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Schiff Base Complexes of Organotin(IV): Infrared and Mössbauer Studies on the Addition Complexes of Mono- and Di-organotin(IV) Chlorides with N-Alkyl(aryl)-2-hydroxyacetophenylideneimines

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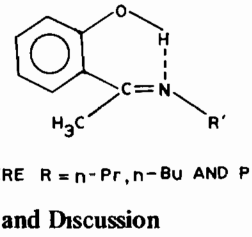
Eighteen new addition complexes of the type $RSnCl_3\cdot 2HOC_6H_4CMe\ NR'$ (R = Et, n-Bu and Ph, R' = n-Pr, n-Bu and Ph) and $R_2SnCl_2\cdot 2HOC_6H_4$-CMe NR' (R = Me, Et, n-Bu and Ph, R' = n-Pr, n-Bu and Ph) have been synthesized and characterized by molar conductance, infrared and Mossbauer measurements

Introduction

In spite of a considerable interest in the adducts of organotin(IV) halides with ONNO tetradentate β-ketoamine [1–3] and Schiff base [4–6] ligands, complexation reactions of these moieties with bidentate Schiff base ligands have received little attention We have recently described [7] the synthesis of adducts of diorganotin dichlorides with N-alkyl-(aryl)salicylideneimines Srivastava and Chauhan [8, 9] have also reported that mono- and di-organotin-(IV) chlorides form 1 2 adducts with N-aryl-salicylideneimines and -2-hydroxy-1-naphthylideneimines In this paper, we wish to report the results of our studies on the adducts of mono- and di-organotin(IV) chlorides with following N-alkyl(aryl)-2-hydroxyacetophenylideneimines



(WHERE R = n-Pr, n-Bu AND Ph)

Results and Discussion

Irrespective of the molar ratio of the reactants, reactions of $RSnCl_3$ and R_2SnCl_2 with the ligands in n-hexane yield 1 2 adducts, which are either precipitated or can be crystallized from the reaction mixture The adducts are straw to yellow coloured solids which are insoluble in solvents like n-hexane, benzene, chloroform and carbon tetrachloride but dissolve in alcohols, dioxane and dimethylformamide The molar conductances of these adducts in nitrobenzene solution were found to be in the range of 1 2–4 2 $ohm^{-1}\ cm^2\ mol^{-1}$, indicating their non-electrolytic nature [10] In view of the propensity of tin to attain six coordination in the adducts of organotin(IV) halides [11], the ligands appear to act as monodentate species in these complexes, making tin atoms only 6-coordinate (Table I)

In the infrared spectra of the ligands and the complexes (Table II), the band due to the stretching vibrations of the free phenolic hydroxyl group has not been observed It appears, therefore, that due to strong intramolecular hydrogen bonding, the frequency of the absorption band is lowered considerably and its intensity also is very much diminished making it difficult to identify this band in the spectra [12, 13] The C=N stretching vibration appears at ~1620 cm^{-1} in the spectra of the ligands whereas it splits up into two bands appearing at 1640–1620 cm^{-1} and ~1600 cm^{-1} in the spectra of the adducts It appears that the higher frequency band of the above two is mainly due to νC=N while the lower frequency band arises due to coupling of νC=N with aromatic C=C stretching vibration which appears at ~1575 cm^{-1} as a shoulder in the spectra of the ligands [16] Srivastava and Chauhan [8, 9] have suggested that νC=N increases by 15–35 cm^{-1} as a result of coordination through nitrogen atoms However, on the contrary, Randaccio [5] has determined the structure of the adduct of dimethyltin dichloride with N,N'-ethylenebis (salicylideneimmine) and it has been observed that the ligand coordinates through the phenolic oxygen atoms, although an increase in νC=N by ~15 cm^{-1} was also observed in the infrared spectra of the adduct [4, 6]

A strong band appearing at ~1280 cm^{-1} has been attributed to the stretching vibration of the phenolic

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TABLE I. Analyses, Melting Points and Molar Conductances (in Nitrobenzene) of the Addition Complexes.

S. No.	Adduct (% yield)	Analyses (%)			Melting Point (°C)	Molar Conductance (ohm^{-1} cm^{2} mol^{-1})
		Sn Found (calcd.)	Cl Found (calcd.)	N Found (calcd.)		
1.	Me$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPr-n (93)	20.57 (20.67)	12.36 (12.35)	4.74 (4.88)	175d	1.56
2.	Me$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NBu-n (91)	19.63 (19.71)	11.74 (11.77)	4.53 (4.65)	97	1.95
3.	Me$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPh (74)	18.57 (18.48)	10.98 (11.04)	4.30 (4.36)	83	1.25
4.	Et$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPr-n (91)	19.76 (19.71)	11.70 (11.77)	4.57 (4.65)	112	1.27
5.	Et$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NBu-n (86)	18.75 (18.84)	11.44 (11.25)	4.31 (4.44)	92	2.34
6.	(n-Bu)$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPr-n (85)	18.12 (18.03)	10.70 (10.76)	4.17 (4.25)	75	1.19
7.	Ph$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPr-n (90)	17.12 (17.00)	10.01 (10.15)	4.07 (4.01)	140	3.00
8.	Ph$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NBu-n (94)	16.43 (16.35)	9.73 (9.86)	3.80 (3.86)	135	3.40
9.	Ph$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPh (85)	15.63 (15.49)	9.13 (9.25)	3.59 (3.66)	118	2.50
10.	EtSnCl$_3$·2HOC$_6$H$_4$CMe:NPr-n (96)	19.65 (19.76)	17.80 (17.70)	4.70 (4.66)	155	3.00
11.	EtSnCl$_3$·2HOC$_6$H$_4$CMe:NBu-n (93)	18.77 (18.64)	16.59 (16.70)	4.27 (4.40)	165	3.12
12.	EtSnCl$_3$·2HOC$_6$H$_4$CMe:NPh (91)	17.62 (17.54)	15.81 (15.71)	4.08 (4.14)	159	2.17
13.	n-BuSnCl$_3$·2HOC$_6$H$_4$CMe:NPr-n (91)	18.49 (18.64)	16.85 (16.70)	4.30 (4.40)	102	2.29
14.	n-BuSnCl$_3$·2HOC$_6$H$_4$CMe:NBu-n (91)	17.78 (17.85)	15.92 (16.00)	4.33 (4.21)	138	3.12
15.	n-BuSnCl$_3$·2HOC$_6$H$_4$CMe:NPh (89)	16.95 (16.85)	15.21 (15.10)	3.88 (3.97)	105	4.16
16.	PhSnCl$_3$·2HOC$_6$H$_4$CMe:NPr-n (94)	18.00 (18.07)	16.10 (16.19)	4.17 (4.26)	265d	2.60
17.	PhSnCl$_3$·2HOC$_6$H$_4$CMe:NBu-n (95)	17.31 (17.38)	15.57 (15.53)	4.01 (4.09)	259d	3.12
18.	PhSnCl$_3$·2HOC$_6$H$_4$CMe:NPh (95)	16.42 (16.37)	14.60 (14.68)	3.75 (3.86)	270d	3.95

TABLE II. Important Infrared Absorption Frequencies of the Addition Complexes.

S. No.	Adduct	ν(C=N) (cm^{-1})	ν(C–O) (cm^{-1})	ν_{as}(Sn–C) (cm^{-1})	ν(O $\rightarrow$ Sn) (cm^{-1})	ν_{as}(Sn–Cl) (cm^{-1})
1.	Me$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPr-n	1620sh	1265s	574vs	416vs	240s
2.	Me$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NBu-n	1625s	1270s	574vs	408s	246s
3.	Me$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPh	1610sh	1270s	574vs	416vs	248s
4.	Ph$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPr-n	1620s	1275s	290s	412vs	240s
5.	Ph$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NBu-n	1620vs	1265sb	290s	408vs	242s
6.	Ph$_2$SnCl$_2$·2HOC$_6$H$_4$CMe:NPh	1620sh	1265w	296m	390vs	236s
7.	EtSnCl$_3$·2HOC$_6$H$_4$CMe:NPr-n	1620vs	1275s	–	–	–
8.	EtSnCl$_3$·2HOC$_6$H$_4$CMe:NBu-n	1630sh	1280vs	–	–	–

(continued on facing page)

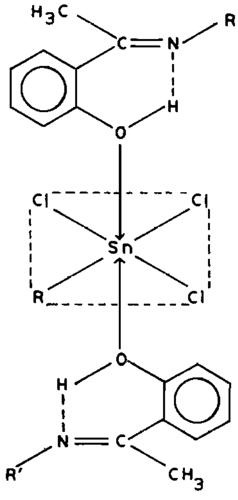
TABLE II. *(continued)*

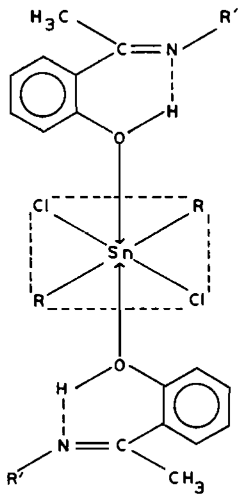
S. No.	Adduct	ν(C=N) (cm^{-1})	ν(C–O) (cm^{-1})	ν_{as}(Sn–C) (cm^{-1})	ν(O → Sn) (cm^{-1})	ν_{as}(Sn–Cl) (cm^{-1})
9.	$EtSnCl_3 \cdot 2HOC_6H_4CMe{:}NPh$	1600vs	1280vs	–	–	–
10.	$n\text{-}BuSnCl_3 \cdot 2HOC_6H_4CMe{:}NPr\text{-}n$	1635vs	1265m	–	–	–
11.	$n\text{-}BuSnCl_3 \cdot 2HOC_6H_4CMe{:}NBu\text{-}n$	1635vs	1265s	–	–	–
12.	$n\text{-}BuSnCl_3 \cdot 2HOC_6H_4CMe{:}NPh$	1610s	1270s	–	–	–
13.	$PhSnCl_3 \cdot 2HOC_6H_4CMe{:}NPr\text{-}n$	1630vs	1270s	–	–	–
14.	$PhSnCl_3 \cdot 2HOC_6H_4CMe{:}NBu\text{-}n$	1630vs	1270s	–	–	–

C–O group of the Schiff bases derived from salicylaldehyde [17]. Therefore, a strong band appearing at ~1315 cm^{-1} in the spectra of these ligands may tentatively be assigned to the ν(C–O) in these ligands. The ν(C–O) at this position may also couple with O–H deformation vibration [16]. In the spectra of the adducts, two bands in the regions 1335–1310 cm^{-1} and 1280–1260 cm^{-1} have been observed. Following the above discussion, the lower and higher energy bands may be attributed to the phenolic ν(C–O) and to the O–H deformation vibrations respectively.

In the sepctra of the adducts of dimethyltin and diphenyltin dichlorides, the absorption bands due to tin–carbon symmetric stretching vibration could not be detected. However, the tin–carbon asymmetric stretching vibrations appeared at ~575 cm^{-1} and ~290 cm^{-1} respectively. These observations tend to indicate that in these octahedral adducts the two methyl [1, 18–22] or two phenyl [8, 18, 20, 22, 23] groups attached to tin occupy *trans* positions.

Symmetric and asymmetric tin–chlorine stretching vibrations occur at ~356 and ~360 cm^{-1} respectively in the spectra of diorganotin dichlorides [24, 25]. A further increase in the coordination number of tin decreases ν(Sn–Cl) [26], as expected by the increase of the electronic charge located on the tin atom which would give rise to an increase of percent ionic character of tin–chlorine bonds. A multiplicity of ν(Sn–Cl$_2$) bands is also observed for octahedral adducts of diorganotin dichlorides if the two chlorine atoms occupy the *cis*-position [18, 23, 27]. The strong single band detected near 240 cm^{-1} in the infrared spectra of the adducts of dimethyltin and diphenyltin dichlorides attributable to ν_{as}(Sn–Cl) would suggest a *trans* > SnCl$_2$ geometry also. Therefore, the remaining *trans*-position may be occupied by the two donor atoms of the ligand molecules and a strong new band appearing in the region 420–408 cm^{-1} in the spectra of these complexes may be attributed to ν(O → Sn) [19–21]. In view of the above observations, the adducts may be assigned the following plausible structures:





Further support at least for the structures of the latter type proposed above for the adducts of diorganotin dichlorides may be drawn from the Mössbauer data (Table III). The large quadrupole splittings (4.003–4.148 mm sec^{-1}) observed for the three adducts of dimethyltin dichloride are consistent with *trans*-R$_2$ (R = Me) structures [28] proposed above. It has been previously mentioned [29, 30] that hexa-

TABLE III. Mössbauer Parameters of the Adducts of Dimethyltin Dichloride at 78 K.

S. No.	Adduct	Quadrupole Splitting, ΔE (mm sec^{-1})	Isomer shift, δ (mm sec^{-1})
1.	$Me_2SnCl_2 \cdot 2HOC_6H_4CMe{:}NPr\text{-}n$	4.148	1.248
2.	$Me_2SnCl_2 \cdot 2HOC_6H_4CMe{:}NBu\text{-}n$	4.003	1.271
3.	$Me_2SnCl_2 \cdot 2HOC_6H_4CMe{:}NPh$	4.003	1.320

coordinate tin compounds with two *trans*-alkyl or -aryl groups exhibit quadrupole splitting of ~4.0 mm sec^{-1}. Conversely, if the two organic groups occupy *cis*-positions, quadrupole splittings of ~2.0 mm sec^{-1} are observed. Parish and Platt [31] have reported that in octahedral R_2SnX_4 and $R_2SnX_2 \cdot 2L$ systems, the majority of *trans*-R_2 complexes have isomer shifts greater than 1.2 mm sec^{-1} whereas very few *cis*-R_2 compounds exhibit isomer shifts greater than 1.0 mm sec^{-1}.

Experimental

Special precautions were taken to exclude moisture. The solvents were dried by usual methods. Organotin(IV) chlorides (M & T Chemicals) were purified by sublimation or distillation under reduced pressure.

The Schiff bases were synthesized by the condensation of 2-hydroxyacetophenone with primary amines in refluxing benzene. These were further purified by distillation under reduced pressure. The addition complexes were synthesized as previously described [7]. Analytical data on these complexes are summarized in Table I.

Tin was estimated as SnO_2 [32]. 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 0.78 cm^{-1}.

Infrared spectra of the ligands and the adducts were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 621 instrument and on a Carl-Zeiss Jena instrument either in KBr pellets or as nujol mulls in KBr plates. The spectra of the ligands and their adducts with dimethyltin and diphenyltin dichlorides in the region 650–200 cm^{-1} were measured on a Beckman IR 12 spectrophotometer as nujol mulls in polythene plates.

Mössbauer spectra of the adducts of dimethyltin dichloride were measured at 78 °K using a constant acceleration spectrometer fitted with a Ba $^{119m}SnO_3$ source. The chemical isomer shifts are given relative to a room temperature source of $CaSnO_3$.

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