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NOTE

Coordination Polymers Involving Organotin Derivatives as Lewis Acids

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Nine complexes of α,α′-dipyridyldisulphide with some diorganotin derivatives possessing the general formulae $[RSnL-]_nX_{2n}$ where R = phenyl, benzyl, n-butyl and $X = Cl^-$, ClO_4^- and NO_3^- have been prepared and assigned polymeric octahedral structures on the basis of IR and ^1H NMR spectral studies. The ligand behaves as tetradentate in nature coordinating through its both sulphur and nitrogen atoms but steric factors prevent the coordination of all four donors to the same tin atom and hence polymeric octahedral structures are suggested in which the organic group is bonded axially to the tin atom.

A large number of polymeric complexes in which nitrogen and sulphur atoms behave as donors and transition metal ions as Lewis acids, have been reported in the literature. The present communication describes the synthesis and characterisation of some organometallic polymers involving the title ligand as Lewis base and organotin moieties as Lewis acids.

All the chemicals used were AR grade and the solvents used were chemically pure. The polymeric complexes were prepared in the following steps.

1. Preparation of α-mercaptopyridine

α-Chloropyridine (10 ml) and thiourea (6 gms) in 40 cc of ethanol (95%) were refluxed for 2 hrs. 30 cc of conc. NH_4OH was added after cooling the reaction mixture. The mixture was kept at room temperature for five days. Distillation of ethanol under reduced pressure, and acidification of the distillate to a pH 4.0 with glacial acetic acid gave a product which was extracted with chloroform, washed with water dried over anhydrous sodium sulphate and distilled under reduced pressure to remove chloroform. This on cooling gave yellow crystals of α-mercaptopyridine. (M.pt. = 124°C; Yield 26%).

2. Preparation of α,α′-Dipyridyl Disulphide

α-Mercaptopyridine (0.5 g) was dissolved in 4.5 ml of 25% sodium

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hydroxide solution and iodine (1.2 g) dissolved in 25 ml of 10% potassium iodine solution was added dropwise. At the first appearance of reddish colour, the solid which had separated out gradually was filtered and washed with water. The crude disulphide was recrystallized from pet. ether (M.pt = 57°C, Yield = 80%).

3. (a) Synthesis of Organotin Derivatives

Commercially available diphenyl and dibutyltin dichlorides were used, while dibenzyltin dichloride was prepared by reported method[1].

Dinitrate and diperchlorate derivatives were prepared by adding diphenyltindichloride (0.1 mol) in methanol (20 ml) to silver nitrate/perchlorate (0.2 mol) also in methanol (20 ml). After stirring the mixture at room temperature for 4 hrs the solid silver chloride was filtered off and the resulting solutions were used as such.

(b) Synthesis of Polymeric Complexes $[R_2SnL-]_nX_{2n}$

α,α'-Dipyridyl disulphide (0.01 mole) in absolute dry methanol was added to the appropriate organotin derivatives (0.01 mol) also in dry methanol (50 ml) and the solution was stirred at room temperature for 10–15 hrs. After distilling off methanol the polymeric complexes were crystallised out using either dry petroleum ether or 1 : 1 petroleum ether-acetone mixture. The resulting polymers were dried and characterised.

On the basis of the analytical data (Table 1) the molecular formulae of the complexes are $[-R_2Sn(L)-]_nX_{2n}$ where R = phenyl, benzyl or n-butyl and $X = Cl^-$, NO_3^- or ClO_4^-. The conductance measurements in DMF correspond to the electrolytic nature of the complexes.

In the IR spectra of the free ligand a few bands of measurable intensities are observed at 1600–1440 cm^{-1} which are the C=C and C=N mixed ring stretches and skeletal in plane vibrations[2]. The bands at 3000–3100 cm^{-1} are due to the C–H ring stretching whereas the C–H out-of-plane bending vibrations occur at 705 cm^{-1}. Either all or some of these bands appear at slightly higher positions in the spectra of the complexes, which is indicative of the coordination through the pyridine nitrogen[3]. The S–S-stretching vibration appears[4] as a very weak band at 500–400 cm^{-1} and the band due to ν(CS) vibration is seen at 940 cm^{-1} in the IR spectra of the free ligand. This band in the complexes disappears completely and a new band is observed in its place at 725 cm^{-1} which is indicative of the formation of polymeric structure through the involvement of both the sulphur atoms, because the band at 940 cm^{-1} normally splits into two components both with negative shifts if only one S- atom is coordinated[5]. The bands at 425 ± 5 and 370 ± 5 cm^{-1} in the complexes are attributed to the Sn–C bond of the organometallic moieties coordinated to the ligands[6]. The bands at 511 cm^{-1}, 1405 cm^{-1} and 1110 and 630 cm^{-1} are due to the uninegative uncoordinated chloride, nitrate and perchlorate ions respectively[7–9].

TABLE 1

ANALYTICAL DATA OF THE COMPLEXES

Sl.	Complexes	Sn	% Found (Calcd.) C	H	N
1.	$C_{10}N_2S_2H_8$		5.35 (5.45)	3.82 (3.63)	12.34 (12.73)
2.	$[Ph_2Sn(L)-]_nCl_{2n}$	20.82 (21.09)	46.64 (46.81)	3.41 (3.19)	4.56 (4.97)
3.	$[Ph_2Sn(L)-]_n(ClO_4)_{2n}$	16.94 (17.22)	38.76 (38.22)	2.85 (2.60)	4.25 (4.05)
4.	$[Ph_2Sn(L)-]_n(NO_3)_{2n}$	19.56 (19.29)	42.22 (42.79)	2.64 (2.92)	9.32 (9.08)
5.	$[Bz_2Sn(L)-]_nCl_{2n}$	20.34 (20.10)	48.15 (48.65)	3.56 (3.72)	4.42 (4.73)
6.	$[Bz_2Sn(L)-]_n(ClO_4)_{2n}$	16.84 (16.55)	39.23 (40.05)	3.24 (3.05)	3.63 (3.89)
7.	$[Bz_2Sn(L)-]_n(NO_3)_{2n}$	18.92 (18.45)	44.12 (44.65)	3.82 (3.41)	8.51 (8.68)
8.	$[Bu_2Sn(L)-]_nCl_{2n}$	22.25 (22.75)	41.38 (41.30)	4.45 (4.97)	5.82 (5.35)
9.	$[Bu_2Sn(L)-]_n(ClO_4)_{2n}$	18.63 (18.28)	33.46 (33.23)	3.81 (4.00)	4.68 (4.29)
10.	$[Bu_2Sn(L)-]_n(NO_3)_{2n}$	20.18 (20.65)	37.12 (37.50)	4.72 (4.51)	9.29 (9.72)

In the ^1H NMR spectra of the complexes of the diphenyl tin derivatives, a doublet at 6.4–6.6 δ and a triplet at 7.4–7.6 δ is due to the phenyl ring protons of the ligand part of the complexes whereas the doublet at 8.4–8.6 δ and triplet at 7.7–8.2 δ is due to the phenyl ring protons of the diphenyl tin part of the complexes. In ^1H NMR spectra of the complexes of dibenzyl tin derivatives in addition to the above signal an additional singlet is observed at 2.3 δ which is due to the additional $-CH_2$ protons. The ^1H NMR spectra of the complexes of dibutyltin derivatives show doublet at 6.5–6.7 δ and triplet at 7.2–7.6 δ attributed to the phenyl ring protons whereas a triplet at 1.2–1.6 δ is due to the CH_3 protons of n-butyl group. A broad multiplet at 2.20–2.50 δ is probably a result of the merging together of all the $-CH_2$ protons of n-butyl group.

From the above discussion, we suggest that the ligands in these complexes behave as tetradentate in nature coordinating through all its nitrogen and sulphur atoms. The polymeric structures for the complexes are a result of the steric factors which prevent the coordination of all the donors of one ligand to the same Lewis acid and the octahedral structures are proposed for the complexes.

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