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# Complexes of Diorganotin(IV) Dichlorides & Diacetates with Some Nitrogen Heterocyclics

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Addition compounds of dialkyltin dichloride and diacetate of the type, $R_2SnX_2$-L and $R_2SnX_2$-$L_2$ (where R = methyl, butyl; X = chloride, acetate and L = pyrrolidine, acridine, 1,10-phenanthroline, 2,2′-bipyridyl and piperazine) have been characterized on the basis of elemental analyses, molar conductance measurements and IR spectral studies. These adducts are non-electrolytes in nitromethane and nitrobenzene. Adducts of acridine appear to be trigonal-bipyramidal while those of piperazine have presumably an octahedral polymeric structure attained through ligand bridging. *cis*-Octahedral geometry for the phenanthroline and the 2,2-bipyridyl adducts, and *trans*-octahedral configuration for pyrrolidine adducts have been proposed.

In continuation of our earlier work on[1-3] group(IV) metal halide complexes with different nitrogen containing ligands, we present herein the results of study on the adducts of dimethyltin dichloride, dibutyltin dichloride and dibutyltin diacetate with pyrrolidine, piperazine, acridine, 1,10-phenanthroline and 2,2′-bipyridyl.

Dimethyltin dichloride (DMC), dibutyltin dichloride (DBC), dibutyltin diacetate (DBA), piperazine hexahydrate (Pz), acridine (Acr), pyrrolidine (Pyrr), phenanthroline (Phen) and 2,2′-bipyridyl were of standard quality and used without further purification. The solvents, ethanol, nitromethane, nitrobenzene and chloroform were distilled and dried by conventional methods.

### *Preparation of the complexes*

The ligand (0.002 mol) dissolved in ethanol was added to $R_2SnX_2$ (0.002 mol) (where X = chloride or acetate) in the same solvent. The adducts appeared instantaneously or on standing for a few days. They were washed three times with ethanol and dried *in vacuo* (Table 1).

The complexes studied in this work have a 1:1 stoichiometric (metal:ligand) ratio except for the pyrrolidine adducts which have a 1:2 ratio. The molar conductances of $10^{-3}$ *M* solutions in nitromethane and nitrobenzene exhibit their non-electrolytic nature ($0\text{-}3.0 \times 10^{-4}$ ohm$^{-1}$ cm$^2$ mol$^{-1}$).

Table 1—Analytical Data of Dialkyltin(IV) Dichloride and Diacetate Adducts

| Complexes (m.p., °C) | Found (Calc.), % | | | | |
|---|---|---|---|---|---|
| | C | H | N | Sn | Cl |
| DMC $(Pyrr)_2$ | 33.18 | 6.68 | 7.74 | 32.79 | 19.59 |
| (310) | (33.19) | (6.69) | (7.75) | (32.80) | (19.60) |
| DBC $(Pyrr)_2$ | 43.09 | 8.15 | 6.28 | 26.61 | 15.90 |
| (195) | (43.08) | (8.13) | (6.28) | (26.60) | (15.89) |
| DBA $(Pyrr)_2$ | 48.69 | 8.58 | 5.69 | 24.08 | — |
| (300) | (48.70) | (8.58) | (5.68) | (24.06) | |
| DMC (Pz) | 23.59 | 5.28 | 9.18 | 38.80 | 23.20 |
| (225) | (23.57) | (5.27) | (9.16) | (38.81) | (23.19) |
| DBC (Pz) | 36.98 | 7.26 | 7.19 | 30.42 | 18.19 |
| (105) | (36.96) | (7.24) | (7.18) | (30.44) | (18.18) |
| DBA (Pz) | 43.97 | 7.86 | 6.43 | 27.16 | — |
| (145) | (43.96) | (7.84) | (6.41) | (27.15) | |
| DMC (Acr) | 45.19 | 3.80 | 3.53 | 29.75 | 17.75 |
| (80) | (45.17) | (3.79) | (3.51) | (29.76) | (17.78) |
| DBC (Acr) | 52.20 | 5.60 | 2.89 | 24.54 | 14.67 |
| (85) | (52.22) | (5.63) | (2.90) | (24.57) | (14.68) |
| DBA (Acr) | 56.60 | 6.26 | 2.63 | 22.29 | — |
| (46) | (56.63) | (6.27) | (2.64) | (22.30) | |
| DMC (Phen) | 42.06 | 3.54 | 7.00 | 29.66 | 17.72 |
| (210) | (42.05) | (3.53) | (7.01) | (29.68) | (17.73) |
| DBC (Phen) | 49.67 | 5.41 | 5.77 | 24.50 | 14.62 |
| (170) | (49.66) | (5.41) | (5.79) | (24.52) | (14.65) |
| DBA (Phen) | 54.23 | 6.03 | 5.29 | 22.30 | — |
| (85) | (54.26) | (6.07) | (5.27) | (22.34) | |
| DMC (Bipy) | 38.34 | 3.76 | 7.42 | 31.55 | 18.85 |
| (55) | (38.35) | (3.75) | (7.45) | (31.58) | (18.87) |
| DBC (Bipy) | 47.01 | 5.69 | 6.05 | 25.81 | 15.40 |
| (165) | (47.00) | (5.70) | (6.09) | (25.80) | (15.41) |
| DBA (Bipy) | 52.11 | 6.35 | 5.53 | 23.41 | — |
| (50) | (52.10) | (6.36) | (5.52) | (23.40) | |

An absorption band (in cm$^{-1}$) at 3268 in the IR spectrum of pyrrolidine is due to $\nu$(N−H). Coordination of tin through the nitrogen atom of pyrrolidine results in the weakening of N−H bond with a consequent decrease[4] in $\nu$(N−H). The appearance of only one $\nu$(M-Cl) band at 330 is an indication of *trans* configuration since two closely associated (M-Cl) bands result for a *cis* octahedral compound[5,6]. Following the above criteria of Beattie and coworkers[7] based on the normal coordinate analysis, these compounds may be suggested to have a *trans* octahedral geometry.

Piperazine shows a tendency to form unstable compounds with group(IV) metal halides[1]. Dimethyltin dichloride, dibutyltin dichloride and dibutyltin diacetate form 1:2 complexes ($R_2SnX_2$:2Pz) with piperazine in solution (detected by conductometric titration), but they could not be isolated. However, the solid complexes of piperazine with the above alkyltin octahedral ligand arrangement is suggested in conformity with earlier reports[17,18].

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## References

1 (a) Maffii G, Testa E & Fusco R, *Sci*, **13** (1958) 629.

(b) Hassert G L, Poutsiava J W, Papadrianos D, Barke J C & Craver B N, *Toxicol & Appl Pharmacol*, **3** (1961) 726.

2 Ramalingam T, Deshmukh A A, Sattur P B, Seth U K & Naik S R, *J Indian chem Soc*, **58** (1981) 269.

3 Hockfelt B & Jonson A, *J mednl Chem*, **5** (1962) 247.

4 Hiroshik, Isao H & Shigekio O, *Zassokenkyn*, **8** (1969) 46; *Chem Abstr*, **73** (1970) 108544.

5 Vogel A I, *A text book of quantitative inorganic analysis* (The ELBS & Longman) 1961, 358, 389, 453, 480, 482, 486, 492, 532.

6 Sharma Y R, *Elementary organic absorption spectroscopy* (S Chand, New Delhi) 1980, 29.

7 Dyer J R, *Application of absorption spectroscopy to organic compounds* (Prentice Hall, New Jersey) 1965, 37.

8 Rao C N R, *Chemical applications of infrared spectroscopy* (Academic Press, New York & London) 1963.

9 Verma I K & Geetha C K, *Indian J Chem*, **16A** (1978) 352.

10 Singh J & Singh N B, *J inorg nucl Chem*, **40** (1978) 919.

11 Satpathy K C & Mahana T D, *J Indian chem Soc*, **56** (1979) 1173.

12 Satpathy K C, Mishra H P & Pradhan G C, *J Indian chem Soc*, **58** (1981) 844.

13 Satpathy K C, Mishra H P & Patel B N, *J Indian chem Soc*, **59** (1982) 40.

14 Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, London) 1968.

15 Benerjie V & Dey A K, *J Indian chem Soc*, **59** (1982) 991.

16 Ballhausen C J, *Introduction to ligand field theory* (McGraw Hill, New York) 1962, 245.

17 Ghose C & Poddar S N, *Indian J Chem*, **15A** (1977) 248.

18 Panda P K & Mohapatra B K, *J Indian chem Soc*, **57** (1980) 137.