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### Synthesis & Characterisation of Bis-dithiocarbamate Complexes of Bis-*p*-biphenyltin (IV)

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**Bis-dithiocarbamate complexes of bis-*p*-biphenyltin(IV) of the type  $(C_6H_5-C_6H_4)_2Sn(S_2CNRR')$  (where  $R = R' =$  methyl, ethyl, isopropyl, tetramethylene, pyrrolidine or  $R =$  methyl;  $R' =$  phenyl) have been prepared by the reaction of bis-*p*-biphenyltin(IV) dichloride with anhydrous sodium derivative of the respective dithiocarbamic acid. The complexes have been characterized on the basis of elemental analyses, IR and PMR data. Molecular weight determination in benzene and conductivity measurements in nitrobenzene indicate the complexes to be monomeric and non-electrolytic respectively. IR and PMR data indicate the bidentate character of the ligand in these complexes.**

**A** GREAT deal of work has been reported on the synthesis and structure of organotin dithiocarbamate complexes<sup>1</sup>. The present note reports the synthesis and characterization of some new bis-*p*-biphenyltin(IV) bis-dithiocarbamate (dtc) com-

plexes of the type  $(C_6H_5-C_6H_4)_2Sn(S_2CNRR')_2$  where  $R = R' =$  Me, Et, *i*-Pr, tetramethylene or pyrrolidine and  $R =$  Me,  $R' =$  Ph.

Well-dried and purified benzene, dichloromethane, acetone, petroleum ether and nitrobenzene were used.

Bis-*p*-biphenyltin (IV) dichloride was prepared by the reaction between tetrabiphenyltin and tin tetrachloride in 1:1 molar ratio in a sealed tube<sup>2,3</sup>. Tetrabiphenyltin was prepared by the reaction of *p*-bromo biphenyl, tin tetrachloride and sodium in dry benzene (Wurtz reaction).

Sodium salts of *N*-substituted dithiocarbamic acids were prepared by the reaction of an appropriate secondary amine, carbon disulphide and sodium hydroxide as described by Kloppeing *et al.*<sup>4</sup>. The water of crystallization from the sodium salt was removed by drying *in vacuo* over  $P_2O_5$  first at room temperature then at 110°C (using boiling toluene) in a drying pistol.

**Bis-*p*-biphenyltin (IV) *N,N*-dimethyldithiocarbamate**—To a solution of bis-*p*-biphenyltin dichloride (0.01 mol) in dry acetone (50 ml) was added dropwise with stirring a solution of sodium salt of *N,N*-dimethyldithiocarbamate (0.02 mol) in dry acetone (50 ml). The mixture was kept at room temperature for 30 min, filtered and the filtrate concentrated *in vacuo* to leave behind a white solid which on crystallization from petroleum ether-dichloromethane as a white crystalline solid, yield ~90%, m.p. 195°.

The other bis-*p*-biphenyltin dithiocarbamates, viz. bis-*p*-biphenyltin *N,N*-diethyl-, *N,N*-diisopropyl-, *N,N*-methyl phenyl-, tetramethylene- and *N*-pyrrolidine-dithiocarbamates were prepared similarly.

Analytical and physical data of these complexes are given in Table I.

The complexes are white crystalline solids with sharp melting points. They are soluble in chloroform, benzene, acetone, dichloromethane, carbon tetrachloride and insoluble in petroleum ether, and are stable at room temperature in the absence of moisture. Conductivity determination reveal that the complexes behave as non-electrolyte in nitrobenzene at a concentration in the range  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-5}$  *M*.

The IR spectra of the complexes in KBr matrix (Perkin-Elmer 621 grating) indicate bidentate character of the dtc ligands in these complexes because of the following reasons :

(1) The complexes exhibit two bands ~1500  $cm^{-1}$  ( $\nu_{C-N}$ ) and 1000  $cm^{-1}$  ( $\nu_{C-S}$ ). Similar observations have been recorded earlier<sup>5,6,7</sup>. If the ligands were to behave as unidentate ligand these bands would have appeared as split band with a separation of 20  $cm^{-1}$  (ref. 8-11).

In the far IR region the presence of two bands 580  $cm^{-1}$  and 540  $cm^{-1}$  may be assigned to  $\nu_{as}Sn-C$  and  $\nu_sSn-C$  respectively. This indicate that C-Sn-C moiety is not linear. A strong band in the region  $380 \pm 10$   $cm^{-1}$  is assignable<sup>12</sup> to  $\nu_{Sn-S}$ .

The room temperature PMR spectra (chemical shift in  $\tau$ -scale), TMS internal reference of various

TABLE 1 — ANALYTICAL DATA FOR BIS-BIPHENYL TIN BISDITHIOCARBAMATO COMPLEXES

Complex	m.p. (°C)	Found (Calc) (%)				M.W. Found (Calc.)
		C	H	N	Sn*	
1. (C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Sn(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	195	53.80 (54.15)	4.60 (4.51)	4.10 (4.21)	17.45 (17.75)	670.8 (664.7)
2. (C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Sn(S <sub>2</sub> CN Et <sub>2</sub> ) <sub>2</sub>	198	55.96 (56.62)	5.06 (5.28)	3.58 (3.89)	16.01 (16.48)	715.2 (720.7)
3. (C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Sn(S <sub>2</sub> CN ipr) <sub>2</sub>	170	58.08 (58.71)	5.61 (5.92)	3.41 (3.6)	14.96 (15.25)	770.10 (776.7)
4. (C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Sn(S <sub>2</sub> CN MePh) <sub>2</sub>	218	60.25 (60.85)	4.17 (4.31)	3.70 (3.55)	14.84 (15.05)	780.1 (786.7)
5. (C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Sn[S <sub>2</sub> CNCH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> ] <sub>2</sub>	205	57.81 (58.27)	4.61 (4.75)	3.42 (3.91)	16.02 (16.57)	706.0 (716.7)
6. (C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Sn(S <sub>2</sub> CN-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> ) <sub>2</sub>	215	55.01 (55.75)	4.10 (4.35)	3.85 (4.07)	16.86 (17.24)	680.5 (688.7)

\*Estimated as SnO<sub>2</sub>

dithiocarbamato complexes of bis-*p*-biphenyltin (IV) recorded in CDCl<sub>3</sub> show two types of signals, viz. due to Sn-bis-*p* biphenyl group and NR<sub>2</sub> protons. Proton signals due to NR<sub>2</sub> proton show that N-bonded R groups are equivalent in these complexes due to the following reasons.

The N-Me protons in the complexes (C<sub>6</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> appear as a three proton singlet. In the analogous ethyl dtc complex only one type of quartet at 6.15 due to N-CH<sub>2</sub> proton and a triplet ~8.6 due to CH<sub>3</sub> protons of the ethyl group. In the case of isopropyl dithiocarbamate complex

there appear a multiplet at 5.25 due to N-CH and

a doublet at 8.52 due to the CH<sub>3</sub> protons of the isopropyl group.

In the spectra of (C<sub>6</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn(S<sub>2</sub>CNCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> N-CH<sub>3</sub> protons appear at 6.25 and N-C<sub>6</sub>H<sub>5</sub> proton at 2.5. Two types of multiplets ~6.2 and 7.92 in tetramethylene complex and ~6.5 and 7.89 in pyrrolidine complex due to methylene group again confirm the equivalence of NR<sub>2</sub> protons. The resonance signals due to biphenyl protons appear as a doublet, a triplet and a doublet between 2.0 and 3.0<sup>13,14</sup>.

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#### Nickel(II) & Copper(II) Complexes of 5(3)-Methylpyrazole-3(5)-carboxamide

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Nickel(II) and copper(II) complexes of 5(3)-methylpyrazole-3(5)-carboxamide (MPA) have been synthesised and characterised. Magnetic and electronic (diffuse reflectance and in solution) spectral data of the species, M(MPA)<sub>2</sub>X<sub>2</sub>.nH<sub>2</sub>O (X = Cl/Br/I/CIO<sub>4</sub>/NO<sub>3</sub>/½SO<sub>3</sub>/BF<sub>4</sub>/SCN), classify them as grossly octahedral ones. The IR data suggest that the ligand (MPA) acts as a neutral bidentate one bonding through the ring (pyrazole) nitrogen and amide-oxygen, the counterion (X) is preferentially coordinated to the metal ion in the solid species and is released in aqueous solution, as revealed by ΔM values).

AS a part of our programme<sup>1-3</sup> of investigating the coordination behaviour of pyrazole-based ligands which might have biological implications we report here the isolation and physico-chemical characterisation of bis-complexes of Ni(II) and Cu(II) with 5(3)-methylpyrazole-3(5)-carboxamide (I, hereinafter abbreviated as MPA) as a ligand. 5(3)-Methylpyrazole-3(5)-carboxamide (MPA) was prepared by the reaction of liquor ammonia with