

Synthesis and Characterization of Monochloro and Bis-Complexes of Tin(II) with Various Schiff Bases Containing 'O' and 'N' Donor Atoms

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Abstract: Some new and novel complexes of tin(II) of types $[(Cl)Sn(S.B.)]$ and $[Sn(S.B.)_2]$ [where S.B. = Schiff bases, salicylidene-4-methyl-1-aminobenzene (p-smab), salicylidene-3-nitro-1-aminobenzene (snab), salicylidene-1-aminobenzene (sab), and salicylidene-2-methyl-1-aminobenzene (o-smab)] have been prepared by the interactions of anhydrous $SnCl_2$ with sodium salts of Schiff bases in 1:1 and 1:2 molar ratio(s), respectively, in the presence of THF-benzene mixture. All these complexes are soluble in common organic solvents such as methanol, ethanol, chloroform, DMF, DMSO etc. and are characterized by elemental analysis and spectral (Infrared, Electronic, 1H -NMR and FAB-mass) studies.

Introduction

Due to the pronounced catalytic¹ and biological activities² of tin(II) complexes and favourable environmental and toxicological properties, research interest in this area continues to be pursued actively and due to these observations we undertake the synthesis and characterization of Schiff base complexes of tin(II) with the view that the newly synthesised complexes may find use as bioactive material.

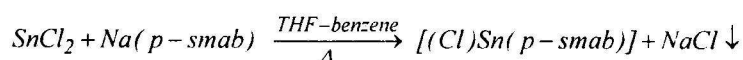
Experimental

Synthesis of Ligands:

The ligands, salicylidene-4-methyl-1-aminobenzene (p-smab)¹, salicylidene-3-nitro-1-aminobenzene (snab)², salicylidene-1-aminobenzene (sab)³ and salicylidene-2-methyl-1-aminobenzene (o-smab)^{4,5} were synthesised according to previously established literature methods.

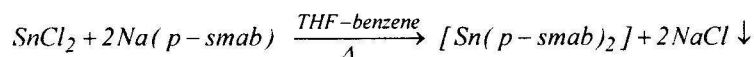
Synthesis of Complexes:

(I) Synthesis of monochloro complexes of tin(II) containing Schiff bases of the type [(Cl)Sn(p-smab)]. To a suspension/solution (THF~20 ml + MeOH ~20 ml) of anhydrous SnCl_2 (0.3g, 1.58 mmol) a methanolic solution of Na(p-smab) (0.349g, 1.58 mmol) was added. The reaction mixture was stirred and then refluxed for ~5 hrs, during which time the colour of the solution was changed from light yellow to dark yellow. The precipitated NaCl was removed by filtration and filtrate was concentrated by distillation and dried in vacuo to afford yellow powdered solid [(Cl)Sn(p-smab)] [0.37g, 65%] (m.p. 146-148°C). Analysis : %Cl, 9.3 (9.7); %Sn, 31.80(32.89)



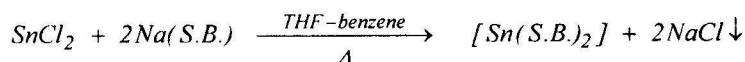
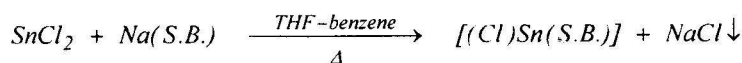
In a similar manner other complexes, [(Cl)Sn(snab)], [(Cl)Sn(sab)] and [(Cl)Sn(o-smab)] have been prepared and purified by recrystallisation in THF-benzene mixture.

(II) Synthesis of bis-complexes of tin(II) containing Schiff bases of the type [Sn(p-smab)₂]. The bis-complexes of tin(II) have been prepared by adopting similar procedure as described for monochloro-complexes by using 1:2 stoichiometric ratio of SnCl_2 and Schiff bases. Synthetic and analytical details for monochloro and bis-complexes are collected in table-1.



Results and Discussion

The complexes of tin(II) containing Schiff bases have been prepared by the reaction of anhydrous SnCl_2 with sodium salts of Schiff bases in different molar ratio(s); which can be represented by the following chemical equations:



(where, S.B. = Schiff bases, p-smab, snab, sab and o-smab)

These complexes are coloured solids and are soluble in common organic solvents such as methanol, ethanol, chloroform, THF-benzene etc.

Table 1: Synthetic and analytical details for complexes of tin(II) containing various Schiff bases

S.No.	Reactants (g. mmol)	Products (g, % yield)	% Analysis : Found (Calcd.)	
			Sn	Cl
1.	SnCl ₂ + Na(p-smab) (0.3, 1.58) (0.349, 1.58)	[(Cl)Sn(p-smab)] (0.37, 65)	31.80 (32.89)	9.5 (9.7)
2.	SnCl ₂ + Na(snab) (0.274, 1.45) (0.383, 1.45)	[(Cl)Sn(snab)] (0.42, 74)	29.95 (30.55)	8.7 (8.9)
3.	SnCl ₂ + Na(sab) (0.26, 1.37) (0.32, 1.37)	[(Cl)Sn(sab)] (0.32, 68)	33.00 (33.70)	9.8 (10.1)
4.	SnCl ₂ + Na(o-smab) (0.257, 1.36) (0.316, 1.36)	[(Cl)Sn(o-smab)] (0.38, 76)	28.90 (29.87)	8.5 (8.9)
5.	SnCl ₂ + Na(p-smab) (0.25, 1.31) (0.61, 2.62)	[Sn(p-smab) ₂] (0.51, 72)	21.00 (21.90)	–
6.	SnCl ₂ + Na(snab) (0.28, 1.47) (0.776, 2.94)	[Sn(snab) ₂] (0.58, 65)	19.15 (19.72)	–
7.	SnCl ₂ + Na(sab) (0.43, 2.26) (1.0, 4.52)	[Sn(sab) ₂] (0.93, 81)	22.80 (23.09)	–
8.	SnCl ₂ + Na(o-smab) (0.3, 1.58) (0.698, 3.16)	[Sn(o-smab) ₂] (0.57, 67)	21.30 (21.90)	–

Infra-red Spectral Studies

The IR absorption bands due to the presence of $\nu_{(C=N)}$ in the Schiff bases are observed in the range 1638-1612 cm⁻¹ whereas, the metal complexes showed negative shift in the range 1615-1585 cm⁻¹ suggesting coordination through azomethine group⁶. The $\nu_{(C-O)}$ (phenolic) bands, appeared in the region 1282-1261 cm⁻¹ in Schiff bases, shifted to higher frequency region 1299-1276 cm⁻¹ in the complexes indicating the participation of phenolic oxygen⁷. Asymmetric and symmetric bands observed at 906, 752 cm⁻¹ due to C-O-C stretching frequencies of THF in the metal complexes suggesting the coordination of THF (solvent).

The IR spectra of monochloro complexes exhibited characteristic IR frequencies in the region 330-320 cm⁻¹, which have been assigned for $\nu_{(M-Cl)}$ vibration⁸. In all the complexes medium to strong bands, observed in the region 483-449 cm⁻¹ and 559-533 cm⁻¹ may be attributed to $\nu_{(M-N)}$ and $\nu_{(M-O)}$ respectively⁹.

UV-Visible Spectral Studies

The UV-visible spectra of complexes, in THF, exhibited a broad band in the region 25641-23980 cm⁻¹ indicating complex formation with transfer of charge from ligand to metal¹⁰.

¹H-NMR Spectral Studies

In the ¹H-NMR spectra of the ligands (Schiff bases) a sharp signal observed at δ 8.28 ppm correspond to the azomethine proton which on complexation undergoes some shielding and gave signals at δ 9.4-8.6 ppm indicating thereby involvement of azomethine nitrogen in coordination¹¹. A strong signal appeared in the region δ 12.80-12.40 ppm in the ¹H-NMR spectra of the ligands may be attributed to the phenolic proton whereas spectra of corresponding complexes are devoid of signals due to (OH) proton indicating coordination to metal through phenolic oxygen¹².

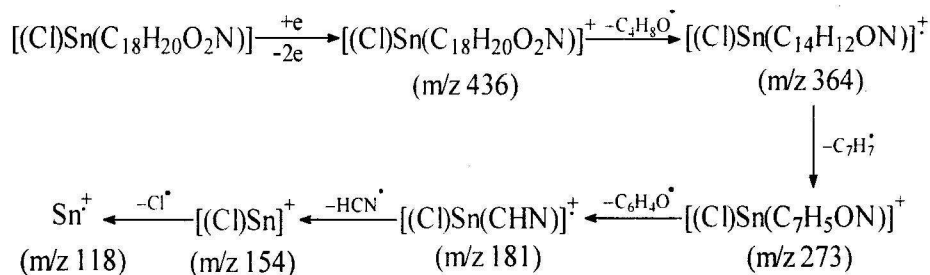
In Schiff bases, the signals due to other protons and their shifts in the corresponding complexes, are congruous with proposed structures (Table 2).

Table 2: Characteristic IR frequencies (cm⁻¹) and ¹H-NMR data (δ , ppm) of monochloro and bis-complexes of tin(II) containing various Schiff bases

S.No.	Complexes	IR					¹ H-NMR	
		$\nu_{\text{Sn-Cl}}$	$\nu_{\text{Sn-N}}$	$\nu_{\text{Sn-O}}$	$\nu_{\text{C-O (phenolic)}}$	$\nu_{\text{C=N}}$	HC=N	Benzene
1.	[(Cl)Sn(p-smab)]	323	458	548	1277	1612	9.28	7.21–6.87
2.	[(Cl)Sn(snab)]	320	453	543	1280	1597	9.21	7.56–7.08
3.	[(Cl)Sn(sab)]	321	449	559	1299	1601	9.35	7.35–6.92
4.	[(Cl)Sn(o-smab)]	327	467	553	1287	1610	9.08	7.84–7.35
5.	[Sn(p-smab) ₂]	–	483	556	1276	1585	8.60	6.64–6.09
6.	[Sn(snab) ₂]	–	472	538	1296	1603	9.19	7.25–7.02
7.	[Sn(sab) ₂]	–	459	546	1278	1599	9.40	7.32–6.98
8.	[Sn(o-smab) ₂]	–	461	536	1283	1615	8.95	7.15–6.84

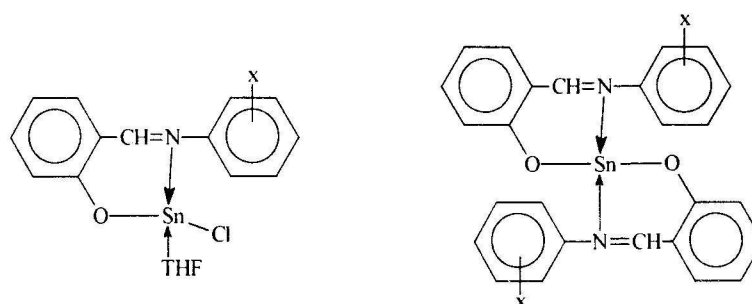
Mass Spectral Studies

The FAB-mass spectrum of mono (salicylidene-4-methyl-1-aminobenzene)tin(II) chloride, [(Cl)Sn (p-smab)] THF showed the molecular ion peak at m/z 436 corresponded to the molecular weight of the compound suggesting monomeric nature of the complex. Other important peaks observed at m/z 363, 273, 210, 180, 154, 118 indicated fragmentation of the complex (See Scheme-1).



Scheme-1: Mass spectral fragmentation pattern of mono (salicylidene-4-methyl-1-aminobenzene) tin(II) chloride [(Cl)Sn(p-smab)]THF

On the basis of above studies following tentative structures have been proposed for tin(II) complexes



x = p-CH₃ (for p-smab), o-CH₃ (for o-smab), H (for sab), m-NO₂ (for snab)

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