ = 690s; ν_sSnC_2 = 590m; νNH_2 = (2960s-2920s- 2840s); δNH_2 = (1560s)
2. Mossbauer data ($mm s^{-1}$): δ = 1.574 QS = 3.82 Γ = 1.05

Elemental Analysis:-

for $C_{30}H_{39}NO_4SSn$: %found (%calculated) : C= 38.45 (38.99) H= 7.32 (7.16) N= 2.67 (2.84); yield: 74%

Results and discussion:-

$CyNH_3C_2O_4SnMe_3$ complex (A)

The presence of strong bands at 1627vs, 1556 cm^{-1} in one case and 1340, 1298 in another case due to the oxalate anion- ν_{as} and ν_s - respectively, in the infrared spectrum of $CyNH_3C_2O_4SnMe_3$ (A) indicates its involvement in the bonding within structures. The apparition of ν_sSnMe_3 as a very weak band at 517 cm^{-1} is indicative of the presence of an almost planar $SnMe_3$ residue allowing to consider the environment around the $SnMe_3$ residue being as trans trigonal bipyramidal.

The value of the ^{119}Sn chemical shift – 198 ppm (\approx 200 ppm) is consistent with the presence of a trans pentacoordinated $SnMe_3$ residue (Wrackmeyer, 1999).

The shape of NH_3 group bands urges us to conclude to a presence of hydrogen bonds of types $\text{NH} \cdots \text{O}$. Indeed, this series of three bands can be explained by the resulting Fermi resonances between νNH and the overtones $2\delta\text{NH}$ and $2\gamma\text{NH}$ (Diallo and al., 2014).

The suggested structure is similar of the crystallographic structure of $(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4\text{SnPh}_3$ reported by Ng and Rae. The structure is dimeric, the $[\text{C}_2\text{O}_4\text{SnMe}_3]^{2-}$ are linked by CyNH_3^+ via $\text{NH} \cdots \text{O}$ hydrogen bonds. The oxalate anion is monochelated and the SnMe_3 is cis coordinated (Ng and al., 2000) (Figure 1).

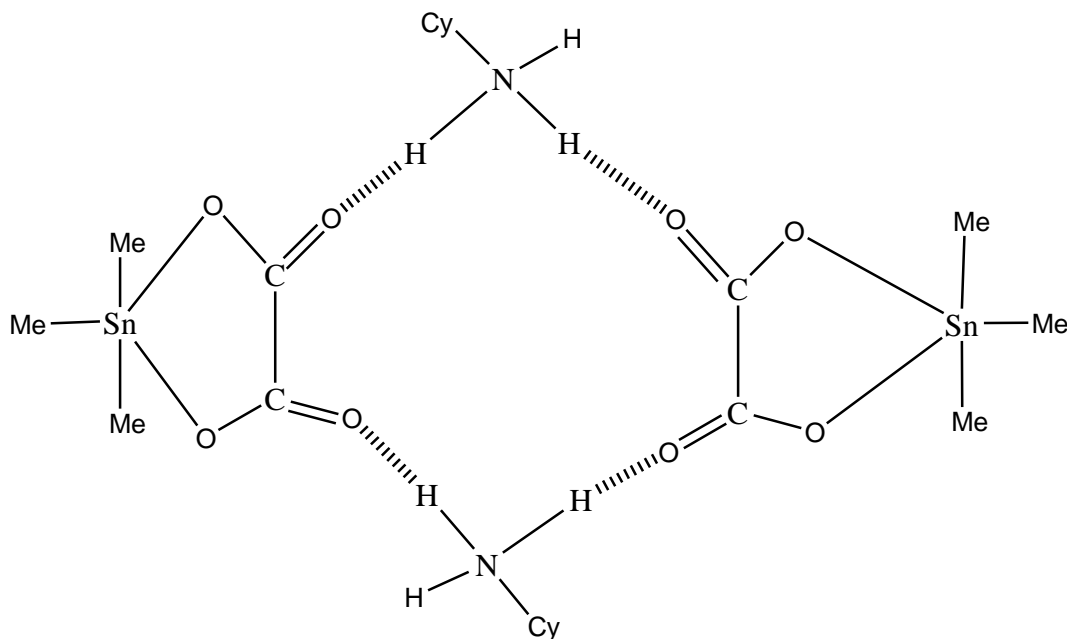


Figure 1:- dimeric structure of of $\text{CyNH}_3\text{C}_2\text{O}_4\text{SnMe}_3$

$\text{CyNH}_3\text{C}_2\text{O}_4\text{SnR}_2\text{Cl}$ ($\text{R}=\text{Ph}$, Bu) complexes (**B**), (**C**)

The infrared spectra of **B** and **C** revealed in particular the presence of strong absorption bands (at 1619 and 1580 for **B**; 1616 and 1682 cm^{-1} for **C** due to the splitting of νasCOO^- ; 1297 and 1270 cm^{-1} for **B**; 1482 and 1462 cm^{-1} for **C**) due to the splitting of νsCOO^- is showing that the oxalate anion is not centrosymmetry (Nakamoto, 1997).

In the IR spectrum of **C**, the presence of νsSnBu_2 as medium band shows that the SnBu_2 residu is slightly bend. This value of the ^{119}Sn chemical shift in CDCl_3 (-278 ppm) shows a trans pentacoordinated tin (IV) central according to (Holecek and al., 1996-1990).

The suggested structure is discrete, the oxalate anion being bi-unidentate and the environment around the tin (IV) centre is trans trigonal bipyramidal (Figure 2).

When hydrogen bonds are involved by cations a supramolecular architecture may be obtained.

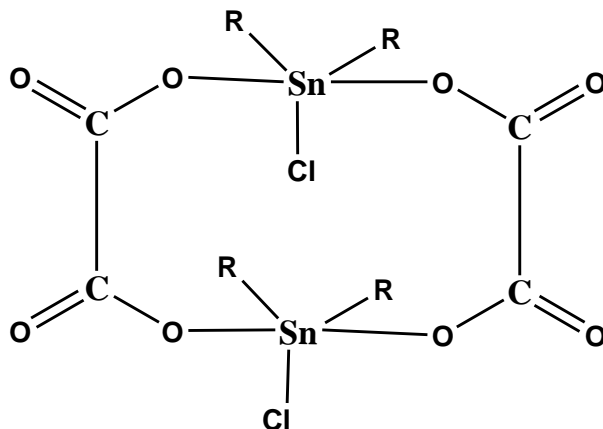


Figure 2 :- Dimeric Structure Of $\text{CyNH}_3\text{C}_2\text{O}_4\text{SnR}_2\text{Cl}$ ($\text{R}=\text{Ph}, \text{Bu}$)

$\text{HC}_2\text{O}_4\text{SnR}_2\text{Cl}$ ($\text{R}=\text{Ph}, \text{Bu}$) derivatives (**D**), (**E**)

The infrared spectra of $\text{HC}_2\text{O}_4\text{SnPh}_2\text{Cl}$ **D** and $\text{HC}_2\text{O}_4\text{SnBu}_2\text{Cl}$ **E** exhibit characteristic absorptions of hydrogenoxalate anion (at 1625 and 1585 cm^{-1} for **D**; 1681 and 1603 cm^{-1} for **E**, 1360 and 1270 cm^{-1} for **D**; 1348 and 1307 cm^{-1} for **E**). In the ir spectrum of **E**, appears ν_{SnC_2} at 580 cm^{-1} as weak band, showing that the SnBu_2 residue being not linear.

The values of the ^{119}Sn chemical shift for **D** and **E** (-277 ppm and -260 ppm respectively) are consistent with a trans pentacoordinated tin (IV) central according to (Holecek and al., 1986- 1990)

The suggested structure is consistent of a dimer of $(\text{HC}_2\text{O}_4)(\text{SnR}_2\text{Cl})$. The SnR_2Cl residue is trans trigonal bipyramidal and the hydrogenoxalate is bidentate (Figure 3).

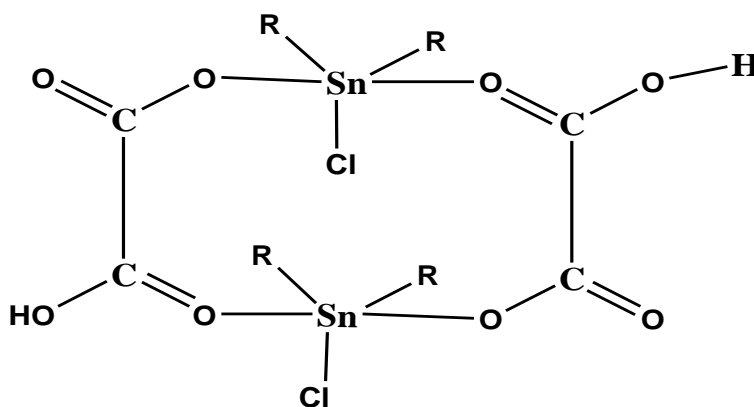


Figure 3:- Discrete Structure Of $\text{HC}_2\text{O}_4\text{SnR}_2\text{Cl}$ ($\text{R}=\text{Ph}, \text{Bu}$)

$\text{CyNH}_3\text{SO}_4\text{SnPh}_2\text{Cl}$ complex (**F**)

The infrared spectra $\text{CyNH}_3\text{SO}_4\text{SnPh}_2\text{Cl}$ (**F**) show strong characteristic bands of sulfate (at 985 , 1025 , 1041 cm^{-1} and 1062 , 1143 cm^{-1} due to ν_s and ν_{as} respectively) shows that SO_4^{2-} anion is not T_d symmetry (Nakamoto, 1997). The very wide absorption around 3000 cm^{-1} in the spectrum due to the cations involved through hydrogen bonds, and generated supramolecular structure.

The value of the ^{119}Sn chemical shift -183 ppm for SnPh_2Cl residue is consistent with the presence of a pentacoordinated tin (IV) centre according to (Holecek et al., 1990). The suggested structure is dimeric when $[\text{SO}_4\text{SnPh}_2\text{Cl}]^-$ anion is considered, the monomers are linked via $\text{NH}\cdots\text{O}$ hydrogen bonds. The sulfate anions are monchelated and the environment around tin (IV) centre is trigonal bipyramidal (Figure 4).

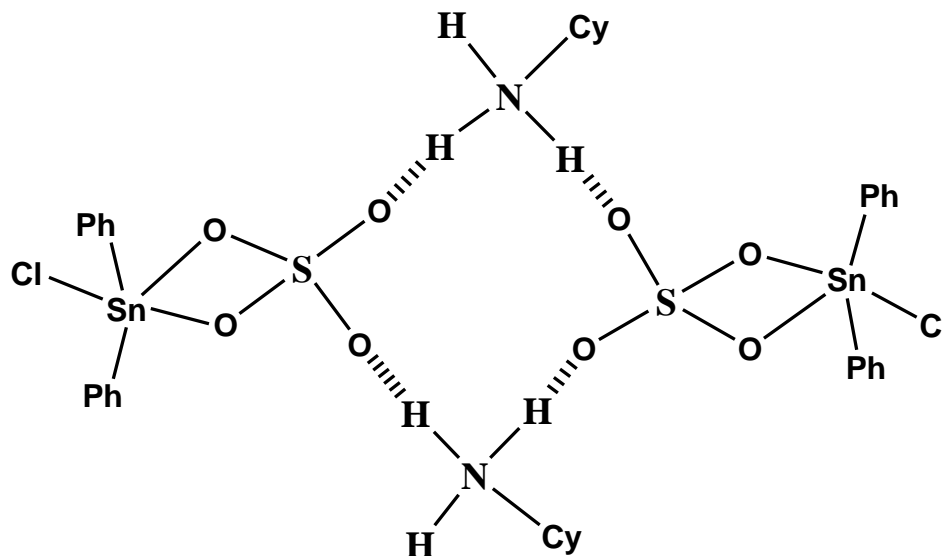


Figure 4:- Dimeric Structure Of $\text{CyNH}_3\text{SO}_4\text{SnPh}_2\text{Cl}$

$\text{CyNH}_3\text{SO}_4\text{SnPh}_3\text{SnPh}_3\text{Cl}$ (**G**)

The infrared spectrum of **G** exhibits characteristic absorptions of sulfate anion bands at 990 , 1035 , 1052 cm^{-1} and 1147 , 1061 cm^{-1} due to ν_s and ν_{as} respectively showing that sulfate anion is not Td (Nakamoto, 1997)

The ^{119}Sn NMR in CDCl_3 shows two signals at -247 ppm and -260 ppm which are consistent with a trans pentacoordinated tin (VI) centre (Bancroft and al., 1972; Parish and al., 1984).

The suggested structure is an infinite chain. The SnPh_3 residues are trans trigonal bipyramidal and the sulfate anion is bi-unidentate coordinated (Figure 5).

NB: When hydrogen bonds are considered, supramolecular architecture is obtained.

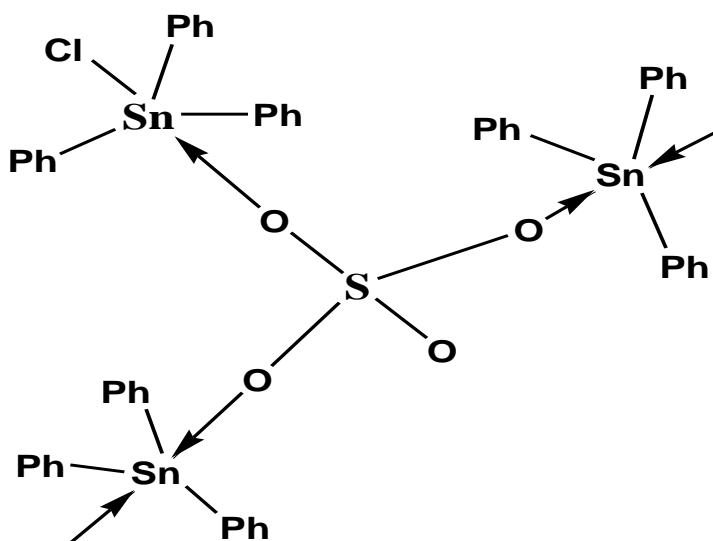


Figure 5:- Infinite Chain Of $\text{CyNH}_3\text{SO}_4\text{SnPh}_3\text{SnPh}_3\text{Cl}$

$\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnR}_3$ (R=Me, Ph) complexes (**H**), (**I**)

The infrared spectra $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnR}_3$ (**H** and **I**) show characteristic bands of sulfate in valence areas. The $\nu_3 \text{ T}_2$ specie splits into to three components (A_1 , B_1 et A_2 species) and the apparition of ν_1 (A_1 specie) is consistent with a SO_4^{2-} anion C_{2v} symmetry (Nakamoto ; 1997).

Intense absorptions bands, observed around 3000 cm^{-1} and 1600 cm^{-1} in many components indicate the presence of $\text{NH}\cdots\text{O}$ hydrogen bonds.

In the $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnMe}_3$ infrared spectrum, the presence of νSnC_3 as a very weak band is indicative of the presence of an almost planar SnC_3 skeleton.

The Mossbauer data of $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnMe}_3$ show that one type of tin (IV) central. The value of quadrupole splitting $3,67 \text{ mm}^{-1}$ is consistent with a trans coordinated SnMe_3 residue (Bancroft and al., 1972 ; Parish and al., 1984).

The suggested structures are similar with those reported by (Ma and al, 2004 ; Gielen and al., 1995). Two sttructures : an infinite chain and oligomer, the sulfate anion is bi-unidentate and SnMe_3 transcoordiné (Figure 6a and b).

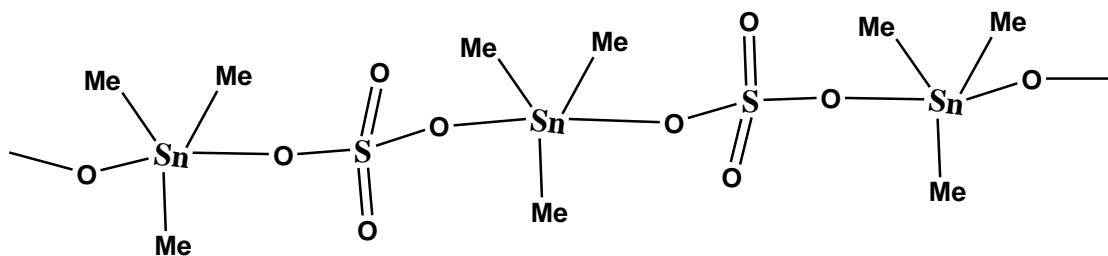


Figure 6a:- Infinite Chain Structure Of $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnR}_3$ (R=Me, Ph)

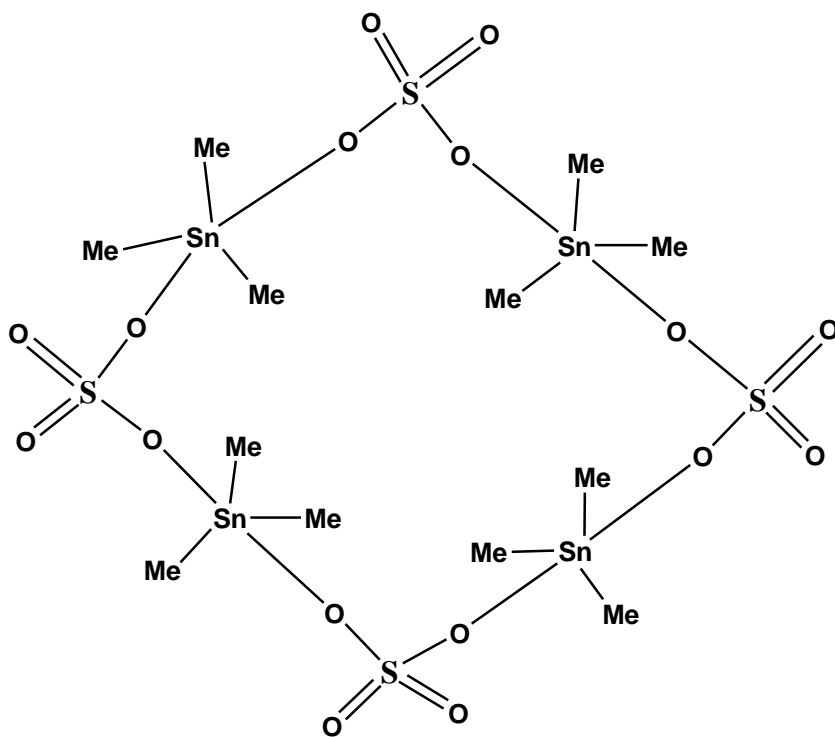


Figure 6b:- oligomer (arbitrary a tetramer) structure of $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnR}_3$ (R=Me, Ph)

NB: When hydrogen bonds are considered, supramolecular architecture is obtained.

SnBu₂(HSO₄)₄(Cy₂NH₂)₂ complex (J)

The forms of characteristic absorption bands in the infrared spectrum of SnBu₂(HSO₄)₄(Cy₂NH₂)₂ (J) between 2800 and 3000 cm⁻¹ (νNH), around 1600 cm⁻¹ are showing the presence of NH---O hydrogen bonds. The presence of νSnC₂ at 590 cm⁻¹ as a medium band is showing that SnC₂ residue is slightly bend. The value of quadupole splitting of Mossbauer spectrum (3.82 mm⁻¹) is indication a slight distorted octahedral geometry around the tin (IV) centre (Bancroft and al., 1972; Parish and al., 1984).

The suggested structure is discrete with a trans hexacoordinated tin (IV) central, the SnC₂ residue are occupied the trans position. The hydrogensulfate anions are monodentate and are linked via NH---O hydrogen bonds (Figure 7).

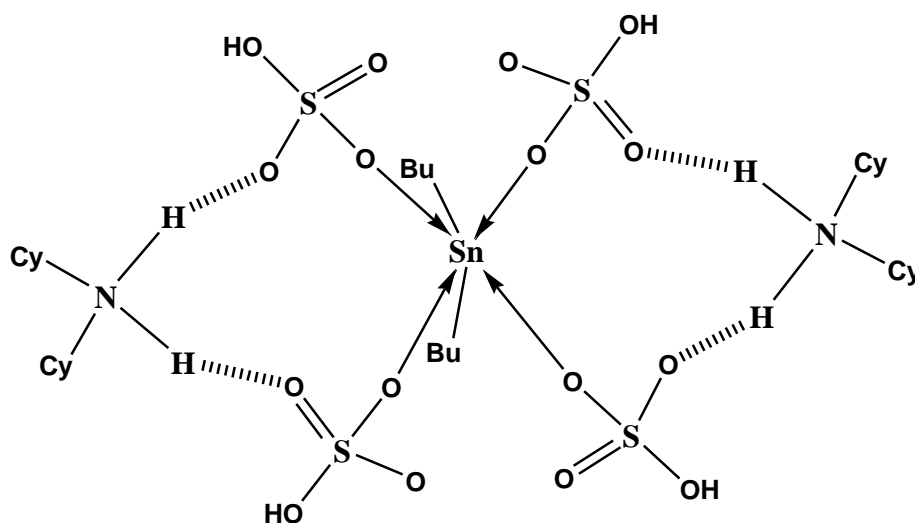


Figure 7:- Discrete Structure Of SnBu₂(HSO₄)₄(Cy₂NH₂)₂

Conclusion:-

The studied di- and triorganotin (IV) residues containing derivatives and complexes have discrete and dimeric structures when they contain oxalate anion and infinite chain or an oligomeric structure when they contain sulfate anion. The environment around the tin (IV) centre being cis or trans trigonal bipyramidal, the oxalate and sulfate ligands are bidentate or monochelated.

In SnBu₂(HSO₄)₄(Cy₂NH₂)₂, the anion is a monodentate ligand, the SnBu₂ residue being slightly bend. The environment around the tin (IV) centre is octahedral.

When the cations involved in hydrogen bonding are considered, supramolecular architectures may be obtained.

Acknowledgment:-

We thank Ph. D. L. Plasseraud (University of Burgundy-Dijon-France) for equipment support.

References:-

1. Bancroft, G.M., Platt, R.H. (1972): Mössbauer spectra of inorganic compounds: Bonding and structure, *Advances in Inorganic Chemistry and Radiochemistry*, 15(14), 59-258.
2. Basu Baul T. S., Linden A. (2015): Synthesis and Structural Facets of Dialkyltin(IV) Complexes Constructed from 2-(2-(3,5-Dimethyl-4-oxocyclohexa-2,5-dien-1 ylidene)hydrazinyl)benzoate, *Z. Anorg. Allg. Chem.*, 641, 1581–1588
3. Brainard R. L.; Denbeaux G., Steven Grzeskowiak; Amrit Narasimhan; Michael Murphy; Lee Napolitano; Daniel A. Freedman (2017) : ,Reactivity of metal-oxalate EUV resists as a function of the central metal, 10146, 1014605

4. - Davies, A. G. and Smith, P. J. (1982): Tin in Comprehensive Organometallic chemistry- the Synthesis, Reactions and Structures of Organometallic compounds (Pergamon Press, vol 2, *Ch11*), S. G. Wilkinson, F. G. A. Stones and E. W. Abel editors,
 - Davies A. G. (1997): Organotin Chemistry, (VCH)
 - Diallo W., Gueye N., Crochet A., Plasseraud L. and Cattey H. (2015) : Crystal structure of dimethylammonium hydrogenoxalate hemi(oxalic acid) Acta Cryst. E71, 473-475
5. Diallo W., Diop L., Plasseraud L. and Cattey H. (2014): [n-Bu₂NH₂]₃[SnPh₃(SeO₄)₂]: the first triorganotin(IV) complex with terminally coordinated selenate ligands, Main Group Met. Chem. 37(3-4): 107–112
6. Diop M. B., Diop L., Plasseraud L. and Maris T. (2015): Crystal structure of 2-methyl-1*H*-imidazol-3-ium aquatrichlorido(oxalato-κ²O,O')stannate(IV), Acta Cryst. E71, 520-522
7. Diop T., Lee A. van der and Sidibé M., (2013) : Poly[tetrabutylammonium [chloridohexamethyl-κ₃-sulfato-distannate(IV)]], Acta Cryst. E69, m406-m407
8. Döring C., Lueck J. F. D. and Jones P. G., (2017) : Crystal structure of the 1:2 adduct of bis(piperidinium) sulfate and 1,3-dimethylthiourea, Acta Cryst. E73, 651-653
9. Evans, C. J.; Karpel, S. (1985). Organotin Compounds in Modern Technology (J. Organomet. Chem. Library Vol. 16, pp. 1 – 279) ; Ed. Elsevier Science Ltd: Amsterdam,
10. Rathod K. T. and Patel I. B., (2017) : Spectroscopic study of gel grown L-Valine Zinc Glycine Thiourea Sulfate (VZGTS) crystal: A novel NLO crystal AIP Conference Proceedings 1837, 040057
11. Gielen, M., Bouhdid, A., Kayser, F., Biesemans, M., de Vos, D., Mahieu, B., Willem, R. (1995): Di(nbutyl)tin bis(dihydroxybenzoate)s: Synthesis, spectroscopic characterization and in vitro antitumour activity, Applied Organometallic Chemistry, 9(3), 251-257
12. Gueye N., Diop L. and Stoeckli-Evans H., (2014) : Tetrakis(dipropylammonium) tetrakis(oxalato-κ²O¹,O²)stannate(IV) monohydrate: a complex with an eight-coordinate Sn^{IV} atom, Acta Cryst. E70, m49-m50
13. - Guèye, O., Qamar, H., Diop, L., Diop, C.A., Russo, U. (1993): A new synthetic route for mono- and polytin (IV) oxalate adducts: IR and Mössbauer study, Polyhedron, 12(10), 1245-1249
14. Holeček, J., Lyčka, A., Handlíř, K. and Nádvorník M., (1990) : ¹³C and ¹¹⁹Sn NMR spectra of diphenyl- and dibenzyltin(IV) compounds and their complexes, Collect. Czech. Chem. Commun., 55, 1193-1207
15. Holeček, J., Lyčka, A., Handlíř, K. and Nádvorník M., (1983) : ¹³C and ¹¹⁹Sn NMR Study of some four- and five-coordinate triphenyltin(IV) compounds, J. of Organometallic Chem. 241(2), 177-184
16. Holeček J., Nádvorník M., Handlíř K., A. Lyčka, J. Organomet. Chem., (1986): ¹³C and ¹¹⁹Sn NMR spectra of Di-n-butyltin(IV) compounds, 315(3), 299-308
17. Ma C., Han Y., Zang R. and Wang D., (2004) : Self-assembly of diorganotin (IV) moieties and 2-pyrazinecarboxylic acid: synthesis, characterizations and crystal structures of monomeric, polymeric or polynuclear macrocyclic compounds, J. Chem. Soc. Dalton Trans, 1832-1840
18. Nakamoto K. : (1997): Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, 5th Edition,
19. Ng S. W. and Rae A. D., 2000 : The pseudo symmetric structure of bis(dicyclohexylammonium) bis(oxalato-triphenylstannate), Zeitschrift für Kristallographie - Crystalline Materials, 215(3), 199-204
20. Sarr M., Diassé-Sarr A., Diallo W., Plasseraud L. and Cattey H., (2013) : Bis(cyclohexylammonium) tetrachlorido(oxalato)stannate(IV), Acta Cryst., E69, m473-m474
21. Parish R. V., 1984: "Structure and bonding in tin compounds" dans "Mössbauer spectroscopy applied to inorganic chemistry", G. L. Lond Ed., Plenum Press, New York, 1 p530
22. Smith G. and Wermuth U. D., (2017) : Unusual 4-arsonoanilinium cationic species in the hydrochloride salt of (4-aminophenyl)arsonic acid and formed in the reaction of the acid with copper(II) sulfate, copper(II) chloride and cadmium chloride, Acta Cryst. C73, 325-330
23. Sougoule A. S., Han X., Balde C. A., Sakho A. M., Zhu D., (2015): An Organotin(IV) Carboxylate Based on Amide Carboxylic Acid: Synthesis, Crystal Structure, and Characterizations, Heteroat. Chem, 26(4), 270–276
24. Xuan H.-Z. Zhang J.-H., Wang Y.-H. Fu C.-L. Zhang W., (2016) :
25. Anti-tumor activity evaluation of novel chrysin–organotin compound in MCF-7 cells
26. Bioorganic & Medicinal Chemistry Letters, 26(2), 570-574
27. Yang Y. g., Hong M., Xu L. d., Cui J. c., Chang G. l., Li D. c., Li C.-z., (2016) : Organotin(IV) complexes derived from Schiff base N'-[(1E)-(2-hydroxy-3-methoxyphenyl)methylidene]pyridine-3-carbohydrazone: Synthesis, in vitro cytotoxicities and DNA/BSA interaction, J. of Organomet. Chem., 804, 48-58
28. Wrackmeyer B., (1999): Application ¹¹⁹Sn-NMR Parameters, Annu. Rep. NMR Spectrosc., 38, 203-264