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RESEARCH ARTICLE

SOME NEW OXALATO AND SULFATO SNR$_3$ (R=Me, Ph) AND SnR'$_2$Cl (R'=Ph, Bu) RESIDUES CONTAINING DERIVATIVES AND COMPLEXES: SYNTHESIS, INFRARED, NMR AND MÖSSBAUER STUDIES.

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Abstract

Ten new oxalato and sulfato complexes and derivatives containing SnR$_3$ or SnR$_2$ (R=Ph, Me, Bu) have been synthetized and studied by infrared, NMR and Mossbauer spectroscopies. The suggested structures are discretes, 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.

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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; Dôring 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 strcuture with a distorted octahedral coordination sphere around the Sn(IV) centre. Cations and anions are linked through N-H⋯O and N-H⋯Cl interactions into a layered arrangement parallel (Sarr and al., 2013).
2. The structure $[(C_4H_9)_4N][Sn_2(CH_3)_6Cl(SO_4)]$ 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).

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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:-
$H_2C_2O_4$ and H_2SO_4 (98%) were purchased from Merck Chemicals, Hohenbrunn bei München, Germany while $CyNH_2$, Cy_2NH, *n*-Bu_2NH, SnR_3Cl, SnR_2Cl_2 (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^{TM} ATR device (Infrared data are given in cm^{-1}) [IR abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak].

^{119}Sn NMR spectrum was recorded on a Bruker Avance 400 MHz spectrometer with a wide band sensor BBFO. Spectra are reported downfield from Me_4Sn, as the internal standard and chemical shifts (□□□are given in ppm.
^{119}Sn 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 $(CyNH_3)[C_2O_4SnMe_3]$:-
An ethanolic solution (25 ml) containing (1.500mmol; 0.148g) of $CyNH_2$, (1.500mmol; 0.135g) of $H_2C_2O_4$, (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 (**A**). The white powder thus formed was washed with hot ethanol and dried in.

Spectroscopic data:-
1. IR data (cm^{-1}) : υasCOO= (1627vs,1556vs) ; υsCOO= (1340s, 1298s) ; υNH_3= (3070vs, 2925vs, 2853vs); δNH_3= (1981m); $\upsilon_{as}SnC_3$= 549m, υ_sSnC_3= 517vw
2. ^{119}Sn NMR data ($CDCl_3$) : δ=-198 ppm

Elemental Analysis:-
for $C_{11}H_{23}NO_4Sn$-% found (% calculated) : C=37.48 (37.53) H=6.37 (6.59) N=4.01 (3.98); yield: 78.21%

Procedure for synthesis of $(CyNH_3)[C_2O_4SnPh_2Cl]$:-
A methanolic solution (20 ml) containing (0.3g; 3.027 mmol) of $CyNH_2$, (0.272g; 3.027 mmol) of $H_2C_2O_4$ and (6.05 mmol; 2.082g) of $SnPh_2Cl_2$ 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}): υasCOO=(1619vs, 580vs); υsCOO=(1297vs, 1270s) ; υNH_3= (2931vs-2857vs), δNH_3=1504s
2. ^{119}Sn NMR data ($CDCl_3$) : δ=-278 ppm

Elemental Analysis:-
for $C_{20}H_{24}ClNO_4Sn$- % found (% calculated) : C=48.21 (48.37) H=4.75 (4.87) N=3.04 (2.82) yield: 35.14%

Procedure for synthesis of $(Bu_2NH_2)[C_2O_4SnBu_2Cl]$:-
An ethanolic solution (20 ml) containing (0.987mmol; 0.344g) of $(Bu_2NH_2)_2C_2O_4$ (obtained from an aqueous mixture of Bu_2NH and $H_2C_2O_4$ in 1 : 1 ratio) 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 (**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}) : υNH_2= (2959vs, 2877vs); υasCOO = (1682s, 1606s); υsCOO =(1482vs, 1462s), $\upsilon_{as}SnC_2$=636vs; υ_sSnC_2= 583m

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 dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : υasCOO = (1625vs, 1585vs); υsCOO= (1360s, 1270s) ; υOH=3720s; δOH=1590s
2. ^{119}Sn NMR data($CDCl_3$) : δ= -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 dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : υasCOO= (1681vs,1603vs); υsCOO= (1348s, 1307s) ; υOH=3432s; δOH=1600s ; $υ_{as}SnC_2$= 645s; $υ_sSnC_2$= 580m
2. ^{119}Sn NMR data ($CDCl_3$) : δ=-260ppm

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 dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : $υ_{as}SO_4$=(985s, 1025vs, 1041vs); $υ_sSO_4$=(1143s, 1062vs); $υNH_3$ (3245, 3035, 2995)L; $δNH_3$= 1599m
2. ^{119}Sn NMR data ($CDCl_3$): δ=-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 dried in an oven at 60° C.

Spectroscopic data:-

1. IR data (cm^{-1}) : : $υ_{as}SO_4$= (990s, 1035vs, 1052vs); $υ_sSO_4$= (1147s, 1061vs); $υNH_3$= (3080, 2996, 2857)L ; $δNH_3$= 1537m
2. ^{119}Sn NMR data ($CDCl_3$) : δ=-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 $Cy_2NH_2HSO_4.H_2O$ (–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 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), $\upsilon_{as}SnC_3$= 520s, υ_sSnC_3=505vw ; υNH_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; 0.0.242g) of $Cy_2NH_2HSO_4.H_2O$ (-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 dried in an oven at 60° C.

Spectroscopic data:-

IR data (cm^{-1}) : $\nu_{as}SO_4^{2-}$= (971s, 1035vs) ; νsSO_4^{2-}= (1080vs, 1120vs) ; υNH_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 dried in an oven at 60° C.

Spectroscopic data:-

1. IR(cm^{-1}) : νas=SO_4^{2-}=(980s-1020vs) ; νas=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 (mms^{-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- υ_{as} and υ_s- respectively, in the infrared spectrum of $CyNH_3C_2O_4SnMe_3$ (**A**) indicates its involvement in the bonding within structures. The apparition of $\upsilon sSnMe_3$ 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 (≈ 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 bands of types NH----O. Indeed, this series of three bands can be explained by the resulting Fermi resonances between υNH and the overtones 2δNH and 2γNH (Diallo and al., 2014).

The suggested structure is similar of the crystallographic structure of $(Cy_2NH_2)_2C_2O_4SnPh_3$ reported by Ng and Rae. The structure is dimeric, the $[C_2O_4SnMe_3]^{2-}$ are linked by $CyNH_3^+$ via NH---O hydrogen bonds. The oxalate anion is monochelated and the $SnMe_3$ is cis coordinated (Ng and al., 2000) (Figure 1).

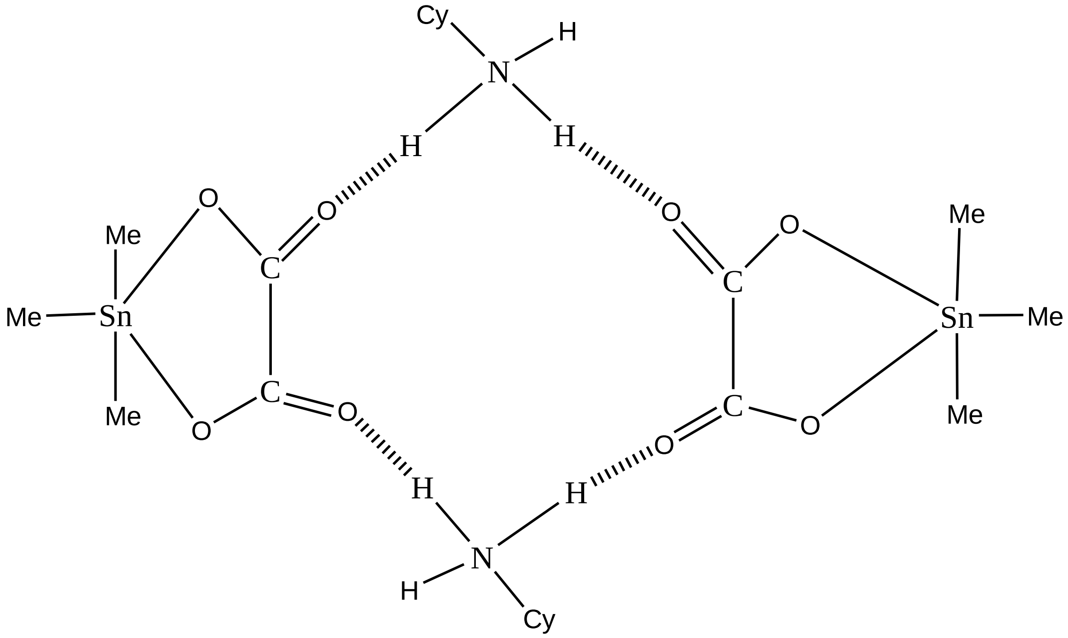

Figure 1:- dimeric structure of of $CyNH_3C_2O_4SnMe_3$

$CyNH_3C_2O_4SnR_2Cl$ (R=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 υasCOO$^-$;1297 and 1270 cm^{-1} for **B** ; 1482 and 1462 cm^{-1} for **C**) due to the splitting of υsCOO$^-$ is showing that the oxalate anion is not centrosymetry (Nakamoto, 1997).

In the IR spectrum of **C**, the presence of υs$SnBu_2$ 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.

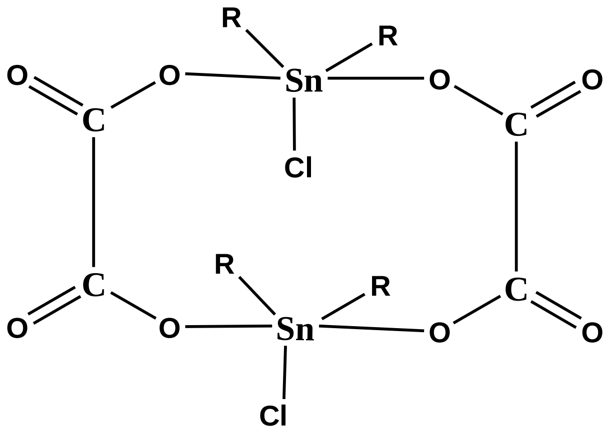

Figure 2 :- Dimeric Structure Of $CyNH_3C_2O_4SnR_2Cl$ (R=Ph, Bu)

$HC_2O_4SnR_2Cl$ (R=Ph, Bu) derivatives (**D**), (**E**)

The infrared spectra of $HC_2O_4SnPh_2Cl$ **D** and $HC_2O_4SnBu_2Cl$ **E** exhibit characteristic absorptions of hydrogenooxalate 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 $\upsilon sSnC_2$ at 580 cm^{-1} as week band, showing that the $SnBu_2$ residu being not linear.

The values of the ^{119}Sn chemical shift for **D** and **E** (-277ppm 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 $(HC_2O_4)(SnR_2Cl)$. The SnR_2Cl residue is trans trigonal bipyramidal and the hydrogenooxalate is bidentate (Figure 3).

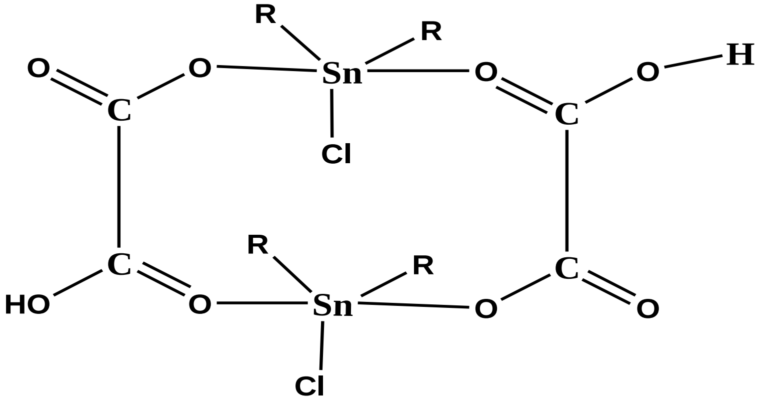

Figure 3:- Discrete Structure Of $HC_2O_4SnR_2Cl$ (R=Ph, Bu)

$CyNH_3SO_4SnPh_2Cl$ complex (**F**)

The infrared spectra $CyNH_3SO_4SnPh_2Cl$ (**F**) show strong characteristic bands of sulfate (at 985, 1025, 1041 cm^{-1} cm^{-1} and 1062, 1143 cm^{-1}dues to υ_s and υ_{as}- respectively) shows that SO_4^{2-} anion is not Td 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 $[SO_4SnPh_2Cl]^-$ anion is considered, the monomers are linked via NH---O hydrogen bonds. The sulfate anions are monchelated and the environment around tin (IV) centre is trigonal bipyramidal (Figure 4).

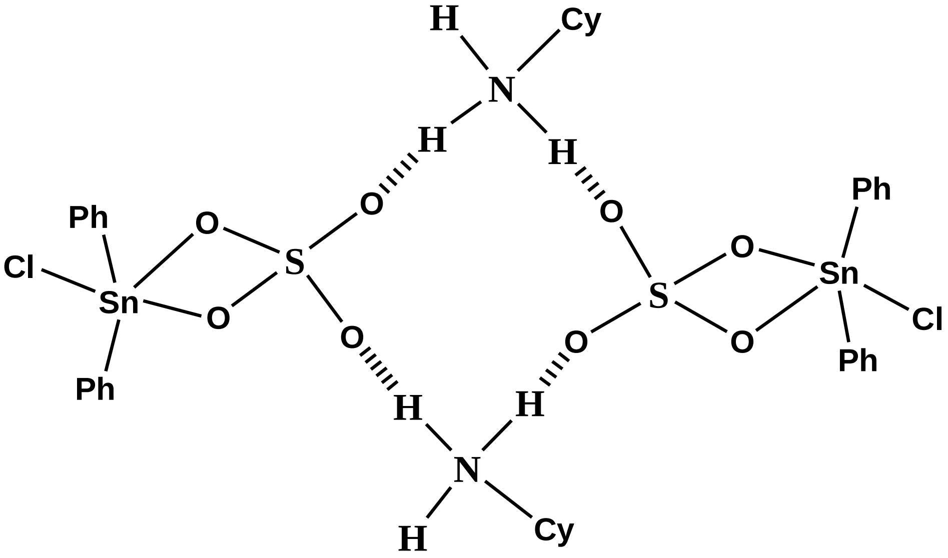

Figure 4:- Dimeric Structure Of $CyNH_3SO_4SnPh_2Cl$

$CyNH_3SO_4SnPh_3SnPh_3Cl$ (**G**)
The infrared spectrum of **G** exhibits characteristic absorptions of sulfate anion bands at 990, 1035, 1052 cm^{-1} and 1147, 1061cm^{-1}dues to υ_s and υ_{as}- respectively showing that sulfate anion is not Td (Nakamoto, 1997)

The ^{119}Sn NMR in $CDCl_3$ shows two signals at -247 ppm et -260 ppm which 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.

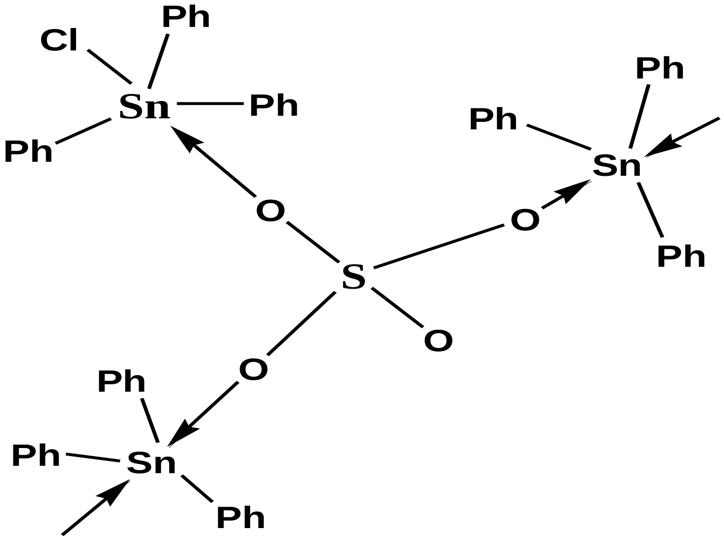

Figure 5:- Infinite Chain Of $Cynh_3so_4snph_3snph_3cl$

$Cy_2NH_2SO_4SnR_3$ (R=Me, Ph) complexes (**H**), (**I**)

The infrared spectra $Cy_2NH_2SO_4SnR_3$ (**H and I**) show characteristic bands of sulfate in valence areas. The υ3 T_2 specie splits into to three components (A_1, B_1 et A_2 species) and the apparition of $υ_1$ (A_1 specie) is consistent with a SO_4^{2-} anion C_{2v} symetry (Nakamoto ; 1997).

Intense absorptions bands, oberserved around 3000 cm-1 and 1600 cm^{-1} in many components indicate the presence of NH….O hydrogen bonds.

In the $Cy_2NH_2SO_4SnMe_3$ infrared spectrum, the presence of υsSnC_3 as a very weak band is indicative of the presence of an almost planar SnC_3 skeleton.

The Mossbauer data of $Cy_2NH_2SO_4SnMe_3$ show that one type of tin (IV) central. The value of quadrupole splitting 3,67 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 sttuctures : an infinite chain and oligomer, the sulfate anion is bi-unidentate and SnMe3 transcoordiné (Figure 6a and b).

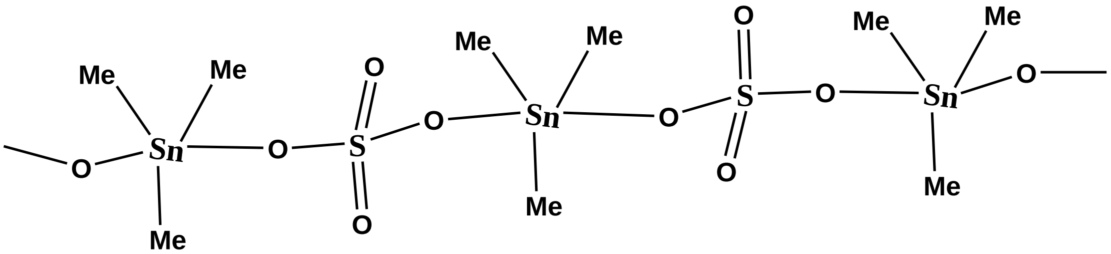

Figure 6a:- Infinite Chain Structure Of $Cy_2NH_2SO_4SnR_3$ (R=Me, Ph)

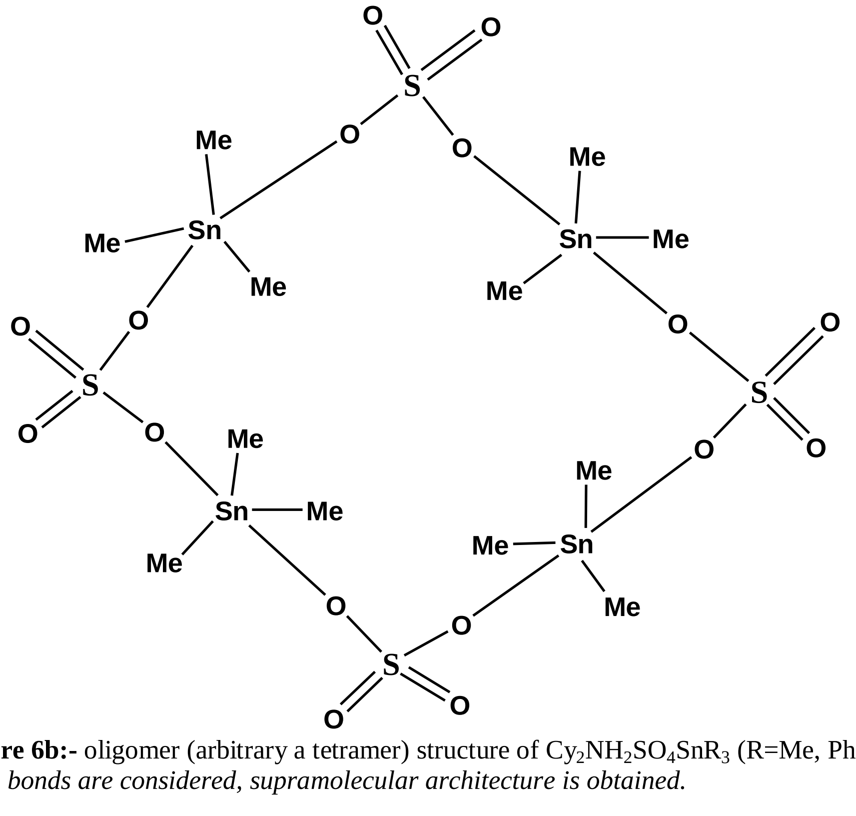

Figure 6b:- oligomer (arbitrary a tetramer) structure of $Cy_2NH_2SO_4SnR_3$ (R=Me, Ph)

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

$SnBu_2(HSO_4)_4(Cy_2NH_2)_2$ complex (**J**)

The forms of characteristic absorption bands in the infrared spectrum of $SnBu_2(HSO_4)_4(Cy_2NH_2)_2$ (**J**) between 2800 and 3000 cm-1 (υNH), around 1600 cm^{-1} are showing the presence of NH----O hydrogen bonds. The presence of $\nu sSnC_2$ at 590 cm^{-1} as a medium band is showing that SnC_2 residu 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 SnC_2 residu are occupied the trans position. The hydrogenosulfate anions are monodenttate and are linked via NH---O hydrogen bonds (Figure 7).

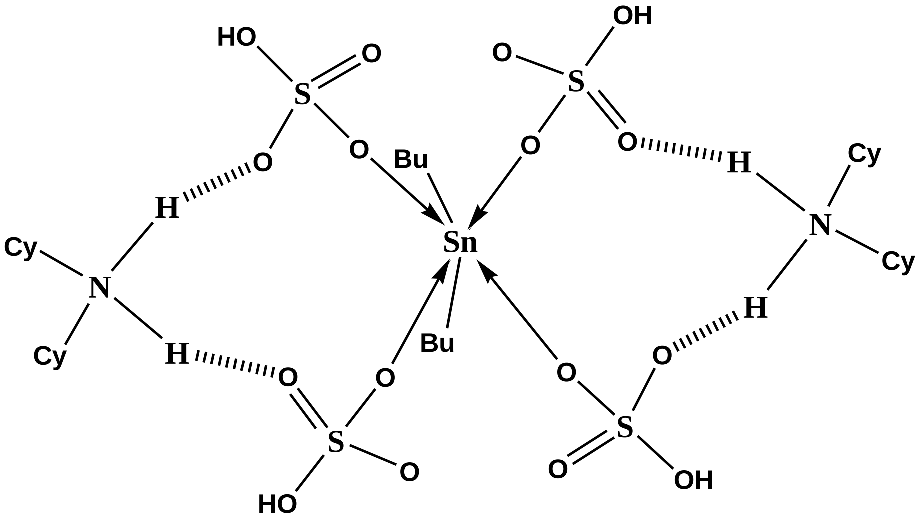

Figure 7:- Discrete Structure Of $SnBu_2(HSO_4)_4(Cy_2NH_2)_2$

Conclusion:-

The studied di- and triorganotin (IV) residues containing derivatives and complexes have discrete and dimeric structures when they contains 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 $SnBu_2(HSO_4)_4(Cy_2NH_2)_2$, the anion is a monodentate ligand, the $SnBu_2$ 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.

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