RESEARCH ARTICLE

TRIORGANOTIN PHOSPHONATES POLYMERIC CHAINS– SYNTHESIS, INFRARED, MÖSSBAUER AND SINGLE CRYSTAL CHARACTERIZATION:THE FIRST ORGANOTIN(IV) PH₂⁻BRIDGED

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Abstract

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Two triorganotin(IV) phosphonate compounds were isolated and structurally investigated by infrared and Mössbauer spectroscopies and X-ray crystallography. The reaction oftrimethyltin(IV) chloride ($SnMe_3Cl$) and hexamethylene tetraammonium hydrogen methylphosphonate $[CH_3PO_3H][N_4(CH_2)_6H]$ led to the formation of $[C_{10}H_{34}O_4P_2Sn_3]$ (**1**) which crystallizes in the Monoclinic space group *Pn* with $Z = 2$, $a = 8.4955$ (2) Å, $b = 11.318$ (3) Å, $c = 11.902$ (2) Å, $\beta = 90.9340$ (10)° and $V = 1144.2$ (4) Å³. An uncommon decomposition of methylphosphonate occurred during the reaction process giving rise to the formation of dimers of $[SnMe_3PH_2SnMe_3]^+$. The structure of **1** consists of an anionic chain of $[CH_3PO_3(SnMe_3PH_2SnMe_3)]^−$ linked to $[SnMe_3(H_2O)]^+$ moieties through Sn—O bonds involving the remaining oxygen atoms of the methylphosphonates. In the chain, each $SnMe_3$ residue is coordinated by one methylphosphonate and one phosphor atom, in a *trans*-trigonal bipyramidal $PSnC_3O$ geometry. The environment at tin atoms in both $SnMe_3$ moieties is an octahedron. The methylphosphonate anion is otherwise in a general position and behaves as a tri-coordinating ligand. The reaction oftriphenyltin(IV) hydroxide ($SnPh_3OH$) and phosphorous acid ($HPO(OH)_2$) led to the formation of $[C_{36}H_{31}O_3PSn_2]$ (**2**) which crystallizes in the Monoclinic space group *P2/n* with $Z = 4$, $a = 11.7966$ (4) Å, $b = 10.1953$ (4) Å, $c = 27.6715$ (10) Å, $\beta = 94.600$ (2)° and $V = 3317.3$ (2) Å³. The structure of **2** is comprised of an anionic chain of $[HPO_3(SnPh_3)]^−$ linked to $SnPh_3$ moieties through Sn—O bonds involving the remaining oxygen atoms of the hydrogenphosphonates. In the chain the $SnPh_3$ residues are each one coordinated by two hydrogenphosphonates in a *trans*-trigonal bipyramidal $OSnC_3O$ arrangement. The geometry at tin atoms within the monocoordinated $SnPh_3$ moieties connected to the chain is a

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distorted tetrahedron. The hydrogenphosphonate anion is in a general arrangement and behaves as a tri-O-coordinating ligand.

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Introduction:-

Metal phosphonate and organotin(IV) classes of compounds aroused and still arouse a great interest because of the wide properties and applications they display in various fields (Bao and Zheng, 2016;Hamchaoui*et al.*, 2013a; Clearfield and Demadis, 2012; Mao, 2007; Fernandez-Armas *et al.*, 2004a,Malllouk *et al.*, 1996; Cao *et al.*, 1992;Etaiw*et al.* 2019;Mao *et al.*, 2015; Devendra *et al.*, 2015;Carraher *et al.*, 2019, 2018; Roner *et al.*, 2014). Numerous organic phosphonate compounds were isolated and widely used as anti-HIV, antiviral in AIDS treatment (Troev, 2006). Few organic salt structures involving methylphosphonate anion were reported in the past three decades (Mahmoudkhani and Langer, 2002; Fleck *et al.*, 2000; Paixao *et al.*, 2000; Honle *et al.*, 1990). To date, several hydrogenphosphonate compounds with different metals such as Mn, Co, Ga, Cr, V, Fe, Cd, In and U have earlier been reported in the literature (Ouarsal *et al.*, 2016; Larrea *et al.* 2016; Berrocal *et al.*, 2014; Oh and Burns, 2014; Hamchaoui *et al.*, 2013a, 2013b; Li *et al.*, 2009; Fernandez-Armas *et al.*, 2004a, 2004b). In some of these structures, the hydrogenphosphonate anion behaves as multidirectional synthons. Contributing to widen phosphonate family compounds, the Dakar group has already reported the spectroscopic (Infrared, Mössbauer and NMR) studies of some $RPO_3(SnPh_3)_2(R = H$ or $CH_3)$ (Diop *et al.*, 1999), the crystal characterization of dibutylammonium bis(hydrogen methylphosphonato-κO)triphenylstannate(IV)(Diop *et al.*, 2012a) as well as numerous phenylphosphonato triphenyltin(IV) crystalline structures which, through hydrogen bonding interactions, exhibit various structures that give rise to supramolecular diverse topologies (Diop *et al.*, 2013a, 2012b, 2011a, 2011b). To the best of our knowledge (CSD version 5.40), very few, only three tin(IV) methylphosphonate and five tin(IV) hydrogenphosphonate containing crystalline compoundsare known (Diop *et al.*, 2012a; Ribot *et al.*, 2001; Adair *et al.*, 1998; Chandrasekhar*et al.*, 2003, 2005; Mairychova *et al.*, 2014). The organotin(IV) methylphosphonate cores have discrete structures, monomeric (Diop *et al.*, 2012a) or dimeric (Ribot *et al.*, 2001) with monodentate and, bidentate and monodentate anions, respectively. Though, the inorganic tin(IV) methylphosphonate complex is polymeric with tri-O-coordinating ligands. Contrary to the firsts, the organotin(IV) hydrogenphosphonatecompounds have a dimeric structure with bidentate ligands (Mairychova *et al.*, 2014) or an hexameric cage structure in a double O-capped cluster with tri-O-coordinating ligands (Chandrasekhar*et al.*, 2003, 2005). Thus,continuing to focus in phosphonato organotin(IV) family compounds, we investigated in this work, in organic solvents,the interactions between a salt of methylphosphonic acid, $CH_3PO(OH)_2$ andhexamethylene tetraamine (**L**) and, trimethyltin(IV) chloride in one hand and, phosphorous acid, $HPO(OH)_2$and triphenyltin(IV) hydroxide in another hand.These interactionsyielded single crystals of compounds**1**, $[SnMe_3(PH_2)SnMe_3][CH_3PO_3][SnMe_3(H_2O)]$ and **2**, $HPO_3(SnPh_3)_2$(Scheme 1) whose X-ray and spectroscopic characterization arecarried out and reported herein.
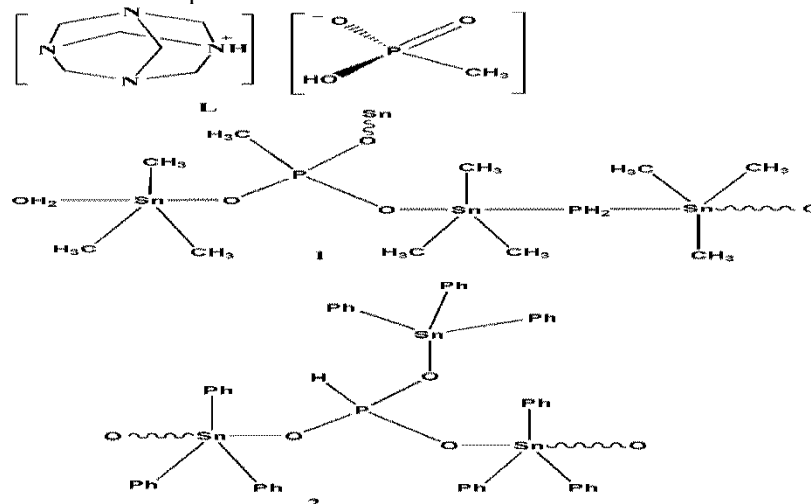
Scheme 1:-Molecular representations of hexamethylene tetraammonium hydrogen methylphosphonate reagent and compounds related to this study.

Experimental section:-
Triphenyltin hydroxide, SnPh$_3$OH(99 % purity) and trimethyltin chloride, SnMe$_3$Cl (99 % purity), phosphorous acid, HPO(OH)$_2$(99 % purity), N$_4$(CH$_2$)$_6$(99 % purity) and CH$_3$PO(OH)$_2$(99 % purity)were purchased from Sigma-Aldrich, Steinheim am Albuch, Germany and were used without any further purification.

Infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate^{TM} ATR device. [IR abbreviations: (vs) very strong, (s) strong, (m) medium, (br) broad, (sh) shoulder].

Elemental analyses were performed at the Institut de Chimie de la Matière Condensée, Université de Bordeaux, France and atthe Institut de Chimie Moléculaire, Université de Bourgogne Franche-Comté, Dijon, France.

^{119}Sn Mössbauer data were collected as reported in (Bouâlam*et al.*, 1991) and in (Diop *et al.*, 2013b), respectively. Mössbauer parameters are given in mm.s^{-1} [Mössbauer abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height).

Synthesis and isolation of [SnMe$_3$(PH$_2$)SnMe$_3$][CH$_3$PO$_3$][SnMe$_3$(H$_2$O)](1):-
The isolation of **1** follows a two steps procedure. The salt hexamethylene tetraammonium hydrogen methylphosphonate, [CH$_3$PO$_3$H][N$_4$(CH$_2$)$_6$H](**L**) was first collected as a white powder from reaction between equimolar aqueous solutions of methylphosphonic acid, CH$_3$PO(OH)$_2$(600mg, 6.25mmol) and hexamethylene tetraamine, N$_4$(CH$_2$)$_6$ (876mg, 6.25mmol). To 15 mL methanol solution of **L**(469mg, 1.98mmol) was added 10 mL dichloromethane solution of SnMe$_3$Cl (395mg, 1.98mmol). The clear obtained mixture was stirred 2h at room temperature (303K)then submitted to a slow solvent evaporation. After four days of a slow evaporation at room temperature (303K), in a not-controlled atmosphere, colourless crystals (melting point = 386K) suitable for an X-ray analysis were picked up from the solution and were finally characterized as **1**.

Spectroscopic data:-
1.   IR data (cm^{-1}):νOH$_2$3389(br), 3192(sh),νPO$_3$$^{2-}$1112(s), 1060(s), 995(s), νPC 850(m),νasSnC$_3$545(s)
2.   Mössbauerparameters (mm.s^{-1}): IS= 1.47, QS = 3.60, Γ= 0.96

Elemental Analysis:-
[SnMe$_3$(PH$_2$)SnMe$_3$][CH$_3$PO$_3$][SnMe$_3$(H$_2$O)] (**1**), C$_{10}$H$_{34}$O$_4$P$_2$Sn$_3$,[%calculated (%found)]:- C = 18.87 (18.63), H = 5.38 (5.19); yield: 55%
[CH$_3$PO$_3$H][N$_4$(CH$_2$)$_6$H](**L**),[%calculated (%found)]:-C= 35.60 (35.22), H= 7.25 (7.39), N= 23.72 (23.75); yield: 85%

Synthesis and isolation of [HPO$_3$(SnPh$_3$)$_2$] (2):-
To 15mL methanol solution of triphenyltin hydroxide, SnPh$_3$OH(551mg, 1.50mmol) was added an equimolar solution of phosphorous acid, HPO(OH)$_2$(123mg, 1.50mmol) preliminary dissolved in 15mLof methanol,giving rise to a clear solution. The resulting mixture was stirred 2h at room temperature (303K) before being submitted to evaporation. After five days of slow solvent evaporation at room temperature(303K), in a not-controlled atmosphere, colourless crystals, suitable for an X-ray crystallographic analysisgrew from the solution and were finally characterized as **2**.

Spectroscopic data:-
1.   IR data (cm^{-1}):νPH2495 (s), νPO$_3$$^{2-}$1132(vs), 1109(vs), δPH 1075(vs), νCC and νCH (phenyl groups) 735(vs), 697(s)
2.   Mössbauerparameters (mm.s^{-1}): IS$_1$= 1.26, QS$_1$ = 2.84, Γ$_1$= 0.89; IS$_2$= 1.34, QS$_2$ = 2.51, Γ$_2$= 0.92

Elemental Analysis:-
[HPO$_3$(SnPh$_3$)$_2$] (**2**), C$_{36}$H$_{31}$O$_3$PSn$_2$,[%calculated (%found)]:- C=55.43 (55.77), H= 4.01 (3.98);yield: 75%.

X-ray crystallographyof [SnMe$_3$(PH$_2$)SnMe$_3$][CH$_3$PO$_3$][SnMe$_3$(H$_2$O)](1):-
A crystal of approximate dimensions 0.25×0.12×0.12 mm was used for data collection. The X-ray crystallographic data were collected using a Nonius KappaCCD diffractometerat T = 150 (2) K. Data were measured using φ and ω scans using Mo*K*α radiation (λ = 0.71073 Å) using a collection strategy to obtain a hemisphere of unique data determined by*COLLECT*(Nonius, 2003). Cell parameters were determined and refined using the

SCALEPACK(Otwinowski and Minor, 1997). Data were corrected for absorption by the empirical absorption correction using *DENZO* (Otwinowski and Minor, 1997). The structure was solved using *SHELXS* (Sheldrick, 2008) and the structure refined using least-squares minimization *SHELXL* (Sheldrick, 2008).

Programs used for the representation of the molecular and crystal structures: *Olex2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008). The Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

CCDC 805143 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

X-ray crystallographyof [HPO$_3$(SnPh$_3$)$_2$] (2):-
A crystal of approximate dimensions 0.32×0.23×0.12 mm was used for data collection. The X-ray crystallographic data were collected using a Bruker Venture Metaljet diffractometer, at T = 100 K. Data were measured using φ and ω scans using Ga*K*α radiation (λ = 1.34139Å) using a collection strategy to obtain a hemisphere of unique data determined by *Apex2* (Bruker AXS Inc., Madison, WI 53719-1173., 2013). Cell parameters were determined and refined using the *SAINT* program (SAINT (2013) V8.35A). Data were corrected for absorption by multi-scan absorption correction using *SADABS2014/5* (Krause *et al.*, 2015). The structure was solved using *Olex2* (Dolomanov *et al.*, 2009) and the structure refined using least-squares minimization *SHELXL*(Sheldrick, 2008).

Programs used for the representation of the molecular and crystal structures: *Olex2* (Dolomanov *et al.*, 2009) and *Mercury*(Macrae *et al.*, 2008). The Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

CCDC 1917005 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Table 1:-Crystal data and structure refinement for compounds (**1**) and (**2**)

Parameters	Compound	
	(**1**)	(**2**)
Empirical formula	$C_{10}H_{34}O_4P_2Sn_3$	$C_{36}H_{31}O_3PSn_2$
Formula weight	636.38	779.96
Temperature	150 (2) K	100 K
Wavelength	0.71073 Å	1.34139 Å
Crystal system	Monoclinic	Monoclinic
Space group	*Pn*	*P2/n*
Unit cell dimensions	a = 8.4955 (2) Å	a = 11.7966 (4)Å
	α = 90°	α = 90°
	b = 11.318 (3) Å	b = 10.1953 (4) Å
	β = 90.934(1)°	β = 94.600 (2)°
	c = 11.902 (2) Å	c = 27.6715 (10) Å
	γ = 90°	γ = 90°
Volume	1144.2 (4)Å^3	3317.3(2)Å^3
Z	2	4
Calculated density	1.847 g cm^{-3}	1.562g cm^{-3}
Absorption coefficient	3.394 mm^{-1}	8.628 mm^{-1}
F(000)	612	1544
Crystal size	0.25 × 0.12 × 0.12 mm^3	0.32 × 0.23 × 0.12 mm^3
Theta range for data collection	2.48–34.96°	3.271–60.733°
Limiting indices	-13≤ h ≤13, -18≤ k ≤ 18, -19≤ l ≤19	-14≤ h ≤15, -13≤ k ≤ 13, -35≤ l ≤31
Reflections collected/unique	16601/9234	45257/7609
R$_{int}$	0.0215	0.0537

Absorption correction	Empirical	Multi-scan
Max. and min. transmission	0.6862 and 0.4841	0.3107and 0.0900
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	9234/2/182	7609/0/385
Goodness-of-fit on F^2	1.034	1.043
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0229$, $wR_2 = 0.0539$	$R_1 = 0.1014$, $wR_2 = 0.0356$
R indices (all data)	$R_1 = 0.0259$, $wR_2 = 0.0524$	$R_1 = 0.1007$, $wR_2 = 0.0363$
Largest diff. peak and hole	0.891and -0.445 e Å^{-3}	1.835and -0.804 e Å^{-3}

$w = 1/[s^2(F_o^2) + (0.0257P)^2 + 0.0154P]$ for **1** and $w = 1/[s^2(F_o^2) + (0.0571P)^2 + 6.2522P]$ for **2**, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2:- Selected bond lengths(Å) for **1** and **2**

(1)		(2)	
Atom—Atom	Bond length	Atom—Atom	Bond length
Sn2—C4	2.122 (3)	Sn1—O2^i	2.196 (2)
Sn2—C2	2.123 (3)	Sn1—O2	2.196 (2)
Sn2—C3	2.125 (3)	Sn1—C1	2.146 (5)
Sn2—O3	2.1621 (19)	Sn1—C5^i	2.134 (3)
Sn2—P2	2.8407 (7)	Sn1—C5	2.134 (3)
Sn1—C6	2.124 (3)	Sn2—O3^{ii}	2.242 (2)
Sn1—C5	2.127 (3)	Sn2—O3	2.242 (2)
Sn1—C7	2.129 (3)	Sn2—C11	2.126 (5)
Sn1—O1	2.1313 (19)	Sn2—C15^{ii}	2.128 (3)
Sn1—O4	2.416 (2)	Sn2—C15	2.128 (3)
Sn3—C10	2.119 (3)	Sn3—O1	2.001 (2)
Sn3—C8	2.124 (3)	Sn3—C21	2.114 (3)
Sn3—C9	2.128 (3)	Sn3—C27	2.120 (3)
Sn3—O2^i	2.140 (2)	Sn3—C33	2.121 (3)
Sn3—P2	2.8190 (10)	P1—H1	1.42 (4)
P1—O1	1.512 (2)	P1—O1	1.553 (2)
P1—O2	1.519 (2)	P1—O2	1.502 (2)
P1—O3	1.538 (2)	P1—O3	1.510 (2)
P1—C1	1.786 (3)		
O2—Sn3^{ii}	2.140 (2)		

Table 3:- Selected angles(°) for **1** and **2**

(1)		(2)	
Atom-atom-atom	Angle value	Atom-atom-atom	Angle value
C4—Sn2—C2	122.58 (13)	O2^i—Sn1—O2	177.03 (12)
C4—Sn2—C3	117.54 (15)	C1—Sn1—O2^i	91.48 (6)
C2—Sn2—C3	118.05 (13)	C1—Sn1—O2	91.48 (6)
C4—Sn2—O3	94.18 (10)	C5—Sn1—O2	85.89 (10)
C2—Sn2—O3	96.54 (10)	C5^i—Sn1—O2	92.61 (10)
C3—Sn2—O3	92.68 (10)	C5—Sn1—O2^i	92.61 (10)
C4—Sn2—P2	85.82 (9)	C5^i—Sn1—O2^i	85.89 (10)
C2—Sn2—P2	86.18 (8)	C5—Sn1—C1	120.39 (8)
C3—Sn2—P2	84.45 (9)	C5^i—Sn1—C1	120.39 (9)
O3—Sn2—P2	176.74 (5)	C5^i—Sn1—C5	119.22 (17)
C6—Sn1—C5	118.83 (14)	O3^{ii}—Sn2—O3	178.22 (13)
C6—Sn1—C7	119.86 (14)	C11—Sn2—O3^{ii}	90.89 (6)
C5—Sn1—C7	119.90 (15)	C11—Sn2—O3	90.89 (6)
C6—Sn1—O1	96.92 (11)	C11—Sn2—C15^{ii}	120.12 (9)
C5—Sn1—O1	93.34 (11)	C11—Sn2—C15	120.12 (9)
C7—Sn1—O1	91.63 (11)	C15^{ii}—Sn2—O3^{ii}	91.42 (10)

C6—Sn1—O4	85.33 (11)	C15^{ii}—Sn2—O3	87.69 (10)
C5—Sn1—O4	86.63 (10)	C15—Sn2—O3^{ii}	87.69 (10)
C7—Sn1—O4	86.17 (11)	C15—Sn2—O3	91.42 (11)
O1—Sn1—O4	177.44 (10)	C15^{ii}—Sn2—C15	119.76 (18)
C10—Sn3—C8	120.71 (17)	O1—Sn3—C21	110.27 (11)
C10—Sn3—C9	120.70 (17)	O1—Sn3—C27	99.28 (11)
C8—Sn3—C9	117.31 (16)	O1—Sn3—C33	105.40 (12)
C10—Sn3—O2^{i}	91.46 (11)	C21—Sn3—C27	110.70 (13)
C8—Sn3—O2^{i}	94.99 (10)	C21—Sn3—C33	113.76 (13)
C9—Sn3—O2^{i}	94.92 (10)	C27—Sn3—C33	116.18 (12)
C10—Sn3—P2	85.40 (10)		
C8—Sn3—P2	87.46 (9)		
C9—Sn3—P2	85.86 (9)		
O2^{i}—Sn3—P2	176.71 (5)		

Symmetry codes: for **1**: (i) *x*+1/2, -*y*, *z*-1/2; (ii) *x*-1/2, -*y*, *z*+1/2, for **2**: (i) -*x*+1/2, *y*, -*z*+3/2; (ii) -*x*+3/2, *y*, -*z*+3/2

Results and discussion:-

The infrared spectrum of **1** exhibits a broad band at 3389 cm^{-1} with a shoulder at 3192 cm^{-1} assigned to νOH vibrations involving the water molecule (Nakamoto, 1997). Vibration bands located at 1112, 1060 and 995 cm^{-1} correspond to νPO$_3^{2-}$vibrations while that at 850 cm^{-1} is attributed to the νPC corroborating presence of the methylphosphonate anion. It is noteworthy to outline absence of a band about 515-520 cm^{-1} that may be attributed to νsSnC$_3$vibration, and presence of a band at 545cm^{-1} that is assigned to νasSnC$_3$vibrations, indicating a planar SnC$_3$ group (Nakamoto, 1997). Tetrahedral tin(IV) centre has a quadrupole splitting about 2.89 mm.s^{-1} (Bancroft and Platt, 1972; Parish, 1984). Thus, the quadrupole spliting value higher than 2.89 mm.s^{-1}, is in accordance with coordination at tin atom. The value of 3.60 mm.s^{-1} is in the range of pentacoordinated tin centres (Bancroft and Platt, 1972; Parish, 1984) in a trigonal bipyramidal arrangement.

The complex **1** which crystallizes in the monoclinic *Pn* space group as colourless prism-like crystal, results from a decomposition (cleavage and formation of new bonds) processover the hydrogen methylphosphonate anionof **L**used as starting material, when the reaction is carried out in a 3:2 methanol/dichloromethanemixture and in a non-controlled atmosphere.In the past, the in-situ formation of hydrogenphosphonate, HPO$_3^{2-}$ from a P—O bond cleavage decomposition has been evidenced (Chandrasekhar*et al*., 2003). In this compound, the formation of the [PH$_2$]$^-$ is owed to a decomposition, P—O and P—C bonds cleavage. A molecular view of the asymmetric unit is depicted in Fig. 1. Present in**1** is the [PH$_2$]$^-$ bridging anion connecting two SnMe$_3$moieties.
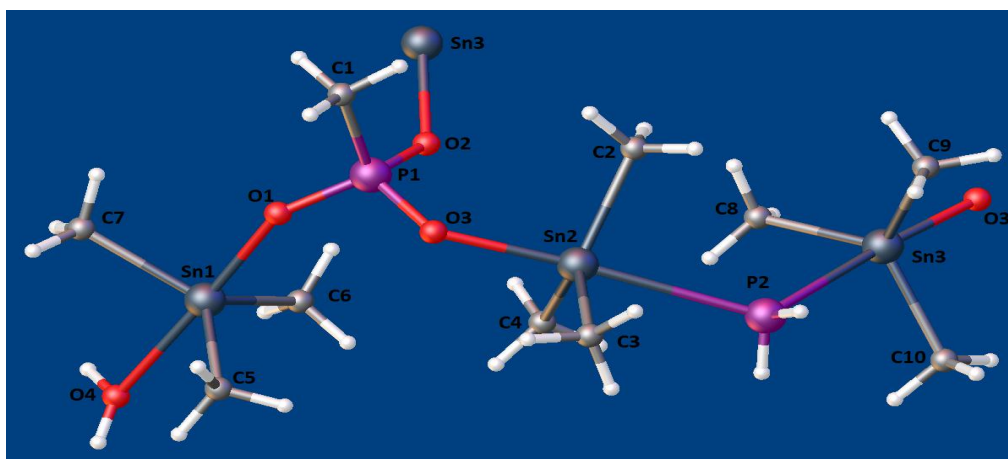
**Fig 1:**-Molecular structure of [SnMe$_3$(PH$_2$)SnMe$_3$][CH$_3$PO$_3$][SnMe$_3$(H$_2$O)] (**1**) showing 50% probability ellipsoids and the crystallographic numberingScheme.

Within the structure of **1**is described an infinite ionic chain of [CH$_3$PO$_3$(SnMe$_3$PH$_2$SnMe$_3$)]$^-$ with methylphosphonate anionbridges. To this chainare then linked aquatrimethyltin(IV), [SnMe$_3$.H$_2$O]$^+$ cations*via* the

third remaining phosphonate oxygen atoms through Sn—O bonds (Figs. 2 and 3). The methylphosphonate dianion behaves as a tri O-coordinating ligand. TheSnMe₃residues are*trans*-coordinated, the environment around the tin(IV) atom being trigonal bipyramidal (tbp). Thus,in the *trans*-coordinated SnMe₃ moiety the methyl groups occupy the equatorial positions and the apical positions are occupied by a phosphor atom from the [PH₂]⁻ bridge and an oxygen atom from a methylphosphonate anion for Sn2 and Sn3 while for Sn1the apical positions are occupied by two oxygen atoms; one from the methylphosphonate and another from the water molecule of crystallization which complete the tbp coordination sphere at tin atom. The sum of the angles at tin centres equal to 358.59°, 358.17° and 358.72° indicate almost planar SnC₃ groups; tin atoms are slightly out the C₃ planes.
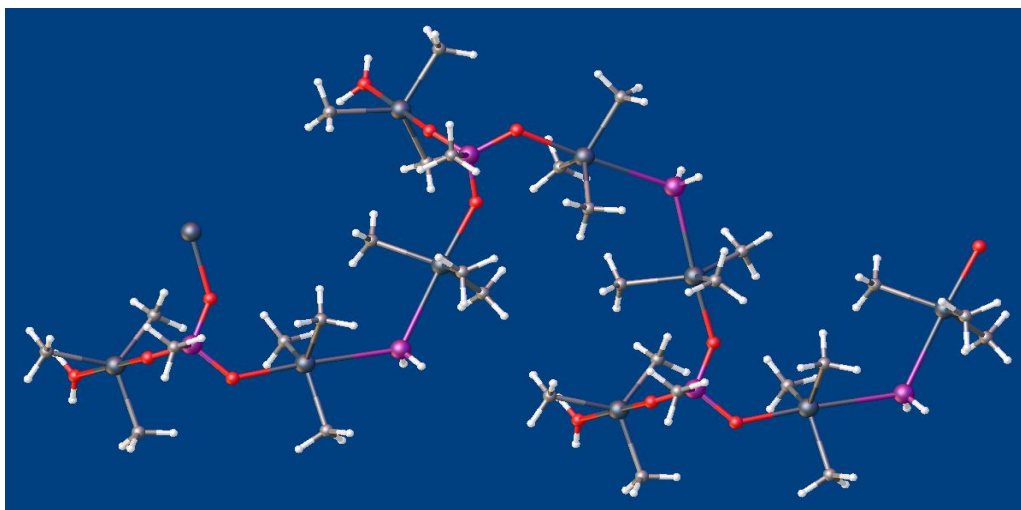

Fig 2:-Molecular structure of **1**showing the infinite ionic chain and [SnMe₃(H₂O)]⁺ cations set on. Ellipsoids are drawn at 50% probability.
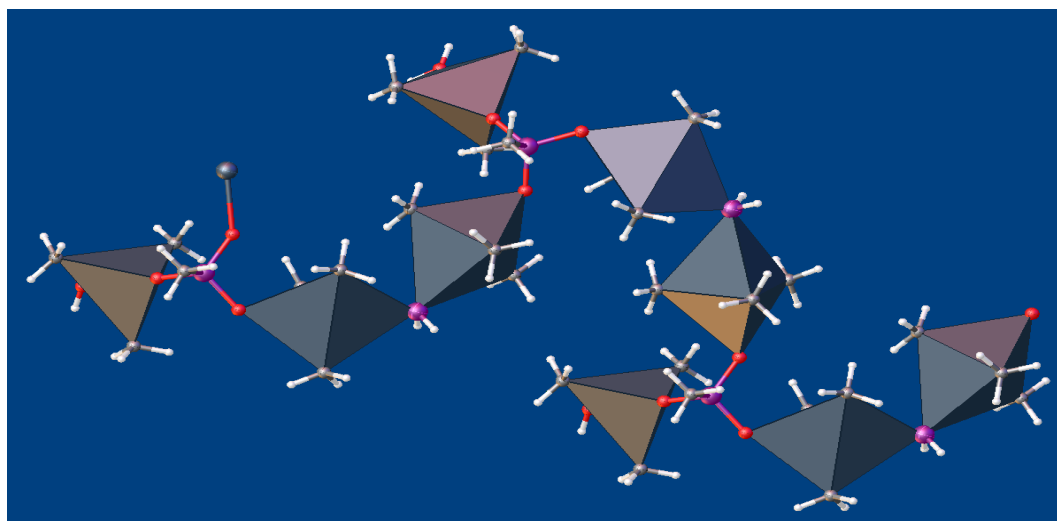
Fig 3:-Molecular structure of **1**showing the trigonal bipyramidal polyhedron at tin atoms. Ellipsoids are drawn at 50% probability.

The Sn—C distances are in the range of those found in tbp SnMe₃ moieties (Diop *et al*., 2013a, 2012b, 2011a). The Sn1—O4 bond of 2.416 (2) Å is longer, weaker than the Sn1—O1 one of 2.1313 (19) Å: these values are in a typical range of Sn—O phosphonate (Diop *et al*., 2013a, 2012a, 2012b) and Sn—O water (Diop *et al*., 2015), respectively. Meanwhile theSn—P bond lengths of 2.8407 (7) and 2.8190 (10)Å are in the range of that previously reported for related PR₂ bridging organotin(IV) compounds (Mertens *et al*., 1995), they are above those found in organotin(IV) PH bridged and PH₂ terminally bonded (Driess *et al*., 1995; Hanssgen *et al*., 1990). The O—Sn—O angle [O1—Sn1—O4 177.44 (10)°] as well as O—Sn—P angles [O3—Sn2—P2 176.74 (5)° and O2ⁱ—Sn3—P2 176.71 (5)°]

reveal a slight deviation from linearity. The P—O bond distances[from 1.512 (2) to 1.538 (2) Å] and P—C[1.786 (3)Å] are in the range of those found in the literature (Hamchaoui *et al.*, 2013a, 2013b; Diop *et al.*, 2012a; Mahmoudkhani and Langer, 2002). The angle values at phosphor atom from 106.23 (13) to 113.67 (12)° are otherwise not exceptional and show a distorted tetrahedral geometry for the methylphosphonate anion as expected. In the crystal, chains are connected through O—H⋯O hydrogen bonding interactions involving water molecules and oxyanions giving rise to a supramolecular two dimensional structuredepicted in Fig.4.
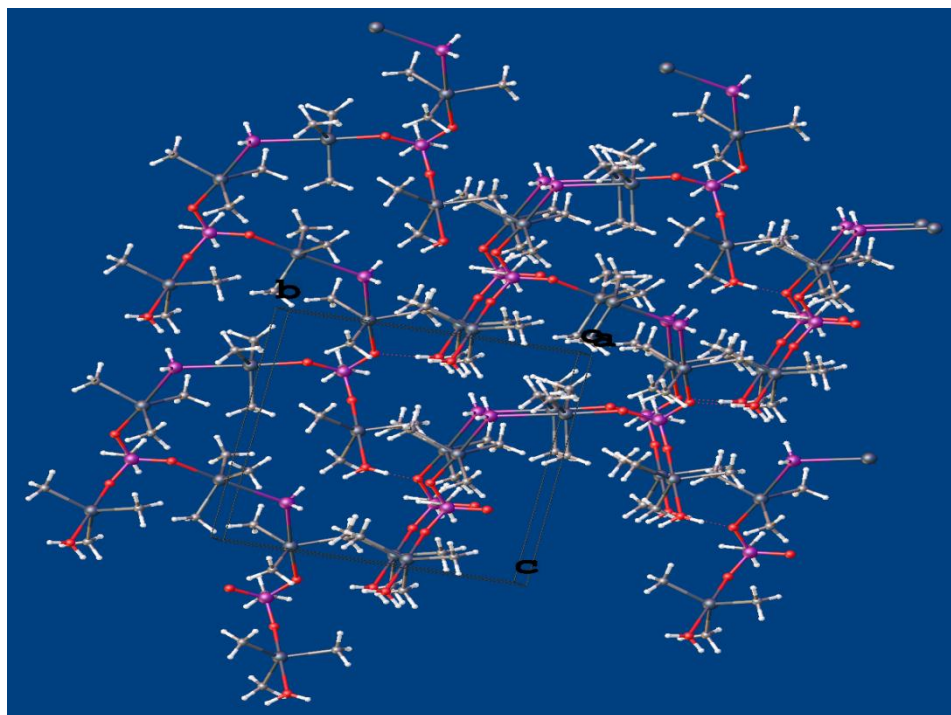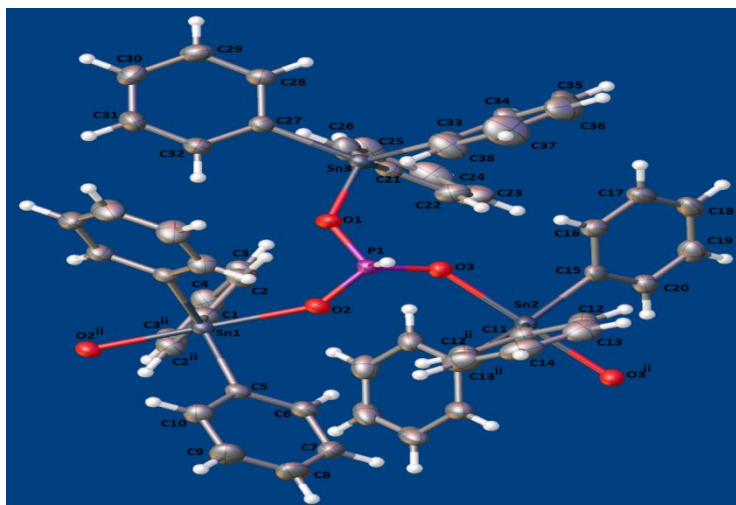

Fig 4:-3D structure of **1**showing 50% probability ellipsoids.

Crystals of **2** were investigated by FT-IR spectroscopy in ATR mode. FT-IR data evidence absorption bands that can be assigned to hydrogenphosphonate and$SnPh_3$ moiety.The vibration bands located at 1132 and 1109 cm^{-1}are assigned to νPO_3^{2-}(Nakamoto, 1997). Vibration bands, characteristic of phenyl ligands, are observed at 735 and 697 cm^{-1} corresponding to $\delta(Csp^2$-H) and$\delta(C = C)$ elongations, respectively. The Mössbauer parameters show two different tin centres: the quadrupole splitting values of 2.84 mm.s^{-1} and 2.51 mm.s^{-1} indicate a trigonal bipyramidal and a tetrahedral arrangement at tin atom, respectively (Bancroft and Platt, 1972; Parish,1984).

The compound **2** crystallizes in the monoclinic P2/n space group as clear light colourless block-like crystal. There are one hydrogenphosphonate ion and two $[SnPh_3]^+$moieties in the molecular structure which view is shown in Fig. 5. The structure of **2** corresponds to an infinite anionic chain of $[HPO_3(SnPh_3)]^-$ with bridging hydrogenphosphonate anions and $[SnPh_3]^+$moieties connected to the chain *via* the third remaining hydrogenphosphonate oxygen atoms through Sn—O bonds (Fig. 5).
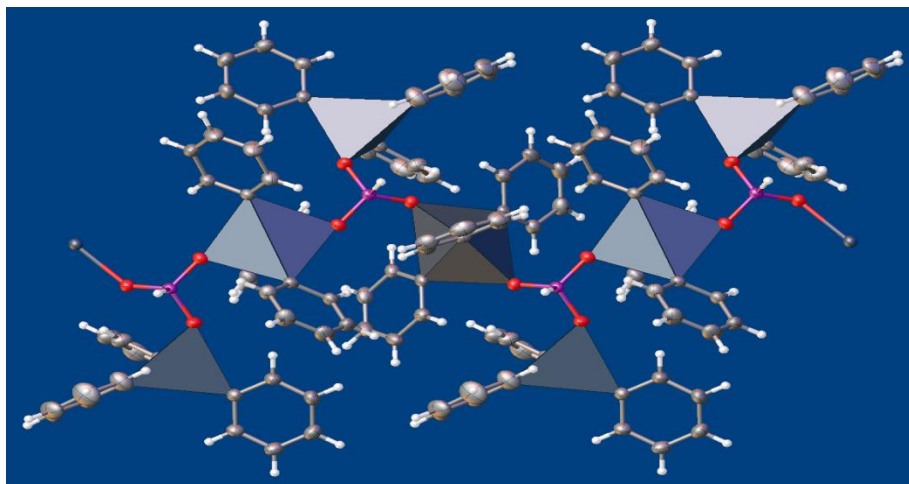
Fig 5:-Molecular structure of $HPO_3(SnPh_3)$ (**2**) showing 50% probability ellipsoids and the crystallographic numberingScheme.

Thus, the hydrogenphosphonate dianion behaves as a tri O-coordinating ligand. There are two types of $SnPh_3$; a *trans*-coordinated one, the environment around the tin(IV) atom being trigonal bipyramidal (tbp) and a monocoordinated one, the environment around the Sn(IV) centre being tetrahedral (td) (Figs. 6 and 7). In the *trans*-coordinated $SnPh_3$ moiety, the phenyl groups occupy the equatorial positions. The tin centres around each hydrogenphosphonate are differently coordinated by this last.
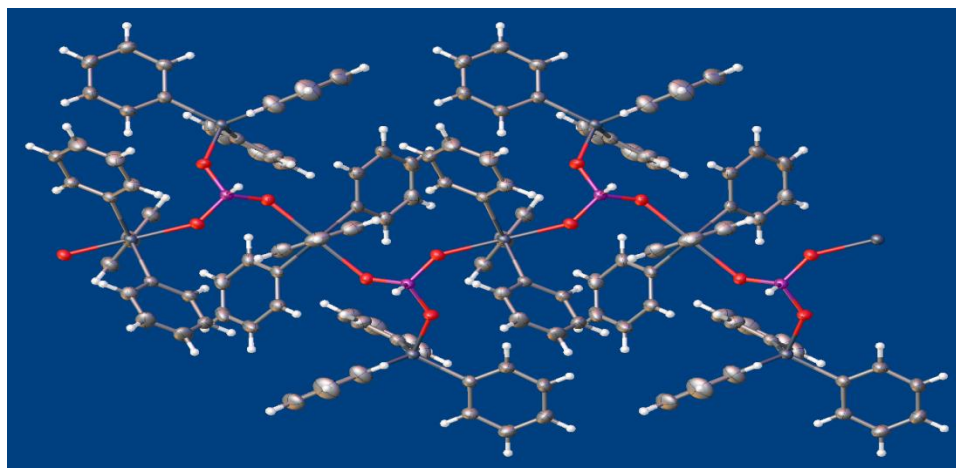

Fig 6:-Molecular structure of **2**showing the infinite ionic chain and $[SnPh_3]^+$ cations set on. Ellipsoids are drawn at 50% probability.

Fig 7:-Molecular structure of **2**showing the two polyhedron types at tin atoms. Ellipsoids are drawn at 50% probability.

The sum of the angles at tin about the *trans*-coordinated SnPh$_3$ moieties are equal to 360 ° indicating a perfect planar SnC$_3$ group. The angle values at the Sn centre for the monocoordinated SnPh$_3$ moieties from 99.28 (11) to 116.18 (12)° indicate a distorted tetrahedron around Sn3 atom. The Sn—C distances are in the range of those found in tbp and td SnPh$_3$ moieties (Diop *et al.*, 2013a, 2012a, 2011b). In the *trans*-coordinated moieties the apical positions of each SnC$_3$O$_2$ framework are occupied by similar oxygen atoms of the hydrogenphosphonates [Sn1—O2 2.196 (2); Sn2—O3 2.242 (2) Å]: these distance values are higher than the Sn—O distance (2.001 (2) Å) in the tetrahedral arrangement. The O—Sn—O angles [O2^i—Sn1—O2 177.03 (12) and O3^{ii}—Sn2—O3 178.22 (13)°] reveal a slight deviation from linearity. The P—O distances [1.502   (2), 1.510 (2) and 1.553 (2) Å] are in the range of those found in the literature (Larrea *et al.*, 2016; Ouarsal *et al.*, 2016; Hamchaoui *et al.*, 2013a, 2013b; Oh and Burns, 2014; Berrocal *et al.*, 2014). The P—H bond distance of 1.42 (4) is in the range of those found in the literature (Ouarsal *et al.*, 2016; Hamchaoui*et al.*, 2013a). The angle values at phosphor atom from 103.2 (17) to 115.16 (13)° show a distorted tetrahedral geometry in the hydrogenphosphonate anion as expected. In the crystal of complex **2**, chains are arranged within the lattice(Fig. 8).
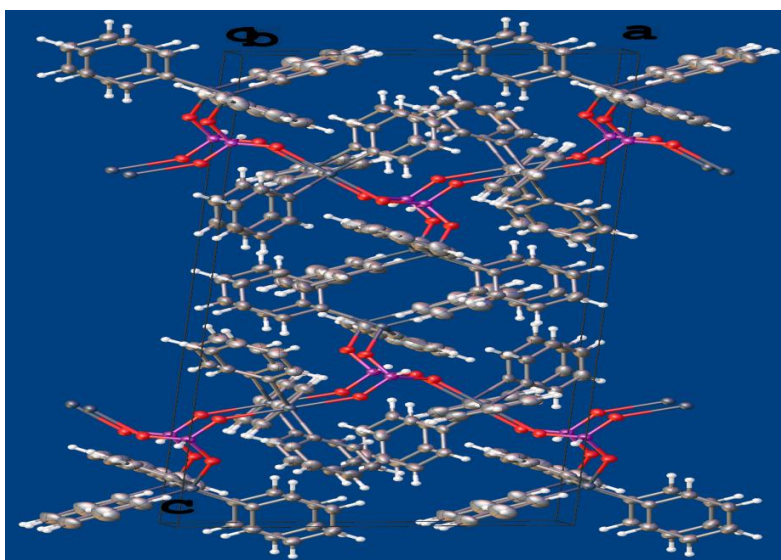
Fig 8:-Packing diagramof **2**showing 50% probability ellipsoids.

Conclusion:-

In this work, the studied triorganotin(IV) phosphonates **1** and **2** describe an ionic infinite chain connected to SnR$_3$ residues. In the case of the structure of **1**, the tin atom about the SnR$_3$ moiety is coordinated to an O water molecule. Thus, the main difference between the structures is that in **1**, all tin atoms are at the centre of a trigonal bipyramidal

polyhedron while **2** exhibits two polyhedra types: a trigonal bipyramidal polyhedron within the chain and, a tetrahedron for the SnR_3 moiety set on the chain. In **1**, the water molecule is involved in inter-chains hydrogen bonding interactions, enabling to growa 3D structure. In contrast, in **2**, chains stacking expand within the lattice. In both structures the phosphonate anion behaves as a tri-O-coordinating ligand towards tin centres. The infrared and mössbauer spectroscopic characterization presents somewhat a little limit, for instance the difference between the two present trigonal bipyramidal polyhedra in **1**. Completion of the studies with single crystal X-ray diffraction highlighted this coordination. Further works in investigation of orther triorganotin(IV) phosphonate compounds with or without a PH_2 bridge are in progress.

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