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PII: S0020-1693(15)00497-1
DOI: http://dx.doi.org/10.1016/j.ica.2015.10.012
Reference: ICA 16722

To appear in: *Inorganica Chimica Acta*

Received Date: 1 August 2015
Revised Date: 23 September 2015
Accepted Date: 9 October 2015

Please cite this article as: M. Roy, S. Roy, K.S. Singh, J. Kalita, S. Sureshkumar Singh, Synthesis, characterization and anti-diabetic activities of triorganotin(IV) azo-carboxylates derived from amino benzoic acids and resorcinol: Crystal structure and topological study of a 48 membered macrocyclic-tetrameric trimethyltin(IV) complex, *Inorganica Chimica Acta* (2015), doi: http://dx.doi.org/10.1016/j.ica.2015.10.012

Synthesis, characterization and anti-diabetic activities of triorganotin(IV) azo-carboxylates derived from amino benzoic acids and resorcinol: Crystal structure and topological study of a 48 membered macrocyclic-tetrameric trimethyltin(IV) complex

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Abstract

Triorganotin(IV) complexes of azo-carboxylic acids derived from amino benzoic acids and resorcinol were synthesized by the reaction of 2/4-(2,4-dihydroxy-phenylazo)-benzoic acids with appropriate triorganotin(IV) chlorides [R= Me (**1** and **3**), Ph (**2** and **4**) and Bu (**5**)] in presence of triethylamine. The characterization of the complexes was accomplished by elemental analyses, UV, IR and multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR spectroscopy. Structure of compound **3** was established by X-ray crystal structure analysis. X-ray crystal structure of **3** revealed that the compound exhibits a 48 membered macrocyclic-tetrameric structure with trigonal bipyramidal geometry around the tin atoms in which the three methyl groups occupy the equatorial positions while the apical positions are being occupied by the oxygen atom of carboxylate group of one ligand and the phenoxide oxygen atom of another ligand. The coordination network in **3** has also been analysed from the topological viewpoint. All the complexes display a sharp singlet ^{119}Sn resonance in the range specified for the four coordinate structures suggesting that complexes have tetrahedral structures in solution. The five coordinate structure of the complexes in solid state dissociated into monomeric species with four coordinate structures in solution. Anti-diabetic activities of the complexes were studied and the results showed that the compounds **2**, **3** and **4** exhibited effective activity even higher than the standard compound.

Key Words: Azo-carboxylates; triorganotin(IV) complexes; NMR spectroscopy; macrocyclic tetramer; anti-diabetic activities.

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1. Introduction

Organotin(IV) complexes of carboxylate ligands have been extensively studied because of their wide range of intriguing structures [1-6] and potential biological activities such as antitumor, antibacterial, antifungal, cytotoxic, insecticidal, urease inhibition, anti-proliferative and anti-tuberculosis etc. [5-10]. Organotin(IV) complexes with azo-carboxylates have been also explored owing to their structural diversity [11-15] and promising biological properties [11-13]. Moreover, organotin(IV) azo-carboxylates derived from amino benzoic acids and salicylaldehyde have been studied in great details in recent years because of their ability to exhibit diverse molecular structures [12-15] and larvicidal properties [12-13]. X-ray crystal structures of tri-n-butyl(IV) complexes with azo-carboxylic acids derived from *ortho*-amino benzoic acids exhibited polymeric structures with *trans*-trigonal bipyramidal geometry around tin atoms while triphenyltin(IV) complexes showed polymeric or dimeric structures with distorted *trans*-trigonal bipyramidal geometry [13-14]. However, triorganotin(IV) complexes with *para*-analogues resulted monomeric distorted tetrahedral structures [12]. Recently, we have also explored structures and antimicrobial activities of triorganotin(IV) complexes [R= methyl, n-butyl and phenyl] with azo-dicarboxylic acids derived from amino benzoic acids (*ortho*- and *para*-) and salicylic acid [16]. Molecular structure of tri-butyltin(IV) complex with *ortho*-azo-carboxylates showed that the complex exhibits polymeric structure in which one of the carboxylate group in the ligand bonded to tin atoms in bi-dentate bridging mode while the second carboxylate coordinates to tin atom in mono-dentate fashion. The structure of the complex is slightly distorted *trans*-trigonal bipyramidal geometry around tin atoms where oxygen atoms of carboxylate and hydroxy group bridge the adjacent tin atoms giving rise to a polymeric structure [16]. The structure of trimethyltin(IV) complex with the same ligand analogue was also found to be polymeric with *trans*-trigonal bipyramidal geometry around tin

atoms. However, in this complex both the carboxylate group of the ligand coordinated to the adjacent tin atoms exclusively in bridging bi-dentate fashion and unlike tributyltin(IV) complex, the hydroxyl group did not take part in the bonding [16].

On the other hand, diabetes Type 2 (diabetes mellitus) is a metabolic disorder which is often characterized by hyperglycaemia i.e. blood containing high level of sugar due to insulin resistance and relatively lack of insulin [17]. Insulin regulates the metabolism of carbohydrates and fats by promoting the absorption of glucose from the blood to skeletal muscles and fat tissue and it also inhibits the production of glucose by the liver [18]. Diabetes occurs when the secretion and activity level of insulin is deteriorated and exogenous insulin is required to treat the diabetic state [17]. Intestinal α-glucosidase controls postprandial hyperglycaemia by inhibiting digestion and carbohydrates absorption and it has been reported that by inhibiting α-glucosidase, diabetes mellitus may be controlled [19]. Triglyceride and postprandial insulin levels can also be reduced and controlled by α-glucosidase inhibitors [20,21]. In the literature, anti-diabetic activities of some metal complexes have been reported and have shown effective activities [22-24]. However, less attention has been paid to the study of anti-diabetic properties of organotin(IV) complexes even though these class of compounds possess potential biological properties [5-10].

Therefore, keeping in view the possibility of designing various interesting molecular structures with potential biological activities that have been exhibited by the organotin(IV) azo-carboxylates [12-16], we became interested to explore further, the chemistry of organotin(IV) complexes with azo-carboxylates derived from amino-benzoic acids. Thus, in this present contribution we have chosen amino benzoic acids and resorcinol for diazo-coupling reaction of carboxylate ligands and then synthesized a series triorganotin(IV) complexes [R = Me (**1** and **3**);

Ph (**2** and **4**) and Bu (**5**)] using these ligands. The synthesized complexes were fully characterized by elemental analysis, IR, multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy. Structure of a representative trimethyltin(IV) complex **3** was determined by X-ray crystallography and its topological analysis was also carried out. In addition, we have studied anti-diabetic activities of the complexes and compared with the standard drug acarbose.

2. Experimental

2.1 Materials and methods

Trimethyltin(IV) choride, Tributyltin(IV) chloride, Triphenyltin(IV) chloride, *ortho*-aminobenzoic acid, *para*-aminobenzoic acid and resorcinol were purchased from Merck as commercial source and used without further purification. Solvents were purified and dried using standard procedure. Carbon, hydrogen and nitrogen analyses were performed with a Perkin Elmer 2400 series II instrument. Electronic spectra for the ligands and compounds were recorded on UV-1800 Shimadzu spectrophotometer in DMF in the range 200-800 nm while IR spectra were obtained on Shimadzu FT-IR-8400S spectrophotometer in the range of 4000-400 cm^{-1} using KBr discs. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62 and 149.18 MHz respectively. ^{1}H and ^{13}C chemical shifts were referred to Me_4Si set at 0.00 ppm while Me_4Sn was employed as external reference compound for ^{119}Sn chemical shifts set at 0.00 ppm. For anti-diabetic assay, α-glucosidase (Maltase) (SRL74854), p-nitrophenyl α-D-glucopyranoside (SRL144969) and acarbose (A8980) were purchased from SRL India and Sigma Aldrich. Na_2HPO_4, NaH_2PO_4, Na_2CO_3, calcium chloride and other chemicals were of highest purity grade and purchased from Merck, India. Milli-Q water was used for all the enzymatic assays.

2.2. Synthesis

2.2.1. Synthesis of 2-(2,4-dihydroxy-phenylazo)-benzoic acid (H_3L^1)

The ligand 2-(2,4-dihydroxy-phenylazo)-benzoic acid (H_3L^1) was synthesized by diazotization of amino-benzoic acids and resorcinol following the analogous procedure [16] described below. To 5.0 g (36.45 mmol) of *o*- amino benzoic acid, 12 mL conc. HCl and 32 mL water was added and the mixture was digested on water bath for 1 hour. It was then cooled to 5°C and diazotized with ice cold aqueous $NaNO_2$ solution (2.51 g in 18mL water). A cold solution of resorcinol (4.03 g, 36.45 mmol) dissolved in 10% NaOH solution (5g, 50 mL) was added to the cold diazonium salt solution with vigorous stirring at 0 to 2°C. A deep red colour appeared immediately and the stirring was allowed to continue for an hour. The reaction mixture was kept overnight in a refrigerator and then kept at room temperature for about 3-4 hours. It was then acidified with dilute acetic acid to afford red precipitate of the desired product. The precipitate was filtered, washed thoroughly with water so as to remove excess acetic acid and water soluble materials, washing was continued till the filtrate became almost neutral and finally the product was dried on water bath. The solid product was then washed with hexane, dried in vacuum and recrystallized from methanol to yield the desired crystalline pure ligand (H_3L^1). Yield: 75 %; m.p.: 242-245 °C. *Anal.* Found: C, 60.77; H, 3.83; N, 10.96%. Calc. for $C_{13}H_{10}N_2O_4$: C, 60.46; H, 3.90; N, 10.85%. UV-visible (DMF) λ_{max}(nm): 265, 412. IR (KBr, cm^{-1}): 1681 ν_{asy}(COO), 1599, 1486, 1450, 1282 . ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H: 7.99 [d, 1H, H-3, J = 7.2 Hz], 7.92 [d, 1H, H-6´, J = 8.4 Hz], 7.69 [m, 2H, H-4 and H-6], 7.53 [t, 1H, H-5, J = 6.8 Hz], 6.57 [d, 1H, H-5´, J = 8.4 Hz], 6.29 [s, 1H, H-3´] ppm; Signals for –OH and –COOH were not observed due to solvent exchange. ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 167.58

[COOH], 164.23 [C-4´], 158.87 [C-1 and C-2´], 147.78 [C-1´], 134.48 [C-5], 132.90 [C-4], 130.86 [C-3], 128.84 [C-6´], 126.12 [C-6], 115.79 [C-2], 110.70 [C-5´], 103.21 [C-3´] ppm.

2.2.2. Synthesis of 4-(2,4-dihydroxy-phenylazo)-benzoic acid (H_3L^2)

The above procedure was also followed in case of H_3L^2 except that *p*-amino benzoic acid was used instead of *o*-amino benzoic acid for the diazo-coupling reaction. Yield: 70%; m.p.: 248-251 °C. *Anal.* Found: C, 60.71; H, 3.91; N, 10.72%. Calc. for $C_{13}H_{10}N_2O_4$: C, 60.46; H, 3.90; N, 10.85%. UV-visible (DMF) λ_{max}(nm): 265, 408. IR (KBr, cm^{-1}): 1686 ν_{asy}(COO); 1603, 1506, 1456, 1426, 1287. ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H: 8.10 [d, 2H, H-3 and H-5, J = 7.2 Hz], 7.94 [d, 2H, H-2 and H-6, J = 7.2 Hz], 7.71 [d, 1H, H-6′, J = 8.4 Hz], 6.53 [d, 1H, H-5´, J = 8.4 Hz], 6.39 [s, 1H, H-3´] ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 166.75[COOH], 163.95 [C-4´], 157.44 [C-1], 153.21 [C-2´], 132.73 [C-4], 131.25 [C-1´], 130.53 [C-3 and C-5], 129.53 [C-6´], 121.50 [C-2 and C-6], 109.65 [C-5´], 102.97 [C-3´] ppm. The numbering scheme and ligand skeleton are shown in **Scheme 1**.

<Scheme 1>

2.2.3. Synthesis of $Me_3SnH_2L^1$ (**1**)

2-(2,4-dihydroxy-phenylazo)-benzoic acid (0.5g, 1.93mmol) was dissolved in 50 mL anhydrous methanol and triethylamine (0.19g, 1.93 mmol) was added. The reaction mixture was then refluxed for 2 hours. To this mixture, trimethyltin(IV) chloride (0.38 g, 1.93 mmol) was added as solid with continuous stirring and then again refluxed for 5 hours. The precipitate containing Et_3NHCl was filtered off and the filtrate was evaporated using rotary evaporator. The solid product was washed with hexane and recrystallized from chloroform which afforded red

crystalline compound. Yield: 50 %; m.p.: 96-100 °C. *Anal*. Found: C, 45.87; H, 4.39; N, 6.72%. Calc. for $C_{16}H_{18}N_2O_4Sn$: C, 45.64; H, 4.31; N, 6.65%. UV-visible (DMF) λ_{max}(nm): 265, 412, 479. IR (KBr, cm^{-1}): 1621 ν_{asy}(COO); 1340 ν_{sym}(COO), 1591, 1483, 1442, 1133, 668 ν(Sn-C), 523 ν(Sn-O).^{1}H NMR ($CDCl_3$, 400 MHz) δ_H, Ligand skeleton: 13.14 [s, 1H, OH], 8.32 [d, 1H, H-3, *J*= 8.4 Hz] 8.05-7.99 [m, 3H, H-6´, H-4 and H-6], 7.89-7.85 [m, 3H, H-5, H-5´ and H-3´]; Sn-CH_3 skeleton: 0.69 [s, 9H, (Sn-CH_3)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C, Ligand skeleton: 168.78 [COO], 164.56 [C-4´], 158.76 [C-1 and C-2´], 147.01 [C-1´], 134.99 [C-5], 133.60 [C-4], 131.20 [C-3], 129.04 [C-6´], 126.29 [C-6], 116.21 [C-2], 110.89 [C-5´], 103.52 [C-3´];Sn-CH_3 skeleton: -1.84 [Sn-CH_3] ppm.^{119}Sn NMR ($CDCl_3$, 149 MHz): 69.8 ppm. Other triorganotin (IV) complexes were synthesized by reacting appropriate triorganotin(IV) chlorides and ligands following the analogous procedure described above.

2.2.4. Synthesis of $Ph_3SnH_2L^1$ (**2**)

Yield: 46%; m.p.: 118-120 °C. *Anal*. Found: C, 61.46; H, 3.91; N, 4.69%. Calc. for $C_{31}H_{24}N_2O_4Sn$: C, 61.31; H, 3.98; N, 4.61%. UV-visible (DMF) λ_{max}(nm): 265, 408, 489. IR (KBr, cm^{-1}): 1618 ν_{asy}(OCO); 1479, 1451, 1427,692 ν(Sn-C), 485ν(Sn-O).^{1}H NMR ($CDCl_3$, 400 MHz) δ_H, Ligand skeleton: 7.76-7.41 [m, 7H, Ar-H]; Sn-Ph skeleton: 7.67 [m, 6H, H-2*], 7.46 [m, 9H, H-3* and H-4*] ppm.^{13}C NMR ($CDCl_3$, 100 MHz) δ_C, Ligand skeleton: 170.78 [COO], 164.43 [C-4´], 158.92 [C-1 and C-2´], 147.80 [C-1´], 135.93 [C-5], 132.97 [C-4], 130.95 [C-3], 128.96 [C-6´], 126.90 [C-6], 115.81 [C-2], 110.78 [C-5´], 103.28 [C-3´]; Sn-Ph skeleton: 137.27 [C-1*], 136.41 [C-2*], 130.50 [C-4*], 128.87 [C-3*] ppm. ^{119}Sn NMR ($CDCl_3$, 149 MHz): - 46.5 ppm.

2.2.5. Synthesis of $Me_3SnH_2L^2$ (**3**)

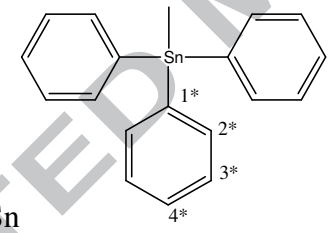
Yield: 56 %; m.p.: 206-209 °C. *Anal*. Found: C, 45.39; H, 4.37; N, 6.58%. Calc. for $C_{16}H_{18}N_2O_4Sn$: C, 45.64; H, 4.31; N, 6.65%. UV-visible (DMF) λ_{max}(nm): 265, 408, 497. IR (KBr, cm^{-1}): 1631ν_{asy}(COO); 1361 ν_{sym}(COO), 1599, 1523, 1502, 1454, 1228, 665 ν(Sn-C), 513 ν(Sn-O).^{1}H NMR ($CDCl_3$, 400 MHz) δ_H, Ligand skeleton: 13.88 [s, 1H, OH], 8.22 [m, 2H, H-3 and H-5], 7.86-7.79 [m, 3H, H-2, H-6 and H-6´], 6.59 [m, 1H, H-5´], 6.45 [d, 1H, H-3´, J = 2.0 Hz]; Sn-CH_3 skeleton: 0.71 [s, 9H, (Sn-CH_3)] ^2J [^{119}Sn-H (58 Hz)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C, Ligand skeleton: 174.54 [COO], 164.01 [C-4´], 157.47 [C-1], 152.60 [C-2´], 132.76 [C-3 and C-5], 131.32 [C-4], 130.51 [C-1´], 129.63 [C-6´], 121.57 [C-2 and C-6], 109.74 [C-5´], 102.31 [C-3´]; Sn–CH_3 skeleton: -2.76 [Sn-CH_3].^{119}Sn NMR ($CDCl_3$,149 MHz): 69.5 ppm

2.2. 6. Synthesis of $Ph_3SnH_2L^2$ (**4**)

Yield: 52%; m.p.: 94-96 °C. *Anal*. Found: C, 61.49; H, 3.89; N, 4.78%. Calc. for $C_{31}H_{24}N_2O_4Sn$: C, 61.31; H, 3.98; N, 4.61%. UV-visible (DMF) λ_{max}(nm): 238, 408, 495. IR (KBr, cm^{-1}): 1635 ν_{asy}(COO); 1597, 1475, 1418, 685 ν(Sn-C), 575ν(Sn-O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H, Ligand skeleton: 7.81[m, 2H, H-3 and H-5] 7.45-7.65 [m, 5H,H-2 and H-6; H-3′, H-5′ and H-6′]; Sn-Ph skeleton: 7.73 [m, 6H, H-2*], 7.46 [m, 9H, H-3* and H-4*] ppm.^{13}C NMR ($CDCl_3$, 100 MHz) δ_C, Ligand skeleton: 173.24 [COO], 164.04 [C-4´], 157.82 [C-1], 154.10 [C-2´], 131.75 [C-4], 131.27 [C-1´], 129.56 [C-6´], 129.05 [C-3 and C-5], 119.72 [C-2 and C-6], 111.34 [C-5´], 103.01 [C-3´]; Sn-Ph skeleton: 137.88 [C-1*], 136.44 [C-2*], 130.32 [C-4*], 128.74 [C-3*] ppm.^{119}Sn NMR ($CDCl_3$, 149 MHz): - 44.5 ppm.

2.2.7. Synthesis of $Bu_3SnH_2L^2$ (**5**)

Yield: 58%; m.p.: 133-138 °C. *Anal*. Found: C, 55.27; H, 6.50; N, 5.26%. Calc. for $C_{25}H_{36}N_2O_4Sn$: C, 54.86; H, 6.63; N, 5.12%. UV-visible (DMF) λ_{max}(nm): 239, 411,497. IR (KBr, cm^{-1}): 1635 ν_{asy}(COO); 1392ν_{sym}(COO), 1537, 1418, 659ν(Sn-C), 530 ν(Sn-O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H, Ligand skeleton: 8.17 [d, 2H, H-3 and H-5, J = 7.6 Hz], 7.63 [m, 1H, H-6´], 7.76 [d, 2H, H-2 and H-6, J =8.4 Hz], 6.55 [d, 1H, H-5´, J = 10.4 Hz], 6.31 [s, 1H, H-3´]; Sn-^{n}Bu skeleton: 1.69 [m, 6H, H-1*], 1.37 [m, 12H, H-2* and H-3*], 0.94 [t, 9H, H-4*] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C, Ligand skeleton: 173.93 [COO], 164.12 [C-4´], 157.96 [C-1], 154.02 [C-2´], 133.97 [C-3 and C-5], 132.49 [C-4], 131.29 [C-1´], 129.56 [C-6´], 119.92 [C-2 and C-6], 114.04 [C-5´], 103.98 [C-3´]; Sn-^{n}Bu skeleton: 29.68 [C-2*], 27.82 [C-3*], 17.85[C-1*], 13.69 [C-4*] ppm.^{119}Sn NMR ($CDCl_3$, 149 MHz): 114.8 ppm. The numbering scheme for Sn-Bu and Sn-Ph in the complexes is given below:



$^{*4}CH_3$-$^{*3}CH_2$-$^{*2}CH_2$-$^{*1}CH_2$-Sn

2.3. X-ray crystallography and Topological analysis

For complex **3**, data collection was made using Bruker SMART APEX II CCD area detector area detector equipped with graphite monochromatedMo Kαradiation (λ = 0.71073 Å) at 293(2) K. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using Bruker SAINT [25]. The absorption correction was applied using SADABS [26]. The structure was solved with SIR-92 [27] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-97 [28]. All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated geometrically

and refined using the riding model. The crystallographic data and structure refinement parameter for compound **3** is given in **Table 1**.

<Table 1>

Topological analysis was performed with the ToposPro program package and the TTD collection of periodic network topologies [29]. The RCSR three-letter codes [30] were used to designate the network topologies. Those nets that are absent in the RCSR are designated with the TOPOS ND_n nomenclature [31], where N is a sequence of coordination numbers of all non-equivalent nodes of the net, D is periodicity of the net (D= M, C, L, T for 0-,1-, 2-, 3-periodic nets), and n is the ordinal number of the net in the set of all non-isomorphic nets with the given ND sequence.

2.4. Anti-diabetic activity

Anti-diabetic properties of the compounds **1-5** were screened by α-glucosidase inhibitory assay and performed according to Kumar *et al*. [32]. In brief, 25 µL of sample solution in ethanol (1 mg/mL) and 25 µL of the enzyme were added in the well and the solution was mixed gently and incubated at $37^oC \pm 1^oC$ for 10 min. Then, 25 µL of the substrate (*p*-nitrophenyl α-D glucopyranoside in 0.5 mM concentration in the buffer, pH 6.8) was added in the mixture and incubated again at 37^o C for 30 min. The reaction was terminated by adding 100 µL of 0.2M sodium carbonate solution. Amount of *p*-nitrophenol released from the substrate was quantified on a UV-Vis spectrophotometer at 405 nm (Multiskan™ GO Spectrophotometer, Thermo-Fisher, Finland). Inhibition concentration (IC_{50}) of enzyme activity was also calculated by following the same enzyme assay. A gradient concentration of 33.3, 66.6 and 99.9 µg/mL was used for each of the synthesized compounds analyzed along with the drug, acarbose as the standard inhibitor of α-

glucosidase (positive control). Appropriate controls were used for each sample and all the analysis were done in triplicate. Percentage enzyme inhibition was calculated by using the following formula: Enzyme inhibition (%): [Control OD-Sample OD/Control OD] x100; [Where, Sample OD = (Sample OD- Sample Blank OD) and Control OD= (OD of the control reaction without inhibitor-blank OD)]

3. Results and discussion

3.1. Synthesis

Triorganotin (IV) complexes, **1**-**5** were synthesized by reacting 2-(2,4-dihydroxy-phenylazo)-benzoic acid (H_3L^1) for compounds [**1** and **2**] or 4-(2,4-dihydroxy-phenylazo)-benzoic acid (H_3L^2) for compounds [**3**-**5**] with appropriate triorganotin(IV) chorides [R= Me (**1** and **3**), Ph (**2** and **4**) and Bu (**5**)] in presence of triethlylamine in methanol. The reaction scheme for the synthesis of complex **1** as one of the representative complex is shown in **Scheme 2** along with the line diagram of the structure. Reaction produces moderate to good yield and complexes are soluble in all common organic solvents.

<Scheme 2>

3.2. X-ray crystal structure description and topological study of compound **3**

The free azo-carboxylic acid ligand contains two hydroxyl groups (2, 4 disposition). Upon complexation, the hydroxyl group at 2-position loses its proton, so the phenoxide O-atom acquires negative charge and the imino N-atom becomes protonated, leading to a zwitterionic ligand. In related systems, existence of such zwitterionic form is a common occurrence [33-37]. The zwitterionic azo-carboxylate ligand bridges the Sn-atoms via a carboxylate O-atom and the phenoxide O-atom. The molecular structure and packing diagram of complex **3** is shown in **Fig.**

1 and **2**; selected bond lengths and bond angles are listed in **Table 2**. In the molecular structure of complex **1**, Me_3Sn and the ligand alternately link into a cyclotetrameric 48 membered $Sn_4C_{28}O_8N_8$ ring. Each tin atom is trigonal bipyramidal (3C, 2O) with two oxygen atoms from the two ligands occupying the axial positions and the equatorial positions occupied by the methyl groups. The tin oxygen distances are in the range 2.095(2)–2.790(4) Å. The distances of $Sn(1)\cdots O(7)^1$ and $O(7)\cdots Sn(1)^1$ [1:^{1}2-x,1-y, 2-z], 2.790(4) Å, is greater than the sum of the covalent radii of Sn and O (2.56 Å), but is considerably less than the sum of the van der Waals radii (3.68 Å) and are considered as part of the primary coordination environment. Sn···O interactions in the range 3.274 (4) to 3.420 (3) Å [Sn(1)···O(2) and Sn(2)···O(6)], although, are well inside of the sum of the van der Waals radii of the Sn and O atoms, these Sn···O distances are too long to be considered bonding.

<Fig. 1>

<Fig. 2>

<Table 2>

The width of the cavity of the macrocyclic derivative can be evaluated by the transannular Sn···Sn distances, which is 16.81 x 15.27 $Å^2$. Analogous triorganotin(IV) tetrameric macrocycles have been found in triphenyltin[((E)-1-{2-hydroxy-5-[(E)-2-phenyl-1-diazenyl]phenyl}methylidene)-amino]acetate [36], tributyltin(IV) 2,6-difluorobenzoate [38] and tributyltin(IV) (Z)-3-(4-nitrophenyl)-2-phenyl-2-propenoate [39]. Both intramolecular and intermolecular hydrogen bonds are foreseen in the structure. The N^+–H group is involved in intramolecular hydrogen bonding with the phenoxide O-atom. Intermolecular O–H···O hydrogen bond between two adjacent hydroxyl/carboxylate groups also occurs.

To provide further insight into the H-bonding and coordination network, we have performed topological analysis. In compound **3**, in addition to intramolecular H-bonding interactions that occur within a molecule, each molecule is engaged in eight intermolecular hydrogen bonds which connect four neighbouring molecules, resulting in a layer structure. The H-bonded layer structure can be topologically classified as **sql** (**Figs. 3, 4**), the most frequent underlying topology observed for H-bonded layers (see Supporting Information for further details). The layers stack along [100] as (AB) (**Fig. 5**).

<Fig. 3>

<Fig. 4>

<Fig. 5>

A more detailed topological description where Sn atoms are considered as the nodes of the underlying net while both coordination and hydrogen bonds are taken into account leads to a 2-periodic three-dimensional **6^3Ia** topology (also known as sphere-packing graph for layer groups) [40] (**Fig. 6, 7**). We have found 41 molecular structures with the same **6^3Ia** topology in the standard representation (in the Supporting Information) [41].

<Fig. 6>

<Fig. 7>

3.3. Spectroscopic characterization

3.3.1. UV-visible spectroscopy

The electronic spectra for compounds **1–5** were recorded in DMF solution (10^{-4} M) at room temperature. The electronic spectra of the ligands $H_3L^1$and H_3L^2 show UV absorptions near 265 nm as a result of $\pi \rightarrow \pi^*$ of the aromatic ring [42]. UV-Visible spectra of the compounds **1-5**

exhibited three absorption bands near 265-275, 408-412 and 475-497 nm, respectively. The new band observed at 475-479 nm indicates ligand to metal charge transfer [43].

3.3.2. IR spectroscopy

IR spectroscopy is a useful tool to ascertain the mode of coordination of the ligands to the metal atom in complexes in solid state. In the complexes **1-5**, the IR absorption bands for -COO^- stretching frequencies were observed at lower frequencies as compared to the corresponding ligands indicating the carboxylate coordination of the ligand to the tin atom [13]. The asymmetric [ν_{asym}(OCO)] stretching vibration for the free ligands were detected near 1681 cm^{-1}; in the complexes, these bands were observed at 1618-1635 cm^{-1}. The value of $\Delta\nu$ [ν_{asy}(OCO) - ν_{sym}(OCO)] also provides useful information to determine the mode of coordination of carboxylate to tin(IV) atom in organotin(IV) complexes [44]. In general, $\Delta\nu$ below 200 cm^{-1} indicates bi-dentate mode and greater than 200 cm^{-1} is the indication of the mono-dentate mode of coordination of the carboxylate ligands to the tin in the complexes [16,44]. In case of the triphenyltin(IV) complexes **2** and **4**, IR absorption band for ν_{sym}(OCO) could not be assigned due to the complex pattern of the spectra. The magnitude of $\Delta\nu$ [$\Delta\nu = \nu_{asy}$(OCO) - ν_{sym}(OCO)] for the complexes **1** and **3** were found to be in the range 270-278 cm^{-1} indicating mono-dentate mode of coordination of the carboxylate ligands in these complexes [45]. Strong bands observed at 650-690 cm^{-1} and 485-575 cm^{-1} in all the complexes may be assigned to ν(Sn-C-Sn) and ν(Sn-O-Sn) mode of vibration [42].

3.3.3 Multinuclear (^1H, ^{13}C and ^{119}Sn) NMR spectroscopy

The ^{1}H, ^{13}C and ^{119}Sn NMR spectral data of the complexes **1**-**5** were recorded in $CDCl_3$ and the data are given in the experimental section and spectra for few representative complexes have been provided in the Supporting Information. The complete assignment of the ligands was achieved by examining their chemical shift values, integration values and multiplicity patterns and also by careful comparison of proton NMR data with the similar type of azo-ligands derived from either amino benzoic acid or resorcinol reported earlier [13,46]. In case of the complexes, assignments of the chemical shifts of the protons was done by extrapolating the conclusions drawn from the ligand assignments to the spectra of the corresponding complexes owing to the similarity of the spectra. In complex **1** and **3**, the singlet peaks appeared at 0.69 and 0.71 ppm are assigned to methyl tin protons. In case of the triphenyl tin(IV) complexes **2** and **4**, the two distinct multiplicities due to phenyl tin protons were observed at around 7.41-7.69 ppm while three multiplets appeared in compound **5** in the range 0.93 to 1.69 ppm are assigned to butyl tin protons. ^{2}J (^{119}Sn-H) coupling constant value for complex **3** was found to be 58 Hz which is in consistent with four coordinate structure [37,47]. Further, the angle between C-Sn-C in **3** was also calculated using Lockhart and Mander's equation [48]{θ(C-Sn-C) = 0.0161 $|^{2}J$(Sn-H)$|^{2}$ -1.32 $|^{2}J$(Sn-H)| + 133.4} and the angle was found to be 111.3° thereby supporting 4-coordinate tetrahedral geometry around tin atom in solution [45]. In ^{13}C NMR spectra of all the complexes, the δ(COO) signals were found to be shifted to the downfield region (174.5-168.7 ppm) as compared to the free acid ligands (167.5-166.7 ppm) indicating that the carboxylate anions are coordinated to tin atom [16,47]. In all complexes, the expected ^{13}C signals were able to detect and the number of carbon signals are completely in consistent with the formulation of expected products. All the complexes were subjected to ^{119}Sn NMR study to determine geometry around tin atom. The complexes displayed a sharp singlet ^{119}Sn resonance peak near + 69.8 and + 69.5

ppm for **1** and **3**; - 46.5 and - 44.5 ppm for **2** and **4** while +115 ppm was observed for **5**. ^{119}Sn resonances of the complexes **1**-**5** suggest four coordinate tetrahedral structures in solution state [47,49-51]. From the above discussion it is evident that the five coordinate structures of the complexes in solid state are dissociated into four coordinate structures in solution state.

3.4. Anti-diabetic activities

The screening of the anti-diabetic activities of the synthetic complexes and ligands using α-glucosidase enzyme revealed that compounds **2**, **3** and **4** have shown significant results by inhibition of more than 50% of α-glucosidase activity. These compounds were further analysed for calculation of IC_{50} as compared to the standard drug, acarbose. The ligands and other compounds **1** and **5** have shown lower activities than the standard drugs in the preliminary screening, so we have determined IC_{50} values for only those complexes which showed significant activities. The pictorial representation in terms of percentage of enzyme activity inhibition and IC_{50} (μg/mL) values for the complexes **2, 3** and **4** along with the standard compound acarbose are given in **Fig. 8** and **Table 3** respectively**.** As can be seen from the diagram, with the change in concentration from 33.33μg/mL, to 66.66 and 99.99 μg/mL, the activity for compounds **2** and **3** increased while for the standard drug acarbose the activity was found to be almost same.From the table, it is also clear that compound **2**showed lowest IC_{50} values at 6.43 μg/mL followed by compound **3** and **4** at 9.70 and 11.19 μg/mL respectively against the standard compound, acarbose with IC_{50} value at 12.15 μg/mL. This promising result of the test is important finding for consideration of *in-vivo* test in near future. These compounds could be better candidate for anti-diabetic studies provided the complexes show permissible toxicities level and increased solubility in water.

<Fig. 8>

<Table 3>

4. **Conclusions**

A new series of triorganitin(IV) complexes with azo-caboxylic acids derived from amino benzoic acids and resorcinol were synthesized and complete characterization of the complexes were accomplished by elemental analysis, UV, IR and multinuclear NMR spectroscopy. IR spectral study indicates the presence of mono-dentate mode of coordination of carboxylate ligands in trimethyl and tri-n-butyltin(IV) complexes. Complexes display a single sharp ^{119}Sn NMR resonance in the range specified for the four coordinate structures thus suggesting that complexes have four coordinate tetrahedral geometry around tin atoms in solution. Molecular structure of trimethyltin(IV) complex **3** was determined by X-ray crystallography. Crystal structure of the complex reveals a 48 membered macrocyclic tetrameric structure in which tin atoms show *trans*-trigonal bipramidal geometry with the three methyl groups occupying the equatorial plane while the apical positions are being occupied by the oxygen atom of carboxylate and phenoxide oxygen atom of another ligand. The complex also exhibits zwitterionic form where a hydrogen atom of one of the hydroxyl groups is shifted to the nearby nitrogen atom of the azo-group. In **3**, H-bonding results in a layer structure with **sql** topology. A more detailed analysis reveals an overall 2-periodic three-dimensional **6^{3}Ia** topology. Anti-diabetic activities of the complexes were also studied on α-glucosidase enzyme and showed better results than the standard drug acarbose. Since the compounds exhibited effective anti-diabetic activity than the standard compound, these compounds could be further studied to explore the possibility of anti-

diabetic therapeutic uses. This promising result will also open a new avenue to the researcher to investigate organotin (IV) azo-carboxylates for their anti-diabetic activities.

Acknowledgements

Authors thank to SAIF, IIT Madras for providing X-ray crystal data for compound **3** and IISc, Bangalore for NMR spectra.

Supplementary materials

CCDC 1415981 contains the supplementary crystallographic data for complex **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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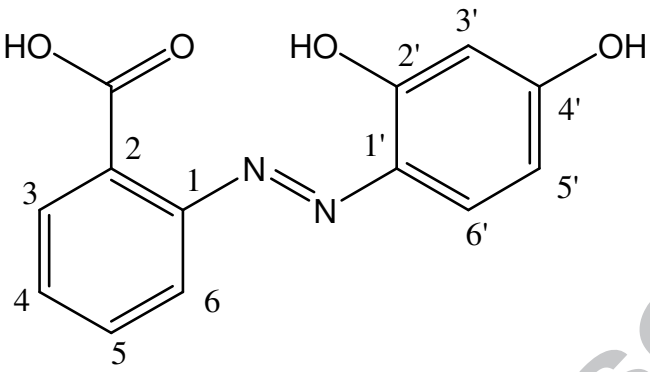
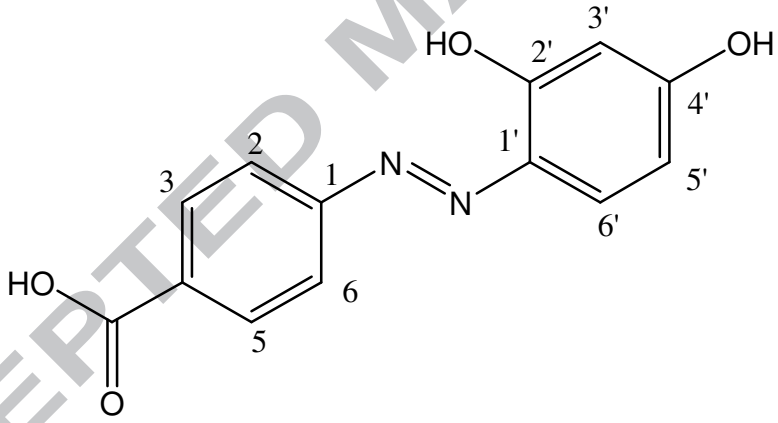
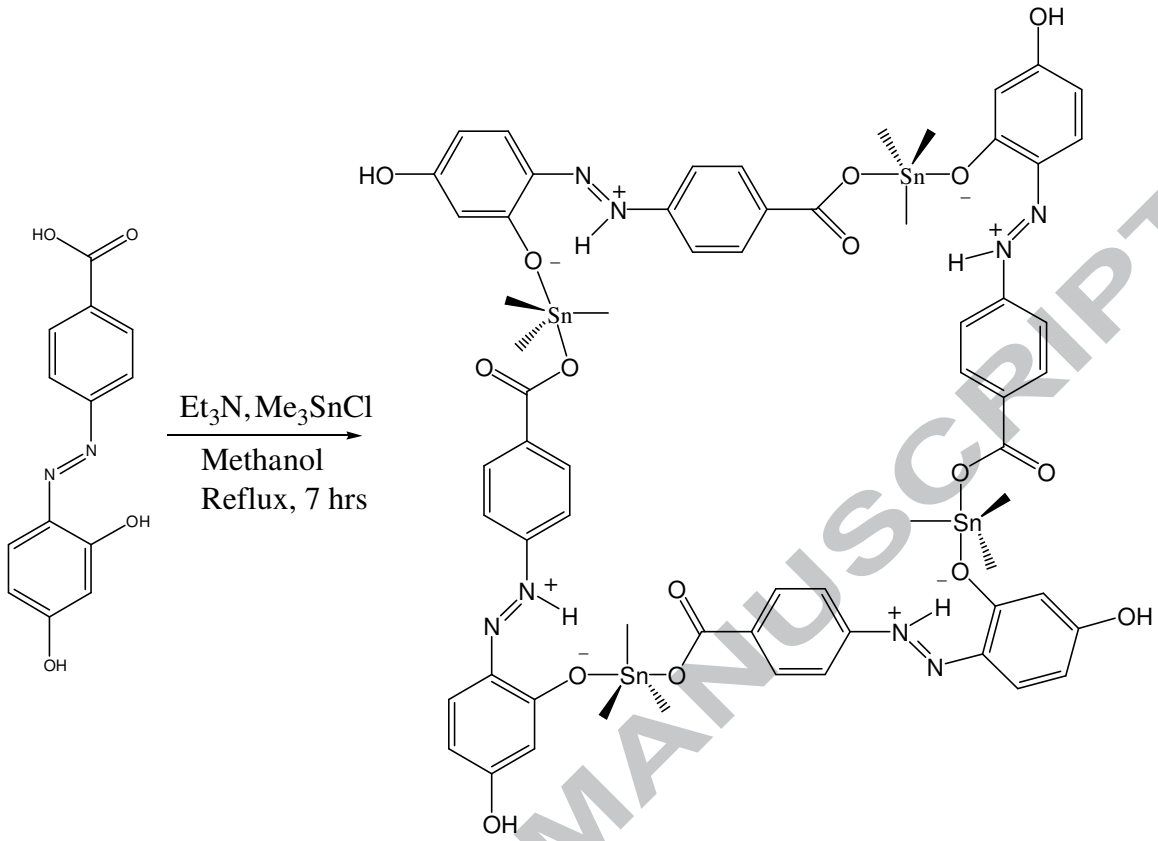


2-(2,4-dihydroxy-phenylazo)-benzoic acid (H_3L^1)



4-(2,4-dihydroxy-phenylazo)-benzoic acid (H_3L^2)

Scheme 1. Ligand skeleton and numbering scheme for H_3L^1 and H_3L^2.



Scheme 2. Reaction scheme for the synthesis of macro-cyclic tetrameric trimethyltin(IV) complex **3**.

Table 1. Crystallographic and structure refinement data for compound **3**.

Empirical formula	$C_{64}H_{72}N_8O_{16}Sn_4$
Formula weight	1684.06
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
a/Å	9.852(5)
b/Å	13.975(5)
c/Å	14.530(5)
α/°	110.354(5)
β/°	107.778(5)
γ/°	98.906(5)
Volume/Å^3	1708.0(12)
Z	1
ρ_{calc}g/cm^3	1.637
μ/mm^{-1}	1.516
F(000)	840
Crystal size/mm^3	0.30 x 0.20 x 0.20
Radiation	MoKα (λ = 0.71073)
Theta range for data collection/°	1.63 to 26.00
Index ranges	$-12 \le h \le 12$, $-17 \le k \le 17$, $-17 \le l \le 17$
Reflections collected	35400
Independent reflections	6714 [R_{int} = 0.0266]
Data/restraints/parameters	6714/1/ 429
Goodness-of-fit on F^2	1.114
Final R indexes [I>=2σ (I)]	R_1 = 0.0268, wR_2 = 0.0660
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0752
Largest diff. peak/hole / e Å^{-3}	0.845 and -0.592

Table 2. Selected bond distances and angles of compound **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(1)	Sn(1)	2.110(4)	C(20)	O(6)	1.227(4)
C(2)	Sn(1)	2.107(4)	C(20)	O(5)	1.271(4)
C(3)	O(2)	1.219(4)	C(3)	O(1)	1.280(4)
C(4)	Sn(1)	2.095(4)	C(28)	O(7)	1.290(4)
C(12)	O(3)	1.289(3)	C(30)	O(8)	1.336(4)
C(14)	O(4)	1.322(4)	N(1)	N(2)	1.298(3)
N(3)	N(4)	1.287(4)	O(1)	Sn(1)	2.095(2)
Sn(1)	O(7)[1]	2.790(4)	C(17)	Sn(2)	2.109(3)
O(3)	Sn(2)	2.364(2)	C(18)	Sn(2)	2.109(4)
O(5)	Sn(2)	2.149(2)	C(19)	Sn(2)	2.108(3)

[1]2-x,1-y,2-z

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O(1)	Sn(1)	C(2)	98.37(15)	O(1)	Sn(1)	C(1)	92.52(13)
C(2)	Sn(1)	C(1)	116.7(2)	C(4)	Sn(1)	C(1)	118.49(18)
C(4)	Sn(1)	C(2)	119.40(18)	O(1)	Sn(1)	O(7)[1]	177.96(10)
C(17)	Sn(2)	O(3)	83.71(11)	C(18)	Sn(2)	O(3)	88.75(12)
C(18)	Sn(2)	C(17)	114.86(16)	C(19)	Sn(2)	C(18)	125.52(15)
C(19)	Sn(2)	C(17)	119.08(15)	C(17)	Sn(2)	O(5)	90.01(12)
C(18)	Sn(2)	O(5)	95.00(13)	C(19)	Sn(2)	O(5)	92.14(13)
O(5)	Sn(2)	O(3)	173.61(8)	O(2)	C(3)	O(1)	125.1(3)

[1]2-x,1-y,2-z

Table 3. IC_{50} values for triorganotin(IV) complexes **2**, **3**, **4** and standard drug acarbose.

Sl. No.	Complexes/reference	IC_{50} value (µg/mL)	SD
1	$Ph_3SnH_2L^1$ (**2**)	6.43	3.12
2	$Me_3SnH_2L^1$ (**3**)	9.70	1.18
3	$Ph_3SnH_2L^2$ (**4**)	11.19	2.70
4	Acarbose	12.15	1.94

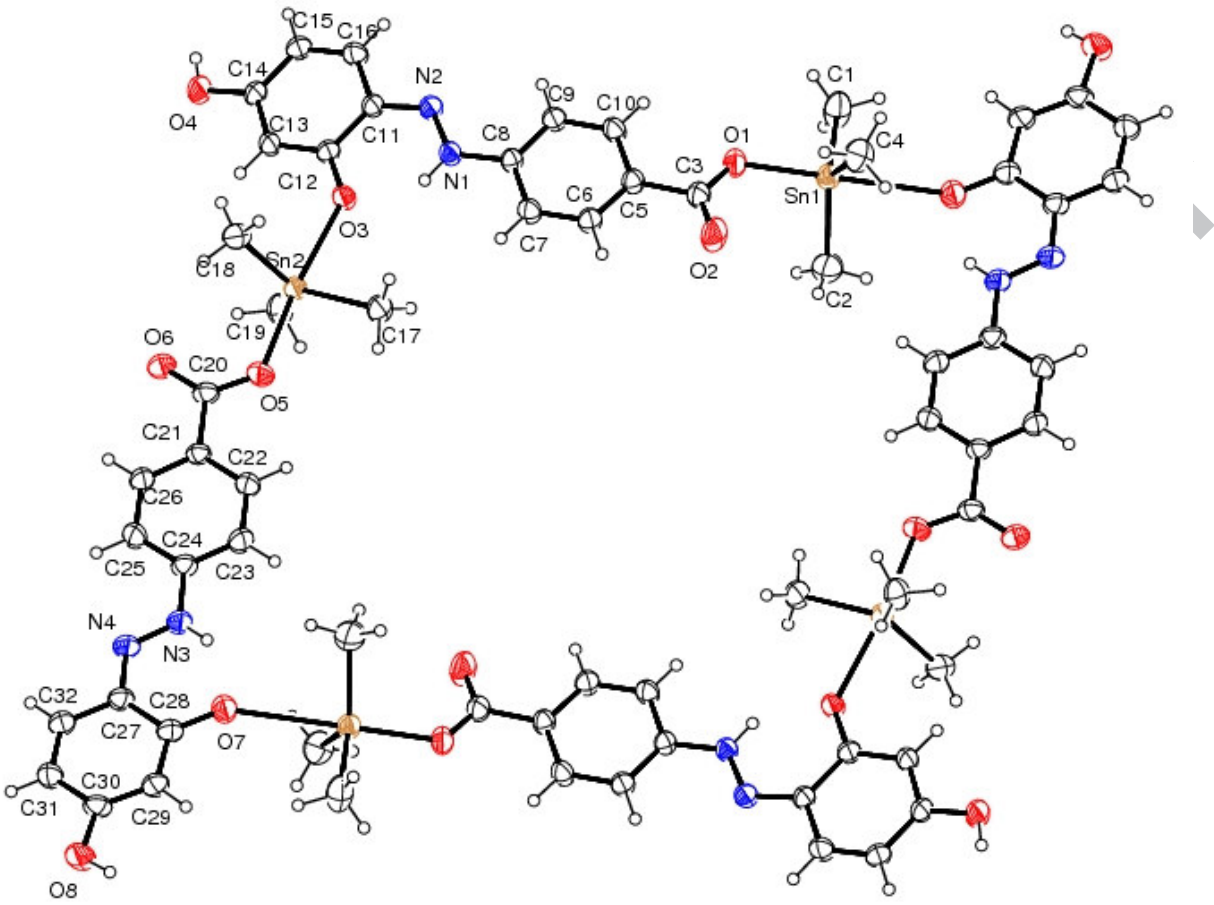


Fig. 1. Molecular structure of compound **3** showing trigonal bipyramidal geometry around tin atoms in the tetrameric macrocycle (50% probability ellipsoids).

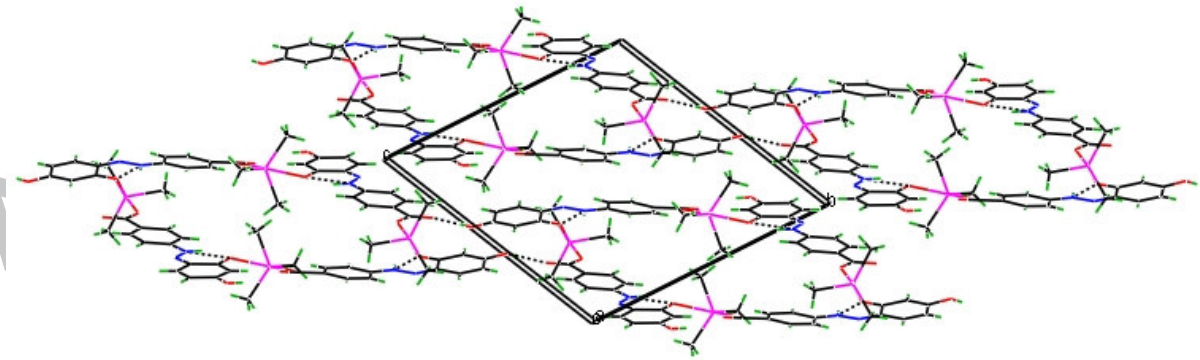


Fig. 2. Packing diagram of complex **3**.

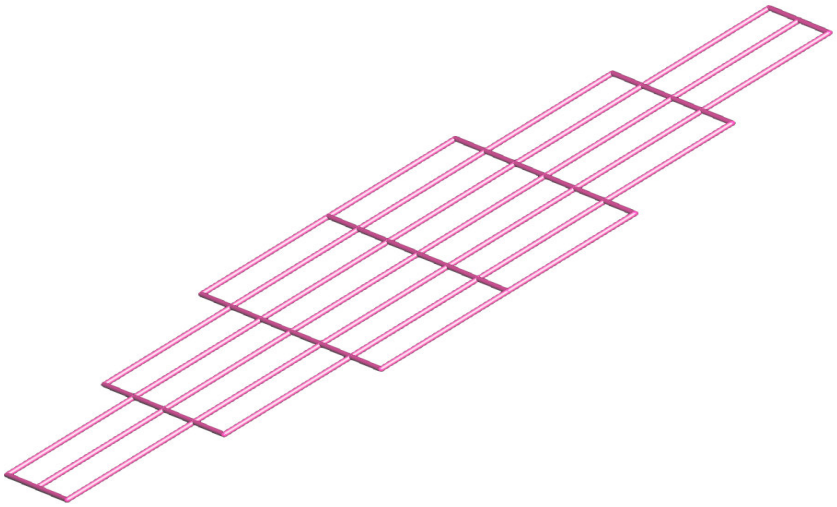


Fig. 3. Underlying net 2-periodic **sql** in the standard representation.

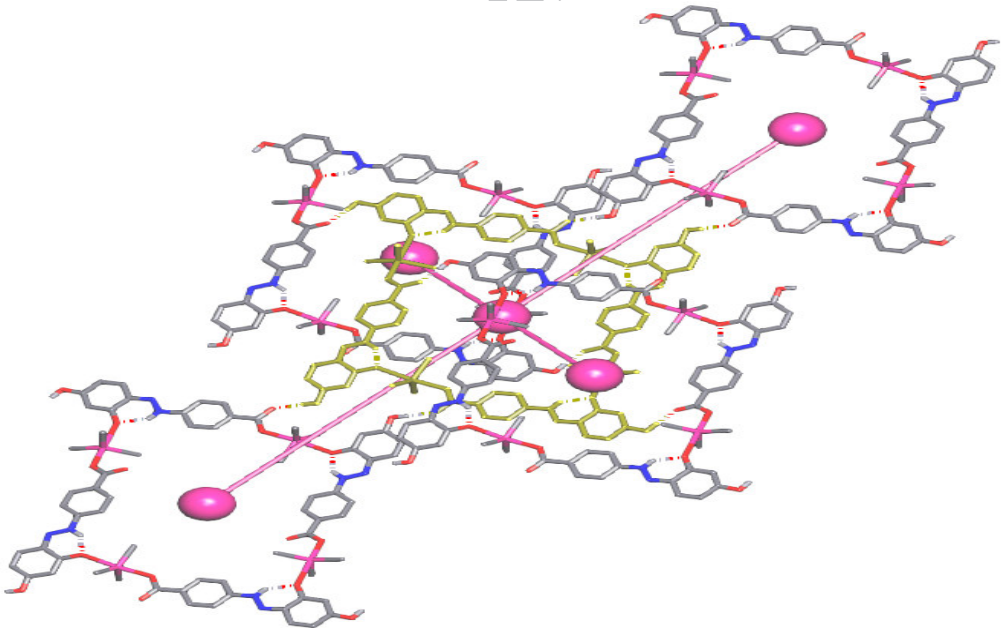


Fig. 4. Underlying net **sql** in the standard representation merged with initial molecular network.

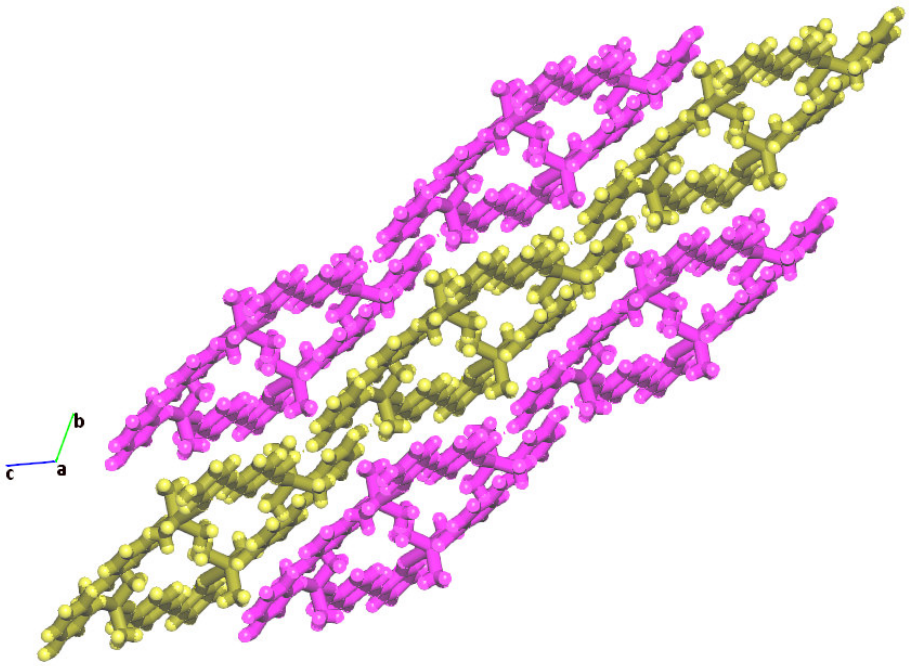


Fig. 5. Stacking (AB) of the H-bonded layers. Layers A and B are differently highlighted.

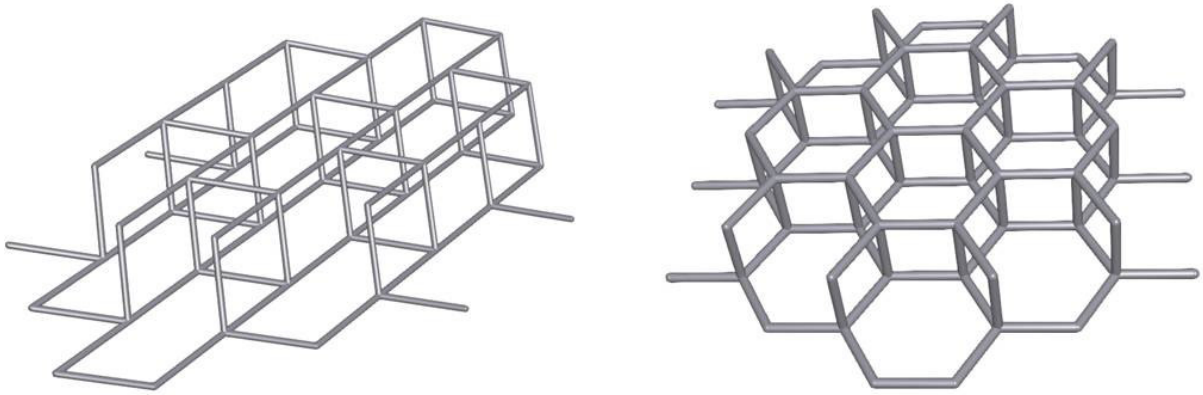


Fig. 6. Underlying net 2-periodic **6^3Ia** in the standard representation (left); Ideal net 2-periodic **6^3Ia** (right).

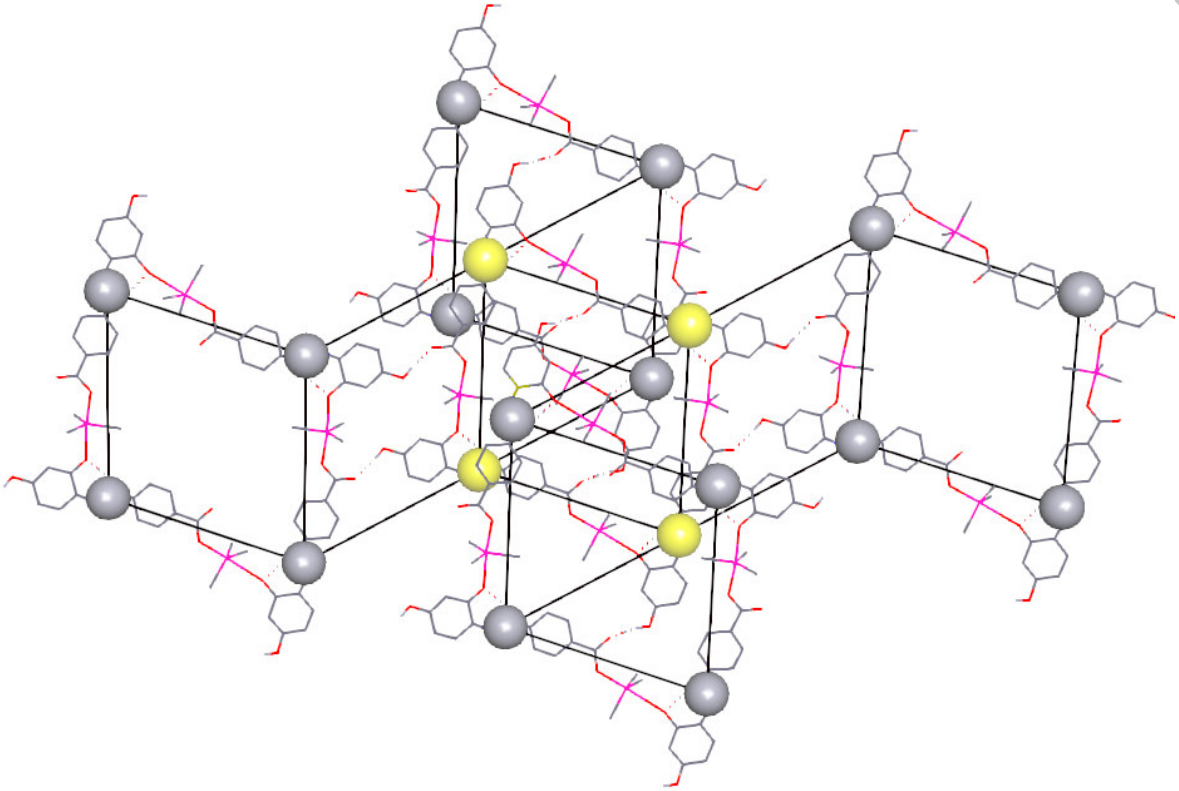


Fig. 7. Underlying net **6^3Ia** in the standard representation merged with initial molecular network.

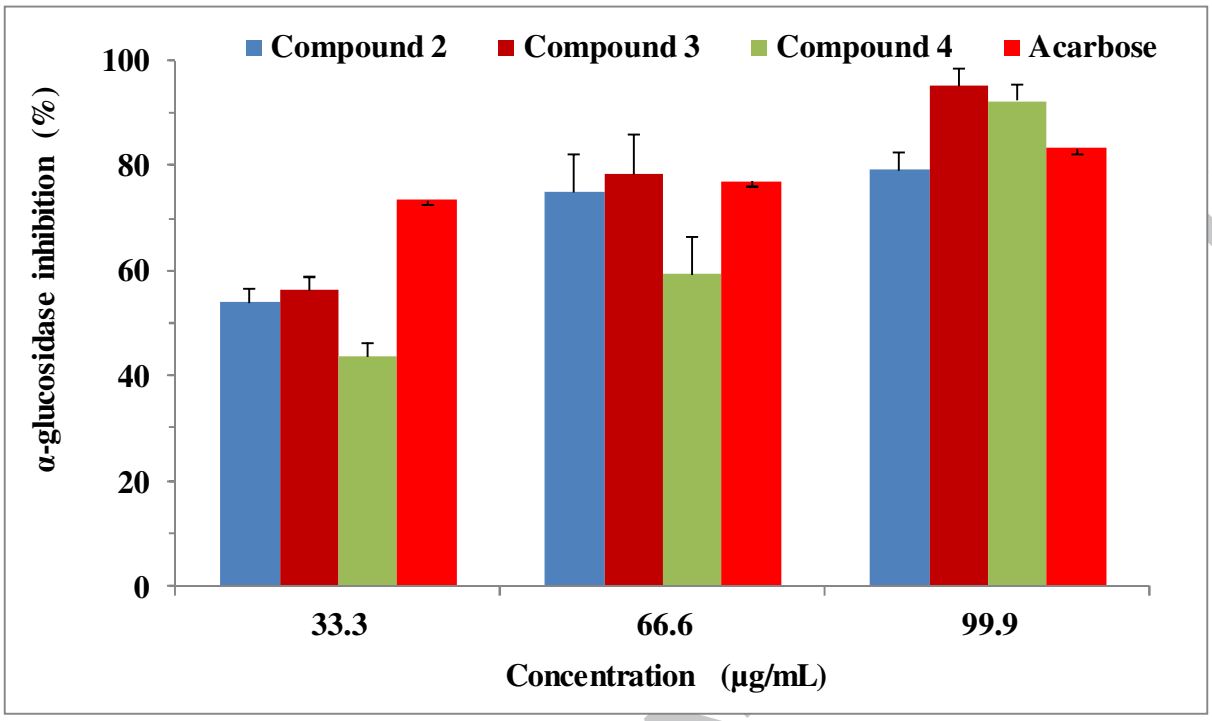
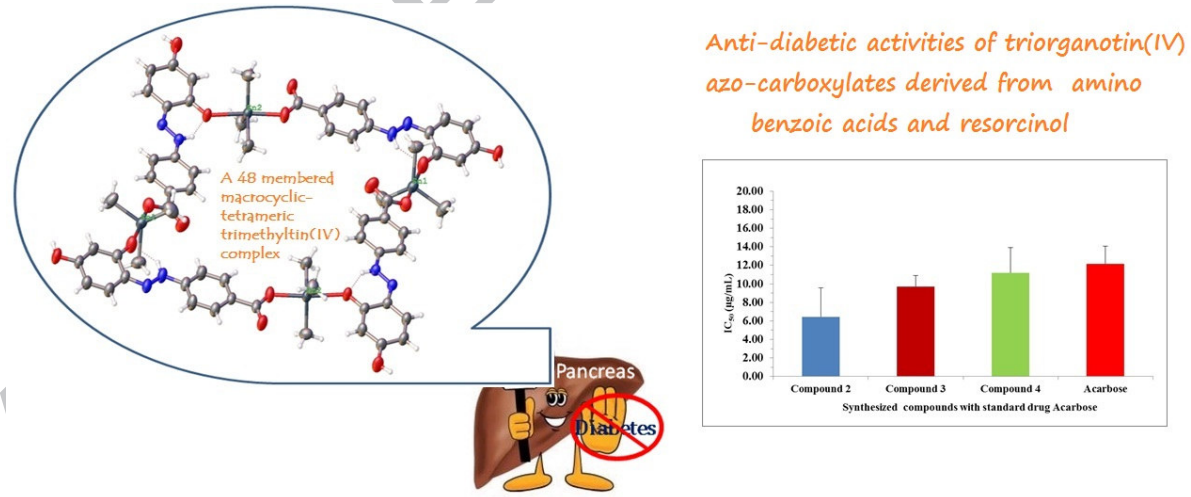


Fig. 8. Comparison of α-glucosidase (%) inhibition for triorganotin(IV) complexes **2**, **3**, **4** and standard drug acarbose at different gradient concentrations (T-bars on the histogram represents SD).

Synopsis

Triorganotin(IV) complexes of azocarboxylic acids were synthesized by the reaction of 2/4-(2,4-dihydroxy-phenylazo)-benzoic acids with appropriate triorganotin(IV) chlorides [R= Me (**1** and **3**), Ph (**2** and **4**) and Bu (**5**)] in presence of triethylamine. X-ray structure of **3** reveals that the compound exhibits a 48 membered macro-cyclic tetramer with *trans*-trigonal bipyramidal geometry around tin atoms. Topological analysis of **3** was also carried out. ^{119}Sn- NMR study of the complexes suggests tetrahedral structures in solution. Anti-diabetic activity studies of the complexes show better results than the standard compound.

Graphical abstract



Highlights

- Triorganotin(IV) azo-carboxylates **1**-**5** derived from amino benzoic acids and resorcinol were synthesized and characterized.
- Structure of compound **3** was determined by X-ray crystallography and its topological analysis was carried out.
- **3** is a 48 membered macrocylic tetrameric compound with *trans*-trigonal bipyramidal geometry around tin atoms.
- Complexes exhibit better anti-diabetic activities than the standard compound.