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Synthesis, Characterization and Formation Kinetics of Sn(II) and (IV)-Schiff Base Complexes

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The synthesis and characterization of Sn(II) and Sn(IV) complexes of nitrogen and oxygen ligands, *p*-dimethyl aminophenylenesalicyladimine (DPS), N,N'phenylenebis(salicylaldimine)(PBS) and N, N'-triethylenetetramine bis (salicylaldimine)(TTS) are reported. The structure of free ligands and their tin complexes were determined by elemental analysis, ir and nmr measurements. The kinetics of formation of the complexes were studied by stopped-flow technique at several temperatures with μ=0.100 M ($NaClO_4$). Activation parameters ΔH^* and ΔS^* were determined.

Introduction

Schiff bases derived from the reaction of salicylaldehyde with primary amines represent a versatile series of ligands. Spectral properties of the metal complexes with transition elements have been widely studied[1-5]. In recent years, there has been considerable interest in the study of the structural properties of metal complexes of bi, tetra and hexadentate nature. The present article describes the synthesis, characterization and formation kinetics of tin(II) and tin(IV) chelates. Many of the main group elements, like the transition elements, also exhibit multiple oxidation states. Heavier members of group 4A can achieve a higher coordination number through the use of d orbitals[6]. Sn(II) and Sn(IV) form Sn(TTS) and Sn(PBS) complexes with tetra and hexadentate ligands, while Sn(II) and (SnIV) form Sn(DPS)2 type complexes with bidentate ligand. These complexes posses chelate rings which provide extra stability for the complexes. These findings are consistent with infra-red and kinetic data. Characterization of the Schiff bases and their tin complexes was done by nmr, ir and elemental analysis. The effects of the number of donor atoms on reactivity and structure are discussed.

Experimental

Absorption spectra were recorded on a Boush-Lomb spectronic 2000 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM 60 L spectrometer in $CDCl_3$ with TMS as internal reference. Ir spectra were recorded on a KBr pallet on a Jasco 300E instrument. Reaction kinetics was studied using Hi-Tech scientific rapid kinetic accessory, SFA-12. Data from those experiments were analyzed with a PC 386 DX 40 modified with an Analog/ Digital converter.

Synthesis of the Schiff bases- 12.21 g (0.1 mol) salicylaldehyde was dissolved in 50 ml ethylacetate at room temperature 15.25 g (0.1 mol). *p*-N,N′ dimethylaminoaniline was dissolved in 50 ml ethylacetate and added to the salicylaldehyde solution. Half an hour was allowed for the reaction to be completed. As *p*- dimethylaminophenylene (salicylaldimine) (DPS) was produced, the yellow colour of the solution intensified. The solution was chilled in an ice water bath and the product was precipitated. Purity of schiff bases was checked by thin layer chromotography and melting points. The other schiff bases, N. N′-phenylenebis(salicyladimine), (PBS) and N,N′-triethylene tetraminbis (salicyladimine), (TTS) were prepared in the same manner.

Synthesis of the Complexes- The Sn(II) chelates were prepared by addition of the 0.480 g (0.002 mol) DPS in 50 ml ethylacetate to a solution of 0.225 g (0.001 mol) of $SnCl_2$ in 50 ml ethylacetate. An immediate colour change to light-yellow occurred, and after standing overninght at room temperature a fine micro crystalline product was collected by filtration, washed with methanol and dielthylether and dried in vacuum.

Kinetic Measurements- Kinetic measurements were made by using both stopped-flow and UV-VIS spectrophotometer, modified with a cell block thermostated to ± 0.1 °C in the temperature range $15-35°$C by means of external water bath. Complex formation reactions were followed by monitoring at the $\lambda_{\max}$ of the reactant (ligand) or product species[7]. Pseudo-first order condition of excess ligand concentrations were employed. Low concentrations ($5 \times 10^{4-}$ M) of the tin were used. Under these conditons formation of Sn(SB) was shown by spectrophotometry to be quantitative. The plots of ln $(A_\infty - A_t)$ against time were generally linear for three or more half-lives. A_∞ readings were recorded after 7-8 half lives. The reported rate constants represent an average of four to six. All the solutions were prepared at an inonic strength of 0.100 M with added sodiumperchlorate.

Results and Discussion

Uv-vis spectra- The spectrum of Sn(II) complex of *p*- dimenthylaminophenylene (salicyladimine) (DPS) in ethylacetate is shown in Figure 1. The absorption at 462 nm is assigned to a ligand -metal charge transfer transition[8]. Additional band at 254 nm is interligand $(\pi - \pi^*)$ transition centered on coordinated Schiff base. The values of $\lambda_{\max}$ and ε for the series of these complexes where ligands are bi, tetra and hexadentate, are listed in Table 1.

Table 1. UV-Visible band maxima and Molar Absorbence for the formation reactions of Sn-Schiff base complexes in Ethylacetate

Ligands		$\lambda_{CT}(nm)^a$	$\varepsilon 10^{3-} M^{-1} cm^{-1}$
DPS	Sn^{2+}	462	2.02
	Sn^{4+}	497	2.28
PBS	Sn^{2+}	446	2.92
	Sn^{4+}	483	3.32
TTS	Sn^{2+}	434	3.66
DPS	Sn^{4+}	474	3.78

a-CT, charge transfer

Kinetics of complex formation- The addition of exces Schiff base (5.0 x 10^{-3} M) to a dilute solution (5.0

x 10^{-4} M) of the tin results in a shift in the uv-visible spectrum, ascribed to a formation of a Sn-Schiff base complex. Plot of k_{obs} against ligand concentrations as shown in Figure 2 were linear for each ligand under study. For each temperature, four k_{obs} values were obtained for for ligand concentrations. second-order rate constant was obtained from the slope of a plot of k_{obs} vs [SB], which ranged from $5x10^{3-}$ to $1.5x10^{2-}$M. For five temperatures 1/T were calculated and graphed against ln k/T. Activation parameters for the complex formation reactions were calculated from

$$In\, k/T = In\, k_B/h + \Delta S^*/R - \Delta H^*/RT$$

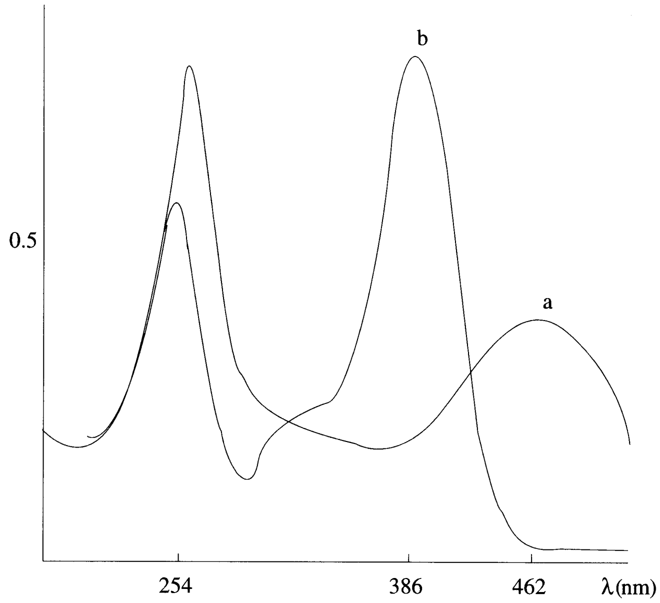


Figure 1. a) Spectral changes on the addition of DPS (1. 5x10^{-4}M) to a solution $SnCl_2(1.5 \times 10^{-4}M)$ in ethylacetate b) UV-visible spectrum of DPS

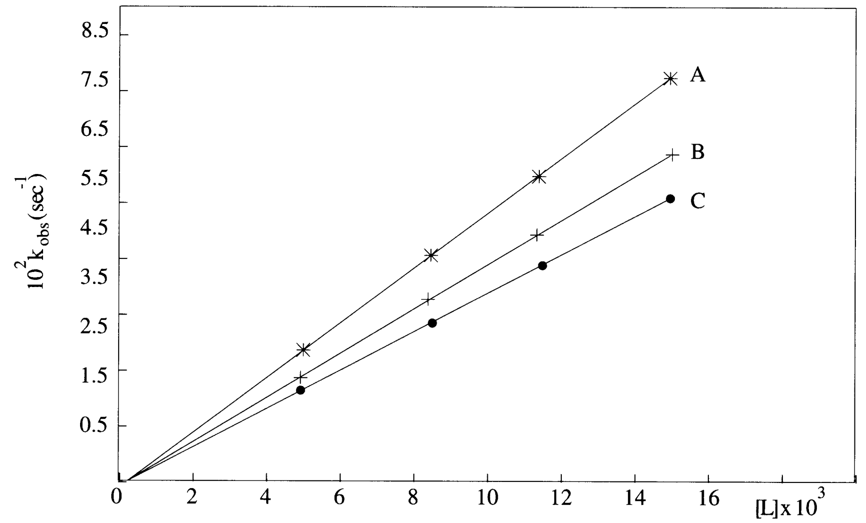


Figure 2. Dependence of k_{obs} on ligand concentrations for the formation reactions of Sn-Schiff base complexes. (25° C, μ=0.10 M) Ligands: a) TTS; b) PBS; c) DPS

Activation entropies and entalpies of the reactions were calculated from the intercept and slope correspondingly by least-squares analysis and collected in Table 2.

Table 2. Rate and activation parameters for complex formation of Schiff bases mwith Sn(II) and Sn(IV) in ethylacetate

Ligands		$k(m^{-1}s^{-1})^b \times 10^{-2}$	$\Delta H^*(kJ/mol)$	$\Delta S^*(J/mol.K)$
DPS	Sn^{2+}	1.72±0.01	25	-113
	Sn^{4+}	2.37±0.02	23	-108
PBS	Sn^{2+}	1.92±0.01	24	-118
	Sn^{4+}	2.64±0.01	22	-130
TTS	Sn^{2+}	2.47±0.02	23	-107
	Sn^{4+}	3.74±0.01	21	-116

b:25°C

No appreciable oxidation is observed in Sn(II) in the doeoxygenated ethylacetate solution. The variations in the formation rate constants in Table 2 indicate that the rate of formation is influenced by the number of coordination sites on the ligand[9]. The enthalpies of activation increase when the charge of the central ion decreases ΔH^* is about 2 kJ/mol higher for Sn(II) complexes. This kinetic behavior with negative entropy of activation is consistent with an associative mechanism[10-12]. The outer-sphere association is primarily controlled by entropic effects[13-14]. The variation in ΔS^* supports an associative mechanism, as in Reaction 1, The general mechanizm for an aquometal ion reacting with simple unidentate ligand is understood in considerable detail.

$$[M(EtAc)_x] + L \overset{K_{os}}{\rightleftharpoons} [M(EtAc)_x] \cdot L \overset{k_{os}}{\rightleftharpoons} [M(L)(EtAc)_{x-1}] + EtAC$$

K_{os} is the equlibrium constants for the formation of an outer sphere complex and k_{os} is the rate constants for the rupture of an inner sphere metal-solvent bond. Then rapid insertion of a ligand donor atom follows. For an open chain multidentate ligand, the overall mechanism of complex formation may be represented as series of steps in which the rupture of a metal-solvent bond is quickly followed by insertion of a donor atom from the attacking ligand at the site being vacated. For strongly coordinated multidentate ligands, this process continues until all donor atoms have formed bonds with the central ions (or until all sites on the central metal ion are occupied by ligand donor atoms). One strong basic donor atom (nitrogen) of the ligand is presumed to have a hydrogen bond to a coordinate solvent molecule to give a stronger outer-sphere complex and to labilise subsequent position on the metal ion so that the other donor atom from the ligand can form an inner-sphere complex.

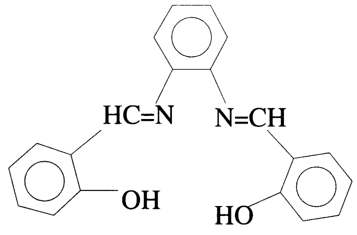
Ir spectra- The **ir** spectra of the complexes do not exhibit any absorption in between 3500-3600 cm^{-1}, indicating that the - OH group of aldehyde is not present in the free state. Instead, the hydrogen of hydroxyl group gets dissociated and takes part in the formation of the Sn-O bond. Similar dissociation is observed in other studies[15]. Amines are expected to show an absorption band near 3400 cm^{-1} due to -NH_2 stretching vibration, but no such bands are observed in Sn-schiff base complexes. Furthermore, the bands due to C=O streching frequencies in the region 1590-1620 cm^{-1} disappear in the case of amines and new bands appear in the region 1620-1630 cm^{-1} cm^{-1}. These new bans are assigned to C=N stretching frequency, which is characteristic of Schiff base, formation and indicates positive involvement of imine nitrogen in bonding[16-17]. C=N-,C-O and C-N stretching frequencies at 1625, 1140 and 1195 cm^{-1} in schiff bases are sligtly changed to lower values (C=N, 1605) after complexation. vC=N band remains almost unchanged upon chalation. This supports the view that the imine group in this type of the ligand is less perturbed by chalation that the carbonyl group. The appearance of new bands at 490-560 and at 495-620 cm^{-1} are characteristic of Sn-N and Sn-O bonds, correspondingly. The results of Ir, UV-VIS, NMR, elemental analysis (Table 3) show that Schiff bases coordinate to tin through the nitrogen and oxygen atoms and form diamagnetic complexes.

Nmr data δ ppm [60 MHz; solvent $CDCl_3$; standard $SiMe_4$]

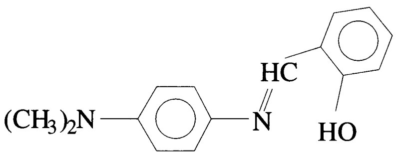
DPS:3.1[6H, s, 2$C\mathbf{H}_3$], 6.2-7.6[8H, m, Ar*H*],8.7[1H, s,-*C***H**=N-]

PBS: 6.9-7.8[12H,m, Ar**H**], 9.1 [2H, s, -C**H**=N-]

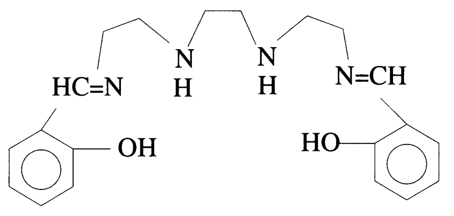
TTS: 2.5-3.2[8H,m, -N-$C\mathbf{H}_{2-}$], 3.3-4.1 [4H, m, =N-$C\mathbf{H}_{2-}$], 6.9-7.4 [8H, m, Ar**H**], 8.9 [2H,s,-C**H**=N]



PBS



DPS



TTS

Structure of the schiff bases studied

Table 3. Elemental analysis[a], and physical data for the Sn- Schiff base complexes

Complex	**Yield (%)**[c]	**Colour**	M.p.,°C	% C	% H	% N
[Sn(TTS)]	71	Dark-orange	152	67.79	7.34	15.81
				(68.12)	(7.66)	(15.83)
[Sn(TTS)]Cl$_2$	79	Orange	168	56.47	6.12	13.18
				(57.11)	(5.99)	(13.47)
[Sn(PBS)]	68	Orange	144	75.94	5.06	8.86
				(76.10)	(5.17)	(8.74)
[Sn(PBS)]Cl$_2$	73	Orange	153	62.01	7.23	4.13
				(62.22)	(7.33)	(4.46)
Sn(DPS)$_2$	66	Yellow	174	75.00	6.66	11.66
				(75.21)	(6.83)	(11.59)
Sn(DPS)$_2$]Cl$_2$	65	Dark-yellow	204	57.88	5.14	9.00
				(57.76)	(5.11)	(8.91)

[a] Calculated values are given in parenthesis, [c] Based on Sn

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