

Synthesis and Characterization of Tin(IV) Complexes with O- and N-Donor Ligands

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The Schiff bases have been prepared by reacting ninhydrin and various substituted amines. The Sn(IV) complexes have been prepared by reacting tin tetrachloride with these Schiff bases in an alcoholic medium. All these complexes are violet to brown in colour and amorphous in nature. The complexes are non-electrolytes in DMF. Elemental analysis confirms the stoichiometry of the type L_2SnCl_4 . The IR spectral observation favours the coordination of C=O to the Sn(IV) ion through oxygen. Sn(IV) exhibits coordination number of six in these complexes

Ninhydrin is a triketo compound used in the detection and estimation of amino acids. Ninhydrin reacts with amino acids producing purple coloured Schiff base. Nenberg¹ has studied the reactions of ninhydrin with various amines. These Schiff bases may be having good biological activities because ninhydrin itself is an important reagent in biomolecular reactions². In view of the considerable physiological and biological importance of ninhydrin and the Schiff bases it is proposed to subject the following Schiff bases (Fig. 1) formed by reaction of ninhydrin and aromatic amines to prepare a few complexes of Sn(IV).

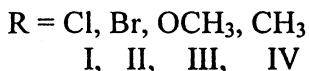
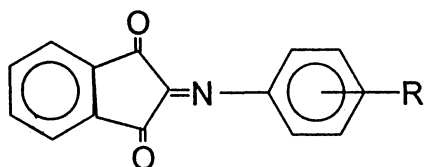


Fig. 1

The chemicals used in the reaction were of reagent grade. Tin(IV) chloride (Reidal) was used without further purification. Distilled alcohol was used as solvent.

Ligands were prepared by refluxing ninhydrin (0.01 mole) and aromatic amines (0.01 mole) in alcohol medium in presence of 2-3 drops of conc. HCl.

The reaction mixture was cooled, the separated mass was filtered, washed with alcohol. The solid obtained was purified by crystallization.

Complexes were prepared by reacting tin(IV) chloride (0.01 mole) in alcohol. The reaction mixture was refluxed with 0.02 mole ligand in alcohol for 3 h on a steam bath. The contents were allowed to cool and transferred to a beaker. The precipitate was filtered, washed with alcohol and dried in vacuum over fused calcium chloride. The dry mass was extracted in soxhlet thimble with dry alcohol.

The elemental analysis (Table-1) was made by the method reported elsewhere³. IR spectra of the complexes and the ligands were recorded on Hitachi 270–50 spectrophotometer in the region 4000–200 cm^{-1} .

All the complexes are violet to brown in colour and complexes undergo decomposition around 300°C. They are amorphous in nature and are insoluble in common organic solvents. However, they are soluble in DMF and DMSO. The insolubility in common organic solvents has thwarted the efforts of determining molecular weight.

The complexes analyse for the stoichiometry of the type SnCl_4L_2 . (Table-1). The molar conductance values obtained for these complexes at the concentration of 10^{-3}M are in the range of 3.0–7.0 $\text{mole}^{-1} \text{ohm}^{-1} \text{cm}^2$. These values are too low to account for any dissociation of the complexes in DMF. Hence these complexes can be regarded as non-electrolytes.

TABLE-1
ANALYTICAL, MOLAR CONDUCTANCE, MELTING POINT AND COLOUR OF THE COMPLEXES

Complex No.	Empirical formula (colour)	% Analysis, found (calcd.)			m.p. (°C)	Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
		Sn	N	Cl		
V	$(\text{C}_{15}\text{H}_8\text{NO}_2\text{Cl})_2\text{SnCl}_4$ (Dark violet)	13.98 (14.84)	3.46 (3.50)	17.65 (17.73)	< 300	3.032
VI	$(\text{C}_{15}\text{H}_8\text{NO}_2\text{Br})_2\text{SnCl}_4$ (Violet)	13.22 (13.36)	3.10 (3.15)	15.93 (15.95)	270	4.138
VII	$(\text{C}_{16}\text{H}_{11}\text{NO}_3)_2\text{SnCl}_4$ (Blackish brown)	15.00 (15.01)	3.46 (3.54)	17.85 (17.93)	> 300	3.198
VIII	$(\text{C}_{16}\text{H}_{11}\text{NO}_2)_2\text{SnCl}_4$ (Dark brown)	15.53 (15.64)	3.63 (3.69)	18.58 (18.68)	> 300	4.015

IR spectra: The important IR frequencies are systematized in Table-2. The ligand exhibits high intensity band around 1720cm^{-1} due to $\nu(\text{C}=\text{O})^4$. In addition to these bands a high intensity band is also observed around 1600cm^{-1} and this band is assigned to $\nu(\text{C}=\text{N})$. A group of medium to high intensity bands observed in the region $1550\text{--}1460 \text{cm}^{-1}$ is considered to due to aromatic $\nu(\text{C}=\text{C})$ vibrations.

In the complexes the following changes are observed: It is observed that the band pertaining to $(\text{C}=\text{N})$ does not indicate any shift in the frequency. Hence it may be concluded that the $(\text{C}=\text{N})$ of the ligand has not taken part in the

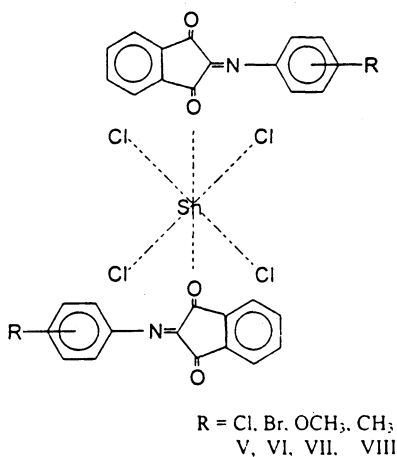
coordination. However the band pertaining to (C=O) shows considerable low frequency shift and is located in the region 1720–1610 cm^{-1} in the complexes. The shift of the order of about 40 cm^{-1} to lower frequency is suggestive of coordination of (C=O) to the Sn(IV) *via*-oxygen.

TABLE-2
THE IR FREQUENCY (cm^{-1}) OF THE SCHIFF BASES AND THEIR TIN(IV)
COMPLEXES

Assignments	I	V	II	VI	III	VII	IV	VIII
$\nu(\text{C}=\text{N})$	1600	1600	1610	1605	1615	1615	1605	1610
$\nu(\text{C}=\text{O})$	1660	1640	1670	1610	1720	1700	1680	1660

The analytical data suggest 1 : 2 stoichiometry for these complexes. The complexes are non-electrolytes in DMF. The IR spectral observations suggest the involvement of only oxygen of the (C=O) in coordination for these complexes.

All these observations put together project the following tentative structure for these complexes wherein Sn(IV) exhibits coordination number of six.



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