



**STRUCTURAL CHARACTERIZATION AND  
ANTIMICROBIAL STUDIES OF SOME NEW  
COORDINATION COMPOUNDS OF TIN (II) AND TIN (IV)  
WITH SEMICARBAZONES AND THIOSEMICARBAZONES  
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**ABSTRACT**

New tetra and hexacoordinated complexes of tin (II) and tin (IV) have been synthesized by the reaction of stannous chloride and dimethyltin dichloride with semicarbazones and thiosemicarbazones prepared by the condensation of aldehydes /ketones with semicarbazide hydrochloride / thiosemicarbazide in absolute alcohol. The bonding pattern and the geometry of these newly synthesized compounds have been suggested on the basis of elemental analysis, electronic, infrared,  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR spectral studies. The monomeric and non-electrolytic nature of these complexes have been confirmed by molecular weight determinations and conductance measurements, respectively. The ligands and their tin complexes have been screened for their antimicrobial activities against several fungi and were found to be quite active in this respect.

**Key words:** Tin complexes, Stannous chloride, Dimethyltin dichloride, Aldehydes/Ketones, Antimicrobial activity.

**INTRODUCTION**

Semicarbazones and thiosemicarbazones are amongst the most important nitrogen-oxygen/sulphur donor ligands. Both of them can act as neutral or charged ligand moieties. These ligands can form complexes by donating an electron pair to metal atom in the formation of coordination compounds. The presence of a second functional group with a replaceable hydrogen atom, preferably a hydroxyl group near enough to the imine group, ( $> \text{C} = \text{N}-$ ), allows the ligand to form a fairly stable four, five or six –membered ring by chelating to the metal atom.

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The real impetus towards developing the coordination chemistry of these potential ligands was probably provided by the remarkable antitumor, antiviral, antimicrobial, antimalarial and anticonvulsant activity<sup>1,2</sup> observed for some of these derivatives, which has been shown to be related to their metal complexing ability.

In view of this, it was considered of interest to synthesize and characterize the semicarbazone and thiosemicarbazone derivatives of tin (II) and tin (IV) and the results of these investigations are reported in this paper. During the course of present investigations, the reactions of stannous chloride and dimethyltin dichloride with different ligands have been carried out. Ligands used were 2-hydroxypropiophenone semicarbazone, 2-hydroxypropiophenone thiosemicarbazone, 1-acetyl-2-naphthol semicarbazone, 1-acetyl-2-naphthol thiosemicarbazone, 2-acetyl-1-naphtholsemicarbazone and 2-acetyl-1-naphthol thiosemicarbazone

## EXPERIMENTAL

All the reactions were carried out in strictly anhydrous condition using quickfit apparatus. All reagents were obtained commercially as analytical grade and were used without further purification.

### Analytical methods and physical measurements

The electronic spectra were taken with a Toshniwal spectrophotometer. The IR spectra were recorded on FT IR spectrophotometer using a Model A-8400s, Shimadzu in KBr pellets<sup>3-5</sup>. <sup>1</sup>H and <sup>119</sup>Sn NMR spectra were recorded on JEOL AL-300. Molecular weight determinations were carried out by the Rast camphor method. The purity of the compounds were checked by thin layer chromatography.

### Synthesis of ligands

All the ligands were synthesized by the condensation of aldehydes/ ketones viz. 2-hydroxypropiophenone, 1-acetyl-2-naphthol, and 2-acetyl-1-naphthol with semicarbazide/ thiosemicarbazide in 1 : 1 molar ratio using absolute alcohol as the reaction medium. The crystals, that separated out, were recrystallized from the same solvent.

### Synthesis of tin (II) and tin (IV) complexes

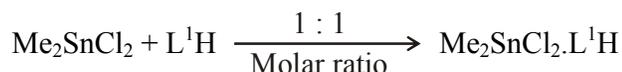
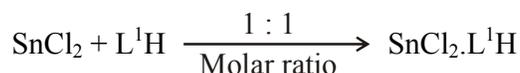
Tin (II) complexes were prepared by the reaction of stannous chloride with semicarbazones and thiosemicarbazones in 1 : 1 molar ratio in dry tetrahydrofuran as

reaction medium. All the contents were stirred with magnetic needle on magnetic stirrer for about two hours. The solvent was removed and the product was finally dried in vacuo.

Tin (IV) complexes were synthesized by the reaction of dimethyltin dichloride with above mentioned semicarbazones and thiosemicarbazones in 1 : 1 molar ratio in dry benzene. The mixture was refluxed on refluxing column for about one hour. The solvent was again removed and the product was recrystallized from the same solvent. Their physical properties and analytical data have been recorded in Table 1.

## RESULTS AND DISCUSSION

Semicarbazones and thiosemicarbazones react with stannous chloride/dimethyltin dichloride in the following manner:



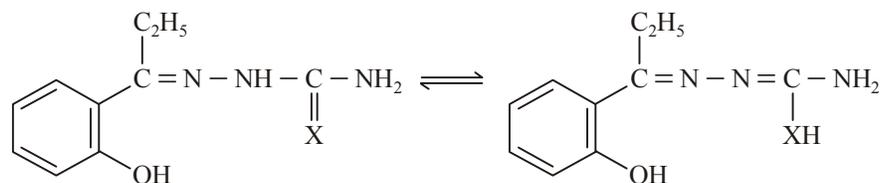
These complexes are coloured solids and are soluble in DMSO and DMF. These are also sensitive to moisture<sup>6,7</sup>.

### Electronic spectra

In the electronic spectra of ligands, two intense maxima were observed at ~ 338 nm and ~ 410 nm, which were due to  $\pi \rightarrow \pi^*$  transition of aromatic ring and  $n \rightarrow \pi^*$  transitions of the  $> \text{C} = \text{N}$  chromophore, respectively. The shifting observed in the later case (~ 410 nm) was due to the polarization in the  $> \text{C} = \text{N}$  bond caused by tin ligand  $\pi$  - electron interaction.

### Infrared spectra

However, in solutions, both the keto and enol tautomeric forms may remain in equilibrium as shown below -



(Where X = O, S)

Table 1: Reactions of stannous chloride/dimethyltin dichloride with semicarbazones and thiosemicarbazones

Reactant	Ligands	Molar ratio	Product colour & state	Melting point (°C)	Analysis: Found (Calcd.) %			Molecular weight : Found (Calcd.)
					N	S	Sn	
SnCl <sub>2</sub>	C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	1 : 1	SnCl <sub>2</sub> .C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> Light yellow solid	95°	10.47 (10.58)	-	29.89 (29.90)	376.73 (396.82)
SnCl <sub>2</sub>	C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> OS	1 : 1	SnCl <sub>2</sub> .C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> OS White solid	115°	10.06 (10.17)	7.65 (7.76)	28.63 (28.74)	402.79 (412.88)
SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	1 : 1	SnCl <sub>2</sub> .C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> Yellow solid	224° (d)	9.69 (9.70)	-	26.31 (27.42)	422.76 (432.85)
SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS	1 : 1	SnCl <sub>2</sub> .C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS Creamy white solid	130°	9.16 (9.36)	7.06 (7.14)	26.19 (26.43)	432.78 (448.91)
SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	1 : 1	SnCl <sub>2</sub> .C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> Orange solid	240°	9.69 (9.70)	-	27.31 (27.42)	422.76 (432.85)
SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS	1 : 1	SnCl <sub>2</sub> .C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS Dark yellow solid	140°	9.16 (9.36)	7.06 (7.14)	26.19 (26.43)	432.78 (448.91)
(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	1 : 1	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> .C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> White solid	180° (d)	9.73 (9.84)	-	27.79 (27.80)	416.79 (426.88)
(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> OS	1 : 1	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> .C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> OS White solid	170° (d)	9.37 (9.48)	7.12 (7.23)	26.68 (26.79)	432.05 (442.94)
(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	1 : 1	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> .C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> Light orange solid	205° (d)	9.06 (9.07)	-	25.52 (25.63)	442.82 (462.91)

Cont...

Reactant	Ligands	Molar ratio	Product colour & state	Melting point (°C)	Analysis: Found (Calcd.) %			Molecular weight : Found (Calcd.)
					N	S	Sn	
(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS	1 : 1	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS White solid	162°	8.69 (8.77)	6.52 (6.69)	23.46 (24.78)	462.84 (478.97)
(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	1 : 1	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> Orange solid	255° (d)	9.06 (9.07)	-	25.52 (25.63)	452.82 (462.91)
(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS	1 : 1	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OS Light yellow solid	156°	8.69 (8.77)	6.52 (6.69)	24.46 (24.78)	462.84 (478.97)

d = decompose

Table 2: Antifungal activity of the ligands and their corresponding tin (II) and tin (IV) complexes

Microorganisms	L <sup>1</sup> H			SnCl <sub>2</sub> ·L <sup>1</sup> H			(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·L <sup>1</sup> H			L <sup>2</sup> H			SnCl <sub>2</sub> ·L <sup>2</sup> H			(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·L <sup>2</sup> H		
	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm
<i>A. flavus</i>	IZ (AI)	20 (1.00)	24 (0.92)	16 (0.80)	22 (0.84)	22 (1.10)	24 (0.92)	18 (0.69)	18 (0.90)	18 (0.69)	20 (1.00)	20 (0.76)	20 (1.40)	28 (1.30)	34			
	IZ (AI)	18 (0.90)	22 (1.00)	22 (1.10)	22 (1.00)	32 (1.45)	22 (1.00)	22 (1.00)	20 (0.90)	22 (1.00)	20 (0.90)	20 (0.90)	20 (1.00)	20 (1.18)	26			
<i>A. niger</i>	IZ (AI)	6 (0.42)	8 (0.25)	10 (0.71)	12 (0.37)	8 (0.57)	16 (0.50)	12 (0.85)	16 (0.50)	16 (0.50)	8 (0.57)	16 (0.50)	8 (1.28)	18 (0.87)	28			

IZ = Inhibition zone (diameter in mm); AI = Activity index (Inhibition zone of test compounds/Inhibition zone of standard)  
L<sup>1</sup>H = C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>; L<sup>2</sup>H = C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>

In the spectra of these ligands, the medium intensity band appearing in the region 3100-3400  $\text{cm}^{-1}$  may be assigned to the hydrogen bonded  $\nu\text{OH}$  vibrations, which disappeared in the resulting complexes.

A sharp and strong band was observed at  $\sim 1620 \pm 10 \text{ cm}^{-1}$ , which may be assignable to  $\nu \text{C}=\text{N}^{12}$  in the spectra of the ligands. This band is shifted to higher frequency ( $\sim 10 \text{ cm}^{-1}$ ) in the spectra of complexes. The ligands exhibited  $\text{NH}_2$  band at  $\sim 3440 \text{ cm}^{-1}$ , which remains unchanged in the spectra of complexes. A band in the region 3350-2850  $\text{cm}^{-1}$  due to  $\sim \text{NH}$  vibration, remains unaffected reflecting the non-involvement of  $\text{NH}$  group in coordination. Some new bands of  $\nu\text{Sn} \leftarrow \text{O}$ ,  $\nu\text{Sn} \leftarrow \text{N}^{13}$ ,  $\nu\text{Sn} \leftarrow \text{S}^{14}$  and  $\nu\text{Sn} - \text{Cl}^{15}$  appear at 550-525  $\text{cm}^{-1}$ , 425-405  $\text{cm}^{-1}$ ,  $325 \pm 20 \text{ cm}^{-1}$  and  $280 \pm 15 \text{ cm}^{-1}$ , respectively.

### **$^1\text{H}$ NMR spectra**

$^1\text{H}$  NMR spectra of ligands and their complexes have been recorded in  $\text{d}_6$  DMSO or  $\text{CDCl}_3$  using TMS as internal standard.

In the proton NMR spectra of the ligands, a broad signal at  $\delta$  3.50 ppm due to  $\text{NH}_2$  protons remain almost unchanged in the spectra of tin complexes, which clearly indicates the non-involvement of this group in complexation. The azomethine proton signal ( $\text{H}-\text{C}=\text{N}$ ) was detected at  $\delta$  8.45 ppm, which appeared at  $\delta$  8.55 ppm in the spectra of complexes due to the coordination of azomethine nitrogen to the metal atom<sup>8,9</sup>. The ligands also exhibited  $\text{NH}$  proton signal at  $\delta$  10.09 ppm, which disappeared in the complexes, showing the involvement of adjacent O or S in bonding with the tin atom.

### **$^{119}\text{Sn}$ NMR spectra**

$^{119}\text{Sn}$  NMR spectra of tin complexes have been recorded using TMT (tetramethyltin) as external standard. Tin (II) complexes gave sharp signals at  $\delta$ -576 ppm and  $\delta$ -578 ppm, which can be attributed to a four coordinated geometry shown in Fig. 1. Tin (IV) complexes also gave sharp signals at  $\delta$ -250 ppm and  $\delta$ -252 ppm, which can be attributed to an octahedral six coordinated geometry shown in Fig. 2.

### **Antimicrobial activity**

Two of ligands and their metal complexes were tested against some of the fungi i.e. *A. flavus*, *F. oxysporum* and *A. niger* at different concentrations. The results are

reported in Table 2. It was observed that metal complexes are much more active than the ligands.

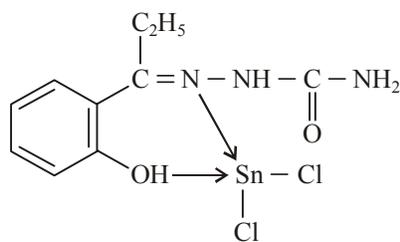


Fig. 1

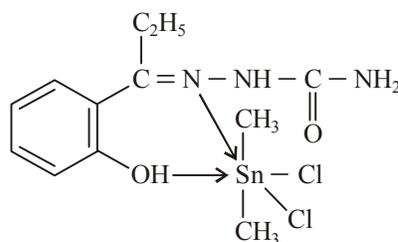


Fig. 2

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