

## NOTE

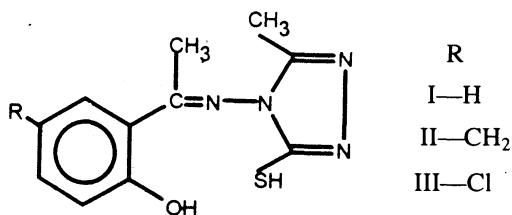
## Synthesis and Characterization of Tin(IV) Complexes with Triazole Schiff bases

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A few complexes of Sn(IV) with Schiff bases derived from 3-methyl-4-amino-5-mercapto-1,2,4-triazoles have been synthesized. These complexes have been characterized by analytical and spectral data. The Schiff bases show bidentate behaviour and form complexes of the type  $\text{SnCl}_2\text{L}_2$ . The Sn(IV) exhibits coordination number of six in these complexes.

In order to obtain some new ligands having O, N and S donor atoms, we have reacted substituted *o*-hydroxy acetophenone with 3-methyl-4-amino-5-mercapto-1,2,4-triazoles. In this paper we wish to report the synthesis and spectral properties of the Sn(IV) complexes with the following ligands:



All the chemicals used were of reagent grade.

The substituted *o*-hydroxy acetophenones were prepared by the method reported in literature.<sup>1</sup> 3-Methyl-4-amino-5-mercapto-1,2,4-triazole was prepared by the reported method.<sup>2</sup>

Ligands were prepared by refluxing a mixture of 3-methyl-4-amino-5-mercapto-1,2,4-triazole and *o*-hydroxy acetophenone in 1 : 1 molar proportion in alcohol containing a few drops of conc. HCl for about 4 h. The product separated was filtered and recrystallised from ethanol.

*Tin(IV) complexes:* Tin(IV) chloride (0.02 M) in alcohol was refluxed with (0.02 M) ligand in alcohol for 3 h on a steam bath. The contents were allowed to cool and the reaction mixture was transferred to a beaker and precipitation of the complex was initiated by adding distilled water containing a few drops of ammonia. 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 analyses were made by the methods<sup>3</sup> reported elsewhere. IR spectra of the ligands and the complexes were recorded on Hitachi-270 spectrometer in the region 4000–250  $\text{cm}^{-1}$ . PMR spectra of typical ligand and its complexes obtained on Varian EM-290 spectrometer.

All the complexes are yellow in colour, amorphous and insoluble in common organic solvents. However, they are soluble to a limited extent in DMF and DMSO. The molar conductance in DMF at the concentration  $10^{-3}$  M shows that these are non-electrolytes in DMF. The elemental analysis shown in Table-1 emphasises that these complexes have stoichiometry of the type  $\text{SnCl}_2\text{L}_2$ , where L is a double deprotonated ligand.

TABLE-1  
ANALYTICAL DATA OF COMPLEXES

L. Complex No.	Complex No.	Empirical formula of complex	% Analysis, Found (Calcd.)			
			M	S	N	Cl
I	1	$(\text{C}_{10}\text{H}_9\text{N}_2\text{OS})_2\text{Sn}\cdot\text{Cl}_2$	18.05 (18.09)	4.79 (4.88)	8.51 (8.53)	10.85 (10.80)
II	2	$(\text{C}_{11}\text{H}_{11}\text{N}_4\text{OS})_2\text{Sn}\cdot\text{Cl}_2$	17.31 (17.35)	4.71 (4.68)	8.15 (8.18)	10.32 (10.32)
III	3	$(\text{C}_{10}\text{H}_8\text{N}_4\text{OSCl})_2\text{Sn}\cdot\text{Cl}_2$	16.35 (16.37)	4.39 (4.42)	8.11 (7.72)	14.69 (14.67)

*IR Spectra:* The triazoles are reported to exhibit thiol-thione tautomerism. The condensation of such triazoles with aldehydes or ketones cannot modify the spectra. The ligands do exhibit tautomerism and one can expect both  $\nu(\text{SH})$  and  $\nu(\text{C}=\text{S})$  vibrations.

A broad weak band with fine structure around  $2700\text{ cm}^{-1}$  is attributed to intramolecular H-bonded OH, on analogy with previous assignments.<sup>4</sup> The medium intensity band observed around  $3250\text{ cm}^{-1}$  is assigned to  $\nu(\text{NH})$ . This suggests that ligands exist in thione form. A medium intensity broad band is observed around  $2350\text{ cm}^{-1}$  and is assigned to  $\nu(\text{SH})$  vibrations. Taking into consideration the previous<sup>5,6</sup> assignments. The high intensity band around  $1640\text{ cm}^{-1}$  observed for ligands can be assigned to  $(\text{C}=\text{N})$  vibration. The high intensity band around  $1280\text{ cm}^{-1}$  is attributed to the phenolic  $\nu(\text{C}-\text{O})$  vibration. The medium intensity band in the region  $760-740\text{ cm}^{-1}$  has been attributed to  $\nu(\text{C}=\text{S})$ .<sup>7</sup>

In the complexes, we observed the following changes:

1. The band due to intramolecular H-bonded OH disappears and phenolic  $\text{C}-\text{O}$  vibrations appear around  $1330\text{ cm}^{-1}$ .

2.  $\nu(\text{C}=\text{N})$  for these complexes appears around  $1620\text{ cm}^{-1}$  suggesting coordination of  $\text{C}=\text{N}$  group through nitrogen.

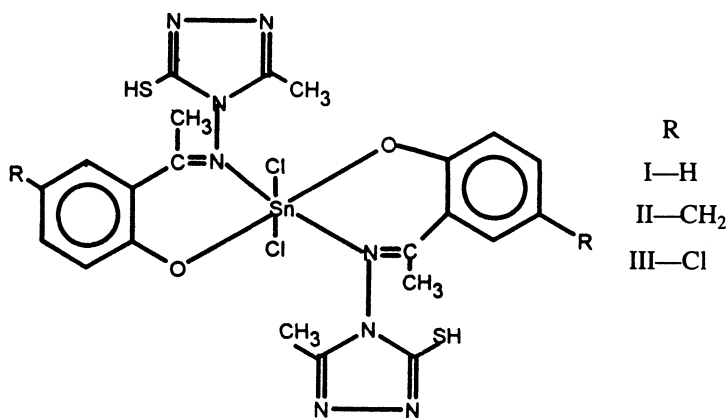
3. The band due to  $\nu(\text{C}=\text{S})$  in the region  $780-740\text{ cm}^{-1}$  of the ligands has remained unperturbed in these complexes. This has suggested the non-involvement of sulfur atom in coordination.

Metal-ligand vibrations are generally located in  $600-250\text{ cm}^{-1}$  region. The skeletal vibrations of the ligand appearing in this region complicate the interpre-

tation. However, comparison of the complex and ligand spectra allows assignment of metal sensitive bands. The assignments are purely tentative and are based on previous assignments.<sup>8,9</sup> The strong bands found around 536 and 502  $\text{cm}^{-1}$  in the complexes may be assigned to  $\nu(\text{Sn}-\text{N})$  vibration. Medium intensity bands found around 480  $\text{cm}^{-1}$  are assigned to the  $\nu(\text{Sn}-\text{O})$  vibrations. In all these complexes, we observe the band around 312  $\text{cm}^{-1}$  is assigned to the characteristic band of hexacoordinated tin(IV), in view of the previous assignments.<sup>10</sup>

**PMR Spectra:** The presence of sharp signals around 12–13 ppm is due to *o*-hydroxy group in ketone. Residue of ligands do not show up in the complexes suggesting that the reactions with tin(IV) chloride have proceeded *via* deprotonation. Other characteristic resonance due to azomethine proton 8.4 ppm shows considerable downfield shift in the complexes appearing around 8.7 ppm, suggesting that coordination of azomethine group to tin(IV) moiety is through nitrogen. These evidences also support the IR conclusions.

Analytical data and spectral observations favour the following structure, where in Sn(IV) exhibits coordination number of six.



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