Journal Homepage: -www.journalijar.com
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)
ISSN NO. 2320-5407
Article DOI:10.21474/IJAR01/8999
DOI URL: http://dx.doi.org/10.21474/IJAR01/8999

RESEARCH ARTICLE

SOME ORGANOTIN (IV) NITRATE ADDUCTS: SYNTHESES, FAR INFRARED AND MÖSSBAUER CHARACTERIZATION.

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Manuscript Info

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Manuscript History
Received: 01 March 2019
Final Accepted: 03 April 2019
Published: May 2019

Key words:-
nitrate, organotin (IV), discrete structures, far infrared, mössbauer.

Abstract

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Nine new organotin (IV) nitrate adducts of $SnPh_3Cl$, $SnMe_3Cl$, $SnMe_2Cl_2$ and $SnBu_2Cl_2$ have been isolated and characterized by far infrared and mössbauer spectroscopies. Within the proposed structures, the nitrate anion behaves as a monodentate, a bidentate, a tridentate or a monochelating ligand. All the structures are discrete and the environments at tin atoms are trigonal bipyramidal with trigonal planar SnR_3 moieties in SnR_3Cl adducts. Two environment types are present in SnR_2Cl_2 containing adducts: an octahedral and a trigonal bipyramidal. The interactions between complex-anions and cations are mainly electrostatic.

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Introduction:-

Interest in organotin(IV) materials is owed to the numerous applications they still arouse. Meneghetti and Meneghetti (2015) as well as Devendra and coworkers (2015) reported interesting catalysis applications while Gielen and coworkers in 2005, Davies and coworkers in 2008 and, Hadjikakou and Hadjiliadis in 2009 reported some biological activities. Potential anticancer activity has been reported for organotin(IV) compounds by Sirajuddin and coworkers and by Amir and coworkers, in 2014. A fungicidal activity has been reported (Mao *et al*., 2015) too. In the past, organotin (IV) nitrate derivatives have been widely studied by Pelizzi and coworkers (Bonardi *et al*., 1991; Franzoni *et al*., 1988, 1989; Pelizzi *et al*., 1983, 1984; Nardelli *et al*., 1985; Dondi *et al*., 1985, 1986). Various other groups have also been involved in seeking new organotin (IV) nitrate compounds (Al-Juaid *et al*., 1998; Ma *et al*., 2004; Shankar *et al*., 2004; Jurkschat *et al*., 2003; Zhong *et al*., 2007). In tin chemistry, bridging bidentate and tridentate nitrates are scarce. In 2003, a bridging nitrate has been isolated and structurally characterized by Jurkschat and Tiekink. Reuter and Reichelt also reported in 2014, some diorganotin(IV) nitrate among which the crystal structure of $Me_2Sn(NO_3)(OH)$ and $Et_2Sn(NO_3)(OH)$, the first, in a one-dimensional chain describes a dimer with two hydroxyl bridges and monodentate nitrates while the second, in a two-dimensional coordination polymer describes a dimeric moiety comprising two hydroxyl bridges and bidentate bridging nitrate ions. The Dakar research work in tin coordination chemistry involves the study of the behaviour of oxyanions as ligands. Thus, we have reported several studies dealing with their coordinating ability (Okio *et al*., 2009; Diallo *et al*., 2009a, 2009b; Kane *et al*., 2009). Carrying interest in organotin(IV) nitrate class of compounds isolation and characterization, the Dakar group has reported the spectroscopic studies of some nitrato compounds including the crystal structure of the complex $[NO_3(SnPh_3NO_3)(SnPh_3Cl)_2][Et_4N]^+$ (Diop *et al.*, 2013) which describes a central tridentate nitrate anion coordinated to tin centres and the infrared study of $SnPh_3(NO_3)_2$.MEIH.$SnPh_3Cl$ (MEIH = 2-methylimidazolium) (Diop and Diop, 2017). As continuation of our contribution in isolation and characterization of new organotin(IV) nitrate compounds, we investigate here the interactions between triorganotin(IV) chloride,

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SnR_3Cl (R = Me, Ph) or diorganotin(IV) dichloride, SnR_2Cl_2 (R = Me, Bu) materials and tetrapropylammonium nitrate or tetrabutylammonium nitrate in one hand and, *n*-hexyltriphenylphosphonium nitrate or benzyltriphenylphosphonium nitrate in another hand. This afforded nine organotin(IV) nitrate adducts reported herein, whose infrared and mössbauer studies have been carried out and their structures suggested on the basis of the spectroscopic data.

Experimental section:-

Silver nitrate, $AgNO_3$, SnR_2Cl_2 (R = Me, Bu, Ph), SnR_3Cl (Me, Ph), tetrapropylammonium chloride, Pr_4NCl (98%), tetrabutylammonium chloride, Bu_4NCl (>97%), benzyltriphenylphosphonium chloride, $PhCH_2Ph_3PCl$ (99%) and *n*-hexyltriphenylphosphonium bromide, *n*-hexylPh_3PBr (95%) were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used without any further purification.

Infrared spectra were recorded on a BX FT-IR-PE 580 (4000-200cm^{-1}) spectrometer at the Cheikh Anta Diop University of Dakar (Senegal) and a FTIR-Nicolet (600-50cm^{-1}) spectrometer at the University of Padua (Italy), the sample being as Nujol mulls using CsI or polyethylene windows. Infrared data are given in cm^{-1} [IR abbreviations: (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak].

The elemental analyses were performed at the CNRS "Service Central d'Analyses" Vernaison-France.

^{119}Sn Mössbauer spectra were obtained as described previously (Bouâlam *et al*., 1991). Mössbauer parameters are given in mms^{-1} [Mössbauer abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height).

Synthesis procedure of $[Pr_4N(NO_3)][SnPh_3Cl]$ (A):-

The isolation of compound **A** follows a two steps procedure. The tetrapropylammonium nitrate salt, $Pr_4N(NO_3)$ was first isolated on allowing equimolar aqueous solutions of tetrapropylammonium chloride, Pr_4NCl (2 g; 9 mmol) and silver nitrate, $AgNO_3$ (1.53 g; 9 mmol) to react, filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. To 15mL ethanolic solution of the tetrapropylammonium nitrate salt, $Pr_4N(NO_3)$ (249 mg; 1 mmol) was added dropwise an equimolar amount of triphenyltin chloride, $SnPh_3Cl$ (386 mg; 1 mmol) preliminary dissolved in 15mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature afforded a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1390(s), 1367(s), ν_1= 1072(s), νCC and νCH (phenyl groups) = 730(vs), 693(s), νSnCl= 334(s), $\nu_{as}SnC_3$= 268(s), ν_sSnC_3= 209(s), νSnO=196(m)
2. Mössbauer parameters (mms^{-1}): QS= 3.08, IS= 1.29, Γ = 0.82

Elemental Analysis:-

$[Pr_4N(NO_3)][SnPh_3Cl]$ (**A**), $C_{30}H_{43}ClN_2O_3Sn$, [% calculated (%found)]:- C = 56.85 (56.84), H = 6.84 (6.85), N = 4.42 (4.32)

Synthesis procedure of $[Bu_4N(NO_3)][SnPh_3Cl]$ (B):-

The tetrabutylammonium nitrate salt, $Bu_4N(NO_3)$ was isolated on allowing equimolar aqueous solutions of tetrabutylammonium chloride, Bu_4NCl (1.95 g; 7 mmol) and silver nitrate, $AgNO_3$ (1.19 g; 7 mmol) to react, filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. The isolation of **B** occurred by adding dropwise 10 mL ethanolic solution of triphenyltin chloride, $SnPh_3Cl$ (285 mg; 0.7 mmol) to an equimolar amount of the previously collected tetrabutylammonium nitrate salt, $Bu_4N(NO_3)$ (214 mg; 0.7 mmol) dissolved in 15 mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature yielded a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1392(s), 1375(s), ν_1= 1076(w), νCC and νCH (phenyl groups) = 736(vs), 695(s), νSnCl= 338(s), $\nu_{as}SnC_3$= 272(s), ν_sSnC_3= 208(w), νSnO= 200(m)
2. Mössbauer parameters (mms^{-1}): QS = 2.83, IS = 1.26, Γ = 0.96

Elemental Analysis:-

$[Bu_4N(NO_3)][SnPh_3Cl]$ (**B**), $C_{34}H_{51}ClN_2O_3Sn$, [% calculated (%found)]:- C = 59.19 (59.22), H = 7.45 (7.41), N = 4.06 (4.11)

Synthesis procedure of $[Bu_4N(NO_3)][(SnPh_3Cl)_2]$ (C):-

The compound **C** was obtained similarly to the previous. At first, the tetrabutylammonium nitrate salt, $Bu_4N(NO_3)$ was isolated by reacting equimolar aqueous solutions of tetrabutyl ammonium chloride, Bu_4NCl (1.95 g; 7 mmol) and silver nitrate, $AgNO_3$ (1.19 g; 7 mmol), filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. The isolation of **C** occurred by mixing 15 mL ethanolic solutions of triphenyltin chloride, $SnPh_3Cl$ (388 mg; 1 mmol) and the previously collected tetrabutylammonium nitrate salt, $Bu_4N(NO_3)$ (153 mg; 0.5 mmol). The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature gave a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1384(s), 1358(s), ν_1= 1078(s), νCC and νCH (phenyl groups) = 734(vs), 697(s), νSnCl= 340(s), $\nu_{as}SnC_3$= 271(vs), ν_sSnC_3= 208(w), νSnO= 200(m)
2. Mössbauer parameters (mms^{-1}): QS= 3.02, IS= 1.31, Γ = 0.92

Elemental Analysis:-

$[Bu_4N(NO_3)][(SnPh_3Cl)_2]$ (**C**), $C_{52}H_{66}Cl_2N_2O_3Sn_2$, [% calculated (%found)]:- C = 58.08 (58.04), H = 6.19 (6.21), N = 2.60 (2.75)

Synthesis procedure of [(*n*-hexyl)$Ph_3P(NO_3)$][$(SnPh_3Cl)_2$] (D):-

The isolation of this compound follows a two steps procedure. The *n*-hexyltriphenylphosphonium nitrate salt, (*n*-hexyl)$Ph_3P(NO_3)$ was first isolated on allowing an aqueous solution of *n*-hexyltriphenylphosphonium bromide, (*n*-hexyl)Ph_3PBr (855 mg; 2 mmol) to react with an equimolar silver nitrate, $AgNO_3$ aqueous solution (340 mg; 2 mmol), filtering off the AgBr precipitate and allowing the solvent to evaporate at room temperature. To 15mL ethanolic solution of the *n*-hexyltriphenylphosphonium nitrate salt, (*n*-hexyl)$Ph_3P(NO_3)$ (164 mg; 0.4 mmol) was added dropwise an amount of triphenyltin chloride, $SnPh_3Cl$ (309 mg; 0.8 mmol) dissolved in 15mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature afforded a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1377(s), 1352(br), ν_1= 1079(m), νCC and νCH (phenyl groups) = 729(vs), 689(s), νSnCl= 341(m), $\nu_{as}SnC_3$= 274(vs), ν_sSnC_3= 211(w), νSnO= 200(m)
2. Mössbauer parameters (mms^{-1}): QS= 3.10, IS= 1.35, Γ = 0.90

Elemental Analysis:-

[(*n*-hexyl)$Ph_3P(NO_3)$][$(SnPh_3Cl)_2$] (**D**), $C_{60}H_{58}Cl_2NO_3PSn_2$, [% calculated (%found)]:- C = 61.05 (61.02), H = 4.95 (5.06), N = 1.19 (1.09)

Synthesis procedure of $[(PhCH_2)Ph_3P(NO_3)][(SnPh_3Cl)_3]$ (E):-

The benzyltriphenylphosphonium nitrate salt, $(PhCH_2)Ph_3P(NO_3)$ was isolated by reacting equimolar aqueous solutions of benzyltriphenylphosphonium chloride, $(PhCH_2)Ph_3PCl$ (974 mg; 2.5 mmol) and silver nitrate, $AgNO_3$ (425 mg; 2.5 mmol), filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. The isolation of **E** occurred by adding dropwise 20 mL ethanolic solution of triphenyltin chloride, $SnPh_3Cl$ (579 mg; 1.5 mmol) to an amount of the previously collected benzyltriphenylphosphonium nitrate salt, $(PhCH_2)Ph_3P(NO_3)$ (208 mg; 0.5 mmol) dissolved in 15 mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature afforded a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1350(vs), νCC and νCH (phenyl groups) = 735(vs), 692(s), νSnCl= 337(m), $\nu_{as}SnC_3$= 273(vs), ν_sSnC_3= 211(w), νSnO= 197(m)
2. Mössbauer parameters (mms^{-1}): QS = 3.08, IS =1.37, Γ = 0.94

Elemental Analysis:-

$[(PhCH_2)Ph_3P(NO_3)][(SnPh_3Cl)_3]$ (**E**), $C_{79}H_{67}Cl_3NO_3PSn_3$, [% calculated (%found)]:- C = 60.37 (60.11), H = 4.30 (4.40), N = 0.89 (0.81)

Synthesis procedure of $[Pr_4N(NO_3)][SnMe_3Cl]$ (F):-

The isolation of compound **F** follows a two steps procedure. The tetrapropylammonium nitrate salt, $Pr_4N(NO_3)$ was first isolated on allowing equimolar aqueous solutions of tetrapropylammonium chloride, Pr_4NCl (2 g; 9 mmol) and silver nitrate, $AgNO_3$ (1.53 g; 9 mmol) to react, filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. To 15mL ethanolic solution of the tetrapropylammonium nitrate salt, $Pr_4N(NO_3)$ (199 mg; 0.8 mmol) was added dropwise an equimolar amount of trimethyltin chloride, $SnMe_3Cl$ (160 mg; 0.8 mmol) dissolved in 10mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature afforded a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1335 (s), 1367(s), ν_1= 1073(m), $\nu_{as}SnC_3$= 546(vs), ν_sSnC_3= 510(w), νSnCl= 333(s), νSnO= 199(s)
2. Mössbauer parameters (mms^{-1}): QS = 3.63, IS = 1.36, Γ = 0.95

Elemental Analysis:-

$[Pr_4N(NO_3)][SnMe_3Cl]$ (**F**), $C_{15}H_{37}ClN_2O_3Sn$, [% calculated (%found)]:- C = 40.25 (39.95), H = 8.33 (8.41), N = 6.26 (6.38)

Synthesis procedure of $[Bu_4N(NO_3)][SnMe_2Cl_2]$ (G):-

The compound **G** was obtained similarly to the previous following a two steps procedure. At first, the tetrabutylammonium nitrate salt, $Bu_4N(NO_3)$ was isolated by reacting equimolar aqueous solutions of tetrabutylammonium chloride, Bu_4NCl (1.95 g; 7 mmol) and silver nitrate, $AgNO_3$ (1.19 g; 7 mmol), filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. The isolation of **G** occurred by reacting 10 mL ethanolic solution of dimethyltin dichloride, $SnMe_2Cl_2$ (220 mg; 1 mmol) and an equimolar amount of the previously collected tetrabutylammonium nitrate salt, $Bu_4N(NO_3)$ (305 mg; 1 mmol) dissolved in 15mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature yielded a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1381(vs), 1353(vs), ν_1= 1064(s), $\nu_{as}SnC_2$= 571(m), ν_sSnC_2= 519(w), νSnCl= 332(vs), νSnO= 200(w)
2. Mössbauer parameters (mms^{-1}): QS = 3.35, IS = 1.32, Γ = 0.86

Elemental Analysis:-

$[Bu_4N(NO_3)][SnMe_2Cl_2]$ (**G**), $C_{18}H_{42}Cl_2N_2O_3Sn$, [% calculated (%found)]:- C = 41.25 (41.15), H = 8.01 (8.10), N = 5.34 (5.20)

Synthesis procedure of $[Pr_4N(NO_3)][SnBu_2Cl_2]$ (H):-

The isolation of compound **H** follows a two steps procedure. The tetrapropylammonium nitrate salt, $Pr_4N(NO_3)$ was first isolated on allowing equimolar aqueous solutions of tetrapropylammonium chloride, Pr_4NCl (2 g; 9 mmol) and silver nitrate, $AgNO_3$ (1.53 g; 9 mmol) to react, filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. To 15mL ethanolic solution of the tetrapropylammonium nitrate salt, $Pr_4N(NO_3)$ (249 mg; 1 mmol) was added dropwise an equimolar amount of dibutyltin dichloride, $SnBu_2Cl_2$ (304 mg; 1 mmol) preliminary dissolved in 10mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature gave a white powder.

Spectroscopic data:-

1. IR data (cm^{-1}): ν_3= 1372(s), 1347(s), ν_1= 1070(vw), ν_4= 591(s), 557(s), νSnCl= 335(s), νSnO= 212(m)
2. Mössbauer parameters (mms^{-1}): QS= 3.54, IS= 1.46, Γ = 0.93

Elemental Analysis:-
$[Pr_4N(NO_3)][SnBu_2Cl_2]$ (**H**), $C_{20}H_{46}Cl_2N_2O_3Sn$, [% calculated (%found)]:- C = 43.50 (42.99), H = 8.40 (8.49), N = 5.07 (5.10)

Synthesis procedure of $[Pr_4N(NO_3)][SnMe_2Cl_2][1/6Pr_4N(NO_3)]$ (I):-
The isolation of **I** also follows a two steps procedure. At first, the tetrapropylammonium nitrate salt, $[Pr_4N(NO_3)]$ was isolated from reaction between equimolar aqueous solutions of tetrapropylammonium chloride, Pr_4NCl (2 g; 9 mmol) and silver nitrate, $AgNO_3$ (1.53 g; 9 mmol), filtering off the AgCl precipitate and allowing the solvent to evaporate at room temperature. The isolation of **I** occurred by reacting 15 mL ethanolic solution of dimethyltin dichloride, $SnMe_2Cl_2$ (110 mg; 0.5 mmol) and an amount of the previously collected tetrapropylammonium nitrate salt, $[Pr_4N(NO_3)]$ (249 mg; 1 mmol) dissolved in 15mL of ethanol. The obtained solution stirred 2h then submitted to a slow solvent evaporation at room temperature afforded a white powder.

Spectroscopic data:-
1. IR data (cm^{-1}): ν_3= 1334(s), 1357(s), $\nu_{as}SnC_2$= 575(m), ν_sSnC_2= 518(m), νSnCl= 337(s), νSnO= 200(m)
2. Mössbauer parameters (mms^{-1}): QS = 3.30, IS = 1.37, Γ = 0.82

Elemental Analysis:-
$[Pr_4N(NO_3)][SnMe_2Cl_2][1/6Pr_4N(NO_3)]$ (**I**), $1/6(C_{96}H_{232}N_{12}N_{14}O_{21}Sn_6)$, [% calculated (%found)]:- C = 37.72 (37.68), H = 7.65 (7.84), N = 6.42 (6.85)

Results and discussion:-

SnR_3Cl adducts (R = Ph, Me)
FT-IR data of **A** evidence absorption bands corresponding to nitrate ion and $SnPh_3$ moiety. The vibration bands located at 1390, 1367 and at 1072 cm^{-1} are assigned to ν_3 and ν_1 vibrations of the nitrate, respectively. Vibration bands, characteristic of phenyl ligands, are observed at 730 and 693 cm^{-1} corresponding to δ(Csp^2-H) and δ(C = C) elongations, respectively. The vibration bands observed in the far infrared data at 334 and at 196 cm^{-1} are attributed in order to νSnCl and νSnO corroborating presence and coordination of the nitrate anion towards the tin atom. The presence, in the far infrared spectrum, of a weak band at 209 cm^{-1} that may be attributed to $\nu sSnC_3$ vibration and a band at 268 cm^{-1} that is assigned to $\nu asSnC_3$ vibrations indicates an almost planar SnC_3 group (Tudela and Calleja, 1993; Nakamoto, 1997).

FT-IR data of **B** exhibits vibration bands at 1392, 1375 and at 1076 cm^{-1} assigned to ν_3 and ν_1 vibrations, respectively. Bands observed at 736 and 695 cm^{-1} correspond to characteristic phenyl groups δ(Csp^2-H) and δ(C = C) elongations, respectively. The vibration bands observed in the far infrared data at 338 and at 200 cm^{-1} attributed in order to νSnCl and νSnO corroborate presence and coordination of the nitrate anion towards the tin centre. The presence, in the far infrared spectrum, of a weak band at 208 cm^{-1} that may be attributed to $\nu sSnC_3$ vibration and a strong band at 272 cm^{-1} that is assigned to $\nu asSnC_3$ vibrations are an indicative of an almost planar SnC_3 skeleton (Tudela and Calleja, 1993; Nakamoto, 1997).

FT-IR data of **F** exhibits vibration bands at 1367, 1335 and at 1073 cm^{-1} assigned to ν_3 and ν_1 vibrations, respectively. The vibration bands observed in the far infrared data at 333 and at 199 cm^{-1} attributed in order to νSnCl and νSnO corroborate presence and coordination of the nitrate anion towards the tin centre. The presence, in the infrared spectrum, of a weak band at 510 cm^{-1} that may be attributed to $\nu sSnC_3$ vibration and a strong band at 546 cm^{-1} that is assigned to $\nu asSnC_3$ vibrations are an indicative of an almost planar SnC_3 group (Nakamoto, 1997).

The Mössbauer quadrupole splitting of tin atom in free $SnPh_3Cl$ is about 2.55mms^{-1} (Bancroft and Platt, 1972; Parish, 1984) while in free $SnMe_3Cl$ it is about 2.89mms^{-1} (Bancroft and Platt, 1972; Parish, 1984); their enhancement is therefore in accordance with the coordination of $SnPh_3Cl$ or $SnMe_3Cl$. Thus, the values of the quadrupole splitting of **A**, **B** and **F** (3.08, 2.83 and 3.63 mms^{-1}, respectively) are all well corroborating presence of a trigonal bipyramidal environment about a pentacoordinated tin atom with alkyne R substituents in equatorial positions and, a nitrate O atom and a chloride in apical ones (Bancroft and Platt, 1972; Parish, 1984; Diallo *et al*., 2018).

These spectroscopic data allow to suggest for these triorganotin adducts a discrete structure with a monodentate nitrate (Figure 1) looking to some nitrate organotin compounds structures specially the crystal structure of

$Et_4NNO_3 \cdot SnPh_2Cl_2$ yet reported (Diop *et al*., 2011, 2013; Reuter and Reichelt, 2014). In the structure the cation interacts electrostatically with the complex-anion.

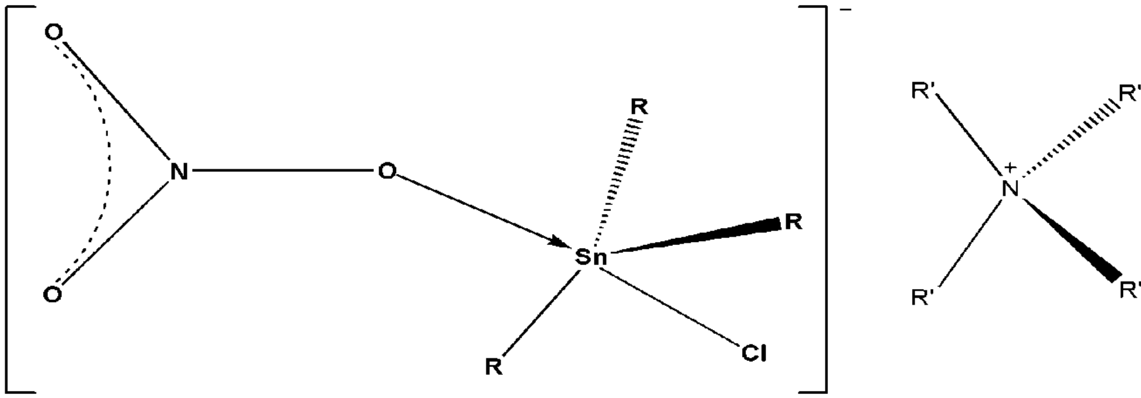

Figure 1:- Discrete mononuclear structure of $[R'_4N(NO_3)][SnR_3Cl]$ (R=Ph, Me; R'=Pr, Bu)

FT-IR data of **C** evidence absorption bands corresponding to nitrate ion and $SnPh_3$ moiety. The vibration bands located at 1384, 1358 and at 1078 cm^{-1} are assigned to ν_3 and ν_1 vibrations of the nitrate, respectively. Vibration bands, characteristic of phenyl ligands, are observed at 734 and 697 cm^{-1} corresponding to $\delta(Csp^2\text{-}H)$ and $\delta(C = C)$ elongations, respectively. The vibration bands observed in the far infrared data at 340 and at 200 cm^{-1} are attributed in order to νSnCl and νSnO corroborating presence and coordination of the nitrate anion towards the tin atom. The presence, in the far infrared spectrum, of a weak band at 208 cm^{-1} that may be attributed to $\nu sSnC_3$ vibration and a band at 271 cm^{-1} that is assigned to $\nu asSnC_3$ vibrations indicates an almost planar SnC_3 group (Tudela and Calleja, 1993; Nakamoto, 1997).
FT-IR data of **D** exhibits vibration bands at 1377, 1352 and at 1079 cm^{-1} assigned to ν_3 and ν_1 nitrato vibrations, respectively. Bands observed at 729 and 689 cm^{-1} correspond to characteristic phenyl groups $\delta(Csp^2\text{-}H)$ and $\delta(C = C)$ elongations, respectively. The vibration bands observed in the far infrared data at 341 and at 200 cm^{-1} attributed in order to νSnCl and νSnO corroborate presence and coordination of the nitrate anion towards the tin centre. The presence, in the far infrared spectrum, of a weak band at 211 cm^{-1} that may be attributed to $\nu sSnC_3$ vibration and a strong band at 274 cm^{-1} that is assigned to $\nu asSnC_3$ vibrations are an indicative of an almost planar SnC_3 group (Tudela and Calleja, 1993; Nakamoto, 1997).

Comparison to free $SnPh_3Cl$ (2.55mms^{-1}) and $SnMe_3Cl$ (2.89mms^{-1}) mössbauer quadrupole splitting shows a variation to higher values. This enhancement of the quadrupole splitting of compounds **C** and **D** (3.02 and 3.10 mms^{-1}, respectively) is consistent with the coordination of $SnPh_3Cl$ or $SnMe_3Cl$. Thus, the values of the quadrupole splitting of **C** and **D** are all well corroborating presence of a trigonal bipyramidal environment about a pentacoordinated tin atom (Bancroft and Platt, 1972; Parish, 1984; Diallo *et al*., 2018) with alkyne R substituents in equatorial positions and, a nitrate O atom and a chloride in apical ones.

These spectroscopic data allow to suggest for these two triphenyltin adducts a discrete structure with a bidentate nitrate (Figures 2a and 2b) in comparison to the dinuclear adduct tetraphenylphosphonium nitratobis (chlorodiphenylstannate)methane, $[Ph_4P]^+[(Ph_2ClSn)_2CH_2.NO_3]^-$ crystal structure as well as the diethyltin(IV) nitrate hydroxide one (Jurkschat and Tiekink, 2003; Reuter and Reichelt, 2014). Within the structures, the ammonium cation as well as the phosphonium cation interacts electrostatically with the anion.

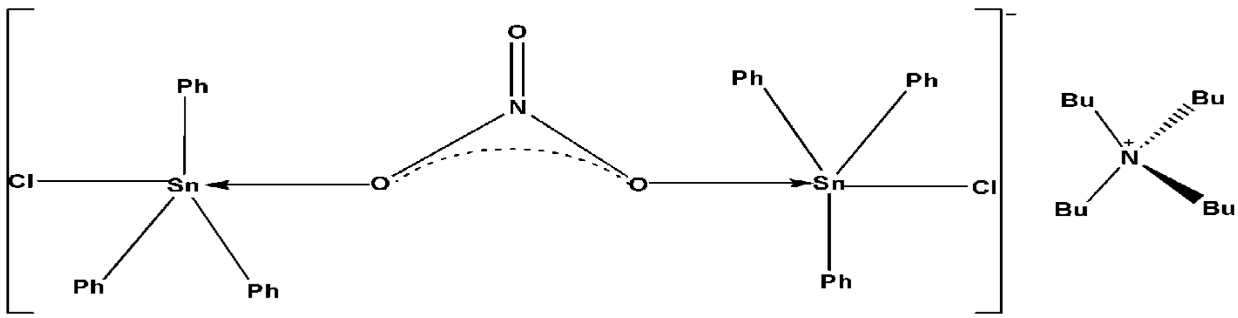

Figure 2a:- Discrete dinuclear structure of $[Bu_4N(NO_3)][(SnPh_3Cl)_2]$

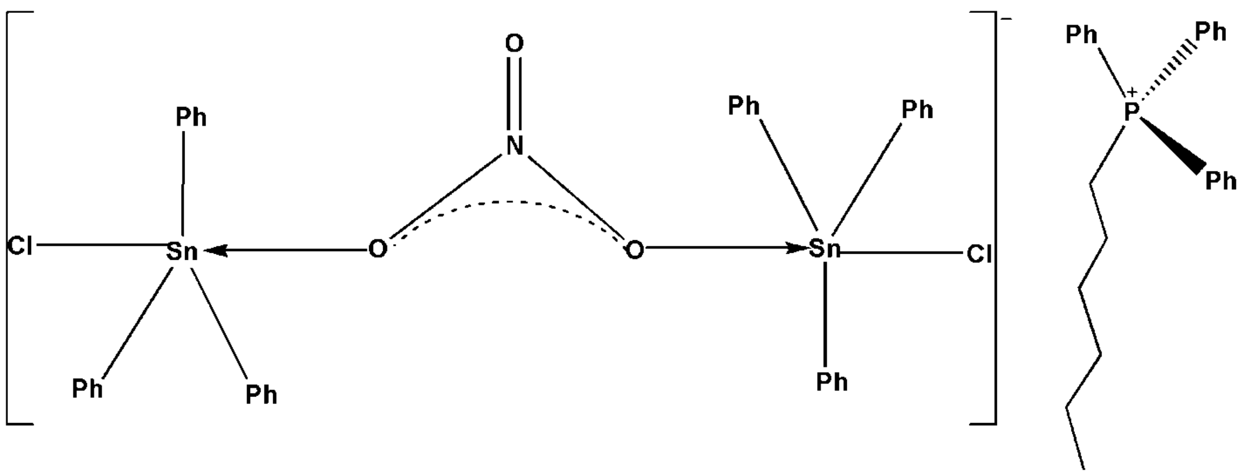

Figure 2b:- Discrete dinuclear structure of $[(n\text{-hexyl})Ph_3P(NO_3)][(SnPh_3Cl)_2]$

FT-IR data of **E** evidence absorption bands corresponding to nitrate ion and $SnPh_3$ moiety. The vibration bands located at 1350 cm^{-1} are assigned to ν_3 vibrations of the nitrate. Vibration bands, characteristic of phenyl ligands, are observed at 735 and 692 cm^{-1} corresponding to $\delta(Csp^2\text{-}H)$ and $\delta(C = C)$ elongations, respectively. The vibration bands observed in the far infrared data at 337 and at 197 cm^{-1} are attributed in order to νSnCl and νSnO corroborating presence and coordination of the nitrate anion towards the tin atom. The presence, in the far infrared spectrum, of a weak band at 211 cm^{-1} that may be attributed to $\nu sSnC_3$ vibration and a band at 273 cm^{-1} that is assigned to $\nu asSnC_3$ vibrations indicates an almost planar SnC_3 skeleton (Tudela and Calleja, 1993; Nakamoto, 1997).

The value of the quadrupole splitting of **E** (3.08 mm^{-1}) well corroborates presence of a trigonal bipyramidal environment about a pentacoordinated tin atom (Bancroft and Platt, 1972; Parish, 1984; Diallo *et al.*, 2018) with alkyne R subsituents in equatorial positions and, a nitrate O atom and a chloride in apical ones.

The spectroscopic data allow suggestion of a discrete trinuclear structure (Figure 3) comprising a central nitrate anion coordinated to three triphenyltin chloride molecules as found in the literature for a close analogue earlier reported, $[NO_3(SnPh_3NO_3)(SnPh_3Cl)_2][Et_4N]^+$ (Diop *et al.*, 2013). In the structure, the benzyltriphenyl phosphonium cation interacts electrostatically with the complex-anion, $[NO_3(SnPh_3Cl)_3]^-$.

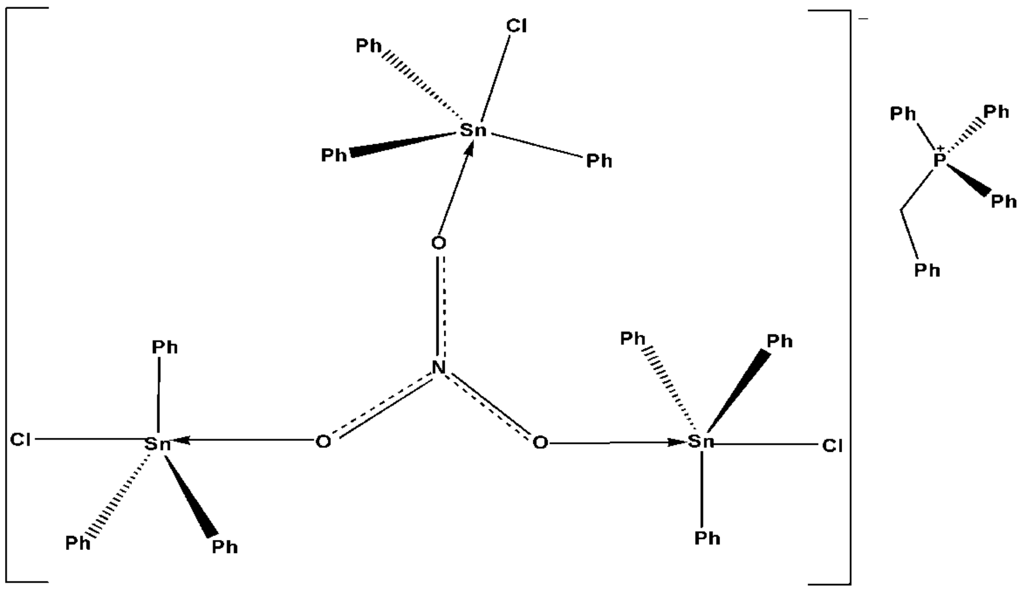

Figure 3:- Discrete trinuclear structure of $[(PhCH_2)Ph_3P(NO_3)][(SnPh_3Cl)_3]$

SnR_2Cl_2 (R = Bu, Me) adducts

FT-IR data of **G** evidence absorption bands corresponding to nitrate ion and $SnMe_2$ moiety. The vibration bands located at 1381, 1353 and at 1064 cm^{-1} are assigned to ν_3 and ν_1 vibrations of the nitrate, respectively. The vibration bands observed in the far infrared data at 332 and at 200 cm^{-1} are attributed in order to νSnCl and νSnO corroborating presence and coordination of the nitrate anion towards the tin atom. The presence, in the infrared spectrum, of a weak band at 519 cm^{-1} that may be attributed to $\nu sSnC_2$ vibration and a band at 571 cm^{-1} that is assigned to $\nu asSnC_2$ vibrations indicates an almost linear SnC_2 group (Nakamoto, 1997).

FT-IR data of **I** evidence absorption bands that correspond to nitrate ion and $SnMe_2$ moiety. The vibration bands located at 1357 and 1334 cm^{-1} are assigned to ν_3 vibrations of the nitrate. The vibration bands observed in the far infrared data at 337 and at 200 cm^{-1} attributed in order to νSnCl and νSnO corroborate presence and coordination of the nitrate anion towards the tin atom. The weak band at 518 cm^{-1} attributed to $\nu sSnC_3$ vibration and the medium one at 575 cm^{-1} assigned to $\nu asSnC_3$ vibrations indicate an almost linear SnC_2 skeleton (Nakamoto, 1997).

The values of the quadrupole splitting of **G** and **I** (3.35 and 3.30mms^{-1}, respectively) are at the border of a distorted *trans*-octahedrally coordinated SnR_2 residue and a SnR_2 residue in a trigonal bipyramidal environment (Bancroft and Platt, 1972).

These spectroscopic data allow to suggest two discrete structures:

1. A first one with a terminal monocoordinating nitrate (Figure 4a) linked to the dimethyltin dichloride molecule, $SnMe_2Cl_2$ meaning a trigonal bipyramidal fashion at tin atom as found in crystal structures of several diorganotin nitrates (Domingos and Sheldrick, 1974; Franzoni *et al*., 1989; Jurkschat and Tiekink, 2003; Svec *et al*., 2010; Reuter and Reichelt, 2014)
2. A second one which is comprised of an unsymmetrical chelating nitrate as found in one of the crystal structures reported by Reuter and Reichelt in 2014, enabling obtainment of a distorted octahedron (Figure 4b).

In both structures, the tetraalkylammonium interacts through electrostatic forces.

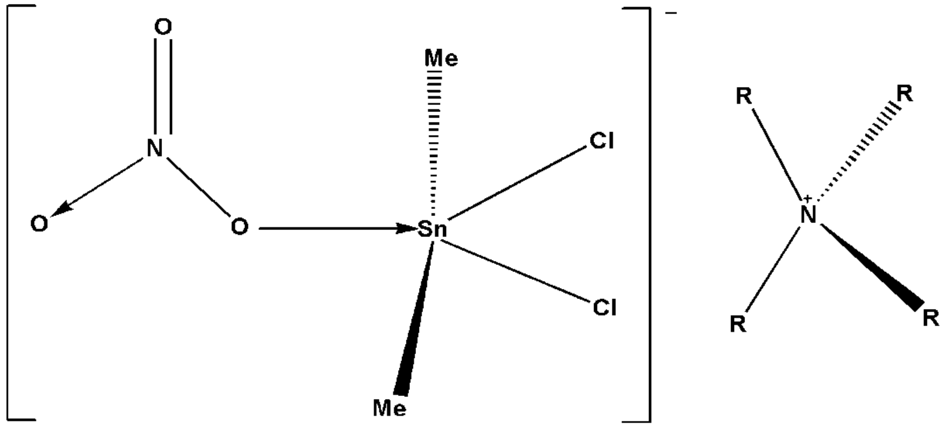

Figure 4a:- Discrete mononuclear structure of $[R_4N(NO_3)][SnMe_2Cl_2]$ (R=Pr, Bu)

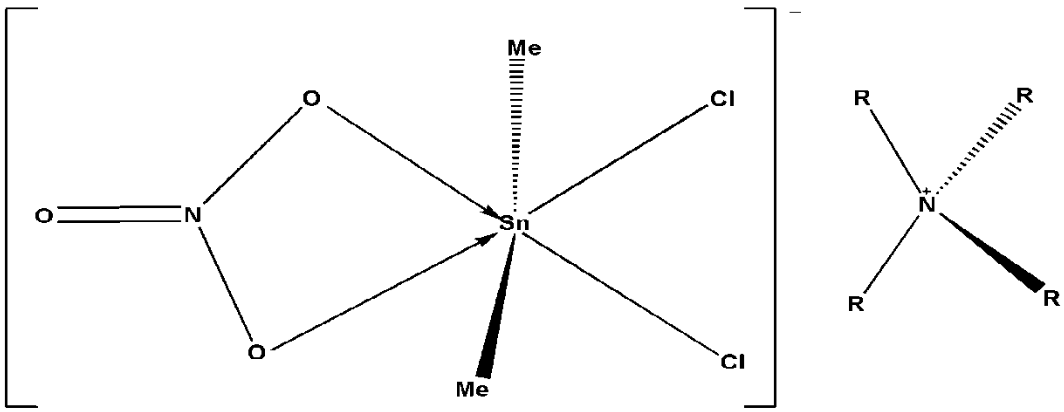

Figure 4b:- Discrete mononuclear structure of $[R_4N(NO_3)][SnMe_2Cl_2]$ (R=Pr, Bu)

FT-IR data of **H** exhibits vibration bands at 1357, 1334 and at 1070 cm^{-1} assigned to ν_3 and ν_1 nitrato vibrations, respectively. The vibration bands observed in the far infrared data at 335 and at 212 cm^{-1} attributed in order to νSnCl and νSnO corroborate presence and coordination of the nitrate anion towards the tin centre. Vibration bands located at 591 and 557 cm^{-1} are attributed to ν_4 nitrate vibrations.

The quadrupole splitting of $Pr_4NNO_3{\cdot}SnBu_2Cl_2$ (**H**) of 3.54mms^{-1} is consistent with an octahedral arrangement at tin atom with *n*-butyl groups in *trans* positions (Bancroft and Platt, 1972).

These spectroscopic data allow to suggest a discrete structure with a monochelating nitrate (Figure **5**), the cation being involved in electrostatic interactions with the complex-anion.

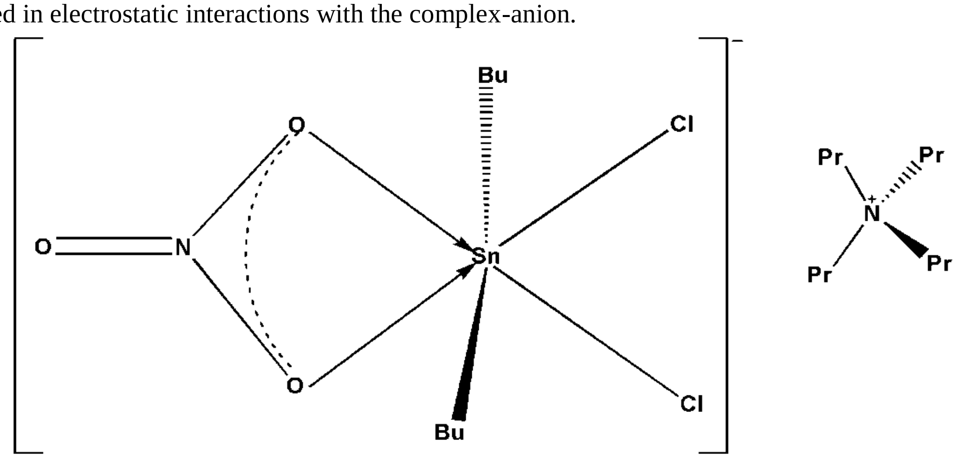

Figure 5:- Discrete mononuclear structure of $[Pr_4N(NO_3)][SnBu_2Cl_2]$

Conclusion:-

All the studied diorgano- or triorganotin nitrato adducts in this work have a discrete structure with one metallic centre, two or three tin centres. These structures are well corroborated to crystal characterization of some analogue compounds. Within this study multiple behaviour of the nitrate such as monodentate, bridging bidentate, tridentate and monochelating have been evidenced. The environment around the tin atom is a trigonal bipyramidal in the case of SnR_3Cl adducts and octahedral or trigonal bipyramidal in SnR_2Cl_2 adducts. A limit of spectroscopy that may be settled by X-ray diffraction has been encountered; selecting the exact behaviour of the nitrate anion between the two borderlines i.e. the distorted *trans*-octahedral coordinated SnR_2 moiety or the *trans*-trigonal bipyramidal fashion one. Further works in attempts to isolate single crystals of the borderlines and other organotin complexes and adducts involving various anions and cations that may interact in hydrogen bonds giving rise to extensive supramolecular topologies are in progress in our laboratory (LA.CHI.MI.A).

Acknowledgment:-

The Dakar group gratefully thanks Professor M. Vidali, University of Padua, Italy and Professor B. Mahieu, University of Louvain-La-Neuve, Belgium, for equipment support.

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