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Synthesis and Characterization of Complexes of Non-transition Elements

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New complexes of bismuth and tin prepared from promethazine hydrochloride (PH), prochlorperazine dimaleate (PCPM) and isopropamide hydrochloride (IPPH) have been characterized by conductivity, spectroscopic and elemental analyses. The conductometric measurements in DMF, DMSO and acetonitrile solution indicate their non-electrolyte nature. TGA data show that Bi(III) complexes are thermally stable up to 135°C whereas Sn(II) complexes are thermally stable upto 230°C. The ligands behave as bidentate in all these complexes. The Bi(III) complexes are assigned octahedral structure while Sn(II) complexes square-planar geometry.

INTRODUCTION

The chemical literature provides information on the complexation of some metals with promethazine and prochlorperazine[1–6]. In the present communication the synthesis and characterization of Bi(III) and Sn(II) complexes with promethazine hydrochloride (PH), prochloroperazine dimaleate (PCPM) and isopropamide hydrochloride (IPPH) have been reported. The complexes are investigated by elemental analyses, conductance measurements, TGA as well as spectroscopic technique.

EXPERIMENTAL

All the chemicals used were of analytical grade. Solvents were used after distillation. Promethazine hydrochloride (British Pharamaceutical Laboratories, Bombay) prochlorperazine dimaleate (British Pharmaceutical Laboratories, Bombay) and isopropamide hydrochloride (Eskayef Ltd., Mysore) were received as gift samples and used as such.

Preparation of the complexes

25 mL of 0.1 M ethanolic solution of metal nitrate or chloride was slowly added to 50 mL of 0.01 M ethanolic solution of PH, PCPM and IPPH separately. The mixture was kept at room temperature for about 10 min and warmed at 60–80°C on a water bath for about 1 h. The solid complex formed was filtered, washed with cold ethanol and then with ether and dried over P_4O_{10} (yield 60–85%)).

Elemental analyses were done by conventional methods. Sulphur and chloride were estimated as $BaSO_4$ and AgCl respectively[7, 8]. Nitrogen content was estimated by Duma's method. Bi(III) and Sn(II) were determined by known method[8]. The results of the analysis are given in Table 1.

RESULTS AND DISCUSSION

All the complexes are pale yellow to dark yellow in colour and they are quite stable at room temperature. They can be stored for a long period. All the complexes are insoluble in water, benzene, toluene, carbon tetrachloride, chloroform, acetone, methanol and cold ethanol but soluble in THF, DMF, DMSO and acetonitrile. All the complexes have 1 : 1 stoichiometry $[BiL(H_2O)(NO_3)_3]$, $[SnLCl_2]$ where L is PH, PCPM and IPPH, which are bidentate ligands. Elemental analyses (Table 1) support this composition. The low molar conductance value (10–25 mhos mol^{-1} cm^{-2}) indicate that all the complexes are non-electrolytes.

The electronic spectra of Sn(II) complexes (Table 1) exhibit two bands at *ca.* 33069 and 37879 cm^{-1}. The Bi(III) complexes give three bands at *ca.* 27115, 29797 and 39432 cm^{-1}. The exact assignment of the bands is complicated because of the considerable overlap of the internal transitions of the ligand with s^2–sp transitions of the central ions.

The heterocyclic nitrogen atom attached to the alkyl group gives characteristic band[9] in the region 2800–2975 cm^{-1}. The stretching frequency of the heterocyclic nitrogen atom attached to the alkyl group in the free ligands PH and PCPM showed the band repectively at 2840–2960 and 2860–2960 cm^{-1}. These bands are shifted to higher frequency region (10–20 cm^{-1}) in the IR specra when PH and PCPM indulge in complexation, thus suggesting that heterocyclic nitrogen atom attached to the alkyl group is the site of coordination. The tertiary nitrogen atom combined with halogen present in the molecule of many organic compounds gives rise to a broad band[9] generally between 2300–2500 cm^{-1}. The stretching frequency of the tertiary nitrogen atom in the ligands PH, PCPM and IPPH completely disappears in the IR spectra of the complexes, thereby indicating that the tertiary nitrogen is also the site of interaction. The C—S stretching frequency of PH and PCPM appears in the same region, 740–760 cm^{-1}, in its complexes, thus confirming that sulphhur atom was not involved in the coordination. In the ligand IPPH, the primary amide gives two bands at 3300 cm^{-1} and 1570 cm^{-1} corresponding to N—H stretching and deformation respectively. These bands have totally disappeared, thereby indicating that the coordination takes place through its nitrogen atom. The new bands at 420–440 cm^{-1}, 350–375 cm^{-1} are assigned to $\nu_{M—N}$ and $\nu_{M—X}$, respectively[10].

TGA curves indicate that Bi(III) complexes are generally stable upto 120–135°C where as Sn(II) complexes are stable upto 210–230°C. Afterwards the oxidation of organic substance begins. It has been found that concurrent with the decomposition and oxidation of organic substance, some volatilization reaction also takes place. The final product obtained in each case has been chemically identified as a pure oxide. On the basis of percentage loss in weight, the thermal decomposition for the complexes can be formulated.

TABLE 1

ELEMENTAL ANALYSES, MOLAR CONDUCTANCE AND ELECTRONIC SPECTRA OF THE COMPLEXES

Complex	Yield (%)	m.p. (°C)	Elemental analysis % Found (Calcd.)				Molar conductance[a] mol^{-1} cm^{-2}	Electronic spectra[b] cm^{-1}
			M	N	Cl	S		
[$Bi(C_{17}H_{20}N_2S)(H_2O)(NO_3)_3$]	78	110–113	29.01 (29.98)	9.86 (10.04)	—	4.35 (4.60)	18.06	26882 29797 40783
[$Sn(C_{17}H_{20}N_2S)Cl_2$]	65	203–206	24.84 (25.06)	5.80 (5.91)	14.75 (14.97)	6.40 (6.77)	11.35	33069 38941
[$Bi(C_{20}H_{24}ClN_3S)(H_2O)(NO_3)_3$]	67	115–118	26.16 (26.57)	11.04 (10.68)	4.25 (4.51)	3.87 (4.08)	15.50	27397 29412 39432
[$Sn(C_{20}H_{24}ClN_3S)Cl_2$]	61	110–112	20.83 (21.08)	7.68 (7.46)	19.01 (18.89)	5.25 (5.69)	13.50	32175 37879
[$Bi(C_{22}H_{30}N_2O)(H_2O)(NO_3)_3$]	84	114–116	27.65 (27.83)	9.50 (9.32)	—	—	20.40	27115 29868 37594
[$Sn(C_{22}H_{30}N_2O)Cl_2$]	80	215–217	22.18 (22.50)	5.20 (5.31)	13.08 (13.44)	—	10.80	33245 38461

[a] 1.0×10^{-3} M solution in DMF/DMSO/CH_3CN.

[b] 1.0×10^{-3} M or 10^{-4}M solution in acetonitrile.

$$[BiL(H_2O)(NO_3)_3] \rightarrow BiL(NO_3)_3 \rightarrow Bi(NO_3)_3 \rightarrow Bi_2O_3$$

$$[SnLCl_2] \rightarrow SnCl_2 \rightarrow SnO$$

On the basis of the above data Bi(III) compounds have been tentatively proposed octahedral geometry while Sn(II) compounds square planar structure.

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