Research Article

Tin(IV) Complexes of Schiff Base Derived from Amino Acid: Synthesis and Characteristic Spectral Studies

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A new series of tin(IV) complexes of general formula $[\text{Sn}(\text{L}-1)(\text{Opr}^i)_2]$ (1), $[\text{Sn}(\text{HL}-1)_2(\text{Opr}^i)_2]$ (2), $[\text{Sn}(\text{L}-2)(\text{Opr}^i)_2]$ (3), $[\text{Sn}(\text{HL}-2)_2(\text{Opr}^i)_2]$ (4), (L is dianion of Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde with glycine (L-1) and β -alanine (L-2)) was synthesized by reaction of tin(IV) tetraisopropoxide with the ligands, in appropriate stoichiometric ratios (1:1 and 1:2). This would result in the replacement of the isopropoxide group from the tin(IV) tetraisopropoxide and hydrogen(s) from ligand with the azeotropical removal of isopropanol. An attempt has been made to prove the structure of the resulting complexes on the basis of elemental analysis, IR, ^1H nuclear magnetic resonance. The binding site of the ligand was identified by IR spectroscopic measurement. In these complexes, the tin(IV) centre is bonded to oxygen atom of the hydroxyl or carboxylate group. The spectra data suggest that the carboxylate group is coordinated to tin(IV) centre in monodentate manner.

1. Introduction

The interest in tin chemistry has attracted considerable attention due to its remarkable industrial, medicinal, and agricultural applications [1–4], and the coordination behavior of tin metal with the biological active ligand has been studied since the last decade due to its wide applications in several areas such as antitumour [5], antiviral [6], bactericides, fungicides [7], marine antifouling paints, surface disinfectants, wood preservatives [8], and many more. Schiff base is an important class of ligand in coordination chemistry and has important and vast biological application in different fields [9]. The interaction of tin metal to the organic group via O–Sn and N–Sn bonds has aroused considerable interest in several research fields. Prompted by these facts, we have synthesized some tin(IV) complexes with Schiff bases and illustrated their geometrical structure by using spectral analysis.

2. Experimental

2.1. Materials and Methods. All the reagents, namely, tin (Merck), 2-hydroxynaphthaldehyde (Aldrich), were used as received. All the chemicals and solvents used were dried and

purified by standard methods, and moisture was excluded from the glass apparatus using CaCl_2 drying tubes.

The melting points were determined in open capillaries with electronic melting point apparatus. C, H, and N analyses of these compounds were carried out in a VarioEL, CHNS elemental analyzer. The tin content in the synthesized compounds was determined gravimetrically as SnO_2 . Infrared spectra of the solid compounds were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer in the range $4000\text{--}400\text{ cm}^{-1}$ from KBr discs. ^1H NMR spectra were recorded on a Bruker DRX 300 (300 MHz FT NMR) spectrometer at the Central Drug Research Institute, Lucknow, India, using CDCl_3 as a solvent and TMS as the internal standard.

2.2. Synthesis of Schiff Bases. Schiff bases were prepared by condensation of hot aqueous (25 mL) solution of glycine or alanine (.013 mole) and 2-hydroxy 1-naphthaldehyde (.013 mole), dissolved in ethanol (50 mL). The reaction mixture was refluxed for about 2 h, and yellow brown polycrystalline precipitate was obtained after standing overnight. It was

TABLE 1: Elemental analysis of complexes.

S. no.	Complexes	Color (yield %)	M.P. (°C)	Elemental analysis % Obsd. (Calcd.)			
				Sn	C	H	N
1	[Sn(L-1)(Opr ⁱ) ₂]	Yellow (58)	69-70	25.68 (25.60)	49.32 (49.17)	4.99 (4.96)	2.98 (3.02)
2	[Sn(HL-1) ₂ (Opr ⁱ) ₂]	Yellow (74)	69-70	17.18 (17.13)	55.49 (55.44)	4.98 (4.91)	3.99 (4.04)
3	[Sn(L-2)(Opr ⁱ) ₂]	Yellow (65)	80-81	24.9 (24.85)	50.31 (50.24)	5.26 (5.23)	2.89 (2.93)
	[Sn(HL-2) ₂ (Opr ⁱ) ₂]	Yellow (76)	80-81	16.42 (16.47)	56.65 (56.61)	5.31 (5.27)	3.85 (3.89)

TABLE 2: IR spectra of complexes (in cm⁻¹).

S. no. ^a	Complexes	$\nu(\text{OH/NH})$	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu(\text{COO})$	$\nu(\text{Sn-O})$	$\nu(\text{N} \rightarrow \text{Sn})$
1	[Sn(L-1)(Opr ⁱ) ₂]	—	1640 s	1398 m	242	538	415
2	[Sn(HL-1) ₂ (Opr ⁱ) ₂]	3400	1641 s	1399 m	242	532	418
3	[Sn(L-2)(Opr ⁱ) ₂]	—	1650 s	1389 m	261	540	430
4	[Sn(HL-2) ₂ (Opr ⁱ) ₂]	3414	1655 s	1390 m	265	535	432

^aNumbers as indicated in Table 2; s: strong; m: medium.

SCHEME 1

SCHEME 2

purified by repeated washing with aqueous-ethanol (1 : 2) and dried in vacuum over fused CaCl₂ (Scheme 1) [10].

2.3. Synthesis of Complexes. The synthetic route used to synthesize complexes is outlined in Scheme 2. In the first step, SnCl₄ was prepared by the action of chlorine gas on pure tin metal in a specially designed apparatus (bubbler). A pale yellow liquid of SnCl₄ thus obtained was purified by distillation. The tin(IV) isopropoxide was synthesized by using literature method [11]. A solution of tin(IV) tetrachloride (2.471 gm, 0.0095 mole) in benzene (10 mL) was treated with sodium isopropoxide (3.116 gm, 0.038 mole) to produce tin(IV) tetraisopropoxide and sodium chloride. The sodium chloride precipitate was removed by filtration, and the solvent was removed by distillation. The solution of tin(IV) tetraisopropoxide (3.528 gm, 0.0095 mole) and ligand

(2.372 gm, 0.01 mole) was refluxed in benzene for 8–10 h. These reactions proceed with the liberation of isopropanol, which is removed azeotropically with benzene.

3. Result and Discussion

All the newly synthesized complexes are colored solids and soluble in common organic solvents. The elemental analysis of these complexes is presented in Table 1.

3.1. Infrared Spectra. The characteristic infrared frequencies of the tin(IV) complexes are given in Table 2. It has been suggested, Schiff bases have a tautomeric structure (Figure 1), which means that pure Schiff bases exist in keto-amine and phenol-imine forms [12], but upon complex formation, they may exist only in the imine form. The complexes

FIGURE 1: Tautomeric form of Schiff base.

FIGURE 2: Structure of tin (IV) complexes.

TABLE 3: NMR spectra of complexes (in δ).

S. no. ^a	Complex	Azomethine proton	Methylene proton	Naphthylidene group proton
1	[Sn(L-1)(Opr ⁱ) ₂]	9.16 (s, 1H)	4.29(s, 2H)	6.91–7.92 (m, 6H)
2	[Sn(HL-1) ₂ (Opr ⁱ) ₂]	9.12 (s, 2H)	4.24 (s, 4H)	6.89–7.88 (m, 12H)
3	[Sn(L-2)(Opr ⁱ) ₂]	8.34 (s, 1H)	3.58 (s, 2H)	6.93–7.93 (m, 6H)
4	[Sn(HL-2) ₂ (Opr ⁱ) ₂]	8.30 (s, 2H)	3.56 (s, 4H)	6.92–7.90 (m, 12H)

^aNumbers as indicated in Table 3; s: singlet; m: multiplet.

1 and **3** do not show a strong band in the region of 3500–3300 cm⁻¹ due to $\nu(\text{OH/NH})$ [13], indicating deprotonation of the phenolic and carboxylic oxygen of the Schiff bases on complex formation with the tin metal. In the complexes, two bands presumably due to asymmetric stretching frequencies $\nu_{\text{as}}(\text{COO})$ and symmetric stretching frequencies $\nu_{\text{s}}(\text{COO})$ are observed at 1640–1655 and 1389–1398 cm⁻¹, respectively. In the complexes, the differences $[\Delta\nu(\text{COO})]$ between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ are >200 cm⁻¹, indicating

the unidentate coordination of the carboxylate group to the tin metal [14]. In the lower frequency region, the medium band observed at about 415–432 cm⁻¹ in the spectra of the complexes has been assigned to the $\nu(\text{N} \rightarrow \text{Sn})$ vibration [15–17].

3.2. ¹H NMR Spectra. Table 3 shows the chemical shifts (δ in ppm) of various protons in metal complexes. The absence

of a signal due to the –OH proton at δ 12.00–13.00 ppm suggests deprotonation of the phenolic/enolic/carboxylic oxygen atoms of the ligand on complexation [15]. The ^1H NMR Spectra of the complexes revealed a signal in the region δ 8.30–9.16 ppm due to the azomethine ($-\text{N}=\text{CH}-$) proton [18]. The multiplets between δ 6.89–7.93 ppm are assigned to the naphthylidene group protons.

4. Conclusion

Based on stoichiometries and the physicochemical studies, penta- and octahedral coordination around tin(IV) has been proposed. The tentatively proposed structures of these complexes are shown in Figure 2.

List of Abbreviations

NaOPr^i :	Sodium isopropoxide
$\text{Sn(OPr}^i)_4$:	Tin(IV) tetraisopropoxide
$\nu_{\text{as}}(\text{COO})$:	Asymmetric stretching frequency
$\nu_{\text{s}}(\text{COO})$:	Symmetric stretching frequency
CDCl_3 :	Deuteriochloroform
IR:	Infrared
NMR:	Nuclear magnetic resonance.

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