

## Synthesis and spectral studies of tin(IV) complexes with Schiff bases derived from sulpha drugs

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**Abstract.** Reactions of tin(IV) chloride with Schiff bases having ONN donor systems have been investigated and on the basis of elemental analysis, IR, PMR and  $^{119}\text{Sn}$  Mössbauer spectral studies, possible structures have been indicated for the resulting new compounds. The Schiff bases used in these studies are the condensation products of salicylaldehyde with sulphathiazole, sulphaphenazole, sulphadiazine, sulphaguanidine, 2-(*p*-aminobenzene sulphonamide)-4,5-dimethyl oxazole, sulphisoxazole, sulphapyridine and sulphaniilamide.

**Keywords.** Tin(IV) chloride; Schiff bases; sulpha drugs; infrared spectra; proton magnetic resonance spectra; Mössbauer spectra.

### 1. Introduction

Compounds containing the sulphonamide group have long been used as drugs for diseases like cancer, tuberculosis (Vaichaulis 1966), diabetes (Dietrich 1968), malaria (Schmidt 1969) and convulsions (Aktiesel and Kabet 1968). It has now been observed that some of these drugs show increased biological activity when administered in the form of metal complexes (Williams 1972; Frust and Haro 1969; Tiwari and Mishra 1980).

A number of references are now available to show that the condensation products of sulpha drugs with aldehydes, ketones or their derivatives are very active biologically, besides having good complexing ability, and their activity increases on complexation with metal ions (Jain and Chaturvedi 1977; Lal and Shukla 1981). It was, therefore, considered of interest to synthesize tin(IV) derivatives of Schiff bases, derived by the condensation of salicylaldehyde with some of the well-known sulpha drugs. In this paper we report the results of these studies.

### 2. Results and discussion

The equimolar reactions of stannic chloride with Schiff bases derived by condensation of salicylaldehyde with various sulpha drugs ( $\text{SBH}_2$ ) can be represented by the following equation



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All the resulting derivatives are light yellow to dark yellow solids, mostly soluble in dimethyl formamide, dimethyl sulphoxide and methanol. They were purified by repeated washing with cyclohexane and their purity was further checked by thin layer chromatography on silica gel G using anhydrous dimethyl formamide as the solvent – all the complexes moved as single spots.

All these complexes of tin(IV) are monomeric as evidenced by their molecular weight determination by the Rast camphor method. The low values of molar conductivity ( $8\text{--}14 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) of the complexes in anhydrous dimethyl formamide show their non-electrolytic nature.

### 2.1 IR spectra

The ligands exhibit two broad peaks in the region  $3400\text{--}3100 \text{ cm}^{-1}$  due to the hydrogen-bonded OH and NH (Varshney and Tandon 1985). In the spectra of the complexes, the band due to OH gets shifted to the higher wave number region showing the coordination of the ligand through the phenolic oxygen. However, the  $\nu$  NH band remains approximately at the same position, which clearly indicates the non-involvement of NH in complexation. A strong band in the region  $1600\text{--}1620 \text{ cm}^{-1}$  assignable to  $\nu\text{C--N}$  is observed in all the ligands. A slight shift of this band towards the higher frequency region in the case of tin(IV) derivatives may be due to an increase in the bond order of the azomethine group (Busch and Bailar 1956).

A medium intensity band in the ligand spectrum at  $\sim 1280 \text{ cm}^{-1}$  due to the C–O vibrations gets shifted to the higher frequency region ( $\sim 1300 \text{ cm}^{-1}$ ) in the complexes suggesting the participation of phenolic oxygen in complexation (Biradar and Kulkarni 1971). Further, new strong bands in all the tin(IV) derivatives, appearing in the region  $420\text{--}400$  and  $500\text{--}530 \text{ cm}^{-1}$  are due to the  $\text{Sn} \leftarrow \text{N}$  (Varshney and Tandon 1985c) and  $\text{Sn} \leftarrow \text{O}$  (Saxena *et al* 1982) respectively.

### 2.2 PMR spectra

The  $^1\text{H}$  NMR spectra of ligands show NH proton signals at  $\delta 10.09$  ppm while all the ligands show an OH proton signal at  $\delta 12.10$  ppm. The signal due to the NH proton remains unchanged in the compounds showing its non-involvement in coordination. However, the signal due to the OH proton gets shifted downfield indicating the coordination of the phenolic oxygen to the tin atom. A signal at  $\delta 8.15$  ppm is observed in the complexes due to the azomethine proton, which moves downfield in comparison to its original position in the free ligand, thereby indicating the coordination of the azomethine nitrogen to the metal atom. An appreciable change is also observed in the position of the aromatic phenyl protons appearing as a complex multiplet at  $\delta 6.44\text{--}7.86$  ppm.

### 2.3 Mössbauer Spectra

The Mössbauer spectrum of one of the complexes ( $\text{SnCl}_4 \cdot \text{C}_{14}\text{H}_{14}\text{N}_4\text{SO}_3$ ) is recorded at  $80^\circ\text{K}$  using a liquid nitrogen cryostat. The isomer shift value is  $0.35 \text{ mm sec}^{-1}$ , which is lower than the  $0.80 \text{ mm sec}^{-1}$  observed in the case of tin(IV) chloride. Thus a decrease in the isomer shift value as compared to

the parent compound indicates complexation, which the magnitude of this fall is directly proportional to the donor strength of the ligand (Huggins *et al* 1969).

Since, the complex has no quadrupole splitting, it can be concluded that the spherical charge distribution around the tin nucleus is unchanged after complexation. This further indicates that there is no marked difference in the polarities of the tin-ligand bonds as reported earlier as well (Saxena *et al* 1984).

Thus on the basis of the above spectral evidence the structures in scheme 1 can be proposed for the resulting tin(IV) complexes.

### 3. Experimental

All the reactions were carried out under strictly anhydrous conditions and analytical grade chemicals were used for all experiments.

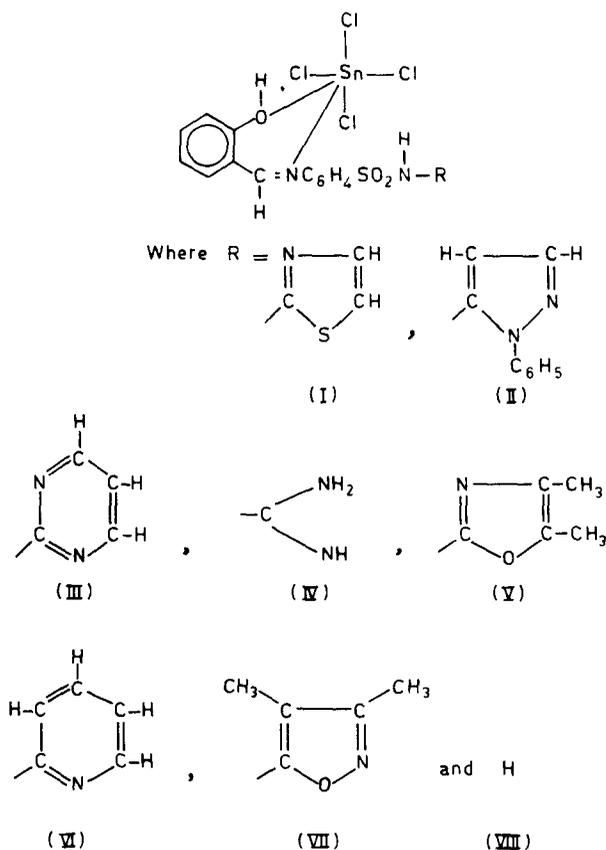
#### 3.1 Preparation of Schiff bases

The Schiff bases have been synthesized by the condensation of salicylaldehyde with sulphathiazole(I), sulphaphenazole(II), sulphadiazine(III), sulphaguanidine(IV), 2-(*p*-aminobenzene sulphonamide)-4,5-dimethyloxazole(V), sulphisoxazole(VI), sulphapyridine(VII) and sulphanilamide(VIII) in 1:1 molar ratio using ethanol as the reaction medium. The solution was refluxed on a water bath for 3–4 h and then allowed to cool to room temperature. The products so obtained were recrystallised from acetone. The ligands used in these studies are as follows.

(1) Salicylaldehyde sulphathiazole (C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> S <sub>2</sub> O <sub>3</sub> ) m.p. 222°C	H <sub>2</sub> ONN-1
(2) Salicylaldehyde sulphaphenazole (C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> SO <sub>3</sub> ) m.p. 185°C	H <sub>2</sub> ONN-2
(3) Salicylaldehyde sulphadiazine (C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> SO <sub>3</sub> ) m.p. 240°C	H <sub>2</sub> ONN-3
(4) Salicylaldehyde sulphaguanidine (C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> SO <sub>3</sub> ) m.p. 230°C	H <sub>2</sub> ONN-4
(5) 2-( <i>p</i> -amino benzene sulphonamide)- 4,5-dimethyloxazole (C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> S) m.p. 140°C	H <sub>2</sub> ONN-5
(6) Salicylaldehyde sulphisoxazole (C <sub>18</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S) m.p. 160°C	H <sub>2</sub> ONN-6
(7) Salicylaldehyde sulphapyridine (C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S) m.p. 200°C	H <sub>2</sub> ONN-7
(8) Salicylaldehyde sulphanilamide (C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S) m.p. 150°C	H <sub>2</sub> ONN-8

#### 3.2 Analytical methods and physical measurements

The complexes were analysed as reported earlier (Varshney and Tandon 1984, 1985) and the infrared spectra were recorded on a Perkin Elmer 577 IR spectrophotometer in the region 4000–200 cm<sup>-1</sup> using KBr optics. A Perkin Elmer Model R12-B spectrometer was used for obtaining the proton magnetic resonance



Scheme 1.

spectra employing deuterated dimethyl sulphoxide or deuterated chloroform as the solvent and tetramethyl silane as the internal standard.

$^{119}\text{Sn}$  Mössbauer spectra were obtained using a constant acceleration micro-processor spectrometer (Cryophysics Ltd., Oxford) with a 512 channel data store. A 15 mci  $\text{Ba } ^{119\text{m}}\text{SnO}_3$  source was used at room temperature and samples were packed in perspex discs and cooled to 80°K using a liquid nitrogen cryostat. The experimental error in the measured values of the isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E_q$ ) parameters was  $\pm 0.05 \text{ mm sec}^{-1}$ .

Molar conductance measurements were made in anhydrous dimethylformamide at  $36 \pm 1^\circ\text{C}$  using a Systronics conductivity bridge Model 305. Molecular weight determinations were carried out by the Rast camphor method.

### 3.3 Preparation of $\text{Sn(IV)}$ complexes

Equimolar amounts of stannic chloride and the ligand were mixed in a flask using benzene as the reaction medium. The colour of the reaction changed immediately. The resulting solution was stirred on a magnetic stirrer for about 4 h. Excess of solvent was removed and the product repeatedly washed with cyclohexane. This was finally dried under vacuum and its purity was checked by TLC.

**Table 1.** Synthesis and characteristics of tin(IV) complexes (the tin compound used in all cases was SnCl<sub>4</sub>, while the molar ratio of compound and ligand was 1:1).

Reactant ligand	Compound colour and state	m.p. °C	Analysis			Mol. Wt obs. (calc.)
			Observed Sn	(calculated) N	S	
H <sub>2</sub> ONN-1	SnCl <sub>4</sub> ·C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> S <sub>2</sub> O <sub>2</sub> Light yellow solid	205	18.86 (19.15)	6.25 (6.78)	9.86 (9.86)	607 (619.7)
H <sub>2</sub> ONN-2	SnCl <sub>4</sub> ·C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> SO <sub>3</sub> Orange solid	180	16.94 (17.49)	8.86 (9.04)	4.92 (5.16)	659 (678.7)
H <sub>2</sub> ONN-3	SnCl <sub>4</sub> ·C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> SO <sub>3</sub> Yellow solid	272	19.42 (19.96)	8.96 (9.42)	4.92 (5.38)	582 (594.7)
H <sub>2</sub> ONN-4	SnCl <sub>4</sub> ·C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> SO <sub>3</sub> Dark yellow solid	190	19.96 (20.51)	9.23 (9.68)	5.21 (5.53)	563 (578.7)
H <sub>2</sub> ONN-5	SnCl <sub>4</sub> ·C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> Dirty yellow solid	145	18.24 (18.79)	6.32 (6.65)	4.92 (5.07)	615 (631.7)
H <sub>2</sub> ONN-6	SnCl <sub>4</sub> ·C <sub>18</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S Yellow solid	170	18.96 (19.34)	6.21 (6.84)	5.01 (5.21)	601 (613.7)
H <sub>2</sub> ONN-7	SnCl <sub>4</sub> ·C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S Canary yellow solid	185	18.86 (19.28)	6.53 (6.82)	4.69 (5.19)	604 (615.7)
H <sub>2</sub> ONN-8	SnCl <sub>4</sub> ·C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S Yellow solid	140	21.95 (22.12)	4.96 (5.22)	5.24 (5.96)	521 (536.7)

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