

for Mn(II), Fe(II), Co(II) and Ni(II) chelates and tetragonal configuration for the Cu(II) chelates. The tetragonal structure of Cu(II) chelates is also expected from Jahn-Teller effect<sup>5</sup>. Infrared analysis of the metal chelates in the region of 3.1 to 4.0  $\mu$  confirms the presence of coordinated water molecules in the complexes.

The Zn(II), Cd(II), Pd(II) and UO<sub>2</sub>(II) chelates show 1:1 (metal-ligand) stoichiometry (Table 1). The molecular weight determination shows the complexes to be monomeric in nature. Therefore, the complexes may be represented by the formula [MLX], where M = metal ion, LH<sub>2</sub> = H<sub>2</sub>NO [C<sub>17</sub>H<sub>13</sub>NSO<sub>4</sub>] or H<sub>2</sub>NT [C<sub>13</sub>H<sub>12</sub>NSO<sub>4</sub>] and X = H<sub>2</sub>O or Py. All the hydrated chelates and their pyridine adducts have been found to be diamagnetic, as expected. These results can be best explained by assigning a tetrahedral structure for Zn(II) and Cd(II) chelates. UO<sub>2</sub>(II) chelates possess an octahedral structure in conformity with the usual behaviour of UO<sub>2</sub>(II) ion<sup>9</sup>.

Pd(II) highly favours a square-planar configuration. Yamada *et al.*<sup>3</sup> have suggested a square-planar configuration for a number of N-alkyl-salicylideneiminato Pd(II) chelates. Solution spectra in dioxane and pyridine of the Pd(II) chelates indicate three absorption bands at 22200, 26500 and 30600 cm<sup>-1</sup> which can be assigned to the transitions <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>1g</sub>, <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>E<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>A<sub>2u</sub> respectively. Thus the Pd(II) chelates exhibit a square-planar configuration.

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### Chlorotellurium Compounds of Aryl Ethers

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Conductance studies and molecular weight measurements on ethoxyphenyltellurium trichloride and bis(methoxyphenyl)tellurium dichloride suggest their presence in molecular form in organic solvents. IR and NMR studies show the presence of TeCl<sub>3</sub> group in the *para* position to ethoxy or methoxy group in the ring, in both the compounds.

IN the present note, structural aspects of *p*-ethoxyphenyltellurium trichloride<sup>1,2</sup> (I) and bis(*p*-methoxyphenyl)tellurium dichloride<sup>3</sup> (II) are discussed. Recently, infrared and NMR studies of *p*-methoxyphenyltellurium trichloride have been reported<sup>4,5</sup>.

Compounds I (m.p. 180-82°) and II (m.p. 190°) were prepared by literature methods<sup>2,3</sup> and crystallized from chloroform and methanol respectively.

Conductivities of these compounds at different concentrations have been measured in acetonitrile at 30° ± 1°. The conductivity increases with dilution. However, the molar conductances are lower than the values expected<sup>6</sup> for 1:1 electrolytes (120-160 ohm<sup>-1</sup> cm<sup>-2</sup> mole<sup>-1</sup>) in the concentration range of 10<sup>-3</sup>M. This suggests that the compounds are present in the solution mainly in the molecular form. Molecular weight determination in benzene by cryoscopic method further supports this contention.

The asymmetric and symmetric C-O-C stretchings in phenetole and anisole appear at 1240 and 1040 cm<sup>-1</sup> whereas compound I exhibits these bands at 1260 and 1050 cm<sup>-1</sup> and compound II at 1270 and 1045 cm<sup>-1</sup>. This shift to higher frequency side indicates *o*- or *p*-substitution of TeCl<sub>3</sub> group in the ring. The appearance of a very intense band (1580 cm<sup>-1</sup>) in both these compounds could be due to a change in the dipole moment because of the presence of *para*-substituted TeCl<sub>3</sub> group in the ring. Further support for *para*-substitution is obtained from the overtone and combination bands which appear at 1880, 1780 and 1710 cm<sup>-1</sup> as expected<sup>7</sup>. A medium intensity band at 455 cm<sup>-1</sup> in compound I and at 480 cm<sup>-1</sup> in compound II corresponds to the tellurium-carbon bond. The compounds I and II show bands at 320 and 290 cm<sup>-1</sup> respectively assigned to Te-Cl bond.

PMR spectra of I and II have been recorded in deutero-acetonitrile. These spectra are of A<sub>2</sub>X<sub>2</sub> type and give a definite proof of the *para*-substitution of chlorotellurium group in the ring. Spectrum (δ scale) of bis(methoxyphenyl)tellurium dichloride shows two quartets at 8.30 and 7.12 ppm. Their intensities show each of them to be due to a pair of protons in identical chemical environment. The J<sub>H<sub>ortho</sub>-H<sub>meta</sub></sub> is 9.0 ± 0.3 Hz. The methoxy groups give rise to a singlet at 3.87 ppm.

The NMR spectrum of II shows even finer structural details. The protons *ortho* to OC<sub>2</sub>H<sub>5</sub> group (H<sub>A</sub> and H<sub>A'</sub>) in II are chemically equivalent as are the protons *ortho* to TeCl<sub>3</sub> group (H<sub>X</sub> and H<sub>X'</sub>). J<sub>A<sub>X</sub></sub> and J<sub>A'<sub>X'</sub></sub> should be the same (~7-10 Hz). The *ortho* and *meta* aromatic protons (with respect to TeCl<sub>3</sub> group) show a multiplet at 8.27 and 7.80 ppm respectively. J<sub>A<sub>X</sub></sub> which is equal to J<sub>A'<sub>X'</sub></sub> is 9.3 ± 0.3 Hz. The spectrum also shows coupling between H<sub>A</sub> and H<sub>A'</sub> (as also between H<sub>X</sub> and H<sub>X'</sub>). J<sub>AA'</sub> is equal to J<sub>XX'</sub> and is 2.2 ± 0.3 Hz. This spectrum can be better described as of the type AA'XX'. A quartet and a triplet appearing at 4.14 and 1.38 ppm respectively are due to the ethyl group (J<sub>C<sub>2</sub>H<sub>5</sub>-CH<sub>3</sub></sub> = 7.0 ± 0.3 Hz).

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### N,N-Diethylamino-oxy Derivatives of Dialkyltin(IV)

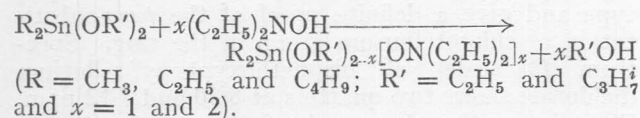
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Diethylamino-oxy derivatives of dialkyltin(IV) have been synthesized and characterized on the basis of elemental analysis, molecular weight determination and IR data.

IN continuation of our previous work on N,N-diethylhydroxylamine derivatives of titanium<sup>1</sup>, boron and aluminium<sup>2</sup>, the derivatives of dialkyltin (IV) are reported in this note.

Dimethyl-, diethyl- and dibutyltin diisopropoxides and dibutyltin diethoxide, prepared by the sodium method, react with diethylhydroxylamine to give products,  $R_2Sn(OR')_{2-x}[ON(C_2H_5)_2]_x$  (Table 1). The reactions can be represented as follows:



The general method of preparation of the compound is as follows: Dialkyltin dialkoxides and diethylhydroxylamine were mixed in benzene in stoichiometric ratios and left overnight. Reaction mixtures were heated at a bath temperature of 80-90° for 4-8 hr. In reactions (1-3) the benzene was removed and the products distilled under reduced pressure. In other cases, insoluble products were separated by filtration and washed subsequently. Dibutyltin derivatives (Table 1, Nos. 1-3) are liquids, miscible with organic solvents. These are volatile and can be distilled with slight decomposition under reduced pressure.

The molecular complexity of soluble diethylamino-oxy derivatives of dibutyltin(IV) was found to be about three as revealed by mol. wt determination. Compounds derived from dimethyl- and diethyltin diisopropoxides are insoluble and can be considered to be polymeric.

IR spectra of the compounds exhibit  $\nu_{as}$  and  $\nu_s$  N-O around 950 and 910 cm<sup>-1</sup> respectively<sup>3</sup>. The characteristic absorptions<sup>4</sup> of isopropoxy group occur at 1140, 1055-1050 cm<sup>-1</sup> and that of ethoxy group at 1180-1103 and 1010 cm<sup>-1</sup>. The bands in the regions 620-609 and 521-510 cm<sup>-1</sup> have been assigned

TABLE 1 — PRODUCTS OF THE REACTIONS OF DIALKYL TIN DIALKOXIDES WITH DIETHYLHYDROXYLAMINE

Sl No.	Molar ratio of reactants	Product	Found (%) (calc.)	
			Sn	N
1	1:1	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(OC <sub>2</sub> H <sub>5</sub> ) [ON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ], b.p. 113-16°/1 mm; 27%	32.39 (32.46)	3.85 (3.83)
2	1:2	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn[ON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> , b.p. 103-6°/1 mm; 40%	29.27 (29.04)	6.83 (6.84)
3	1:1	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(OC <sub>3</sub> H <sub>7</sub> ) <sup>i</sup> [ON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ], b.p. 110°/0.5 mm; 35%	31.29 (31.33)	3.60 (3.64)
4	1:1	(CH <sub>3</sub> ) <sub>2</sub> Sn(OC <sub>3</sub> H <sub>7</sub> ) <sup>i</sup> [ON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ], insoluble and infusible; 99%	39.93 (40.05)	4.70 (4.73)
5	1:2	(CH <sub>3</sub> ) <sub>2</sub> Sn[ON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> , insoluble and in- fusible; 97%	36.72 (36.53)	8.60 (8.62)
6	1:1	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn(OC <sub>3</sub> H <sub>7</sub> ) <sup>i</sup> [ON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ], soluble in hot benzene and infusible; 98%	36.81 (36.64)	4.46 (4.33)
7	1:2	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn[ON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> , insoluble and in- fusible; 96%	33.98 (33.67)	7.93 (7.94)

Products 1-3 are yellow liquids and of 4-7 are white solids.

to  $\nu_{as}$  and  $\nu_s$  Sn-C respectively.  $\nu_{as}$  and  $\nu_s$  Sn-O appear around 572-560 and 475-466 cm<sup>-1</sup> respectively<sup>5</sup>.

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### Mn(II), Fe(II), Co(II), Ni(II) & Cu(II) Complexes with Benzoylhydrazine

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Benzoylhydrazine (BH) complexes of the types  $M(BH)_3SO_4 \cdot 3H_2O$  where M = Ni(II), Co(II) or Fe(II);  $M'(BH)_2SO_4 \cdot 2H_2O$  where M' = Cu(II) or Mn(II);  $M''(BH)_2Cl_2 \cdot 3H_2O$  where M'' = Ni(II), Co(II) or Mn(II) and  $Ni(BH)_3X$  where X = HgCl<sub>4</sub><sup>2-</sup>, HgCl<sub>2</sub>I<sub>2</sub><sup>2-</sup>, HgI<sub>4</sub><sup>2-</sup>, CdCl<sub>2</sub>I<sub>2</sub><sup>2-</sup> or CdI<sub>4</sub><sup>2-</sup> have been synthesized and characterized by analysis and physicochemical studies. The complexes are spin-free and octahedral where BH acts as a bidentate coordinating ligand. Molar extinction coefficient (ε) and approximate oscillator strength (f) of the electronic bands have been calculated for complexes of the type M''(BH)<sub>2</sub>Cl<sub>2</sub>. Sulphate group is bonded to metals directly or to BH by hydrogen bonding.

IN continuation of our work<sup>1,2</sup> on benzoylhydrazine (BH) complexes of Ti(IV) and some non-transition metal ions, the preparation and characteri-

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