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SCHIFF BASE COMPLEXES OF ORGANOTIN(IV): INFRARED AND MÖSSBAUER STUDIES ON THE ADDITION COMPLEXES OF DIORGANOTIN DICHLORIDES WITH *N*-ALKYL(ARYL)SALICYLIDENEIMINES

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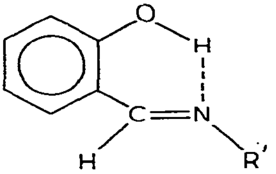
Summary

Fourteen new addition complexes of the type $R_2SnCl_2 \cdot 2\ HOC_6H_4CH{=}NR'$ have been synthesized by the reactions of diorganotin dichlorides, R_2SnCl_2 (where R = Me, Et, n-Bu and Ph), with *N*-alkyl(aryl)salicylideneimines, $HOC_6H_4CH{=}NR'$ (where R′ = Me, Et, n-Bu and Ph), in non-aqueous solvents. The complexes are non-electrolytes in nitrobenzene. Infrared and Mössbauer spectroscopic studies indicate an all-*trans* octahedral geometry for the complexes.

Introduction

During the last few years, the addition complexes of organotin(IV) halides with ONNO bifunctional tetradentate β-ketoamine (1—3) and Schiff base (4—6) ligands have attracted much attention. However, the addition complexes of organotin(IV) halides with monofunctional bidentate salicylideneimines, having ON donor atoms, have been very little investigated [7,8]. Following a preliminary communication on their synthesis [9], we report below our detailed studies on the addition complexes of diorganotin dichlorides with following *N*-alkyl)aryl)salicyclideneimines:



(R′ = Me, Et, n-Bu and Ph)

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Results and discussion

Diorganotin dichlorides react with *N*-alkyl(aryl)salicylideneimines to form 1/2 adducts according to the following equation:

$R_2SnCl_2 + 2\ HOC_6H_4CH{=}NR' \rightarrow R_2SnCl_2 \cdot 2\ HOC_6H_4CH{=}NR'$

(R = R′ = Me, Et, n-Bu and Ph)

When the above reactions were carried out in 1/1 or even 1/4 molar ratios, only the 1/2 adducts could be isolated, leaving half of the chloride or the ligand unreacted in the filtrate. The adducts are yellow coloured microcrystalline solids, insoluble in solvents like n-hexane, benzene, chloroform and carbon tetrachloride but soluble in alcohols, dioxane and dimethylformamide. In some case the adducts were recrystallized from methanol. The addition complexes of dimethyltin and diethyltin dichlorides with *N*-alkylsalicylideneimines showed marked thermal stability and could be sublimed unchanged under reduced pressure (Table 1). In their thermal stability these adducts resemble the 1/2 molecular adduct of stannic chloride with dimethyl sulphoxide [10].

The molar conductances of the adducts in nitrobenzene were of the order of 0.80—2.88 ohm^{-1} cm^2 mol^{-1} (molar conductance expected for 1/1 and 1/2 electrolytes [11] are 25—30 and 44—60 ohm^{-1} cm^2 mol^{-1} respectively), indicating clearly that the adducts are essentially non-electrolytes, and both the chlorine atoms bonded to tin remain in the coordination sphere.

In the infrared spectra of the ligands as well as their adducts with diorganotin dichlorides, no band is observed in the region 3650—3590 cm^{-1} attributable to the stretching vibration of the free phenolic hydroxyl group [12], indicating that the ring formed by intra-molecular hydrogen bond in the ligands is retained in the adducts [5,7]. Weak broad bands are, however, observed in the spectra of the ligands in the region 3200—2600 cm^{-1} which may be attributed to the stretching vibration of the intramolecularly hydrogen bonded hydroxyl group [13,14] of the type OH···N, overlapping with the ν(C—H) in the region 3100—2800 cm^{-1}; the lower frequency bands amongst these appear to be shifted upwards by about 200 cm^{-1} in the adducts.

A strong band due to C=N stretching vibration appears in the region 1640—1615 cm^{-1} in the infrared spectra of the ligands [15,16]. However, this band is shifted slightly towards higher frequencies (1660—1620 cm^{-1}) in the spectra of the addition complexes (Table 2). An increase in ν(C=N) by 15—35 cm^{-1} in the adducts of organotin(IV) chlorides with Schiff base ligands, has been reported earlier [4,7] also. A strong sharp band appearing at ~1285 cm^{-1} in the spectra of these ligands as well as their adducts may be attributed to the phenolic C—O stretching vibration in accord with earlier assignments [7,16,17].

In order to further elucidate the structure, the infrared spectra of the adducts of dimethyltin and diphenyltin dichlorides were also studied in the 650—200 cm^{-1} region. In the spectra of adducts of dimethyltin [1,18—21] and diphenyltin [19,22] dichlorides, sharp strong bands due to ν_{as}(Sn—C) were observed at ~575 and ~295 cm^{-1}, respectively, while the bands due to ν_s(Sn—C) could not be detected. Both the asymmetric and symmetric tin—chlorine stretching vibrations, which appear at ~360 and ~356 cm^{-1} in the

TABLE 1

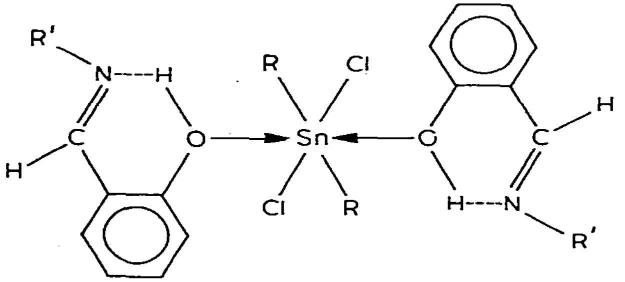
ANALYSES AND PROPERTIES OF THE ADDITION COMPLEXES

Addition Complex	Analyses found (calcd.) (%)			M.p. (°C)	Sublimation temp. (°C/mmHg) (% yield of sublimate)	Molar conductance (ohm^{-1} cm^2 mol^{-1})
	Sn	Cl	N			
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNMe$	24.39 (24.22)	14.31 (14.46)	5.61 (5.71)	152	120/0.5 (97)	1.27
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	22.99 (22.92)	13.51 (13.69)	5.28 (5.40)	136	105/0.1 (96)	1.44
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNBu$-n	20.42 (20.67)	12.42 (12.34)	4.79 (4.87)	96	95/0.5 (96)	1.68
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	19.11 (19.33)	11.36 (11.54)	4.43 (4.56)	128		1.34
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNMe$	22.99 (22.92)	13.60 (13.69)	5.31 (5.40)	138	120/0.5 (95)	1.78
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	21.66 (21.74)	12.84 (12.98)	5.00 (5.13)	92	90/0.5 (96)	2.60
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNBu$-n	19.81 (19.72)	11.72 (11.77)	4.60 (4.65)	65	80/0.3 (95)	1.80
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	18.58 (18.49)	11.26 (11.04)	4.25 (4.36)	103		1.46
$(n\text{-}Bu)_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	19.47 (19.72)	11.68 (11.77)	4.61 (4.65)	48		0.90
$(n\text{-}Bu)_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	16.88 (17.00)	10.06 (10.15)	4.10 (4.01)	55		0.80
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNMe$	19.41 (19.33)	11.45 (11.54)	4.46 (4.56)	195		2.34
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	18.40 (18.49)	11.10 (11.04)	4.40 (4.36)	173		2.88
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNBu$-n	17.08 (17.00)	10.03 (10.15)	3.96 (4.01)	119		2.60
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	15.97 (16.08)	9.51 (9.60)	3.61 (3.79)	186		2.50

spectra of diorganotin dichlorides [18,22], are lowerd by ~100 cm^{-1} on complex formation. Appearance of only a single band in the region 250—230 cm^{-1} and the absence of any multiplicity of the bands (expected for *cis*-compounds), indicates that the two chlorine atoms must be in a *trans* disposition [1,19].

In the infrared spectra of the adducts there is a new, strong band in the 460—408 cm^{-1} region. This may tentatively be assigned to either $\nu(O \rightarrow Sn)$ [20,21] or $\nu(N \rightarrow Sn)$ [1,23], but an unambiguous choice between the two is not possible. However, in view of the oxygen-bonded [5] nature of *N,N'*-ethylenebis(salicylideneimine), as revealed by X-ray crystallography, it is likely that these ligands are also coordinating through the phenolic oxygen atoms, and the band is probably attributable to $\nu(O \rightarrow Sn)$.

In view of the above discussion, it appears that these adducts may also have all-*trans* structures as depicted below:



Mössbauer spectra of the adducts of dimethyltin dichloride have also been measured at liquid nitrogen temperature. Fitzsimmons et al. [24] as well as Parish and Platt [25] have reported that the quadrupole splittings for the octahedral *trans*-R_2SnX_4 structures are twice as large as for *cis*-R_2SnX_4 geometries. Parish and Platt [26] have further suggested that in organotin(IV) compounds, the isomer shift also is a function of the stereochemistry of the molecule. In octahedral R_2SnX_4 and $R_2SnX_2L_2$ systems, it has been found that for comparable R, X and L ligands, the majority of *trans*-complexes have isomer shifts greater than 1.2 mm sec^{-1} whereas very few *cis*-complexes exhibit isomer shifts

TABLE 2

IMPORTANT INFRARED FREQUENCIES OF THE ADDITION COMPLEXES

Addition complex	$\nu(C{=}N)$ (cm^{-1})	$\nu(C—O)$ (cm^{-1})	$\nu_{as}(Sn—C)$ (cm^{-1})	$\nu(O \rightarrow Sn)$ (cm^{-1})	$\nu_{as}(Sn—Cl)$ (cm^{-1})
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNMe$	1653vs	1290vs	575vs	416vs	242s
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	1650vs	1280vs	578vs	458m	232s
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNBu$-n	1650vs	1285s	576vs	436s	240s
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	1630vs	1280m	576vs		240s
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNMe$	1660vs	1285vs			
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	1645vs	1280vs			
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNBu$-n	1645vs	1280s			
$Et_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	1630vs	1285s			
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNMe$	1655vs	1290vs	296s	424vs	242s
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	1650vs	1280vs	298s	408m	224s
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNBu$-n	1650vs	1280vs	292m	424vs	242s
$Ph_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	1620vs	1295vs	290m		228s

TABLE 3

MÖSSBAUER PARAMETERS OF THE ADDUCTS OF DIMETHYLTIN DICHLORIDE [a]

Adduct	Quadrupole splitting, ΔE (mm sec^{-1})	Isomer shift, δ (mm sec^{-1})	Line widths	
			Γ_1 (mm sec^{-1})	Γ_2 (mm sec^{-1})
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNMe$	4.30	1.44	1.10	1.06
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNEt$	4.44	1.52	1.13	1.13
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNBu\text{-}n$	4.23	1.41	1.06	1.13
$Me_2SnCl_2 \cdot 2\ HOC_6H_4CHNPh$	4.30	1.37	0.92	0.92

[a] The accuracy for all these parameters is ±0.06 mm sec^{-1}.

greater than 1.0 mm sec^{-1}. The quadrupole splittings and isomer shifts for these new adducts (Table 3) fall in the ranges 4.23—4.44 mm sec^{-1} and 1.37—1.52 mm sec^{-1} respectively. These large quadrupole splittings and isomer shifts confirm that in the new complexes the two methyl groups attached to tin occupy *trans*-positions.

Experimental

Special precautions were taken to exclude moisture. n-Hexane, benzene, methanol and nitrobenzene were dried by standard methods. Diorganotin dichlorides (M&T chemicals) were purified by sublimation or distillation under reduced pressure.

The Schiff bases were synthesized by literature methods [15,16]. The addition complexes were synthesized as previously described [9]. Analytical data on these complexes are summarized in Table 1.

Tin was estimated as SnO_2 [27]. Chlorine and nitrogen were estimated by Volhard's and Kjeldahl's methods respectively.

Conductance measurements were made at room temperature using a Tesla RLC conductivity bridge with a cell having cell constant of 0.78 cm^{-1}.

The IR spectra of the ligands and the adducts were recorded in the region 4000—400 cm^{-1} on a Perkin—Elmer 621 instrument either as neat liquid films and Nujol mulls in KBr plates or in KBr pellets. The spectra of the ligands and their adducts with dimethyltin and diphenyltin dichlorides were recorded in the 650—200 cm^{-1} region also on a Beckman IR 12 spectrophotometer as neat liquid films and as Nujol mulls in polythene plates.

Mössbauer spectra of the addition complexes of dimethyltin dichloride were recorded at 78 K. The isomer shifts were measured relative to barium stannate at room temperature.

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