Asian Journal of Chemistry Vol. 7, No. 3 (1995), 571—575

Organotin Complexes of 2-Substituted Benzimidazoles

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Some novel complexes of organo-tin derivatives with biologically important benzimidazoles have been synthesized and characterized on the basis of elemental analysis, ultraviolet and IR spectral studies. These derivatives were prepared by reacting R_2SnX_2 (where X = OR′, Cl; R and R′ = CH_3, C_2H_5, C_6H_5) with 2-(*o*-hydroxy phenyl) benzimidazoles and 2-(*o*-amino phenyl) benzimidazoles in 1 : 2 and 1 : 1 molar ratios respectively in dry chloroform and benzene.

INTRODUCTION

The coordination compounds of organotin derivatives with several organic ligands have been extensively investigated[1–7]. These derivatives have aroused special interest particularly in context of their biological[8,9] and pharmacological[10,11] activities. The chelates of dialkyl/diaryl tin(IV) with 8-hydroxyquinoline (8-HQ) have been reported by several workers[12–16] and were found to possess appreciable fungicidal[17] and bactericidal[17] properties. According to Lane[18] 2-(*o*-hydroxy phenyl) benzimidazole behaves in a manner similar to 8-HQ in its coordination and chelating properties. In the present paper we report the synthesis and characterisation of the complexes formed by the reaction of R_2SnX_2 with 2-(*o*-hydroxy phenyl) benzimidazole and 2-(*o*-amino phenyl) benzimidazole derivatives according to the equations (1) and (2).

$$R_2SnX_2 + 2LH \longrightarrow R_2SnL_2 + 2HX \qquad (1)$$

where R = methyl, ethyl, butyl and phenyl
LH = 2-(*o*-hydroxy phenyl) benzimidazole
X = methoxide or isopropoxide
HX represents the corresponding protonated species.

$$R_2SnX_2 + L \longrightarrow R_2SnX_2{\cdot}L \qquad (2)$$

where R = mentioned in (1);
X = Cl
L = 2-(*o*-amino phenyl) benzimidazole.

EXPERIMENTAL

Preparation of the ligands

(i) *2-(o-hydroxy phenyl) benzimidazoles* [2-(*o*-OH phbzIm)]: Equimolar quantities of *o*-phenylene diamine (OPD) and salicylic acid were mixed with sufficient quantity of polyphosphoric acid (PPA) and heated to 250°C in round-bottom flask and the product isolated by the method described by Heins *et al.*[19]

(ii) *2-(o-amino phenyl) benzimidazoles* [2-(*o*-NH_2 ph bzIm)]: Similarly equimolar quantity of OPD and anthranilic acid (1 : 1) were mixed to PPA to give a paste and heated to 250°C in round-bottom flask; the product was isolated by the method described by Heins *et al.*[19]

Synthesis of metal complexes

(i) *Dialkyl/aryl tin diphenoxide benzimidazoles:* the solution of dimethyl tin diisopropoxide (0.002 M) and 2-(*o*-OH ph bzIm) (0.004 M) were mixed thoroughly in 1 : 2 molar ratio in dry $CHCl_3$ and refluxed for $\frac{1}{2}$ h. Isopropanol liberated during the reaction was removed azeotropically.

Similarly the solution of each of the diethyl, dibutyl, diphenyl tin dimethoxide (0.001 M) in dry $CHCl_3$ was added to a solution of 2-(*o*-OH ph bzIm) (0.002 M) in 1 : 2 molar ratio, and refluxed for 3 h on oil bath. Methanol liberated during the reaction was removed azeotropically. The products thus obtained were filtered, well washed with ether and dried under reduced pressure.

(ii) *Dialkyl/aryl tin 2-(o-amino phenyl) benzimidazoles*: Warm solution of each of $(CH_3)_2SnCl_2$, $(C_2H_5)_2SnCl_2$, $(C_4H_9)_2SnCl_2$ (0.001 M) in dry $CHCl_3$ was added to a solution of 2-(*o*-NH_2 ph bzlm) (0.001 M) both in dry $CHCl_3$, and stirred thoroughly for $\frac{1}{2}$ h. The solvent was removed under pressure and after that kept unstirred for 6 h. The products thus obtained were filtered, well washed with ether and dried. Similarly warm solutions of $(C_6H_5)_2SnCl_2$ (0.001 M) and 2-(*o*-NH_2 ph bzlm) (0.001 M), both in dry $CHCl_3$, were refluxed for 2 h and kept unstirred for 2 days. The product was obtained in a similar manner as described above.

RESULTS AND DISCUSSION

The results of the elemental analysis and the composition of the complexes synthesized are recorded in Table-1.

TABLE-1
(A) COLOUR AND COMPOSITION OF DIALKYL/DIARYL DIPHENOXY BENZIMIDAZOLE Sn(IV) DERIVATIVES

S. No	Compound/Colour	Elemental Analysis % Found (Calcd.)			
		C	H	N	Sn
(I)	$(CH_3)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (Yellowish)	58.68 (59.29)	4.12 (4.26)	9.90 (9.87)	20.70 (20.92)
(II)	$(C_2H_5)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (Yellow)	59.97 (60.50)	4.28 (474)	9.44 (9.41)	19.98 (19.93)
(III)	$(C_4H_9)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (yellow)	61.89 (62.69)	5.23 (5.57)	8.41 (8.60)	18.13 (18.22)
(IV)	$(C_6H_5)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (Dirty white)	65.55 (66.01)	4.18 (4.08)	8.21 (8.10)	17.08 (17.16)

(B) COLOUR AND COMPOSITION OF DIALKYL/DIARYL TIN 2-(*o*-AMINO PHENYL) BENZIMIDAZOLE DERIVATIVES

S. No.	Compound/Colour	Elemental Analysis % Found (Calcd.)			
		C	H	N	Sn
(V)	$(CH_3)_2SnCl_2(NH_2C_6H_4{\cdot}C_7H_5N_2)$ (Yellowish)	41.86 (42.00)	3.87 (3.99)	9.77 (9.79)	27.69 (27.69)
(VI)	$(C_2H_5)_2SnCl_2(NH_2C_6H_4{\cdot}C_7H_5N_2)$ (Yellowish)	44.23 (44.68)	4.56 (4.63)	9.16 (9.19)	25.93 (25.97)
(VII)	$(C_4H_9)_2SnCl_2(NH_2C_6H_4{\cdot}C_7H_5N_2)$ (Yellowish)	48.89 (49.16)	5.57 (5.69)	8.18 (8.18)	23.15 (23.13)
(VIII)	$(C_6H_5)_2SnCl_2(NH_2C_6H_4{\cdot}C_7H_5N_2)$ (Yellowish)	53.98 (54.29)	3.79 (3.82)	7.59 (7.59)	21.47 (21.46)

UV spectral data of dialkyl/aryl tin diphenoxide benzimidazole: The ligand 2-(*o*-OH ph bzIm) absorbs at 319 mμ in ethanol. The above mentioned complex in chloroform exhibit a broad absorption band in the region 260–350 mμ. The band consists of 2λ maxima of nearly equal intensity therefore it can be regarded as a split broad band having maxima around 295–300 mμ and 330 mμ. The former is attributed to the absorption band due to benzene ring and associated with vibrational effects on $\pi \rightarrow \pi^*$ transitions; the latter band around 330 mμ in case of complex derivatives is attributed to electronic transitions located in chelate ring (Table-2).

TABLE-2

UV SPECTRAL DATA IN $CHCl_3$ AT 1×10^4 M CONCENTRATION

S. No.	Compound/Colour	λ_{max}	Molar ext.	Coeff.
(I)	$(CH_3)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (Yellowidh)	290–330	1.26×10^4	1.50×10^4
(II)	$(C_2H_5)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (Yellow)	295–325	1.10×10^4	1.45×10^4
(III)	$(C_4H_9)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (yellow)	295–330	1.23×10^4	1.35×10^4
(IV)	$(C_6H_5)_2Sn(OC_6H_5{\cdot}C_7H_5N_2)_2$ (Dirty white)	300–330	1.6×10^4	1.70×10^4

The UV spectrum of the corresponding oxinates $(CH_3)_2Sn(OX)_2$ in ethanol was compared with the spectrum of the above mentioned complex. The absorption peak at 320 mμ in the spectra of 8-HQ shifts to 360–380 mμ on chelation with dialkyl tin[12]. In view of similarity between the coordination behaviour of 8-HQ and 2(*o*-OH ph bzIm), it can be assumed that the absorption at 330 mμ in case of the later is due to the chelation of ligand with dialkyl tin(IV). The formation of chelate structure also gets support from IR spectral measurements.

IR spectral data: IR spectrum (KBr) of the ligand 2-(*o*-OH ph bzIm) shows following prominent peaks in the range 3500–3200 cm^{-1}, 3150–3050 cm^{-1} and

1410 cm^{-1}. These peaks have been assigned to ν(O—H), ν(N—H) and δ(N—H) vibrations in the ligand respectively (Table 3).

TABLE-3
(A) INFRA-RED SPECTRA (cm^{-1}) OF DIALKYL/DIARYL DIPHENOXY BENZIMIDAZOLE Sn(IV) DERIVATIVES

Compound	ν(OH)	δ(OH)	ν_{asym}(NH)	δ(NH)	ν_{asym}(Sn–C)	ν_{asym}(Sn–O)
(I)	3325 s	1250 m	3300 b	1425 w	535 s	515 s
(II)	—	—	3360 b	1425 w	540 s	510 s
(III)	—	—	—	1415 w	545 s	515 s
(IV)	—	—	3444 b	1420 w	530 s	510 s

(B) INFRA-RED SPECTRA (cm^{-1}) OF DIALKYL/DIARYL TIN 2-AMINO PHENYL BENZIMIDAZOL DERIVATIVES

Compound	ν_{asym}(NH)	δ(NH)	ν_{asym}(Sn–C)	ν(Sn–C_6H_5)	ν_{asym}(Sn–Cl)	ν_{asym}(Sn–Cl)
(V)	3380–3370 s	1410 w	520 m	—	355–350 s	347–338 w
(VI)	—	1410 w	520 m	—	356–352 w	345–340 w
(VII)	3360 b–3150 w	1410 w	520 m	—	—	—
(VIII)	3450 b–3090 s	1410 w	515 s	1070 s	365–360 w	357–348 w

The spectra of dialkyl/aryl tin diphenoxide benzimidazole revealed the similarity with the spectra of the ligand except a few conspicuous changes. The peak due to ν(OH) vibration disappears and ν(N—H) is shifted to slightly higher frequency range of 3200–3050 cm^{-1}. In view of above observations, it seems that the phenolic proton is released as shown in eq. (1) and the organotin forms bond with phenolic oxygen atom of the ligand. The position of absorption band due to NH group present in the ligand remains unaffected as a result of the above bonding. The absorption band around 521–510 cm^{-1} may be assigned to ν_{asym}(Sn—O) stretching vibration. Appearance of this new band and absence of OH band of the ligand can be a proof for the formation of chelate ring through displacement of phenolic proton and coordination with tertiary nitrogen atom of the benzimidazole ring.

The presence of absorption band at 545–530 cm^{-1} can be assigned to (Sn—C) asymmetric stretching mode. The Sn—C symmetric stretching vibration present in the IR spectra of tetrahedral organotin derivatives (R_2SnX_2) and which occurs 50–30 cm^{-1} below ν_{asym}(Sn—C) was found to be absent in the spectra of these complexes. The above observation is in accordance with the previous observations[13, 20–22]. The presence of only absorption frequency due to ν_{asym}(Sn—C) mode and absence of its symmetric frequency indicates that both the alkyl/aryl groups are in *trans* position and supports an octahedral chelate structure for these complex derivatives.

Similarly the presence of only ν_{asym}(Sn—C) mode around 545–530 cm^{-1} in the IR spectrum of dichoro dialkylaryl tin 2(*o*-amino phenyl) benzimidazole leads us to believe that the stereochemistry of R_2SnCl_2 undergoes a change from tetrahedral geometry around the organotin moiety.

There are two new bands at 355–350 cm^{-1} and 347–338 cm^{-1} in the spectrum of complex derivative. These bands are associated with asymmetric and symmetric stretching of (Sn—Cl) bonds respectively. It shows that chlorine of R_2SnCl_2 moiety does not react with amino and imino groups of the ligand, as confirmed by the presence of ν_{asym}(NH) (3200–3050 cm^{-1}) and δ NH (1410 cm^{-1}) bands in the spectra of these derivatives. The non-elimination of HCl as shown in equation (2) and formation of addition product is also supportive of the above conjecture.

In view of above observations, the octahedral structure is suggested for these complex derivatives with both the alkyl groups in *trans* positions and chlorines occupying *cis* positions.

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(*Received*: 22 August 1994; *Accepted*: 2 January 1995) AJC-911