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Synthesis and solid-state spectroscopic investigation of some novel diorganotin(IV) complexes of tetraazamacrocyclic ligands

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ABSTRACT

The tetradendate macrocyclic ligands, [H_2L-1 = 5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene] and [H_2L-2 = 6,14-dioxa-8,16-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene] have been prepared by the condensation reaction of 1,2-diaminoethane and 1,3-diaminopropane, respectively, with ethyl acetoacetate in methanol at room temperature. The diorganotin(IV) complexes of general formula [R_2Sn(L-1)/R_2Sn(L-2)] (R = Me, *n*-Bu and Ph) have been synthesized by template condensation reaction of 1,2-diaminoethane or 1,3-diaminopropane and ethyl acetoacetate with R_2SnCl_2 (R = Me or Ph) or *n*-Bu_2SnO in 2:2:1 molar ratio at ambient temperature (35 ± 2 °C) in methanol. The solid-state characterization of resulting complexes have been carried out by elemental analysis, IR, recently developed DART-mass, solid-state ^{13}C NMR, ^{119m}Sn Mössbauer spectroscopic studies. These studies suggest that in all of the studied complexes, the macrocyclic ligands act as tetradentate coordinating through four nitrogen atoms giving a skew-trapezoidal bipyramidal environment around tin center. Since, the studied diorganotin(IV) macrocyclic complexes are insoluble in common organic solvents, hence good crystals could not be grown for single crystal X-ray crystallographic studies. Thermal studies of all of the studied complexes have also been carried out in the temperature range 0–1000 °C using TG, DTG and DTA techniques. The end product of pyrolysis is SnO_2 confirmed by XRD analysis.

1. Introduction

The coordination chemistry of macrocycles is an expeditiously expanding domain of research having a promising and diverse future [1]. Synthetic macrocyclic ligands resemble with natural macrocycles such as porphyrins [2] and cobalamines [3] in electronic properties and reactivity. Metal complexes of macrocyclic ligands are very active part of biologically occurring metalloenzymes [4] and of industrial catalysts [5]. The chemistry of tetraazamacrocyclic ligands has been of growing interest to coordination chemists followed by the earlier work on the metal controlled template synthesis of macrocycles [6]. Studies on azamacrocycles started with serendipitous discoveries of idiosyncratic imine condensations of transition element compounds of suitable configured amines with carbonyl compounds [6]. Much interesting research has focused on the physiological compatibility of azamacrocyclic compounds and the elaboration of substituents that confer biomimetic or biomedically useful properties [7]. Interest in linked azamacrocycles has been spurred by indications that their compounds show antiviral activity and inhibit human immuno-deficiency virus (HIV) replication, at least *in vitro* [8,9]. Reported interactions of azamacrocycle compounds with specific peptide and DNA sequences offer interesting therapeutic possibilities. The ability of azamacrocycles to bind cations (effectively irreversibly), leaving some coordination site labile, has implications for catalytic activity in a variety of fields [10,11]. The tetraazamacrocycles are used as magnetic resonance imaging agents [12], and are able to safely convey radiopharmaceutical nuclei to targeted sites [13,14]. In general, there has been increasing interest in azamacrocycle compounds as biomimetic models and as catalysts, particularly for peroxidation reactions and for electrochemical CO_2 fixation [6].

Azamacrocycles with amide functions (oxo-azamacrocycles) are usually prepared by conventional non-template methods without requiring high dilution techniques. The amide functions of oxo-azamacrocycles are generally reduced by B_2H_6/THF, providing versatile synthesis of cyclic amines. The cyclic amine–amide and cyclic peptides have many properties analogous to linear peptides and their metal complexes show functionalities resembling those of metalloproteins, thereby, making them of biological interest [15]. A large number of workers [16–18] are currently engaged in the synthesis of polyamide macrocycles and their coordination chemistry which is of particular interest in view of two potential donor atoms, i.e., amide nitrogen and amide oxygen [17,19–26]. However, in the most of the polyamide macrocyclic complexes, amide nitrogen is involved in coordination and not oxygen. The

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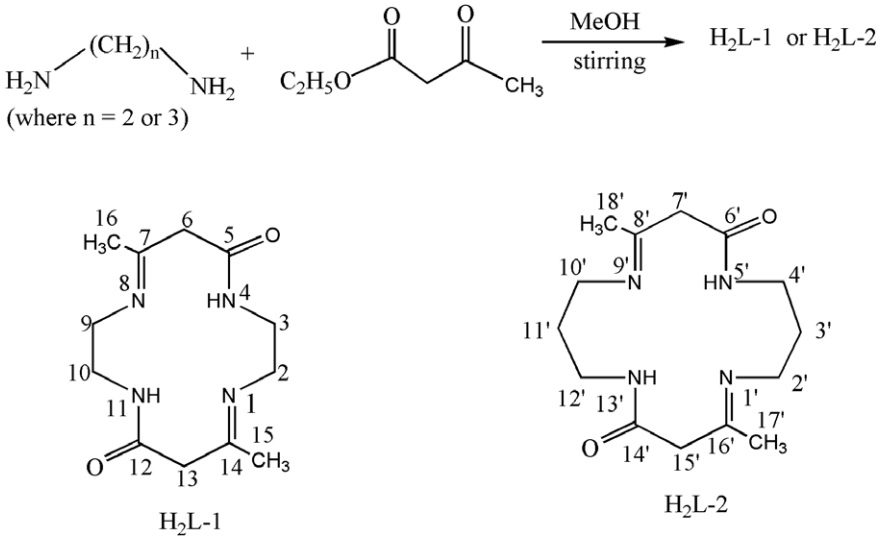


Scheme 1.

tetraazamacrocycle (H_2tmtaa) (H_2tmtaa = dibenzotetramethyltetraaza[14]annulene) and its dianion (tmtaa) have a saddle structure in which the four nitrogen atoms lie in a plane, thereby, creating a natural location (cavity size *ca.* 1.9 Å) for metal encapsulation [27]. In comparison to a large number of transition metal complexes of oxo-tetraazamacrocycles (as cited above), only two references on tin(II) [26] and Si(IV)/Sn(IV) [28] have been reported so far. In view of this, we report herein the synthesis and solid-state characterization of several new complexes of diorganotin(IV) moiety with macrocyclic ligands H_2L-1 and H_2L-2 (Scheme 1), derived from the condensation of ethyl acetoacetate with 1,2-diaminoethane and 1,3-diaminopropane, respectively.

2. Experimental

2.1. Materials

All of the syntheses were carried out under an anhydrous nitrogen atmosphere and precautions to avoid the presence of oxygen were taken at every stage. *n*-Dibutyltin(IV) oxide, dimethyltin(IV) dichloride were purchased from Merk-Schuchardt and used as received. Diphenyltin(IV) dichloride was synthesized according to the reported method [29]. Ethyl acetoacetate (Thomas Baker), 1,2-diaminoethane (BDH) and 1,3-diaminopropane (Merk-Schuchardt) were used as received. Solvents such as methanol and cyclohexane (Qualigens) were dried and distilled, and stored under nitrogen before use.

2.2. Measurements

The melting points of the synthesized complexes were determined on a Toshniwal capillary melting point apparatus and were uncorrected. Carbon, hydrogen and nitrogen were analyzed on elemental analyzer system VarioEL CHNS analyzer. IR and Far-IR spectra of the solid compounds were recorded on a Nicolet NEXUS Aligent 1100 FT-IR spectrometer in the range 4000–400 cm^{-1} in KBr discs and 500–200 cm^{-1} in CsI discs. ^{13}C NMR spectra (at frequency 125 MHz) of the compounds in the solid-state were recorded on a Bruker Avance WB (Wide Bore) 500 MHz FT NMR spectrometer using Adamantane as the external reference at the Tata Institute of Fundamental Research, Mumbai, India. The sample was packed in 4 mm rotor weight ≈ 72 mg and pulse program used was cross-polarization from proton (cp-ramp). ^{13}C and ^{1}H NMR of H_2L-1 and H_2L-2 in $CDCl_3$ were recorded on a Bruker Avance (400 MHz) FT NMR spectrometer using TMS as the internal standard at the Punjab University, Chandigarh, India. The DART-mass spectra of the compounds were recorded on a Jeol AccuTOF DART JMS-T100LC mass spectrometer having TOF mass analyzer and DART (Direct Analysis in Real Time) source at the Central Drug Research Institute, Lucknow, India. The solid samples were subjected directly in front of DART source. Dry helium was used with 4 LPM (liter per minute) flow rate for ionization at 350 °C. The orifice 1 set at 28 V and spectra were collected and print outs are averaged spectra of 6–8 scans. ^{119m}Sn Mössbauer spectra were recorded on a Mössbauer spectrometer model MS-900 according to the procedure reported previously [30], at the Department of Chemistry and Physics, University of The District of Columbia, Washington, DC. Thermal measurements were carried out on a Perkin–Elmer (Pyris Diamond) thermal analyzer in air, in the temperature range 0–1000 °C with heating rate 10 °C/min in a platinum crucible using alumina powder as a reference material at I.I.C., Indian Institute of Technology Roorkee. The X-ray powder diffraction (XRD) of residues obtained by pyrolysis of the studied diorganotin(IV) derivatives of macrocyclic ligands were recorded on a Bruker AXS diffractometer at I.I.C., Indian Institute of Technology Roorkee, using nickel mono chromated Cu Kα radiation (λ = 1.541 Å).

2.3. Synthesis

2.3.1. Synthesis of 5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene H_2L-1 (**1**) and 6,14-dioxa-8,16-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene H_2L-2 (**2**)

The ligand, H_2L-1 was prepared according to the previously reported method [24] and H_2L-2 was synthesized using the similar procedure. To a methanol solution of ethyl acetoacetate (1.301 g, 10.0 mmol) was added 1,2-diaminoethane for H_2L-1 (0.601 g, 10.0 mmol) or 1,3-diaminopropane for H_2L-2 (0.741 g, 10.0 mmol) in 10 ml of methanol with constant stirring. The reaction mixture was stirred for 8–12 h at room temperature (35 ± 2 °C). The contents were then left at room temperature for 12 h which resulted in the formation of fine shining colorless crystalline solid in case of H_2L-1, but H_2L-2 was crystallized after keeping the contents for a few days. The solid product was washed with chilled metha-

nol and dried in vacuo. The purity of these macrocycles was checked by TLC.

*2.3.1.1. H_2L-1 (**1**).* Colorless crystalline; m.p., 133–135 °C [24]; Yield, 71%; Anal. Calc. for $C_{12}H_{20}N_4O_2$ (252.32): C, 57.12; H, 7.99; N, 22.21%. Found: C, 57.01; H, 7.73; N, 21.91%. (MH^+/z) Found (calc.): 253.18 (253.33). Selected IR data (KBr, ν_{max}/cm^{-1}): 1605vs (C=N), 1649s (C=O), 2987vs, 2951vs (C–H), 3296vs (N–H). ^1H NMR ($CDCl_3$, δ/ppm): δ 8.64 (s, 2H, H-4, H-11); 4.09, 4.06 (dd (9.2, 9.2 Hz), 4H, H-2, H-9); 3.36, 3.34 (dd (4.0, 7.3 Hz), 4H, H-3, H-10); 4.46 (s, 4H, H-6, H-13); 1.91s, 1.23t (6.5 Hz, 6H, H-15, H-16).

*2.3.1.2. H_2L-2 (**2**).* Colorless crystalline; m.p., 45–47 °C; Yield, 69%; Anal. Calc. for $C_{14}H_{24}N_4O_2$ (280.37): C, 59.98; H, 8.63; N, 19.98%. Found: C, 59.96; H, 8.74; N, 19.87%. (MH^+/z) Found (calc.): 281.18 (281.38). Selected IR data (KBr, ν_{max}/cm^{-1}): 1606vs (C=N), 1646s (C=O), 2985vs, 2947vs (C–H), 3296m (N–H). ^1H NMR ($CDCl_3$, δ/ppm): δ 8.56 (s, 2H, H-5′, H-13′); 4.04, 4.08 (dd (9.6, 9.4 Hz), 4H, H-2′, H-10′); 2.80 (m, 4H, H-3′, H-11′); 3.27, 3.32 (dd (8.6, 8.6 Hz), 4H, H-4′, H-12′); 3.80 (s, 4H, H-7′, H-15′); 1.91s, 1.24t (9.7 Hz, 6H, H-17′, H-18′).

2.3.2. Synthesis of diorganotin(IV) complexes of H_2L-1 and H_2L-2

The diorganotin(IV) complexes of 5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene (H_2L-1) and 6,14-dioxa-8,16-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene (H_2L-2) have been synthesized by following methods.

2.3.3. Attempted synthesis of dibutyltin(IV) complexes of H_2L-1/H_2L-2 by azeotropic removal of water method

The ligand, H_2L-1 or H_2L-2 (5.0 mmol) dissolved in methanol (30 ml) was added drop wise to a methanol solution (30 ml) of *n*-dibutyltin(IV) oxide (1.245 g, 5.0 mmol) with constant stirring under dry nitrogen atmosphere. The resulting mixture was then stirred for additional 40 h at room temperature (35 ± 2 °C), followed by refluxing for 2–3 h. The excess of solvent was removed under vacuum, but no complexation took place, instead macrocyclic ligand and *n*-dibutyltin oxide separated out. Therefore, this method was not used for synthesis of dimethyltin(IV) and diphenyltin(IV) complexes.

2.3.4. Synthesis of dibutyltin(IV) complexes of H_2L-1/H_2L-2 using template method

The dibutyltin(IV) complexes of H_2L-1/H_2L-2 were prepared by a drop wise addition of methanol (~10 ml for each) solution of ethyl acetoacetate (1.301 g, 10.0 mmol) and 1,2-diaminoethane (0.601 g, 10 mmol)/1,3-diaminopropane (0.741 g, 10.0 mmol) to the suspension of dibutyltin(IV) oxide (1.245 g, 5.0 mmol) (**3**/**6**) in methanol (~30 ml) with constant stirring at room temperature under inert atmosphere of dry nitrogen. The mixture thus obtained was stirred for 40 h at 35 ± 2 °C. The water formed during the reaction was removed azeotropically. The solution was filtered, and the excess of solvent was gradually removed by evaporation under vacuum. The solid product was washed thoroughly with dry cyclohexane, and then dried in vacuo.

*2.3.4.1. n-Bu_2Sn(L-1) (**3**).* Yellow solid; m.p., 230–232 °C; Yield, 80%; Anal. Calc. for $C_{20}H_{36}N_4O_2Sn$ (483.24): C, 49.71; H, 7.51; N, 11.59; Sn, 24.56%. Found: C, 49.76; H, 8.01; N, 11.12; Sn, 24.72%. Selected IR data (KBr, ν_{max}/cm^{-1}): 1566m (C=N), 1634vs (C=O), 2565w (C–H), 648w (ν_{as} Sn–C), 607vw (ν_s Sn–C), 465m (Sn–N), 417m (Sn←N).

*2.3.4.2. n-Bu_2Sn(L-2) (**6**).* White solid; m.p., >320 °C; Yield, 81%; Anal. Calc. for $C_{22}H_{40}N_4O_2Sn$ (511.29): C, 51.68; H, 7.89; N, 10.96; Sn, 23.22%. Found: C, 51.29; H, 7.16; N, 10.76; Sn, 23.69%. (MH^+/z) Found (calc.): 512.12 (512.30). Selected IR data (KBr, ν_{max}/cm^{-1}): 1562s (C=N), 1636vs (C=O), 2954w, 2929w (C–H), 596s (ν_{as} Sn–C), 567s (ν_s Sn–C), 420sh (Sn–N), 419m (Sn←N).

2.3.5. Synthesis of dimethyl/diphenyltin(IV) complexes of H_2L-1/H_2L-2 using template method

The dimethyltin(IV) and diphenyltin(IV) complexes of H_2L-1 and H_2L-2 were prepared by a drop wise addition of methanol solution (~10 ml for each) of ethyl acetoacetate (1.301 g, 10.0 mmol) and 1,2-diaminoethane (0.601 g, 10.0 mmol)/1,3-diaminopropane (0.741 g, 10.0 mmol) to the solution of dimethyltin(IV) dichloride (1.098 g, 5.0 mmol) (**4**/**7**) or diphenyltin(IV) dichloride (1.720 g, 5.0 mmol) (**5**/**8**) in dry methanol (~20 ml) with constant stirring at room temperature under inert atmosphere of dry nitrogen. The mixture thus obtained was stirred for 15 h at room temperature (35 ± 2 °C). The excess of solvent was reduced under vacuum and solid product was washed thoroughly by dry cyclohexane, and then dried in vacuo.

*2.3.5.1. Me_2Sn(L-1) (**4**).* White solid; m.p., 180–182 °C; Yield, 76%; Anal. Calc. for $C_{14}H_{24}N_4O_2Sn$ (399.08): C, 42.14; H, 6.06; N, 14.04; Sn, 29.75%. Found: C, 42.26; H, 6.00; N, 14.39; Sn, 29.64%. (MH^+/z) Found (calc.): 400.11 (400.09). Selected IR data (KBr, ν_{max}/cm^{-1}): 1566s (C=N), 1634vs (C=O), 2982m (C–H), 653w (ν_{as} Sn–C), 620w (ν_s Sn–C), 465m (Sn–N), 410m (Sn←N).

*2.3.5.2. Ph_2Sn(L-1) (**5**).* White solid; m.p., 210 (dec.) °C; Yield, 82%; Anal. Calc. for $C_{24}H_{28}N_4O_2Sn$ (523.22): C, 55.09; H, 5.39; N, 10.71; Sn, 22.69%. Found: C, 54.64; H, 5.31; N, 10.38; Sn, 22.45%. (MH^+/z) Found (calc.): 523.31 (524.23). Selected IR data (KBr, ν_{max}/cm^{-1}): 1562vs (C=N), 1639m (C=O), 2978m (C–H), 279m (ν_{as} Sn–C), 230s (ν_s Sn–C), 456m (Sn–N), 422w (Sn←N).

*2.3.5.3. Me_2Sn(L-2) (**7**).* White solid; m.p., >300 °C; Yield, 75%; Anal. Calc. for $C_{16}H_{28}N_4O_2Sn$ (427.13): C, 44.99; H, 6.61; N, 13.12; Sn, 27.79%. Found: C, 44.85; H, 6.29; N, 13.07; Sn, 27.43%. (MH^+/z) Found (calc.): 428.27 (428.14). Selected IR data (KBr, ν_{max}/cm^{-1}): 1530w, 1565sh (C=N), 1626vs,br (C=O), 2996m, 2920w (C–H), 561vs (ν_{as} Sn–C), 521w (ν_s Sn–C), 446m (Sn–N), 406w (Sn←N).

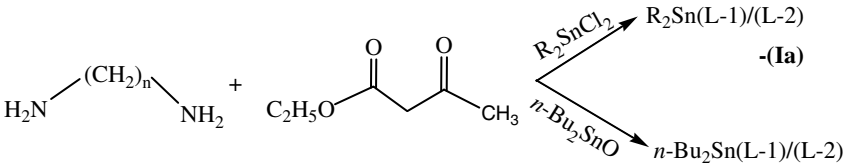
*2.3.5.4. Ph_2Sn(L-2) (**8**).* White solid; m.p., >300 °C; Yield, 80%; Anal. Calc. for $C_{26}H_{32}N_4O_2Sn$ (551.28): C, 56.65; H, 5.85; N, 10.16; Sn, 21.53%. Found: C, 56.72; H, 5.68; N, 9.79; Sn, 21.34%. (MH^+/z) Found (calc.): 552.35 (552.29). Selected IR data (KBr, ν_{max}/cm^{-1}): 1565sh (C=N), 1630vs,br (C=O), 3059m, 2956m (C–H), 279m (ν_{as} Sn–C), 225m (ν_s Sn–C), 470s (Sn–N), 420vs (Sn←N).

Note: vs: very strong; s: strong; m: medium; w: weak; br: broad; sh: shoulder.

3. Results and discussion

3.1. Synthesis, reactivity and solid-state characteristics

The reaction of R_2SnCl_2 (R = Me and Ph) or *n*-Bu_2SnO with the 1,2-diaminoethane or 1,3-diaminopropane and ethyl acetoacetate in 1:2:2 molar ratio at room temperature in a single step (using template method) led to the formation of the complexes according to Eq. (Ia and Ib). The reactions involved in the synthesis of diorganotin(IV) complexes of macrocyclic ligands, H_2L-1 and H_2L-2, were found to be quite feasible and required 15 h of stirring at ambient temperature (35 ± 2 °C), except *n*-Bu_2Sn(L-1)/(L-2), which required 40 h stirring at (35 ± 2 °C). However; even prolonged stirring for 40 h followed by refluxing for 2–3 h of a mixture of macrocyclic ligand, H_2L-1 or H_2L-2, synthesized according to the previously reported method, and *n*-Bu_2SnO in a 1:1 molar ratio in methanol did not result in complexation.



(where n = 2 or 3, R = Me or Ph)

All of the synthesized complexes are white solid, except *n*-Bu_2Sn(L-1), which is yellow in color, and are stable towards air and moisture. The macrocyclic ligands, H_2L-1 and H_2L-2 are soluble in chloroform, toluene, xylene, methanol, dichloromethane, acetone, acetonitrile and nitrobenzene but insoluble in benzene, diethyl ether, carbon tetrachloride, water, kerosene and cyclohexane, while the diorganotin(IV) complexes are insoluble in all of the above mentioned solvents except methanol in which they have very poor solubility. The analytical data of these complexes are in agreement with the proposed 1:1 metal to ligand stoichiometry. In order to confirm the template cyclization of amine and diketone in the resulting diorganotin(IV) macrocyclic complexes, the free macrocyclic ligands, H_2L-1 and H_2L-2, have also been prepared and characterized. The elemental analyses and molecular ion peaks in the mass spectra of H_2L-1 and H_2L-2, supports their proposed macrocyclic ligand frame work (Scheme 1) derived from the condensation of 1,2-diaminoethane or 1,3-diaminopropane with ethyl acetoacetate. Further, the molecular ion peaks observed in the DART-mass spectra of diorganotin(IV) complexes of H_2L-1 or H_2L-2, also support the formation of macrocyclic ligand frame work (Scheme 1) in the synthesized diorganotin(IV) complexes.

The observed spectroscopic data (discussed in subsequent sections) are consistent with a structure (in the solid-state) in which R_2Sn(IV) moiety is bonded to the four nitrogen atoms resulting in a six-coordinated geometry around the tin center. Such an arrangement is depicted in Figs. 2 and 3 with the ligand in its usual saddle conformation and the two substituent group (R) may be *cis* or *trans*. Since, diorganotin(IV) macrocyclic complexes studied herein are insoluble in above mentioned solvents, hence all the solid-state spectral studies, viz. infrared, far-infrared solid-state ^{13}C NMR, ^{119m}Sn mössbauer and recently developed DART-mass have been utilized in order to establish the structural characterization of the synthesized diorganotin(IV) macrocyclic complexes.

3.2. Infrared and far-infrared spectral studies

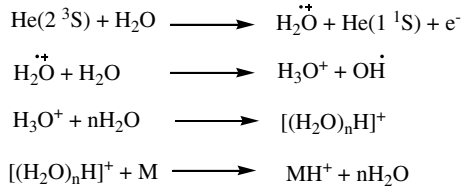
The characteristic infrared absorption bands (in cm^{-1}) of H_2L-1, H_2L-2 and their diorganotin(IV) complexes along with their assignments are given in experimental section. The preliminary identification of the synthesized macrocyclic ligands have been obtained from their IR spectra which show the absence of uncondensed functional groups (NH_2, O–R), stretching modes of starting materials and the appearance of bands characteristic of imine and amide groups. In the IR spectra of the ligands, H_2L-1/H_2L-2, the appearance of a strong absorption band at 1605 ± 1 cm^{-1} corresponds to C=N stretching frequency. In addition to it, four amide bands have also been identified in the IR spectra of H_2L-1/H_2L-2 at 1649(vs)/1646(vs), 1510(vs)/1510(vs), 1260(m)/1259(m) and 724(vs)/725(s) cm^{-1} assignable to amide-I, II, III and IV vibrational modes, respectively, similar to that reported for different tetraazamacrocyclic ligands [31].

A single strong to medium intensity band observed for the macrocyclic ligands at 3296 cm^{-1} corresponds to ν(N–H) assigned for secondary amine [16]. The absorption bands at 2986 ± 1 and 1410–1465 cm^{-1} in free macrocyclic ligands may reasonably correspond to (C–H) stretching and (C–H) bending vibrational modes, respectively. The major changes observed in the IR spectra of the corresponding diorganotin(IV) macrocyclic complexes are the red shift in the ν(C=N) mode which appear in the region 1566–1530 cm^{-1}, and are in agreement with the values reported for other analogues complexes [32]. Whereas the band corresponding to ν(N–H) mode of vibrations are not observed in IR spectra of diorganotin(IV) complexes of macrocyclic ligands indicating the deprotonation of amide group. Since the deprotonated nitrogen is involved in coordination, the amide I band undergoes a small shift in comparison to the free macrocyclic ligands. This may be due to the dispersion of the electronic charge in the coordinated amide group (O=C–N–Sn). However, the positions of amide II, III and IV bands remain unchanged in the spectra of diorganotin(IV) macrocyclic complexes indicating the non-involvement of C=O group in coordination, which was further confirmed by the absence of ν(Sn–O) band. Further, new bands observed in the region (470–406 cm^{-1}) assignable to ν(Sn–N)/(Sn←N) vibrational modes in the spectra of diorganotin(IV) complexes, which are absent in the spectra of free macrocycles, confirm the coordination of azomethine nitrogen (C=N) and deprototonated amide nitrogen to tin center [33]. The ν_{as} (Sn–C) and ν(Sn–C) bands in all dialkyltin(IV) complexes have been observed at 639 ± 36 and 572 ± 35 cm^{-1}, respectively, whereas corresponding vibrational bands in diphenyltin(IV) analogues are observed in far-IR region at 279 and 228 ± 3 cm^{-1}, respectively [34].

3.3. DART-mass spectral studies

The mass spectra of the complexes (**5**–**8**) have been recorded in the solid-state by a recently developed technique DART (Direct Analysis in Real Time) mass spectrometer using Time of Flight (TOF) mass analyzer, which give accurate mass capability. The analysis was performed in the DART beam of excited helium atoms which involves predominantly the formation of ionized water cluster followed by proton transfer reaction. The helium 2 ^{3}S state has energy of 19.8 eV and reacts with water efficiently with an estimated reaction cross section of 100 Å [35] (Scheme 2).

The molecular ion peaks (due to ^{119}Sn isotope) in all the synthesized complexes have been observed at *m*/*z* 400.11, 523.31, 512.12, 428.27 and 552.35, suggesting the proposed molecular formula of (**4**), (**5**), (**6**), (**7**) and (**8**) for these complexes, respectively. It also provides the evidence for the monomeric nature of all the synthesized complexes. The peaks at M+1, M−1 and M−2, have also been observed due to the presence of ^{120}Sn, ^{118}Sn and ^{117}Sn isotopes [36,37]. For illustration, one of depicted in Fig. 1, shows the magni-



Scheme 2.

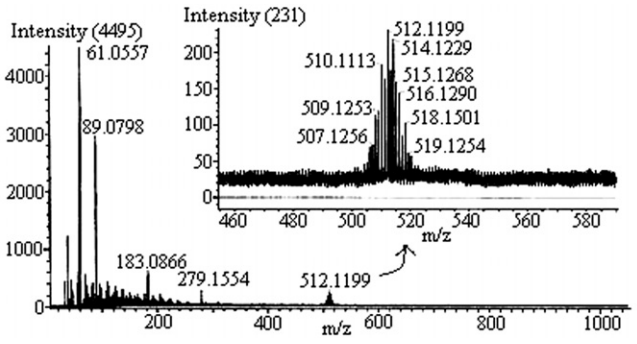


Fig. 1. Mass spectrum of *n*-Bu_2Sn(L-2) (**6**) (with full scan).

fied region of the full scan DART mass spectrum with the characteristic isotopic peaks in complex (**6**).

In complexes (**4**) and (**5**) two peaks other than molecular ion peak have also been observed at *m*/*z* 253 and 239, indicating the fragmentation of complexes and responsible for $[(H_2L\text{-}1)H^+]$ and $[(H_2L\text{-}1\text{-}CH_3)H^+]$, respectively. Whereas in complexes (**6**), (**7**) and (**8**), few more intense peaks have been observed at *m*/*z* 279, 183, 99 and 61 which indicate the fragmentation of complexes in $[(HL\text{-}2)H^+]$, $[(H_2L\text{-}2)\text{-}(NC(Me)CH_2CON)H^+]$, $[(C_4H_6N_2O)H^+]$ and $[(C_2H_6NO)H^+]$, respectively. The mass spectral data provide a little help to establish the structure, but it is more informative about purity and molecular weight of the synthesized complexes.

3.4. NMR spectral studies

3.4.1. ^1H and ^{13}C NMR spectral studies of H_2L-1 and H_2L-2 in solution

The ^1H and ^{13}C NMR spectra of the synthesized macrocyclic ligands, H_2L-1 and H_2L-2, were recorded in $CDCl_3$. The ^1H NMR spectra of the ligands do not show any signal assignable to primary amino protons suggesting that the proposed macrocyclic skeleton have been formed by the condensation reaction. The spectra of both macrocyclic ligands, H_2L-1 and H_2L-2, exhibit a sharp singlet at δ 1.91 ppm and triplet at 1.23–1.24 ppm, which may be assigned to CH_3 protons (6H). The CH_2 (4H) protons of alkyl acetoacetate moiety (i.e., H-6, H-13 in H_2L-1 and H-7′, H-15′ in H_2L-2) are also observed as singlet at δ 4.46 and δ 3.80 ppm, respectively [38]. A broad sharp resonance observed at δ 8.64 ppm and δ 8.56 ppm in H_2L-1 and H_2L-2, respectively, has been assigned to the amide protons (–NHC═O, 2H) [39]. The expected signals of the diaminoethane/diaminopropane moiety have also been observed and assigned.

^{13}C NMR spectral data of H_2L-1 and H_2L-2 recorded in $CDCl_3$ are presented in Table 1. All the magnetically non-equivalent carbons of alkyl groups of macrocyclic frame work have been assigned. The carbonyl (C═O) carbon (C-5, C-12 in H_2L-1 and C-6′, C-14′ in H_2L-2) and imine carbon (C-7, C-14 in H_2L-1 and C-8′, C-16′ in H_2L-2) resonances have been observed at δ 170.36 ± 0.15 ppm and δ 161.30 ± 0.09 ppm, respectively. Since the diorganotin(IV) complexes of both macrocyclic ligands are insoluble in NMR solvents, hence solid-state ^{13}C NMR spectra of the studied complexes have been recorded which are also presented in Table 1 and discussed in the following section.

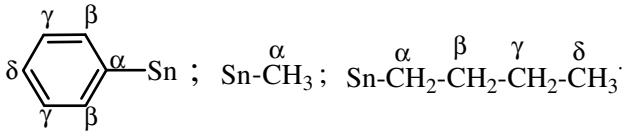
3.4.2. Solid-state ^{13}C NMR spectral studies

X-ray crystallography is the most accurate method of determining molecular structure in the crystalline state, and it has profoundly influenced our understanding of molecular structure and bonding. Few other methods are sufficiently sensitive to structural features to be capable even of questioning X-ray determined structures. In contrast to the solution NMR spectra, the solid-state NMR spectra are very broad, as the full effects of anisotropic or orientation-dependent interactions are observed in the spectrum. High-resolution solid-state NMR spectra can provide the same type of information that is available from corresponding solution NMR spectra, but a number of special techniques/equipment are needed, including magic-angle spinning, cross-polarization, etc. The

Table 1
^{13}C NMR spectral data δ (ppm) of ligands (in solution) and their diorganotin(IV) complexes (in the solid-state)

Carbon no./sl. no.[a]	(**1**)[b]	(**2**)[b]	(**3**)[c]	(**4**)[c]	(**5**)[c]	(**6**)[c]	(**7**)[c]	(**8**)[c]
C-2,9	56.36		61.94	61.39	61.40			
C-3,10	43.77		48.13	47.57	47.63			
C-5,12	170.51		172.65	172.09	172.12			
C-6,13	40.86		39.58	38.08	38.042			
C-7,14	161.21		164.74	164.16	164.20			
C-15,16	14.53		17.51	16.94	16.97			
	19.13							
C-2′,10′		57.88				64.17	62.55	61.93
C-3′,11′		19.32				20.22	21.64	20.93
C-4′,12′		40.23				43.73	42.56	40.38
C-6′,14′		170.21				174.40	174.19	174.22
C-7′,15′		33.59				38.52	36.66	35.55
C-8′,16′		161.39				164.53	164.24	164.19
C-17′,18′		14.24				16.93	16.94	17.02
C-α			27.27	9.530	144.93,139.67	29.94	8.03	141.97
C-β			31.72		137.60	32.72		136.82
			29.95					
C-γ			25.54		130.38	25.53		127.93
C-δ			16.83		133.00	22.32		130.94
$^1J[^{13}C\text{–}^{119}Sn]$[d]			NO	807.63	NO	NO	710.42	719.30
∠C–Sn–C (°)[e]				147.6			139.1	139.9

[a] Sl. no. as indicated in Section 2.
[b] In $CDCl_3$.
[c] In solid-state; NO: not observed.
[d] In Hz.
[e] Calculated by the Eq.: $|^1J| = 11.4(\theta) - 875$;



presence of broad NMR line shapes, once thought to be a hindrance, actually provides much information on chemistry, structure and dynamics in the solid-state. The anisotropies in the local fields of the protons broadened the ^{1}H NMR spectra such that no spectral lines could be resolved. A number of methods have been developed in order to minimize large anisotropic NMR interaction between nuclei and increase S/N in rare spin (e.g. ^{13}C, ^{15}N) high-resolution solid-state NMR spectra. Cross-polarization is one of the most important techniques in high-resolution solid-state NMR. In this technique, polarization from abundant spins such as ^{1}H or ^{19}F is transferred to dilute spins such as ^{13}C or ^{15}N in order to enhance S/N and reduce waiting time between successive experiments. The solid-sate ^{13}C NMR spectral data of the studied diorganotin(IV) complexes of macrocyclic ligands are presented in Table 1.

The comparison of ^{13}C NMR spectral data of the ligands, H_2L-1 and H_2L-2, in $CDCl_3$ and solid-state ^{13}C NMR spectral data of the studied diorganotin(IV) complexes of these macrocyclic ligands indicated that imine carbon and carbonyl carbon resonances under go a small shift towards lower field [28,40]. This suggests the coordination of macrocyclic ligands through the imine nitrogen and deprotonation of amide proton (-NHCO) and its subsequent bonding with tin. Further, all the alkyl carbons of ethyl acetoacetate and diaminoethane/diaminopropane moieties of the macrocyclic frame work are shifted towards lower field which also support the coordination of macrocyclic ligands through all the four nitrogens to tin [28]. All magnetically non-equivalent carbons of the alkyl or phenyl groups attached to tin have been identified and their chemical shift values are in close agreement with reported values [34].

The $^{1}J(^{13}C–^{119}Sn)$ values have been calculated for complexes (**4**), (**7**) and (**8**) from their solid-state NMR spectra which show the satellites. But the ^{117}Sn and ^{119}Sn satellites are not well resolved in the solid-state spectra, so $^{1}J(^{13}C–^{119}Sn)$ was calculated from the distance separating the center of fused ^{117}Sn and ^{119}Sn satellites X 1.023 (because the natural abundances of ^{117}Sn and ^{119}Sn are similar (7.6% and 8.6%, respectively) the differences between the separation of the centers of unresolved satellites and $^{1}J(^{13}C–^{119}Sn)$ is closely approximated by multiplying the separation, in hertz by one half the ratio of the gyromagnetic ratio of ^{119}Sn and ^{117}Sn) [41].

$^{1}J(^{13}C–^{119}Sn)$ values calculated for complexes (**4**), (**7**) and (**8**) were 807.63 Hz, 710.42 Hz and 719.30 Hz, respectively which lie in the range ($\geqslant$630), typical for hexacoordinated diorganotin(IV) complexes [42]. Moreover, the calculated values of ∠C–Sn–C using the observed $^{1}J(^{13}C–^{119}Sn)$ values in the equation given by Lockhart and Manders [43] ($|^{1}J| = 11.4(\theta) - 875$) are in the range of 139.1–147.6° (Table 1) indicating a pseudooctahedral geometry.

The solid-state ^{13}C NMR spectra of a number of structurally characterized methyltin(IV) compounds have reported that the ^{13}C (methyl-Sn) chemical shifts are very sensitive to slight differences in magnetic environment (i.e., slight difference in distance to neighboring atoms) [41]. In the studied Me_2Sn(L-1) and Me_2Sn(L-2), a single methyl resonance has been observed. The narrow single dimethyltin resonance observed in these complexes reflects the presence of mirror plane through tin and the macrocyclic ligands, which interconvert the two methyl groups.

3.5. ^{119m}Sn Mössbauer spectral studies

It is instructive to compare the structural analysis of the studied diorganotin(IV) complexes of macrocyclic ligands by solid-state NMR with the routinely employed ^{119m}Sn Mössbauer technique. Mössbauer isomer shift (I.S.) and quadrupole splitting (Q.S.) parameters are used to obtain information about the coordination number and bonding geometry of organotin compounds. ^{119m}Sn Mössbauer spectral data of all of the studied diorganotin(IV) complexes are given in Table 2. Mössbauer spectra of all the diorganotin(IV) complexes exhibit a doublet centered in the isomer shift (I.S.) value range 0.89–1.24 mm s^{-1} and the quadrupole splitting (Q.S) values in the range 2.11–3.34 mm s^{-1} show that the electric field gradient around tin nucleus is generated by inequalities in tin–nitrogen (ligand) σ bond and is also due to the geometric distortions. The ρ (Q.S./I.S.) value of 2.3–2.7 in the studied diorganotin(IV) complexes indicate a coordination number of tin either 5 or 6 [44]. The low value of Q. S. for Ph_2SnL is due to greater polarizability of the phenyl groups.

Table 2
^{119m}Sn Mössbauer data of diorganotin(IV) complexes of H_2L-1 and H_2L-2

Complex no.	Q.S. (mm S^{-1})	I.S. (mm S^{-1})	ρ(Q.S./I.S.)	τ_1 (L)	τ_2 (R)	∠C–Sn–C (°)
(**3**)	2.312	1.008	2.3	1.116	1.294	107
(**4**)	3.338	1.243	2.7	2.085	2.245	137
(**5**)	2.112	0.892	2.4	1.162	1.363	106
(**6**)	2.147	1.015	2.1	1.814	1.891	100
(**7**)	2.632	1.044	2.5	1.897	1.927	117
(**8**)	1.946	0.895	2.2	2.065	2.159	97

Q.S: quadrupole splitting; I.S: isomer shift; τ_1 (L): half line width left doublet component; τ_2 (R): half line width right doublet component.

The Q.S. values for *trans*- and *cis*-octahedral $[R_2SnX_4]^{2-}$ are around 4.00 and 2.00 mm s^{-1}, respectively [45]. Further, it has been reported [45] that I.S. values for *cis*-$[R_2SnX_4]^{2-}$ are less the 1.00 mm s^{-1} while those for *trans*-$[R_2SnX_4]^{2-}$ are approximately 1.2–1.3 mm s^{-1}. The observed values of Q.S. and I.S. of the studied diorganotin(IV) complexes of macrocyclic ligands are substantially lower than the values for *trans*-octahedral configuration and slightly higher than the values for *cis*-octahedral configuration. Further, the ∠C–Sn–C for the studied diorganotin(IV) complexes has been calculated by using Parish's relationship [46]: Q.S. = $4[R][1 - 3/4\ \sin^2 2\theta]^{1/2}$, where ∠C–Sn–C is $(180 - 2\theta)°$ and [R] is the partial quadruple splitting for alkyl and phenyl groups bonded to tin. The reported values of [R] for alkyl and phenyl groups are −1.03 mm s^{-1} and −0.95 mm s^{-1}, respectively [47,48].

The calculated values of ∠C–Sn–C in the studied diorganotin(IV) complexes of macrocyclic ligands are in the range of 97–137°, which is again intermediate between the corresponding *cis*-octahedral with ∠C–Sn–C = 90° and *trans*-octahedral with ∠C–Sn–C = 180°. Thus, the structures of R_2Sn(L-1) and R_2Sn(L-2) are best described by the highly distorted square bipyramidal/ skew-trapezoidal bipyramidal configuration with the two organic groups (Me, *n*-Bu or Ph) in bent axial position and trapezoidal plane being defined by the four Sn–N coordination/interactions and macrocyclic ligand is in usual saddle conformation (Figs. 2b and 3b). The observed ν_{as}(Sn–C) and ν_s(Sn–C) stretching vibrations in the IR spectra of the studied diorganotin(IV) complexes indicate a non-planar

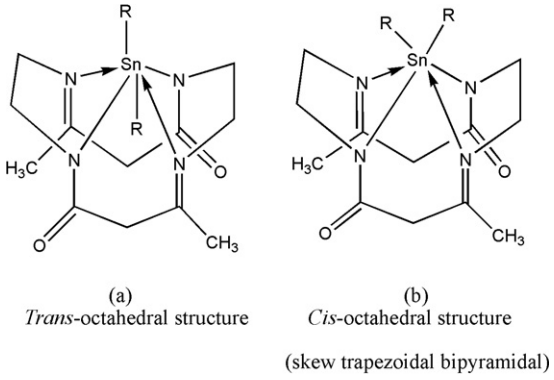


Fig. 2. Proposed structures of diorganotin(IV) complexes of H_2L-1 where R = Me, *n*-Bu or Ph.

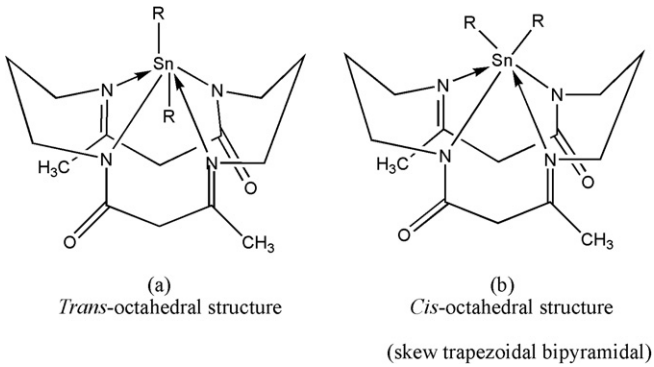


Fig. 3. Proposed structures of diorganotin(IV) complexes of H_2L-2 where R = Me, *n*-Bu or Ph.

SnC_2 fragment and rule out the possibility of *trans*-octahedral structure (Figs. 2a and 3a). The proposed skew-trapezoidal bipyramidal structure for R_2Sn(L-1) and R_2Sn(L-2) has been attributed to an octahedral distortion by steric demands of the ligands [49]. A similar structure has also been reported [28] for [Me_2M(tmtaa)] and [Cl_2M(tmtaa)] (M = Si and Sn, H_2tmtaa = dibenzotetramethyltetraaza[14]annulene). Such as arrangement depicted in Figs. 2b and 3b, with the ligand (tmtaa) in its usual saddle conformation and the two substituent groups (R) mutually *cis*, has also been reported for the group 4(d^0) counterparts [Cl_2M(tmtaa)] (M = Ti [50], Zr [51,52]) and [$(PhCH_2)_2$Zr(tmtaa)] [52] and is, infact, common to all such transition metal complexes [R_2M(tmtaa)], with the sole exception of [$(PMePh_2)_2$Ru(tmtaa)] [53].

3.6. Thermal studies

The thermal decomposition behavior of complex no. (**3**)–(**8**) in air have been studied using TG, DTG and DTA techniques. The TG temperature ranges, peak temperatures in DTA and DTG, percent weight loss along with the species lost as well as enthalpy of DTA peaks are presented in Table 3. The main diffraction lines observed in the residues obtained by the pyrolysis of these organotin(IV) macrocyclic complexes are summarized in Table 4. *n*-Bu_2Sn(L-1) decomposes in three steps in air. The weight loss in the first step of decomposition, which extends from 100 to 240 °C, corresponds to the loss of two butyl groups and a part of ligand moiety (2CO) {$C_{10}H_{18}O_2$; wt. loss obsd. 37.01%: calc. 35.23%}. Thereafter, $C_6H_{10}N_2$ of the remaining ligand moiety is lost (wt. loss obsd. 22.36%: calc. 22.80%) in the second step followed by the loss of rest of ligand moiety ($C_4H_8N_2$) {wt. loss obsd. 15.38%: calc. 17.41%} along with oxidation in the third step of decomposition leaving 2.56 mg (25.25%) residue (relative to 10.13 mg of sample taken) up to 500 °C (for SnO_2: calc. residue 31.24%). The

Table 4
The main diffraction lines (intensity) in residues obtained by pyrolysis of organotin(IV) derivatives of tetraazamacrocyclic ligands

Tin compound/residue of complex	Main diffraction lines *d* (Å) (intensity (%)) (*hkl*)				
	1	2	3	4	5
Sn[a]	2.92 (100) (200)	2.79 (90) (101)	2.06 (34) (220)	2.02 (74) (211)	1.48 (23) (112)
SnO[a]	3.39 (100)	3.00 (50)	2.89 (90)	2.67 (90)	1.77 (80)
SnO_2[a]	3.35 (100) (110)	2.64 (80) (101)	2.37 (25) (200)	1.77 (65) (211)	1.68 (18) (220)
n-Bu_2Sn(L-1)	3.35 (100)	2.64 (92)	2.37 (21)	1.76 (85)	1.68 (19)
Ph_2Sn(L-1)	3.34 (100)	2.64 (80)	2.36 (22)	1.76 (66)	1.67 (15)
n-Bu_2Sn(L-2)	3.35 (100)	2.64 (97)	2.37 (22)	1.76 (87)	1.68 (20)
Me_2Sn(L-2)	3.35 (100)	2.65 (92)	2.37 (24)	1.76 (83)	1.68 (16)
Ph_2Sn(L-2)	3.35 (100)	2.64 (95)	2.37 (26)	1.76 (97)	1.68 (20)

[a] Ref. [54].

Table 3
Thermal analysis data of organotin(IV) derivatives in air

Compound	Step no.	Temperature range in TG (°C)	Peak temperature in DTG (°C)	Peak temperature in DTA (°C)	Enthalpy (mJ/mg)	Loss of mass % Observed (calc.)	Species lost
Bu_2Sn(L-1)	I	100–240	218	123 (endothermic) 232 (exothermic)	40.50 −39.30	37.01 (35.23)	$2CO + 2C_4H_9$
	II	240–308	277	293 (exothermic)	−177	22.36 (22.80)	$C_6H_{10}N_2$
	III	308–500	447	447 (exothermic)	−1368	15.38 (17.41)	$N_2C_4H_8$
Me_2Sn(L-1)	I	99–166	156	120 (endothermic) 159 (endothermic)	161	23.38 (21.57)	$2CH_3 + 2CO$
	II	166–252	196 219	215 (endothermic)	161	56.43 (48.68)	$C_{10}H_{18}N_4$
	III	252–560	526	525 (exothermic)	−465	15.83	Sublimation
Ph_2Sn(L-1)	I	100–245	185	116 (endothermic)	33	41.48 (40.18)	$2CO + 2C_6H_5$
	II	245–286	259 273	276 (exothermic)	−26.3	23.38 (21.05)	$C_6H_{10}N_2$
	III	286–660	435	433 (exothermic) 551 (exothermic) 643 (exothermic)	−61.8 −191 −36	14.28 (16.08)	$C_4H_8N_2$
Bu_2Sn(L-2)	I	99–310	288	302 (exothermic) 885 (broad exothermic)	−914 −86.2	52.95 (54.48)	$C_{14}H_{22}N_4O_2$ Sublimation
Me_2Sn(L-2)	I	100-160	152	153 (endothermic)	46	07.70 (7.04)	$2CH_3$
	II	160–265	186			31.01 (32.35)	$C_8H_{10}O_2$
	III	265–350	268, 293	317 (exothermic)	−664	24.95 (32.82)	$C_6H_{12}N_4$
Ph_2SnL-2	I	100–244	164	164 (endothermic)	27.6	26.60 (27.97)	$2C_6H_5$
	II	244–287	263			24.75 (25.06)	$C_8H_{10}O_2$
	III	287–500	330	401 (exothermic)	−411	19.56 (25.43)	$C_6H_{12}N_4$

amount of the residue left at 1000 °C (maximum temperature recorded) is 24.59% and the residue obtained at ~500–525 °C is SnO_2 which has been identified by XRD (Table 4).

Me_2Sn(L-1) decomposes in two steps. The weight losses in the first and second steps of decomposition correspond to the loss of two methyl groups attached to Sn + 2CO groups and the remaining ligand moiety ($C_{10}H_{18}N_4$), respectively. The unexpected mass loss is observed in the temperature range 252–560 °C leaving a residue of 4.36% (relative to 10.25 mg of sample) at 560 °C and 3.64% at 800 °C, which indicates the slow sublimation of metallic particles. In case of Ph_2Sn(L-1), the decomposition take place in three steps in the temperature range 100–660 °C, corresponding to the loss of phenyl groups attached to tin and the ligand moiety with simultaneous oxidation of the material to SnO_2. The mass of residue left is 20.86% at 660 °C (for SnO_2, calc. 28.86%) which sublimed slowly up to 800 °C leaving 19.6% of the residue (relative to 10.56 mg of sample). The XRD of the residue obtained at 660 °C indicates the formation of SnO_2 (Table 4).

Me_2Sn(L-2) and Ph_2Sn(L-2) decompose in three steps whereas a single step decomposition pattern is observed in *n*-Bu_2Sn(L-2) in the temperature range 99–310 °C. The mass loss observed in case of *n*-Bu_2Sn(L-2) is 52.95% (calc. 54.48%), which corresponds to the loss of macrocyclic ligand moiety along with partial oxidation of material (residue left 45.64% at 800 °C; for SnO_2 calc. residue %: 29.53%). The amount of residue left at 800 °C corresponds to the formation of *n*-Bu_2SnO_2 rather than SnO_2, but XRD of the residue at 350 °C corresponds to that of SnO_2 (Table 4). Me_2Sn(L-2) and Ph_2Sn(L-2) follow the same three steps decomposition pattern involving the loss of 2Me/2Ph groups in the first step followed by the decomposition of the macrocyclic ligand moiety in the second and third steps (Table 3) along with oxidation of the material. The mass of the residue obtained in case of Me_2Sn(L-2) is 36.34% at 300 °C (for SnO_2, calc. 35.35%) which sublimed very slowly leaving 35.97% of the residue at 800 °C. The amount of the residue obtained in the case of Ph_2Sn(L-2) is 29.09% (for SnO_2, calc. 27.39) in the temperature range 500–800 °C. Further, the XRD analysis of the residues confirms the formation of SnO_2 (Table 4).

4. Conclusions

Diorganotin(IV) complexes of tetraazamacrocycles have been synthesized through template method. The solid-state spectral studies along with elemental analysis of all the synthesized complexes, R_2Sn(L-1)/R_2Sn(L-2), suggest a skew-trapezoidal bipyramidal environment around tin center with the two organic groups in bent axial position and trapezoidal plane being defined by four Sn–N interactions. Thermal decomposition of the studied complexes yielded SnO_2, which is confirmed by X-ray diffraction.

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