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Synthesis, spectral, crystal studies and DFT Calculations of new complexes of p-substituted dibenzyltin bromides with 1, 10-phenanthroline

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ABSTRACT

The novel organotin (IV) complexes such as (p-ClBz)2SnBr2. Phen(2a) and (p-BrBz)2SnBr2. Phen(2b) were synthesized and characterized employing 1H, 13C and 119Sn NMR analyses. The spectral studies revealed the complex formation of 1,10-phenanthroline with p-substituted diorganotin dibromides at normal reaction conditions. Single crystal diffraction of 2a and 2b has confirmed that the tin atom is in regular octahedral geometry with the benzyl group in the equidirectional position. The structures of these compounds have been characterized by FT-IR, FT-Raman techniques. The optimized geometrical parameters, vibrational wavenumbers, corresponding vibrational assignments of the complexes 2a and 2b have been investigated by means of the density functional theory. The vibrational frequencies were calculated and scaled values were compared with experimental FT-IR and FT-Raman spectra. The observed and calculated frequencies are found to be in good agreement. Moreover, the molecular electrostatic potential surfaces of the complexes have been constructed and electronic property such as HOMO and LUMO energies were also performed.

1. Introduction

Organotin(IV) complexes have received much attention, both in academic and applied research, because of the ability of the tin to afford stable bonds with carbon as well as with hetero atoms; a wide range of compounds have been reported in organic synthesis and catalysis [1]. The nitrogen containing organic compounds and their metal complexes display a extensive series of biological activities such as antitumor, antibacterial, antifungal and antiviral properties [2]. Especially, 1,10-Phenanthroline is a classic bidentate ligand for transition metal ions or atoms that has played an important role in the development of coordination chemistry [3].

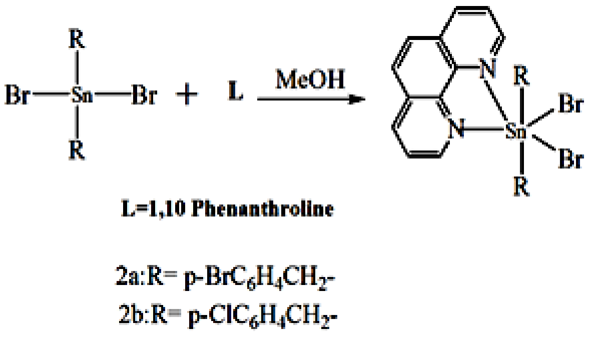
Furthermore, organotin(IV) complexes show a large spectrum of biological activities such as anti tumour and anti-cancer activities [4]. The activity of these complexes depends upon the number and nature of the organo group linked to the tin ion or atom as well as on the ligand.

In recent years, several investigations to test their anti-tumour activities have been carried out and much attention has been focused on these properties and their implications in antioncogensis [5].

It has been previously reported that the 1:1 adducts formed between diorganotin dihalides and ligands with a N─C─C─N skeleton structure, like 2-aminomethyl pyridine and 1,10-phenanthroline, possess anti-tumour activity [6]. The investigation of the cytotoxicity of organotin(IV) compounds remains an important area of research [7–9]. In our previous study, synthesis, spectral and structural studies and DFT calculations of new complexes of p-substituted dibenzyltin chlorides with 1,10-phenanthroline were reported in our recent publication [10, 11].

In this paper, as a part of our ongoing research projects, we report here on the synthesis of new organotin(IV) complexes made by the reaction of (p-ClBz)$_2$SnBr$_2$ or (p-BrBz)$_2$SnBr$_2$ with 1,10-phenanthroline in which tin is bound to the ligand as shown in scheme **2**. These two complexes, **2a** and **2b,** were characterized by FT-IR, FT-Raman, ^{1}H NMR, ^{13}C NMR and ^{119}Sn NMR spectra and X-ray crystallography. These studies revealed that the ligand is bound to the Sn(IV) atom through the nitrogen atoms.

The optimized geometry, vibrational wavenumbers and frontier molecular orbitals for the complexes **2a** and **2b** were calculated at DFT/B3LYP level of theory using LanL2DZ basis set. The results of the theoretical and spectroscopic studies are reported herein.



L=1,10 Phenanthroline

2a:R= p-BrC$_6$H$_4$CH$_2$-
2b:R= p-ClC$_6$H$_4$CH$_2$-

Scheme 2: Synthesis of complexes, 2a and 2b.

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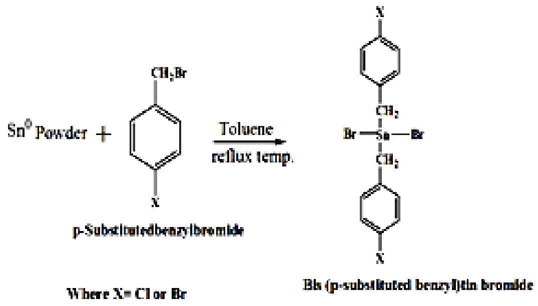

Scheme 1: Synthesis of organotin (IV) compounds 1a and 1b[6]

2. Experimental

p-Chlorobenzyl bromide, p-Bromobenzyl bromide, were commercially purchased from Alfa Aeser; 1,10-Phenanthroline from Qualigens; and is used without further purification; Tin powder from Loba Chemie; All solvents were dried according to a standard procedure.

Computational Method

Thorough information including structural attributes and vibrational modes of complexes **2a** and **2b** have been presented in a comparative way using density functional theory computations with the aid Gaussian 09W software package [12]. Geometry optimization was carried out at DFT method by using B3LYP/LanL2DZ basis set method. To obtain better agreement with the experimental and theoretical results standard scale factors were used. At B3LYP method with the LanL2DZ basis set a scaling factor of 0.9837 has been recommended for all frequencies <1800 cm^{-1}. A scaling factor of 0.9213 was utilized for C-H stretching modes due to large anharmonicities in higher wavenumber region 2700 cm^{-1}. However, for vibrational modes observed in lower wavenumber region, 1500 cm^{-1} a scaling factor 1.0 has been prescribed. Correction factors of B3LYP are therefore much more useful in bringing the experimental and theoretical results closer to each other. The vibrational modes are assigned on the basis of potential energy distribution analysis using Vibrational Energy Distribution Analysis (VEDA) program [13]. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the complexes were analyzed.

Physical Measurements

Melting points were obtained with Sigma Instruments apparatus. The room temperature Fourier transform infrared spectra of the title complexes were measured in the region 4000-450 cm^{-1}, at a resolution ± 1 cm^{-1}, using BRUKER RFS 27 vacuum Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman spectra were recorded on the same instrument with an FRA-106 Raman accessory in the region 3500 – 100 cm^{-1}. The 1064 nm Nd:YAG laser was used as excitation source, and the laser power was set to 200 mW. The observed FT-IR and FT-Raman spectra of the complexes **2a** and **2b** are shown in Figs. 1 and 2, respectively. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded at room temperature in $CDCl_3$ on a Brukar Avance 500 MHz. Me_4Si is used as external standard sample for ^{1}H and ^{13}C NMR spectra and for ^{119}Sn NMR, Me_4Sn is used as reference sample.

X-ray Crystallography:

Suitable crystals of **2a** and **2b** were obtained as pale-yellow plates and pale-yellow rods, respectively, by slow evaporation of solutions in chloroform. The intensity data were collected at 296 K (**2a**) and 293 K (**2b**) on a Bruker APEX2 Diffraction System [14] using MoKα graphite monochromated radiation (99.6% complete). Image plate distance 70mm, ϕ oscillation scans 0 - 163° for **2a** and 0 - 186° for **2b**, with step $\Delta\phi = 1.3°$, exposure time 6 mins, 2θ range 2.20 – 26.00° (**2a**) and 2.194 – 24.998°(**2b**). The structures were solved by Direct methods using the program SHELXS-97 [15]. The refinement and all further calculations were carried out using SHELXL-97[15]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2. Empirical absorption corrections were applied using the multi-scan routine in PLATON [16]. Further crystallographic data and refinement details are given in Table 1. The selected experimental and theoretical bond lengths, bond angles and wavenumbers along with assignments are presented in Tables 2 and 3, respectively.

Table 1. Crystallographic data and refinement details for compound 2a and 2b

Parameters	**2a**	**2b**
Chemical formula	$C_{26}H_{20}Br_2Cl_2N_2Sn$	C26 H20 Br4 N2 Sn
M_r	709.85	798.77
Cell setting, space group	Monoclinic	Monoclinic, $P2_1/c$
Temperature (K)	296(2) K	293(2) K
a, *b*, *c* (Å)	9.0487(3) Å , 18.5093(6) Å, 15.7454(5) Å	9.0187(4) Å, 18.5677(9) Å, 15.8702(8) Å
α, β, γ (°)	90°, 100.138(5)°, 90°	90, 98.154(2), 90
V ($Å^3$)	2595.95(15)	2630.7(2)
Z	4	4
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	4.286 mm^{-1}	7.064
Crystal size (mm)	0.35 x 0.35 x 0.30 mm^3	0.300 x 0.250 x 0.200 mm^3
Diffractometer	Burker APEX 2 diffractometer	Burker APEX 2 diffractometer
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
T_{min}, T_{max}	0.3764 and 0.3101	0.354 and 0.235
R_{int}	0.0401	0.072
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0340, 0.0688, 0.0821	0.024, 0.060, 0.93
No. of reflections	5093	4624
No. of parameters	308	298
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained

Table 2. Selected experimental and calculated bond distances (Å) and bond angles (degrees) for compounds 2a and 2b

Parameters	Bond distances(Å)				Parameters	Bond angles (degrees)			
	Experimental		Calculated			Experimental		Calculated	
	2a	2b	2a	2b		2a	2b	2a	2b
Sn1-Br1	2.648(6)	2.652(11)	2.540	2.581	Br1-Sn1-Br2	104.21(2)	104.43(3)	104.74	104.85
Sn1-Br2	2.686(6)	2.687(10)	2.540	2.540	Br1-Sn1-N1	161.58(9)	90.77(14)	92.09	91.98
Sn1-N1	2.375(3)	2.353(5)	2.430	2.431	Br1-Sn1-N2	91.31(9)	160.83(14)	160.97	161.46
Sn1-N2	2.353(3)	2.380(6)	2.429	2.425	Br1-Sn1-C13	92.17(13)	93.6(2)	92.63	93.17
Sn1-C13(C1)	2.162(4)	2.153(7)	2.149	2.136	Br1-Sn1-C20	93.70(14)	92.3(2)	93.75	93.01
Sn1-C20(C20)	2.165(4)	2.162(7)	2.218	2.216	Br2-Sn1-N1	94.18(9)	164.79(14)	164.06	163.93
					Br2-Sn1-N2	164.46(9)	94.71(14)	94.21	94.44
					Br2-Sn1-C13	86.41(12)	87.3(2)	88.10	88.18
					Br2-Sn1-C20	87.79(14)	86.14(19)	86.43	86.04
					N1-Sn1-N2	70.28(12)	70.08(19)	70.04	69.83
					N1-Sn1-C13	88.05(15)	92.4(2)	92.17	92.37
					N1-Sn1-C20	87.79(16)	92.8(2)	92.53	92.48
					N2-Sn1-C13	92.35(14)	88.3(3)	87.81	88.87
					N2-Sn1-C20	92.01(9)	87.8(2)	87.01	87.52
					C13-Sn1-C20	172.60(18)	172.1(3)	171.49	172.36

Synthesis of bis(p-substituted benzyl)tin bromides.

Bis(p-chlorobenzyl)tin dibromide, **1a,** and bis(p-bromobenzyl)tin dibromide, **1b,** were prepared by the reactions of respective p-substituted benzyl halides with tin powder in toluene, isolated and purified as per the procedure reported in the literature **(Scheme 1)** [17] .

Synthesis of bis(p-Chlorobenzyl)tin bromide, 1a.

To 4.0g (0.034 mol) of tin powder, three drops (or 1-2% of the weight of tin) of water was added and kneaded together. The tin powder was suspended in 150 ml of toluene under efficient stirring and heated to the boiling point of the dispersing agent. To this suspension, 6.90 g (0.034 mol) of p-chlorobenzyl bromide was added dropwise and refluxed for three hours. Yellow solid (6.5 g or 80%) and recrystallized from ethylacetate to give 5.5 g (75%) of white crystals with silky appearance. Extraction of the recovered tin powder (2 g or 0.016 moles) with water gave no inorganic salt. m.p. 180˚C. ^{1}H NMR δ ppm : s 3.211, 4 H, CH_2 groups; $^{2}J_{Sn-H}$ = 72 Hz, m 7.207-7.228 8H Ar protons ^{13}C NMR δ ppm : 32.18 (CH_2), 128.84-129.60, 132.22 12C Ar carbons.

Synthesis of bis(p-Bromobenzyl)tin Bromide, 1b.

The starting compound, **1b,** was prepared by similar procedures of the compound, **1a.** Tin powder 4.0g (0.034 mol): Toluene 150 ml: p-bromobenzyl bromides 8.40 g (0.034 mol). m.p: 218ºC. ^{1}H NMR δ ppm : s 3.196, 4H, -2CH_2 groups,; $^{2}J_{Sn-H}$ = 72 Hz, 7.260 m 7.376-7.360 8H Ar protons ^{13}C NMR δ ppm: 32.27 (CH_2 groups); 129.72, 132.159 12C Ar carbons

Synthesis of (p-chlorobenzyl) (dibromo) (1,10-phenanthroline) tin(IV) complex, 2a.

To the solution of bis(p-chlorobenzyl)tin bromide (1g, 0.001898 mol) in methanol, 1,10-phenanthroline (0.376g, 0.00189mol) in methanol was added drop wise using a pressure equalizing funnel. During the addition, the colour of the reaction mixture slowly turned yellow and the mixture was allowed to stir for one hour. After the completion of the reaction, the solvent was removed completely *in vacuum*. A pale yellow solid was obtained. The obtained product was crystallized by vapour diffusion method as follows. The solid was dissolved in chloroform in a vial and was placed in a beaker containing petroleum ether. Crystals separated after two days. Yield = 0.2 g. 85% m.p: 240ºC decomposed.

^{1}H NMR δ ppm: s 3.447, 4H, 2CH_2 groups,; $^{2}J_{Sn-H}$ = 145Hz,; d 6.097-6.113 2H Ar protons, d 6.202-6.219 2H Ar protons, dd 7.808-7.834 1H Phen protons, s 7.925 1H Phen protons dd 8.480 – 8.499 1H Phen protons; dd 9.499-9.511. 1H Phen protons:

^{13}C NMR δ ppm : 55.88, 2CH_2 groups, 125.15, 126.62,126.94,128.49, 128.60, 129.77,; 6C, Ar carbons 138.09, 139.39. 140.14, 149.27,; 8C Phen carbons (two identical sets).

^{119}Sn NMR δ ppm : −336.69, 1Sn.

Synthesis of (p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin(IV) complex, 2b.

The complex, **2b,** was prepared by similar procedures of complex, **2a.** To the solution of bis(p-bromobenzyl)tin bromide (0.65g, 0.0014 mol), 1,10-phenanthroline (0.29g, 0.0014 mol) in ethyl alcohol was added drop wise using a pressure equalizing funnel. A yellow solid was obtained. Yield: 0.75g, m.p=245˚C.

^{1}H NMR δ ppm : 3.434, 4H, 2CH_2 groups,; $^{2}J_{Sn-H}$ = 140 Hz., d, 6.035-6.051 2H Ar protons, d, 6.334-6.350 2H Ar protons, dd 7.813-7.839 1H Phen proton, s, 7.934, 1H Phen proton, dd 8.490--8.508 1H Phen protons, dd 9.493-9.501 1H Phen protons,

^{13}C NMR δ ppm : 56.03, 2CH_2 groups ; 117.75, 125.17, 126.94, 128.46, 128.97, 129.54,; Ar carbons 138.59, 139.38, 140.02, 149.26, 8C Phen carbons (two identical sets).

^{119}Sn NMR δ ppm : −343.06, 1 Sn.

Table 3. Selected experimental and calculated wavenumbers (cm^{-1}) and assignments for compounds 2a and 2b

2a				2b			
Wavenumbers			Assignments /(PED%)	Wavenumbers			Assignments /(PED%)
FT-IR	FT-Raman	Calculated (Scaled)		FT-IR	FT-Raman	Calculated (Scaled)	
3143		3149	νCH(99)	3090	3092	3092	νCH(98)
	3140	3142	νCH(99)	3089		3089	νCH(98)
	3110	3116	νCH(98)		3073	3075	νCH(97)
3088		3093	νCH(98)	3062		3063	νCH(98)
	3076	3080	νCH(98)		3055	3056	νCH(97)
	3052	3052	νCH(98)		3020	3020	νCH(98)
3043		3048	νCH(97)	3014		3015	νCH(97)
3038		3037	νCH(97)	2990		2992	νCH(97)
	3030	3031	νCH(97)		2984	2984	νCH(96)
	3019	3022	νCH(99)	2932		2931	$\nu_{ass}CH_2$(97)
3012		3019	νCH(99)		2928	2626	$\nu_{ass}CH_2$(97)
3008		3011	νCH(98)	2856		2856	$\nu_{ss}CH_2$(95)
	2993	2996	νCH(98)		2841	2840	$\nu_{ss}CH_2$(95)
2984		2982	νCH(98)	1680		1682	νCC(66), δCH(23)
2949		2950	$\nu_{ass}CH_2$(95)	1653		1651	νCC(67), δCH(22)
2910		2912	$\nu_{ass}CH_2$(95)	1643		1644	νCC(69), δCH(20)
2856		2853	$\nu_{ss}CH_2$(95)	1624	1624	1623	νCC(66), δCH(18)
2825		2830	$\nu_{ss}CH_2$(94)	1590	1593	1590	νCC(65), δCH(20)
1665		1668	νCC(69), δCH(23)	1575		1573	CH_2 sciss.(88)
1622		1628	νCC(68), δCH(23)	1554		1552	CH_2 sciss.(87)
1612	1612	1615	νCC(66), δCH(18)	1540		1543	δCH (64), νCC (20)
1582	1583	1580	CH_2 sciss.(88)	1520	1519	1518	δCH (63), νCC (22)
1575		1573	CH_2 sciss.(87)	1510		1509	δCH (65), νCC (23)
1540		1542	νCH(65), δCC(18)	1490	1490	1492	νCC(58), δCH(20)
	1530	1533	νCH(65), δCC(18)	1461	1460	1463	νCC(58), δCH(20)
	1515	1516	νCH(66), δCC(18)	1432		1432	νCC(66), δCH(18)
1511		1510	νCH(66), δCC(18)	1415	1415	1417	νCC(66), δCH(18)
1467		1468	νCC(68) , δCH(19)	1370		1375	νCC(65), δCH(20)
1450	1451	1457	νCC(68) , νCN (20)	1345	1342	1343	νCC(66), δCH(20)
1428		1430	νCC(66) , νCN (20)	1320		1324	CH_2 rock.(68)
	1420	1421	νCC(66), δCH(22)	1300	1304	1304	CH_2 rock.(68)
1378	1380	1382	νCC(64), δCH(18)	1263	1263	1260	CH_2 wagg.(57)
1345	1345	1343	νCC(63), δCH(18)	1224	1225	1223	CH_2 wagg.(57)
1320		1322	CH_2 rock.(69)		1146	1144	δCH (65), νCC (20)
1305	1304	1306	CH_2 rock.(69)	1143		1142	δCH (65), νCC (18)
1252	1254	1256	CH_2 wagg.(59)	1118		1120	δCH (66), νCC (20)
1220		1224	CH_2 wagg. (59)	1112	1111	1112	δCH (64), νCC (18)
1143	1142	1145	δCH (66), νCC (22)	1089	1088	1088	δCH (64), νCC (18)
1138		1136	δCH (65), νCC (20)		985	982	νCN(66), νCC(18)
1120		1125	δCH (66), νCC (22)	973		970	νCN(67), νCC(18)
1105		1108	δCH (68), νCC (18)		969	968	δCH (63), νCC (20)
1070		1071	δCH (64), νCC (16)	904		904	δCH (63), νCC (17)
	1051	1048	δCH (68), νCC (17)	866		865	δCH (64), νCC (19)
1041		1040	δCH (64), νCC (20)	853	854	853	νCN(65), νCC(21)
1026		1025	δCH (64), νCC (18)	827	825	823	νSnN(65), νSnC(20)
	1019	1021	δCH (68), νCC (17)	807	807	808	νSnN(65), νSnC(20)
	999	998	δCH (65), νCC (18)	775		775	νCN(68), νCC(22)
985	983	983	νCN(68), νCC(20)	750	749	751	νCCl(77), δCH(18)
948	951	950	νCN(67), νCC(16)	725	726	726	νCCl(75), δCH(19)
894	896	892	γCC(68), γCH(18)	620	621	621	νSnC(65)
				608		608	νSnC(65)
865	868	866	γCC(65), γCH(18)	392		401	CH_2 twist. (55)
848		845	νCN(67), νCC(20)	360		364	CH_2 twist. (56)
	838	838	νSnN(66), νSnC(12)		288	290	νSnCl(58)
815	817	817	νSnN(65), νSnC(14)		265	264	νSnCl(59)
777	774	775	νCN(68), νCC(20)				
752		750	γCC(58), γCH(20)				
	740	741	νSnC(59), δCH(19)				
723	724	725	νSnC(59), δCH(18)				
642	643	642	νCBr(48)				
628		627	νCBr(48)				
560		562	νSnC(63)				
476		475	νSnC(62)				
	283	282	νSnBr(49)				
	265	262	νSnBr(50)				
	133	133	CH_2 twist. (56)				
	118	116	CH_2 twist. (56)				

ν: stretching; δ: in-plane bending; ass: assymmetric stretching; ss: symmetric stretching; rock.: rocking; sciss.: scissoring; wagg.: wagging; twist: twisting.

3. Results and Discussion

Some new p-substituted organotin(IV) derivatives of 1,10-phenanthroline complexes were prepared by the reaction of the 1,10-phenanthroline with selected p-substituted dibenzyltin (IV) bromides in methanol in appropriate mole ratio **(Scheme: 2)**. The complexes **2a** and **2b** are quite stable in moist air and are also soluble in common organic solvents.

3.1. Spectroscopic data

The complexes **2a** and **2b** were characterized by FT-IR, FT-Raman [Figs.1 and 2], multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR [Fig.3]

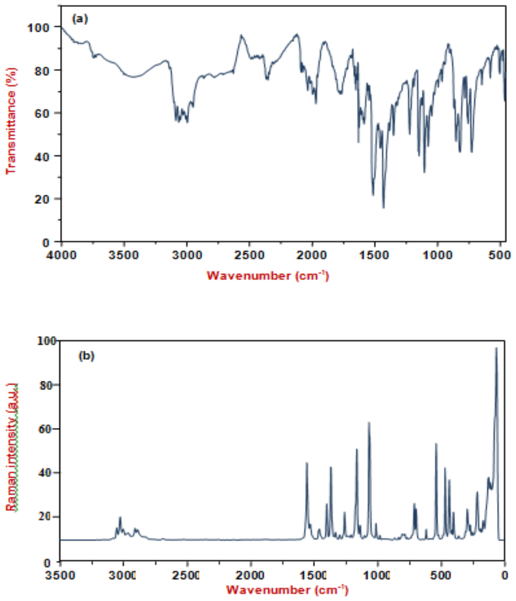

Fig 1. Observed (a) FTIR (b) FT-Raman spectra of Bis(p-methylbenzyl)(dichloro)(1,10-phenanthroline)tin(IV), Complex 2a

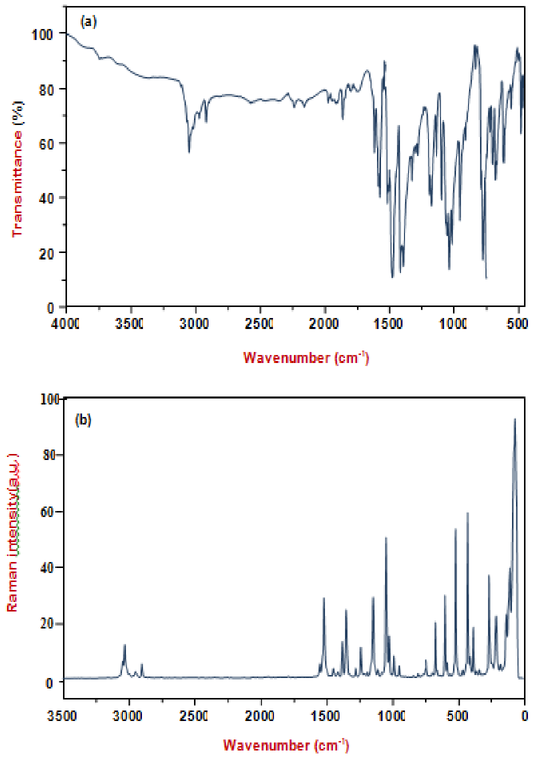

Fig 2. Observed (a) FTIR (b) FT-Raman spectra of (p-chlorobenzyl)(dichloro)(1,10-phenanthroline)tin (IV), Complex 2b.

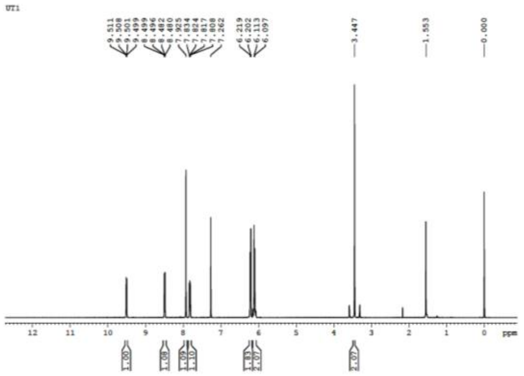

Fig 3 (a). 1H NMR ^{1}H NMR spectrum of the Bis(p-chlorobenzyl)(dibromo)(1,10-phenanthroline)tin(IV), complex 2a.

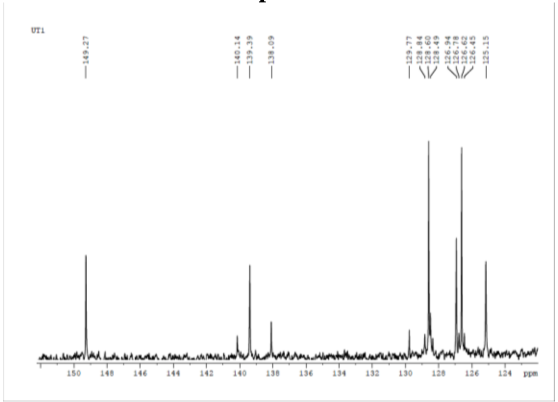

Fig 3 (b). 13C NMR ^{13}C NMR spectrum of the Bis(p-chlorobenzyl)(dibromo)(1,10-phenanthroline)tin(IV), complex, 2a.

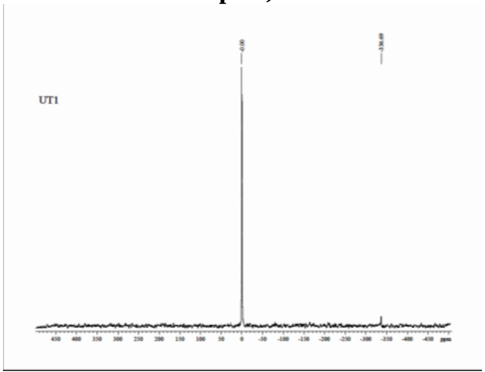

Fig. 3 (c) 119 Sn NMR ^{119}Sn NMR spectrum of the Bis(p-chlrorobenzyl)(dibromo)(1,10-phenanthroline)tin(IV), complex, 2a

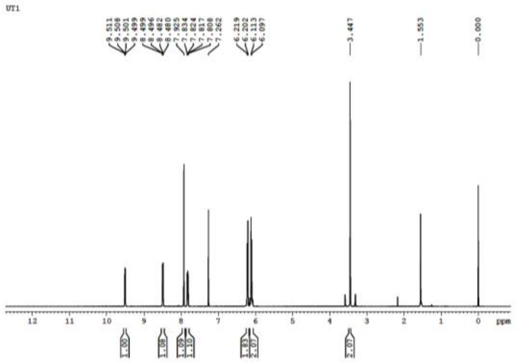

Fig. 3 (d) 1H NMR ^{1}H NMR spectrum of the Bis(p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin(IV), complex, 2b

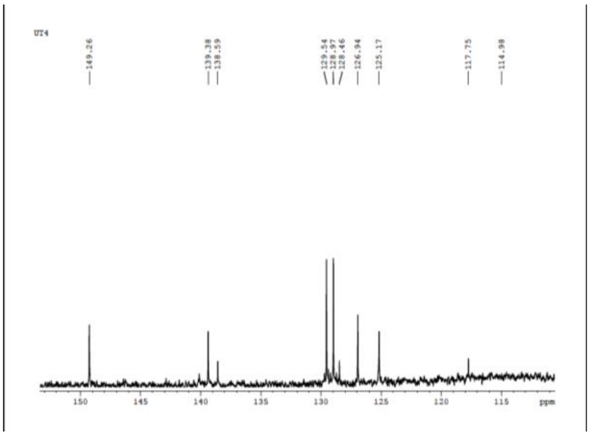

Fig. 3 (e) 13 C NMR ^{13}C NMR spectrum of the Bis(p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin(IV), complex, 2b

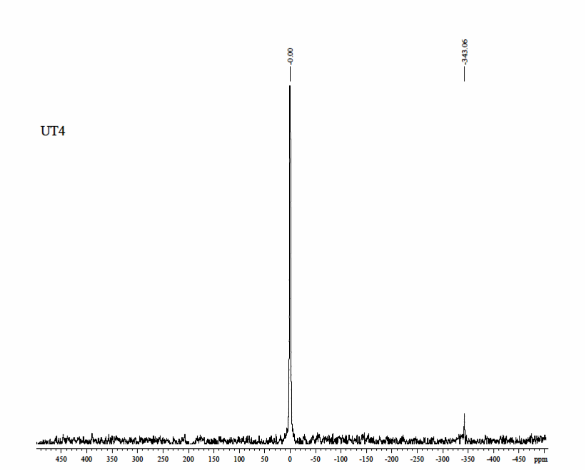

Fig. 3 (f) 119Sn NMR ^{119}Sn NMR spectrum of the Bis(p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin(IV), complex, 2b

spectroscopic techniques and X-ray analysis in combination with melting points. The spectroscopic data have been mentioned in the synthesis section.

The ^{1}H NMR spectra were recorded for the complexes **2a** and **2b** in $CDCl_3$. The characteristic chemical shifts were identified by their intensity and multiplicity patterns. The total number of protons, calculated from the integration values, is in agreement with the expected molecular composition of the complexes. The proton chemical shifts assignment of the carbon attached to Sn exhibits a singlet at 3.447 ppm and at 3.434 ppm for complexes **2a** and **2b**. The protons of the ligand and benzyl tin moieties for the complexes resonate as singlets, doublets and multiplets in the expected range 6.097 – 9.511ppm (**2a**), 6.035-9.501 ppm (**2b**) [18].

The proton chemical shift assignment of the substituted dibenzyltin bromides moiety is a straight forward from the multiplicity pattern. The $^{2}J[^{119}Sn\text{—}^{1}H]$ coupling constant values for **2a** and **2b** complexes are 145Hz and 140Hz respectively. It supports the octahedral environment around Sn atom for the two complexes [19].

The ^{13}C NMR data explicitly resolved the resonances of all the distinct carbon atoms present in the complexes. The aromatic carbon resonances of the p-substituted benzyl moieties and the ligand of complexes, **2a** and **2b** are easily assigned on the basis of signal intensities. The aromatic carbon resonances were assigned by comparison of experimental chemical shift values [20]. The chemical shift values for p-substituted benzyl groups and the ligand of the complexes, **2a** and **2b,** gives signals in the expected range of 125.15−149.27 ppm **(2a)** and 114.98 – 149.26ppm (**2b**) [21]. From the ^{13}C NMR, the formation of the complex is confirmed by the change in the chemical shift observed for the methylene group at 55.88 ppm and at 56.03 ppm observed for the same carbon of bis(p-substituted benzyl)tin chloride for the complexes, **2a** and **2b.** The fact that only one signal is obtained for the above carbon indicate the equivalence of the two methylene groups in the two complexes.

The ^{119}Sn NMR data (in $CDCl_3$) show a single resonance at −336.690 ppm for bis(p-methylbenzyl)(dichloro)(1,10-phenanthroline)tin(IV) **2a**, and at −343.823 ppm for (p-chlorobenzyl)(dichloro)(1,10-phenanthroline)tin(IV) **2b**, complexes. These values are in conformity to hexa coordination around the Sn atom as reported earlier [22]. The chemical shift values observed for these complexes are comparable with corresponding values for similar complexes [23]. This up field signal is attributed to high electron density on tin because of complexation in these complexes [24]. This feature has been confirmed by single crystal XRD studies when two complexes were crystallized in $CHCl_3$ by solvent diffusion method.

Crystallographic study

Figs. 4 and 5 show the ORTEP and Gauss view representation of the molecular structures for the complexes, **2a** and **2b**. The data were corrected for absorption using the w and f scan method of 36811and 45046 intensities, 5093 and 4624 were collected for **2a** and **2b,** respectively; the r values for these **2a** and **2b** complexes are as [R(int)=0.040] and [R(int)=0.072]. The final wR2 were 0.0821 and 0.0958 with a conventional R1 of 0.0340 and 0.0497 for parameters; S=1.07 and 1.159 also for **2a** and **2b,** respectively. There are four independent molecules in the asymmetric unit in both **2a** and **2b** and are discussed here. Tin atom is surrounded by two carbon atoms, two bromines and two nitrogens in octahedral environment. Bidentate nitrogen donor ligand and two bromines are in equatorial positions and two carbons of benzyl groups are in axial positions in these two complexes.

All the Sn bond lengths are close or very close to the mean Sn-Br, Sn-C, Sn-N distances reported in a recent review of diorganodihalotin complexes [5, 25, and 26]. The Sn-Br distances are 2.6476 (6) Å and 2.6856 (6) Å; 2.6515(11) Å and 2.6869(10) Å in **2a** and **2b** respectively lies in the range (2.55 Å - 2.75 Å) of Sn-Br distances found in bromoorganotin (IV) complex in general [27,28]. The Sn-N bond lengths are 2.375 (3) and 2.353 (3) in **2a**; 2.353(5) Å and 2.380(6) Å in **2b** are shorter than the complexes [29]. They are longer than the sum of the covalent radii of tin and nitrogen (2.15 Å) and significantly shorter than the sum of their van der Waals radii (3.75 Å) and thus indicating a substantial bonding interaction [30]. The Sn-C distances 2.153(7) Å and 2.162(7) Å in **2a** and 2.162 (4) and 2.165 (4) in **2b** are quite close to those found in similar type of complexes [31-35].

A significant distortion in octahedral geometry arises from the presence of the bridged ligand. Thus, owing to the coordination angles between each respective *trans* groups are not equal to 180º, the benzyl groups are not precisely perpendicular to the plane [Br (1)-Sn-Br (2), 104.21 (2) in **2a** 104.43(3) in **2b** and N (1)-Sn-N (2), 70.28 (12) in **2a** 70.08(19) **2b** in the complex**.**

The deviation from the regular octahedral geometry (C(13)-Sn-C(20) 172.6 (2) in **2a** and 172.1(3) in **2b** complexes**,** may result from the electronegative Br atoms attached to *p*-positions of both benzyl groups which are bonded to tin atom in axial positions.

Hydrogen Bonding

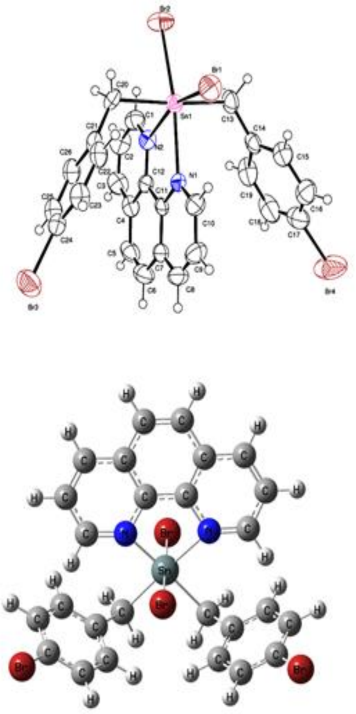

Fig 4. The crystal structure of (p-chlorobenzyl)(dibromo)(1,10-phenanthroline)tin(IV) complex, 2a

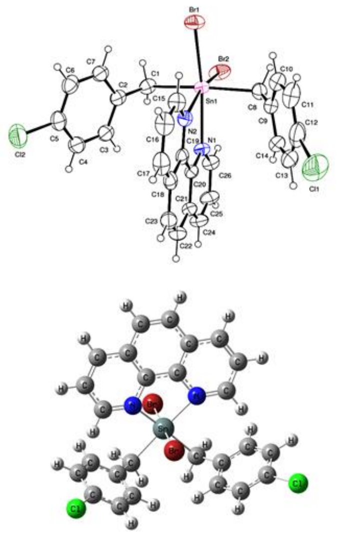

Fig 5. The crystal structure of (p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin(IV) complex, 2b.

The coordination geometry around Sn atom is distorted octahedral due to the presence of moderate hydrogen bonding in both the complexes **2a** and **2b**. The packing diagrams showing the presence of hydrogen bonding in **2a** and **2b** are given in Figs.6 and 7, respectively. Hydrogen bonding formed through bromine and chlorine atoms via C---H…Br (Sn-Br….H-Phen) and C---H…Cl (C--X….H--Benzyl, where X=Cl or Br) interactions forming 2D networks in **2a**. However, only weak C---H…Br hydrogen bondings are observed in **2b.** The hydrogen bonding distances (D--H...A) and bond angles [< (DHA)] for **2a** and **2b** complexes are given in the Tables 4 and 5 and these values are comparable with reported values of similar type of complexes [2,35a].

Table 4. Hydrogen Bonding [Å and °], [2a]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11)...Br(2)^{1}	0.93	3.07	3.686(6)	125.0
C(13)-H(13)...Cl(2)^{2}	0.93	3.01	3.779(9)	140.5
C(15)-H(15)...Br(1)	0.93	2.85	3.531(5)	131.1
C(25)-H(25)...Br(1)3	0.93	3.12	3.802(5)	131.4
C(26)-H(26)...Br(2)	0.93	3.01	3.687(5)	130.6

Symmetry transformations:
[1] x-1,y,z ; [2] x,-y+3/2,z-1/2; [3] -x+1,y+1/2,-z+1/2

Table 5. Hydrogen bonding [Å and °], [2b]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...Br(2)	0.93	3.03	3.709(9)	131.1
C(10)-H(10)...Br(1)	0.93	2.82	3.508(8)	131.5
C(10)-H(10)...Br(3)^{1}	0.93	3.09	3.725(8)	127.3
C(16)-H(16)...Br(2)^{2}	0.93	3.05	3.683(9)	126.7
C(18)-H(18)...Br(3)^{3}	0.93	3.02	3.800(12)	142.5

Symmetry transformations used to generate equivalent atoms:

[1] = -x+2,-y,-z [2] = x+1,y,z [3] = x,-y+1/2,z+1/2

HOMO-LUMO analysis

The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are computed at B3LYP/LanL2DZ level. HOMO and LUMO orbitals for the complexes **2a** and **2b** are shown in Figs. 8 and 9, respectively. Generally the energy values of LUMO, HOMO and their energy gap reflect the chemical activity of the molecule. HOMO as an electron donor represents the ability to donate an electron, while LUMO as an electron acceptor represent the ability to receive an electron [36, 37]. The energies of the HOMO [-0.2286 eV, 0.13367 eV] and LUMO [-0.52761 eV, 0.12837 eV] and the energy gaps are found to be 0.2990 eV and 0.0053 eV The HOMO–LUMO energy gap reveals the intramolecular charge transfer (ICT) interaction occurs within the molecule.

Molecular electrostatic potential

Molecular electrostatic potential (MEP) is a plot of electrostatic potential mapped on to the constant electron density surface. MEP displays molecular size, shape and electrostatic potential value. Electrostatic potential correlates with dipole moment, electronegativity, partial charges and site of chemical reactivity of the molecule. It provides a visual method to understand the relative polarity of a molecule. The negative electrostatic potential corresponds to an attraction of the proton by the concentrated electron density in the molecule. The positive electrostatic potential corresponds to repulsion of the proton by the atomic nuclei in regions where low electron density exist and the nuclear charge is incompletely shielded. By definition, electron density isosurface is a surface on which molecule's electron density has a particular value and that encloses a specified fraction of the molecule's electron probability density [38–40]. The electrostatic potential values are represented by different colors. The positive, negative and neutral electrostatic potential regions of molecules are shown in terms of color grading. Potential increases in the order red < orange < yellow < green < blue. Generally the red color indicates the maximum negative region and the blue color represents the maximum positive region. To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, MEP surface is plotted over optimized geometry of both **2a** and **2b** at B3LYP/LanL2DZ basis set [41, 42]. Figs. 10 and 11 shows electrostatic potential surface map of **2a** and **2b** along with the fitting point charges to the electrostatic potential. In the present study, the value of point charges to the electrostatic potential are predicted with the help of B3LYP level of the theory incorporating LanL2DZ basis set. As easily can be seen in Figs. 10 and 11, investigated molecule has several possible sites for electrophilic (the electrophilic sites are most electro negative and are represented as red color) and nucleophilic attack (the nucleophilic sites are most positive and are represented as blue color).

Vibrational spectral analysis

C-H vibrations

The aromatic ring stretching vibrations are normally found between 3100 and 2900 cm^{-1} [43]. The C-H stretching vibrations of **2a** are observed in 3143, 3088, 3043, 3038, 3012, 3008, 2984 cm^{-1} in FT-IR spectrum and 3140, 3110, 3076, 3052, 3030, 3019, 2993 cm^{-1} in FT-Raman spectrum. The bands 3190, 3089, 3062, 3014, 2990 cm^{-1} in IR spectrum and 3092 3073, 3055, 3020, 2984 cm^{-1} in FT-Raman spectrum are assigned to C-H stretching vibrations for the complex **2b**. The C-H in-plane and out-of-plane bending vibrations modes are found to be well within the characteristic region.

C–C vibrations

The ring C=C and C–C stretching vibrations, known as semicircle stretching usually occur in the region 1625–1400 cm^{-1}. Hence in the present study, the FT-IR bands identified at 1665, 1622, 1612, 1467, 1450, 1428, 1378, 1345 cm^{-1} and the FT-Raman band at 1451, 1420, 1380, 1345 cm^{-1} are assigned to C–C stretching vibrations of the complex **2a**. The bands ascribed at 1680, 1653, 1643, 1624, 1590, 1490, 1461, 1432, 1415, 1370, 1345 cm^{-1} in FT-IR spectrum and 1624, 1593, 1490, 1460, 1415, 1342 in FT-Raman have been designated to C-C stretching modes for the complex **2b**. The theoretically calculated C-C stretching modes for the complexes **2a** and **2b** are found at 1668, 1628, 1615, 1468, 1457, 1430, 1421, 1382, 1343 cm^{-1} and 1624, 1593, 1492, 1463, 1432, 1417, 1375, 1343 cm^{-1}, respectively.

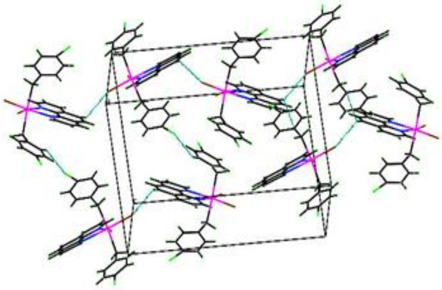

Fig 6. The crystal structure of (p-chlorobenzyl)(dibromo)(1,10-phenanthroline)tin (IV), Complex 2b.

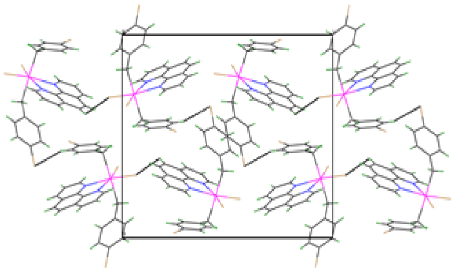

Fig 7. The crystal structure of (p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin (IV), Complex 2b.

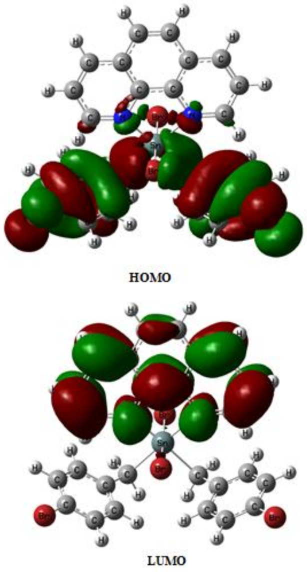

Fig 8. Frontier molecular orbitals of (p-chlorobenzyl)(dibromo)(1,10-phenanthroline)tin(IV) complex, 2a.

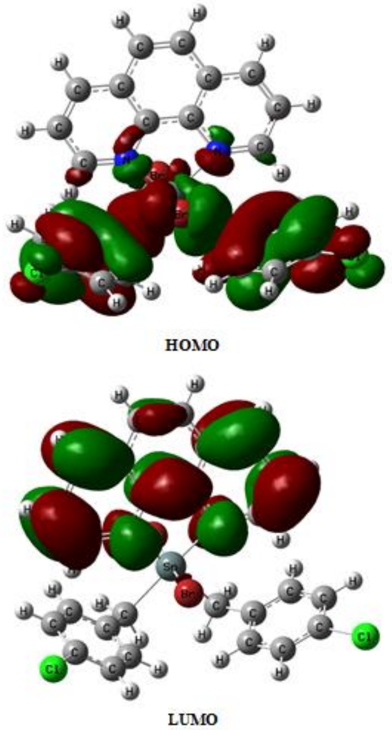

Fig 9. Frontier molecular orbitals of (p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin(IV) complex, 2b.

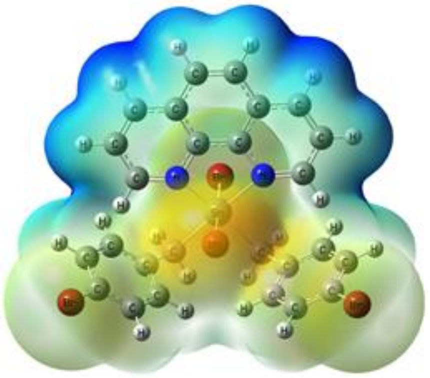

Fig 10. Electrostatic potential surface map of (p-chlorobenzyl)(dibromo)(1,10-phenanthroline)tin(IV) complex, 2a

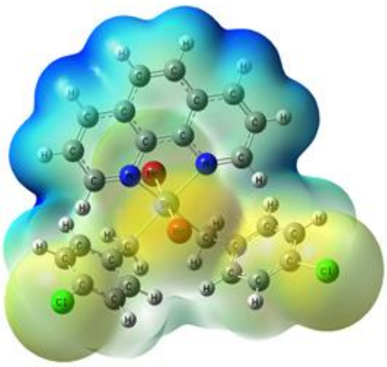

Fig 11. Electrostatic potential surface map of (p-bromobenzyl)(dibromo)(1,10-phenanthroline)tin(IV) complex, 2b.

CH_2 vibrations

For the assignments of CH_2 group frequencies, basically six fun-damentals can be associated with each CH_2 group namely, CH_2 symmetric stretch; CH_2 asymmetric stretch; CH_2 scissoring and CH_2 rocking, which belong to in-plane vibrations and two out-of-plane vibrations, viz., CH_2 wagging and CH_2 twisting modes, which are expected to be depolarized. The asymmetric CH_2 stretching vibrations are generally observed above 3000 cm^{-1}, while the symmetric stretch will appear between 3000 and 2900 cm^{-1} [44]. In the title complexes, the band at 2949, 2910 and 2932, 2928 cm^{-1} in FT-IR spectra is assigned to CH_2 asymmetric stretching modes for the complexes **2a** and **2b**, respectively. The medium strong band at 2856, 2825 cm^{-1} and 2856, 2841 cm^{-1} are attributed to CH_2 symmetric stretching. Theoretically, the value at 2950, 2912, 2856, 2830 and 2931, 2856 and 2840 cm^{-1} by B3LYP/LanL2DZ method exactly correlate with the experimental observations.

Aromatic CH_2 compounds have a band of weak-to-medium intensity of 1500-200 cm^{-1} belong to CH_2 bending vibrations [43]. The CH_2 group of the complex is capable of different bending vibrations such as scissoring, wagging, rocking and twisting. These vibrations give rise to variable intensity bands at lower wavenumber region. In the present study, the prominent bands at 1582, 1575, 1554 cm^{-1} in FT-IR spectrum 1583 cm^{-1} in FT-Raman spectrum are assigned to CH_2 scissoring mode. In aromatic complexes, the wagging modes are expected in the region 1200 – 1000 cm^{-1} with a moderate to strong intensity. For the complexes **2a** and **2b**, the weak bands at 1320, 1305, 1300 cm^{-1} in IR and 1304 cm^{-1} in Raman are assigned to CH_2 rocking vibrations. The CH_2 wagging vibrational modes are attributed at 1252, 1220, 1263 and 1224 cm^{-1} in infrared and 1254, 1263, 1225 cm^{-1} Raman spectrum.

C–Cl vibrations

The C–Cl stretching mode appears as mixed mode. In the lower region, C–Cl stretching vibrations appear in the region 760–505 cm^{-1}. For simple chlorine compounds, C–Cl absorption is in the region 750–700 cm^{-1} [43]. From the above literature the band observed at 775, 750 cm^{-1} in FT-IR spectrum are assigned to C–Cl stretching vibrations. The shift of lower frequency of **2b** is due to much greater electronegativity of Cl as compared to carbon atoms. Thus Cl atom acquires small positive charge and the carbon atom acquires small negative charge. The inductive effect of chlorine attracts electrons from C–Cl bond, which increases the force constants and leads to an increase in the absorption frequency.

Sn–C, Sn–N and Sn–Br vibrations

Infrared spectroscopy has provided valuable information on the molecular geometry of organotin compounds. Particularly important is the criterion established for determining the configuration of SnC3 and SnC2 moieties in chlorotrimethyltin and dichlorodimethyltin derivatives. Characteristic infrared absorptions of some tin-ligand stretching vibrations are m(Sn–C), 600–470 cm^{-1} [45] m(Sn-N), 843 -752 cm^{-1} and m(Sn-Br), 264-222 cm^{-1} [46]. Hence, in the present investigations, the Sn-C stretching vibrations are observed at 560, 476 cm^{-1} and 620, 608 cm^{-1} in FT-IR spectra for **2a** and **2b** complexes, respectively. Similarly the Sn–B stretching vibrations for the complexes **2a** and **2b** are observed at 283, 265 cm^{-1} and 288, 265 cm^{-1} in FT-Raman spectra, respectively. The Sn-N stretching vibrations are observed at 838, 817 cm^{-1} in FT-Raman spectrum for 2a complex. The theoretically computed values are in good agreement with the observed values.

4. Conclusions

We have reported the synthesis of a bis(*p*-chlorobenzyl)(dibromo)(1,10-phenanthroline)Sn(IV) and bis(*p*-

bromobenzyl)(dibromo)(1,10-phenanthroline)Sn(IV) complexes. The spectral and structural studies revealed the formation of complexes in which the tin atom is hexa coordinated. The optimized geometrical parameters and vibrational wave numbers of **2a** and **2b** complexes were analyzed with aid of density functional theory method. The various modes of vibrations are assigned unambiguously using the results of PED output obtained from the normal coordinate analysis. The calculated wavenumbers are good agreement with the experimental results. The HOMO and LUMO energy values suggest the possibility of intermolecular charge transfer within the complexes.

Acknowledgement

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Supplementary data: Crystallographic data (excluding structure factors) for the structures **2a** and **2b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1021619 (**2a**) and CCDC 1449106 (**2b**). Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internet) +44-1223/336-033; E-mail: deposit@ccds.cam.ac.uk].

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