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Tin(IV) Complexes of *Schiff* Bases Derived from Salicylaldehyde and Aminoalcohols

By

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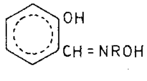
1 : 1 and 1 : 2 molar reactions of tin(IV) chloride with the *Schiff* bases, HO—$C_6H_4CH:NROH$ [where R = —$(CH_2)_2$—, —CH_2—, —$CH(CH_3)$—, —$(CH_2)_3$—, and —$CH(C_2H_5)CH_2$—] have been studied in different stoichiometric ratios and derivatives of the type $SnCl_4(SBH_2)$ and $SnCl_4(SBH_2)_2$ (where SBH_2 represents the *Schiff* base molecule) have been isolated. These have been characterised by elemental analysis, conductivity measurements and I.R. spectral studies.

Introduction

A few derivatives of tin(IV) chloride with the *Schiff* bases have been reported[1–5]. In earlier communications[6–8] from these laboratories, reactions of tin(IV) chloride with the *Schiff* bases derived from the condensation of benzaldehyde, o-hydroxyacetophenone or pentane-2,4-dione with aminoalcohols have been reported and several new derivatives isolated for the first time. In the present paper we wish



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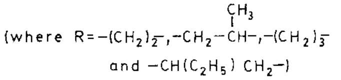

(where $R = -(CH_2)_2-, -CH_2-\overset{CH_3}{\overset{|}{C}H}-, -(CH_2)_3-$ and $-CH(C_2H_5)CH_2-$)

to report the preparation and properties of tin(IV) complexes with the *Schiff* bases derived from salicylaldehyde and aminoalcohols such

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as 2-amino-1-ethanol, 1-amino-2-propanol, 3-amino-1-propanol and 2-amino-1-butanol. These *Schiff* bases having the donor system HO—N—OH may be structurally represented by the general formula (I). They have not been studied so far.

Experimental

All reactions were carried out under strictly anhydrous conditions. Benzene (BDH) was first refluxed over sodium wire for several hours and then distilled azeotropically with ethanol. $SnCl_4$ (Riedel) was kept over copper turnings and redistilled before use. Dimethylformamide (BDH) was purified as described earlier[6]. The middle fraction boiling at 55 ± 1 °C/35 mm was collected and stored in blackened and stoppered pyrex flasks. The specific conductivity of the solvent was found to be 0.5–1.5 × $\times 10^7$ ohm^{-1} cm^{-1} at 25 ± 1 °C.

Table 1. *Physical Properties of the Schiff Bases*

Schiff Base*	State and M.P. (°C)	B.P. (°C/mm)
Salicylidene-2-hydroxy-ethylamine ($C_9H_{11}NO_2$)	Yellow viscous liquid	138/1.0
Salicylidene-2-hydroxy-1-propylamine ($C_{10}H_{13}NO_2$)	Yellow solid (63–65)	136/1.0
Salicylidene-3-hydroxy-1-propylamine ($C_{10}H_{13}NO_2$)	Yellow liquid	152–153/1.5–1.6
Salicylidene-1-hydroxy-2-butylamine ($C_{11}H_{15}NO_2$)	Red liquid	125–126/0.5–0.6

* Analyses (CH, N) were consistent with the formulas given.

Preparation of Schiff Bases

The *Schiff* bases were prepared by refluxing salicylaldehyde with amino-alcohols (molar ratio 1 : 1) in presence of benzene for several hours, followed by the removal of water/benzene azeotrope. These were distilled before use and their characteristics are recorded in Table 1.

Preparation of Tin(IV) Complexes

$SnCl_4$ (1 : 1 and 1 : 2 molar ratios) was dissolved in benzene and the calculated amount of the Schiff base was slowly added with constant shaking. An exothermic reaction took place and the solid compound separated out immediately. It was repeatedly washed with benzene and the products dried under reduced pressure. These have been found to be insoluble in

Table 2. *Synthesis and Characteristics of Tin(IV) Schiff Base Complexes*

S. No.	$SnCl_4$, (g)	*Schiff* base, (g)	Molar ratio	Compound, yield (g) nature	Analysis (%)			Molar conductance (ohm^{-1} cm^2 mol^{-1})
					Sn Found (Calcd)	Cl Found (Calcd)	N Found (Calcd)	
1.	1.92	$C_9H_{11}NO_2$ 1.02	1 : 1	$SnCl_4(C_9H_{11}NO_2)$ (2.84), Yellow solid	27.23 (27.89)	32.53 (33.36)	3.15 (3.28)	8.22
2.	0.60	$C_9H_{11}NO_2$ 0.76	1 : 2	$SnCl_4(C_9H_{11}NO_2)_2$ (1.32), Yellow Solid	20.43 (20.09)	24.83 (24.04)	4.68 (4.74)	7.88
3.	1.05	$C_{10}H_{13}NO_2$ 0.93	1 : 1	$SnCl_4(C_{10}H_{13}NO_2)$ (1.95), Yellow solid	26.71 (27.00)	32.56 (32.29)	3.00 (3.18)	8.31
4.	0.84	$C_{10}H_{13}NO_2$ 1.15	1 : 2	$SnCl_4(C_{10}H_{13}NO_2)_2$ (1.99), Yellow solid	19.56 (19.19)	23.05 (22.95)	4.35 (4.52)	8.60
5.	1.54	$C_{10}H_{13}NO_2$ 1.06	1 : 1	$SnCl_4(C_{10}H_{13}NO_2)$ (2.60), Yellow solid	26.14 (27.00)	32.19 (32.29)	3.09 (3.18)	7.63
6.	0.64	$C_{10}H_{13}NO_2$ 0.89	1 : 2	$SnCl_4(C_{10}H_{13}NO_2)_2$ (1.48), Yellow solid	18.69 (19.19)	23.14 (22.95)	4.38 (4.52)	7.78
7.	1.79	$C_{11}H_{15}NO_2$ 1.33	1 : 1	$SnCl_4(C_{11}H_{15}NO_2)$ (3.06), Yellow solid	25.45 (26.16)	31.65 (31.30)	2.95 (3.08)	8.13
8.	1.44	$C_{11}H_{15}NO_2$ 2.13	1 : 2	$SnCl_4(C_{11}H_{15}NO_2)_2$ (3.55), Yellow solid	18.13 (18.35)	22.09 (21.96)	4.20 (4.33)	8.60

most of the common organic solvents but soluble in *DMF*. The details of their analyses, physical properties and molar conductance are reported in Table 2.

Analytical Methods and Physical Measurements

Tin was estimated gravimetrically as tin oxide. Chlorine was determined as AgCl, and nitrogen by *Kjeldahl*'s method.

Conductance measurements were made using a Tesla RLC bridge, with a cell having cell constant 0.74 cm^{-1}.

The infrared spectra of the ligands and the complexes as nujol mulls were recorded on Perkin Elmer 337 grating I.R. Spectrophotometer in the range, 4000–700 cm^{-1}.

Results and Discussion

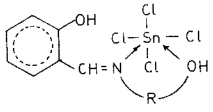
All the ligands have been shown to form 1 : 1 and 1 : 2 complexes, $SnCl_4 \cdot SBH_2$ and $SnCl_4 \cdot (SBH_2)_2$ respectively. Reactions in 1 : 3 and other higher molar ratios have been found to yield $SnCl_4 \cdot (SBH_2)_2$ type of derivatives only.

Their limited solubilities in common organic solvents, however, did not permit the determination of their molecular weights. The molar conductance values as determined in *DMF* at $10^{-3}M$ concentration and 25 ± 1 °C fall in the range 7.63–8.60 $ohm^{-1}\, cm^2\, mol^{-1}$ (Table 2) indicating that these derivatives behave as nonelectrolytes in *DMF*.

Coordination of the azomethine nitrogen to the tin atom is indicated by the shift of ν C=N frequency towards the higher side[1, 5–7]. In the IR spectra of *Schiff* bases, a strong band due to ν C=N appears at 1630 ± 5 cm^{-1}, whereas in the tin complexes this band is observed at 1645 ± 5 cm^{-1}. As the *Schiff* bases possess the functional group NOH and in the case of only nitrogen coordinating to the metal atom, the 1 : 1 complex will be pentacoordinated. However, hexacoordinated complexes in the case of tin(IV) have been reported to be more stable. *Kogan* et al.[1] have shown the formation of 1 : 2 complex only between tin(IV) chloride and the *Schiff* bases of salicylaldehyde and aromatic amines. In these cases, coordination of nitrogen to the metal has been suggested giving an octahedral geometry to the complex and the phenolic OH does not coordinate.

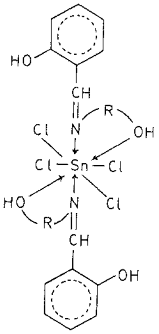
A similar hexacoordinated environment for tin(IV) can be postulated in the derivatives synthesized during the course of the present investigation. This can only be possible, if the oxygen of the alcoholic group may also coordinate to the metal atom forming a Sn ← O band. This Sn ← O band has been reported to occur at 410–385 cm^{-1} in the I.R. spectra of tin(IV) complexes with salicylaldehyde[9]. However, due to lack of facilities of recording the spectra in the lower region, this could not be observed in these complexes.

Thus in the $SnCl_4 \cdot SBH_2$ type of complexes a coordination number of six with an octahedral geometry can be indicated (II).



(II)

Further, in the $SnCl_4 \cdot (SBH_2)_2$ type of derivatives, the central metal atom may probably be octacoordinated[6–8, 10–13] and can be represented by the following structure (III).



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