

Synthesis, characterization and reactions of diorganotin(IV) complexes with some N_2S_2 donor ligands derived from 2-aminothiophenol

(Mrs) P R Shukla*, Ashish K Pathak & Nihal Ahmad
Department of Chemistry, University of Lucknow,
Lucknow 226 007

Received 13 May 1991; revised 23 September 1991;
accepted 16 December 1991

Complexes of some diphenyltin(IV) salts with N_2S_2 donor ligands have been prepared and characterized on the basis of analytical, IR and 1H NMR spectral studies. The reactivity of these complexes with various reagents has also been studied.

A literature survey revealed that not much work has been reported on the reactivity of tin complexes with N_2S_2 donor ligands. This prompted us to carry out the complexation reactions of diphenyltin-dichlorodide/ditetrafluoroborate with four N_2S_2 donor ligands derived from the condensation of 2-aminothiophenol with dichloroethane/dibromoethane and glyoxal. The complexes have been subjected to various substitution, addition and cyclisation reactions in order to study the mode of coordination of the ligands to tin atom and also the relative stability of the Sn - C bond. The complexes have been characterized using various physico-chemical techniques.

Experimental

All the reactions were carried out under dry nitrogen atmosphere. Tin was estimated by the standard method¹. The molar conductances ($10^{-3} M$ in DMF) were measured on a Toshniwal direct reading conductivity bridge using a dip type conductivity cell. The IR spectra were determined on Perkin Elmer-577 spectrophotometer in KBr/CsI in the range $4000-200\text{ cm}^{-1}$ and 1H NMR spectra recorded on a Perkin Elmer-R-32, 90MHz spectrometer in DMSO- d_6 solvent. The elemental analysis were carried out micro-analytically at CDRI, Lucknow.

Diphenyltin dichloride was obtained from E. Merck. The chemicals used were of AR grade. The solvents were distilled and dried before use. Diphenyltin tetrafluoroborate was prepared by

simple metathetical reaction of Ph_2SnCl_2 with $NaBF_4$ in methanol.

Di(2-benzenethiol)ethylenediamine (L_1)/*Di(2-aminophenyl) ethanebisulphide* (L_2)

2-Aminothiophenol (2.50g, 0.02 mol) in 20 ml dry methanol was mixed slowly with glyoxal (0.01 mol) for L_1 or dichloroethane (0.01 mol) for L_2 in methanol (10 ml). The reaction mixture was refluxed for 8-10 h, filtered and concentrated to yield the ligand L_1 or L_2 which was recrystallised from absolute ethanol (10 ml) and washed with diethylether (5 ml).

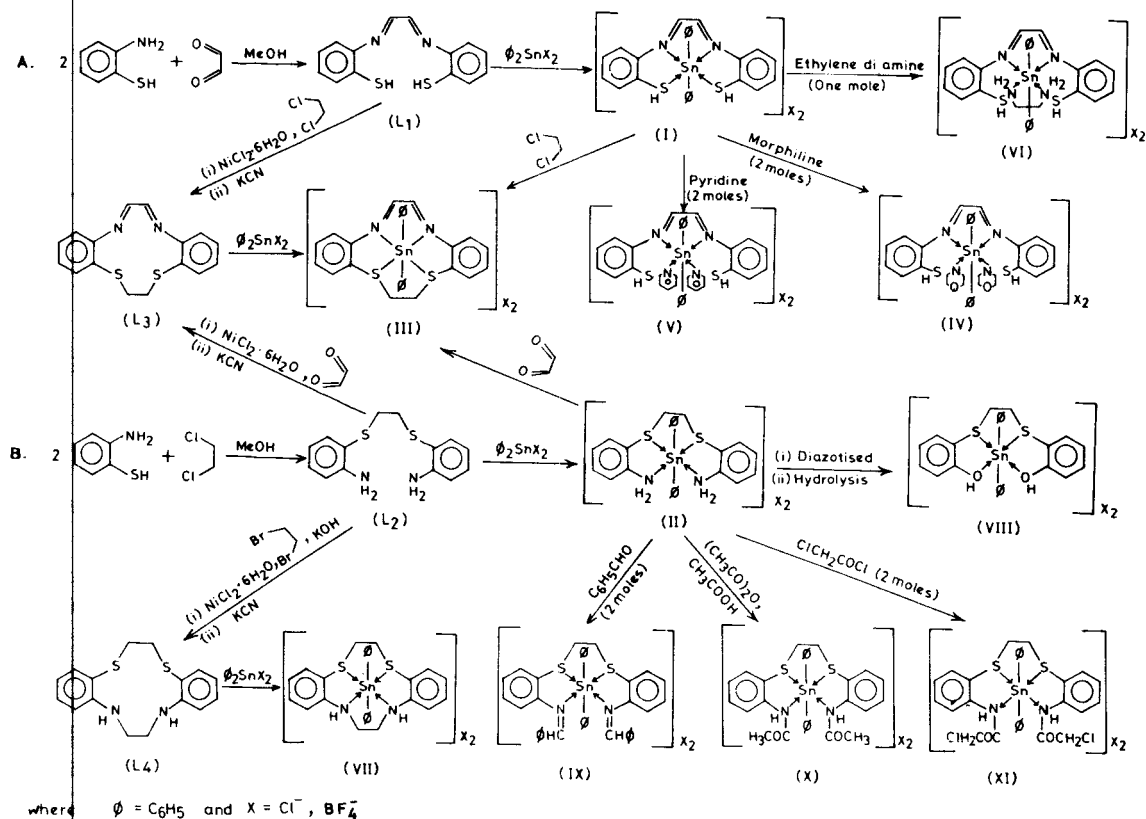
Dibenzo(e,k) 1,4-diaza-7,10-dithiacyclododeca-2,3-diene (L_3).

To a methanolic solution (10 ml) of ligand L_1 or L_2 (0.27 g, 0.001 mol) nickel chloride (0.24 g, 0.001 mol) in methanol (5 ml) was added and refluxed for 5-6 h. To this solution, dichloroethane (0.001 mol) for L_1 or glyoxal (0.001 mol) for L_2 in methanol was added dropwise with constant stirring. It was refluxed for 5 h. To this solution, KCN (0.5 g) was added and again refluxed for 20h and filtered. The filtrate was concentrated and the ligand crystallised from pet-ether. The compound was purified by running it through silica column, eluted with benzene and recrystallised using pet-ether (40-60°C).

Dibenzo (e,k) 1,4-diaza-7,10-dithiacyclododecane (L_4)

To a methanolic solution (10 ml) of L_2 (0.27 g, 0.001 mol), nickel chloride (0.24 g, 0.001 mol) in methanol (5 ml) was added and refluxed for 5 h. The solution was cooled to 0°C and 1,2-dibromoethane (0.20 g, 0.001 mol) added dropwise with constant stirring for about 30 min after which the reaction mixture was heated on a steam bath for 1 h and concentrated to one-third of its original volume. To this solution, KOH pellets (2.0 g) were added and the mixture heated with stirring for 2 h on a steam bath. After cooling to room temperature, the solid was removed by filtration and washed with several portions of diethylether. To the filtrate, KCN (0.5 g) was added and the solution continuously refluxed for 20 h. The precipitate of $[K_2 Ni(CN)_4]$ was removed by filtration. The desired compound was crystallised from the filtrate using pet-ether, purified by running over TLC or through silica column and recrystallised in pet-ether (40-60°C).

Di(2-benzenethiol) ethylenediaminediphenyltin dichloride/ditetrafluoroborate (I) or *di(2-aminophenyl) ethanebisulphidediphenyltin dichloride/ ditetrafluoroborate* (II)



Scheme 1

Anhydrous methanolic solution (5 ml) containing Ph_2SnCl_2 (3.4 g, 0.01 mol) or $\text{Ph}_2\text{Sn}(\text{BF}_4)_2$ (4.4 g, 0.01 mol) was gradually added to ligand L_1 or L_2 (0.01 mol) in methanol (10 ml). The reaction mixture was refluxed for 8 hr and filtered. Upon concentration, the product precipitated out. The product was recrystallised from absolute ethanol (20 ml).

The other derivatives of the compounds I and II were prepared by usual methods as shown in Scheme I.

Results and discussion

The analytical data (Table 1) suggests the molecular formula of the complexes to be $[\text{Ph}_2\text{Sn}(\text{L})]\text{X}_2$ where $\text{X} = \text{Cl}^-, \text{BF}_4^-$ and $\text{L} = \text{di}(2\text{-benzenethiol})\text{ethylenediamine}$ (L_1); $\text{di}(2\text{-aminophenyl})\text{-ethanebisulphide}$ (L_2); $\text{dibenzo}(e,k)1,4\text{-diaz}-7,10\text{-dithiacyclododeca-2,3-diene}$ (L_3) and $\text{dibenzo}(e,k)1,4\text{-diaz}-7,10\text{-dithiacyclododecane}$ (L_4). The molar conductances correspond to 1:2 electrolytic nature of these complexes.

In the IR spectra of ligands L_1 and L_2 , a weak band at 3000 cm^{-1} due to C-H stretching and many sharp bands in the range $1600\text{-}1465\text{ cm}^{-1}$ are observed due to aromatic ring vibrations. The bands around 1015 and 750 cm^{-1} correspond to C-S stretching^{2,3}, and the band at 1300 cm^{-1} is assigned to C-N stretching

vibrations. In addition to these, L_1 also shows a strong band at 1610 cm^{-1} due to $\text{C}=\text{N}$ and a weak band at 2515 cm^{-1} which may be attributed to SH stretching vibrations⁴. The presence of these bands indicates that condensation of 2-aminothiophenol with glyoxal has taken place. The ligand L_2 shows a band at 3310 cm^{-1} corresponding to NH stretch. Presence of this band along with the absence of SH band at 2515 cm^{-1} is an evidence of the condensation of thiol groups of 2-aminothiophenol with dichloroethane.

In the spectra of all the complexes of ligands L_1 & L_2 , the aromatic ring vibrations show a slightly positive shift. The azomethine stretching vibrations in the complex I is observed at 1600 cm^{-1} . This negative shift suggests coordination through the azomethine nitrogen^{5,6}. The SH and C-S stretching vibrations are shifted to higher wavenumbers showing the coordination of sulphur atom of the ligand to the tin atom³. In the IR spectra of complexes II, the bands due to NH and C-S are also shifted, suggesting the coordination through nitrogen and sulphur atoms.

In the IR spectra of complex III, a band at 1600 cm^{-1} is observed which is assigned to coordinated azomethine vibration whereas a lower shift in the NH vibration in case of the complex VII suggest the coordination through imino groups. The C-S

Table 1—Characterization data of the complexes

Compound Emp. formula (m.pt. °C)	Yield (%)	Found(Calc.), %				Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
		Sn	C	H	N	
C ₁₄ H ₁₂ N ₂ S ₂ (L ₁) (143)	87	—	61.55 (61.76)	4.22 (4.41)	9.89 (10.29)	—
C ₁₄ H ₁₆ N ₂ S ₂ (L ₂) (72)	82	—	60.16 (60.86)	5.21 (5.79)	10.51 (10.14)	—
C ₁₆ H ₁₄ N ₂ S ₂ (L ₃) (129)	74	—	63.98 (64.42)	4.55 (4.69)	9.08 (9.39)	—
C ₁₆ H ₁₈ N ₂ S ₂ (L ₄) (240)	64	—	63.08 (63.58)	5.75 (5.96)	9.05 (9.27)	—
C ₂₆ H ₂₂ N ₂ S ₂ SnCl ₂ (I) (82)	65	19.08 (19.31)	49.89 (50.64)	3.04 (3.57)	4.08 (4.54)	140.18
C ₂₆ H ₂₂ N ₂ S ₂ Sn(BF ₄) ₂ (*)	63	16.32 (16.57)	**	**	3.52 (3.89)	146.29
C ₂₆ H ₂₆ N ₂ S ₂ SnCl ₂ (II) (112)	68	19.51 (19.19)	50.70 (50.32)	4.04 (4.19)	4.39 (4.51)	160.09
C ₂₆ H ₂₆ N ₂ S ₂ Sn(BF ₄) ₂ (*)	64	16.22 (16.46)	**	**	3.73 (3.87)	165.28
C ₂₈ H ₂₄ N ₂ S ₂ SnCl ₂ (III) (115)	55	17.99 (18.53)	52.08 (52.33)	3.15 (3.73)	4.17 (4.36)	156.15
C ₂₈ H ₂₄ N ₂ S ₂ Sn(BF ₄) ₂ (*)	56	15.67 (15.98)	**	**	3.53 (3.76)	160.21
C ₃₄ H ₃₈ N ₄ S ₂ O ₂ SnCl ₂ (IV) (160d)	49	15.31 (15.10)	51.22 (51.77)	4.67 (4.82)	7.34 (7.10)	138.77
C ₃₄ H ₃₈ N ₄ S ₂ O ₂ Sn(BF ₄) ₂ (*)	47	13.66 (13.36)	**	**	6.04 (6.28)	133.36
C ₃₆ H ₃₂ N ₄ S ₂ SnCl ₂ (V) (240)	51	15.12 (15.37)	55.67 (55.81)	4.01 (4.13)	7.41 (7.23)	159.66
C ₃₆ H ₃₂ N ₄ S ₂ Sn(BF ₄) ₂ (*)	53	13.33 (13.57)	**	**	6.15 (6.38)	160.08
C ₂₈ H ₃₀ N ₄ S ₂ SnCl ₂ (VI) (240)	49	17.34 (17.60)	49.55 (49.70)	4.07 (4.43)	8.01 (8.28)	161.61
C ₂₈ H ₃₀ N ₄ S ₂ Sn(BF ₄) ₂ (*)	45	15.51 (15.28)	**	**	7.02 (7.19)	160.54
C ₂₈ H ₂₈ N ₂ S ₂ SnCl ₂ (VII) (200d)	54	18.27 (18.42)	50.98 (52.01)	4.12 (4.33)	4.14 (4.33)	149.30
C ₂₈ H ₂₈ N ₂ S ₂ Sn(BF ₄) ₂ (*)	52	15.28 (15.89)	**	**	3.57 (3.74)	153.72
C ₂₆ H ₂₄ O ₂ S ₂ SnCl ₂ (VIII) (240)	41	19.40 (19.13)	50.02 (50.16)	3.66 (3.85)	—	161.04
C ₂₆ H ₂₄ O ₂ S ₂ Sn(BF ₄) ₂ (*)	45	16.12 (16.42)	**	**	—	162.84

(Contd)

Table 1—Characterization data of the complexes—Contd.

Compound Emp. formula (m.pt. °C)	Yield (%)	Found(Calc.), %				Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
		Sn	C	H	N	
C ₃₈ H ₃₆ N ₂ S ₂ SnCl ₂ (IX) (240)	51	14.99 (15.37)	58.70 (58.91)	4.46 (4.65)	3.45 (3.61)	148.72
C ₃₈ H ₃₆ N ₂ S ₂ Sn(BF ₄) ₂ (*)	48	13.42 (13.57)	**	**	3.02 (3.19)	144.09
C ₃₀ H ₃₀ N ₂ S ₂ O ₂ SnCl ₂ (X) (240)	43	16.77 (16.90)	51.08 (51.13)	4.02 (4.26)	3.78 (3.97)	141.37
C ₃₀ H ₃₀ N ₂ S ₂ O ₂ Sn(BF ₄) ₂ (*)	47	14.52 (14.75)	**	**	3.22 (3.47)	139.36
C ₃₀ H ₂₈ N ₂ S ₂ O ₂ SnCl ₂ (XI) (240)	59	15.08 (15.39)	46.82 (46.57)	3.22 (3.62)	3.42 (3.62)	158.17
C ₃₀ H ₂₈ N ₂ S ₂ O ₂ Sn(BF ₄) ₂ (*)	55	13.37 (13.59)	**	**	3.09 (3.19)	160.05

d = decomposition point, * = explodes before melting, ** = due to the explosive character and the presence of fluorine C,H analyses were not possible.

Table 2—¹H NMR spectral data of the complexesChemical shift in δ ppm

Compd.	Aromatic protons	NH protons	SH protons	OH protons	CH protons	CH ₂ protons	CH ₃ protons
L ₁	7.25(4H, t) 6.90(2H, d) 6.60(2H, t)	—	5.50(2H, s)	—	2.25(2H, s)	—	—
L ₂	7.30(4H, t) 6.90(2H, d) 6.50(2H, t)	4.20(4H, s)	—	—	—	1.90(4H, s)	—
L ₃	7.20(4H, t) 6.95(2H, d) 6.65(2H, t)	—	—	—	2.25(2H, s)	1.85(4H, s)	—
L ₄	7.25(4H, t) 6.80(2H, d) 6.60(2H, t)	4.20(2H, s)	—	—	—	1.95(4H, s) 2.05(4H, s)	—
I	8.20-6.40(18H, m)	—	5.60(2H, s)	—	2.50(2H, s)	—	—
II	8.40-6.35(18H, m)	4.45(4H, s)	—	—	—	2.05(4H, s)	—
III	8.25-6.60(18H, m)	—	—	—	2.50(2H, s)	2.05(4H, s)	—
VII	8.30-6.30(18H, m)	4.35(2H, s)	—	—	—	2.15(4H, s) 2.10(4H, s)	—
VIII	8.35-6.45(18H, m)	—	—	6.00(2H, s)	—	2.10(4H, s)	—
IX	8.40-6.35(28H, m)	—	—	—	2.60(2H, s)	2.15(4H, s)	—
X	8.35-6.40(18H, m)	4.40(2H, s)	—	—	—	2.05(4H, s)	1.35(6H, s)
XI	8.25-6.40(18H, m)	4.35(2H, s)	—	—	—	2.20(4H, s) 2.10(4H, s)	—

stretching vibration also undergoes a shift suggesting the coordination through sulphur atoms. The spectra of complex VIII shows a band at $3100 \pm 10 \text{ cm}^{-1}$ which is assigned to coordinated OH stretching⁷. This band along with the absence of band at 3310 cm^{-1} as shown in the spectra of complex II, indicates the conversion of NH_2 groups into OH groups.

The analytical data along with the appearance of the expected IR bands⁸ in case of the complexes IX, X and XI suggest the course of reactions as shown in Scheme 1.

In the spectra of complexes IV, V and VI, bands due to thiol groups do not show any significant shift which indicates their non-participation in the coordination and in their place the secondary ligands morpholine, pyridine and ethylenediamine are coordinated, as the bands due to these are observed at expected positions⁹.

In the far infrared spectra of all the complexes, two bands of weak intensities identified at 425 ± 5 and $370 \pm 5 \text{ cm}^{-1}$, which are absent in the spectra of the ligands are attributed to $\text{Sn} \leftarrow \text{N}$ vibrations¹⁰. Another medium intensity band at $290 \pm 5 \text{ cm}^{-1}$, which may be attributed to $\text{Sn}-\text{C}(\text{Ph})$, clearly indicates the existence of linear $\text{Ph}-\text{Sn}^{2+}-\text{Ph}$ species which shows that the phenyl groups are in *trans* positions¹¹⁻¹³. The presence of ionic tetrafluoroborate and ionic chloride is evidenced by the molar conductance studies whereas the presence of ionic tetrafluoroborate is also shown by the appearance of bands at 1050 cm^{-1} and 620 cm^{-1} (ref. 14). The presence of ionic chloride is confirmed by the precipitation of two moles of AgCl when compounds I & II were made to react with AgNO_3 solution.

The ^1H NMR spectral studies of the ligand and the complexes further support the mode of bonding as indicated by the IR spectral studies. The ^1H NMR data are given in Table 2.

Thus the IR, ^1H NMR, molar conductance and elemental analysis data clearly indicate that all the

complexes obtained by different routes possess 1:1 (metal:ligand) stoichiometry and are 1:2 electrolytes. It is also confirmed on the basis of above discussion that nitrogen as well as sulphur atoms behave as donors coordinating in a planar fashion while the phenyl groups are present at *trans* axial positions giving octahedral geometry to the complexes except in complexes IV, V and VI where the two sulphur atoms are not coordinated and in their place the secondary ligands are coordinated. It is also observed that in all the reactions of complexes I and II, the $\text{Sn}-\text{C}$ bond remains intact and does not cleave during the course of reactions and no change in the structure of the complexes takes place.

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