Asian Journal of Chemistry Vol. 6, No. 1 (1994), 52–55

Synthesis and Characterisation of Some New Diorganotin Derivatives of *p*-Nitrobenzoyl Chloride

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The complexes of diorganotin(IV) with *p*-nitrobenzoylchloride with general formulae $R_2SnL_2X_2$ and $R_2SnL_2Y_2$, (where R = C_6H_5 or C_4H_9, L = *p*-nitrobenzoylchloride, X = Cl^-, SCN^- and Y = ClO_4^-, BF_4^-, NO_3^-) have been reported. The complexes are proposed to have octahedral or tetrahedral geometries on the basis of analytical data, molar conductance, ^1H NMR and IR spectroscopic studies.

INTRODUCTION

The diorganotin derivatives of *p*-nitrobenzoylchloride are expected to have either a coordinate or a covalent bond between the two moieties. In the present report, the diorganotin derivatives of *p*-nitrobenzoylchloride are synthesized to investigate the above two possibilities.

EXPERIMENTAL

All the reactions were carried out under dry nitrogen atomosphere. Tin was estimated by standard method[1]. The molar conductance (10^{-3} molar solution in DMF) was measured on a Toshniwal direct reading conductivity bridge using dip type conductivity cell. The IR spectral studies were determined on a Perkin Elmer-577 spectrophotometer in KBr/CsI in the range of 4000–200 cm^{-1} and ^1H NMR spectra were recorded on Perkin Elmer R-32, 90 MHz spectrometer in DMSO-d_6 with TMS as an internal reference. Carbon, hydrogen and nitrogen were estimated microanalytically.

Diphenyltindichloride and dibutyltindichloride were obtained from E. Merck and all the chemicals used were of AR grade. The solvents were distilled and dried by standard methods before use.

p-Nitrobenzoylchloride was prepared by reported method[2]. The other organotin salts *viz.* R_2SnX_2 (R = Ph, Bu; X = SCN^-) and R_2SnY_2 (R = Ph, Bu; Y = ClO_4^-, BF_4^-, NO_3^-) were prepared by simple metathetical reactions of Ph_2SnCl_2 or Bu_2SnCl_2 with AgX or AgY/NaX or NaY in methanol.

Preparation of Complexes

To a solution of 0.01 mole of appropriate organotin salt in methanol was added 0.02 mole of *p*-nitrobenzoylchloride and the solution was refluxed for 10 hrs over a steam bath and then filtered. The filtrate was concentrated to get the crude product, which was recrystallised with absolute ethanol, washed with petroleum ether and dried over P_4O_{10}. The purity of the compounds was checked by qualitative TLC techniques.

RESULTS AND DISCUSSION

The analytical and conductance data of the complexes (Table 1) suggest the general formulae of complexes to be $R_2SnL_2X_2$ and $R_2SnL_2Y_2$, where R = Ph or Bu; X = Cl^-, SCN^- and Y = ClO_4^-, BF_4^-, NO_3^-. Thus smaller anions like Cl^- or SCN^-, which can be favourably coordinated, form non-electrolyte complexes, while the bigger anions like ClO_4^-, BF_4^- and NO_3^- do not coordinate probably due to their bulky nature and give 1 : 2 electrolytes.

TABLE 1

ANALYTICAL AND MOLAR CONDUCTANCE DATA OF COMPLEXES

S. No.	Complexes	Melting points (°C)	Analysis % Found (Calcd.)				Λ_M† (mole^{-1} cm^2 ohm^{-1})
			Sn	C	N	H	
1.	$[Ph_2SnL_2Cl_2]$	178	15.30 (15.42)	44.15 (44.27)	2.51 (2.55)	2.52 (2.55)	22.15
2.	$[Ph_2SnL_2](ClO_4)_2^*$	—	—	—	—	—	145.70
3.	$[Ph_2SnL_2(SCN)_2]$	195	14.35 (14.49)	44.65 (44.81)	7.40 (7.46)	2.35 (2.40)	18.29
4.	$[Ph_2SnL_2](BF_4)_2^*$	—	—	—	—	—	162.24
5.	$[Ph_2SnL_2](NO_3)_2$	153	13.95 (14.34)	41.03 (41.17)	7.35 (7.39)	2.31 (2.37)	152.14
6.	$[Bu_2SnL_2Cl_2]$	187	16.20 (16.35)	39.65 (39.71)	4.18 (4.21)	3.80 (3.91)	21.86
7.	$[Bu_2SnL_2](ClO_4)_2^*$	—	—	—	—	—	142.90
8.	$[Bu_2SnL_2(SCN)_2]$	215	15.15 (15.31)	40.50 (40.58)	7.81 (7.89)	3.59 (3.66)	19.28
9.	$[Bu_2SnL_2](BF_4)_2^*$	—	—	—	—	—	160.20
10.	$[Bu_2SnL_2](NO_3)_2$	162	15.05 (15.14)	36.58 (36.78)	7.75 (7.80)	3.55 (3.62)	149.92

Ph = C_6H_5, Bu = C_4H_9 *Complexes explosive in nature

L = *p*-Nitrobenzoylchloride †In DMF-solvent.

In the IR spectra of free ligand (L) a few sharp bands are seen in the range 1600–1450 cm^{-1} due to phenyl groups. The formation of *p*-nitrobenzoylchloride from *p*-nitrobenzoic acid is evidenced by the absence of the band due to OH stretching frequency at about 3000 cm^{-1} and the presence of a strong band near 710 cm^{-1} due to C–Cl stretch. Bands due to C=O were found at 1755 and 1700 cm^{-1}, due to NO_2 at 1530, 1455 and 850 cm^{-1} and due to C–N stretch at 1315 cm^{-1}.

In the IR spectra of all the complexes, the following bands are observed which are indicative of the formation of complexes by virtue of the coordination to the tin atom through one of the oxygen atoms of the nitro group.

(i) The bands at 1755, 1700 and 710 cm^{-1} due to COCl group do not show any significant shift, thus giving an evidence in support of non-coordination through COCl group.

(ii) The aromatic vibrations are seen in complexes in the same range (1600–1450 cm^{-1}) but are shifted slightly to higher frequency, thus indicating the formation of a coordinate bond.

(iii) The nitro group vibrations also show a lower shift in their positions and appear at 1515 ± 10 cm^{-1} and 1440 ± 10 cm^{-1} suggesting the coordination through nitro group[8].

(iv) Band due to C–N stretch also shows a lower shifting and is observed at 1300 ± 10 cm^{-1}, indicating the coordination through nitro group.

(v) A weak band at 530 ± 5 cm^{-1}, which is absent in the spectra of the free ligand, may be attributed to Sn–O stretch[3] which is probably a result of the coordination through the oxygen atom of the organometallic moiety.

In the spectra of complexes 1 to 5 a weak band at 290 ± 5 cm^{-1} and in the spectra of complexes 6 to 10 a relatively stronger band at 515 ± 5 cm^{-1} may be attributed to Sn–C stretching vibration as a result of covalent bonds between tin and phenyl, tin and butyl groups respectively. In the spectra of chloro complexes sharp bands at 350 ± 10, 410 ± 10 and 505 ± 10 cm^{-1} are observed which correspond to coordinated chloride ions[4–6], whereas thiocyanate complexes show bands at 2000 ± 5 cm^{-1} due to C=N, at 450 ± 10 cm^{-1} due to N–C–S and at 810 ± 5 cm^{-1} due to CS stretching vibrations of coordinated thiocyanate ion[9–11]. In the spectra of perchlorate complexes the bands at 1120 ± 5 cm^{-1} and 650 ± 5 cm^{-1} show the presence of uninegative uncoordinated perchlorate groups. The bands at 1015 ± 5 and 530 ± 5 cm^{-1} in the spectra of tetrafluoroborate complexes also appear due to presence of uninegative tetrafluoroborate ions which are uncoordinated in nature[12,13]. The presence of ionic nitrate in their complexes is evidenced by the appearence of bands at 1360, 810 and 230 cm^{-1}.

The ^1H NMR spectral data of the complexes are in full accordance with the mode of bonding discussed above. In the ^1H NMR spectra of the ligand L, only phenyl protons appear as doublet in the range 8.50–8.90 ppm (4H). In the ^1H NMR spectra of complexes (where R=Ph) the signals due to the phenyl ring protons of the ligand and the diphenyltin moieties mergre together and are observed in the range 6.70–8.30 ppm as two broad multiplets at 8.30–7.10 ppm (8H) and 6.95–6.70 ppm (9H). The upfield shift and broadening of the signals is an indication of coordination of the ligand to tin atom through oxygen atom of the nitro group. In dibutyltin complexes, the phenyl ring protons are observed at 6.70–8.30 ppm (8H) slightly shifted to upfield due to coordination. In addition to this, an additional multiplet at 1.80 ppm (8H) due to CH_2 protons and a triplet at 1.40 ppm (6H) due to CH_3 protons are also observed.

Thus on the basis of the above discussion an octahedral geometry may be assigned to chloro and thiocyanato complexes in which the anions are coordinated to tin atom of organometallic moiety. The perchlorate and tetrafluoroborate complexes are assigned to have a tetrahedral structure in which two positions of tetrahedron are occupied by two phenyl or butyl groups and the remaining two positions are occupied by nitro groups, being coordinated through one of the oxygen atoms whereas the anions remain outside the coordination sphere owing to their bulky nature.

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(*Received*: 29 June 1992; *Accepted*: 8 March 1993) AJC–5978