Some New Tin(II) Complexes of Schiff Bases Derived from Sulphadrugs

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Summary: Reactions of tin(II) methoxide with the Schiff bases derived by the condensation of salicyladehyde and sulfadrugs have resulted in the isolation of some new tin(II) derivatives. These have been characterized on the bases of elemental analyses, molecular weight determination, conductivity measurement and UV, IR and ^{1}H NMR spectral studies. The bivalent nature and the geometry around tin(II) has been deduced on the basis of Mossbauer spectral data.

Introduction

Only a limited amount of work has so far been carried out on the tin(II) Schiff base complexes [1-7] as the synthesis of pure tin(II) compounds presents difficulties on account of its ease of oxidation in the aqueous solution. However, it is usually possible to prevent this by carrying out the synthesis in deaerated solution in presence of non-oxidising atmosphere. In the present paper, we report the synthesis and characterization of tin(II) complexes of the following Schiff bases derived from sulphadrugs.

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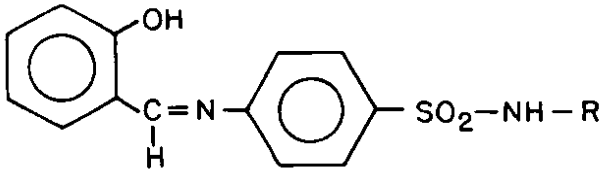

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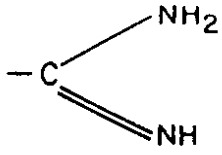
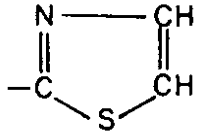


Salicylaldehyde sulfaguanidine

IV

where R =



I

Salicylaldehyde sulfathiazole

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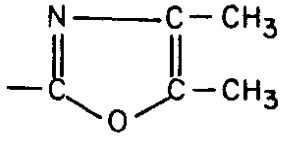

Salicylaldehyde sulfisoxazole

V

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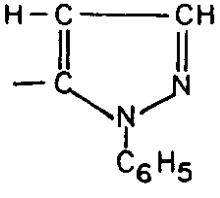

II

Salicylaldehyde sulfaphenazole

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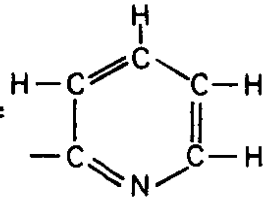

Salicylaldehyde sulfapyridine

VI

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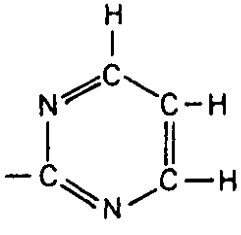

III

Salicylaldehyde sulfadiazine

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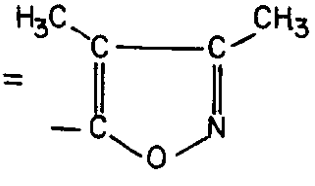


Salicylaldehyde-2-(p-aminobenzene sulfonamide)-4,5-dimethyloxazole

VII

Experimental

Tin(II) methoxide was prepared by the reaction of anhydrous tin(II) chloride with an excess of triethylamine in methanol as described by Gsell and Zeldin [8]. Schiff bases were synthesized by the condensation of salicylaldehyde with sulfa drugs in 96% ethanol. The solution was refluxed on a water bath for 2-3 hours and allowed to cool at room temperature [9]. The ligands used in these studies are as follows:

(i) Salicylaldehyde sulfathiazole ($C_{16}H_{13}N_3S_2O_3$) m.p. 222°C

(ii) Salicylaldehyde sulfaphenazole ($C_{22}H_{18}N_4SO_3$) m.p. 185°C

(iii) Salicylaldehyde sulfadiazine ($C_{17}H_{14}N_4SO_3$) m.p. 240°C

(iv) Salicylaldehyde sulfaguanidine ($C_{14}H_{14}N_4SO_3$) m.p. 230°C

(v) Salicylaldehyde sulfisoxazole ($C_{18}H_{15}N_3O_3S$) m.p. 160°C

(vi) Salicylaldehyde sulfapyridine ($C_{18}H_{17}N_3O_3S$) m.p. 200°C

(vii) Salicylaldehyde-2-(p-aminobenzene sulfonamide)-4,5-dimethyloxazole ($C_{18}H_{17}N_3O_4S$) m.p. 140°C

Tin was estimated gravimetrically as SnO_2. Nitrogen was estimated by the Kjeldahl's method and sulphur as $BaSO_4$ by the Messenger's method.

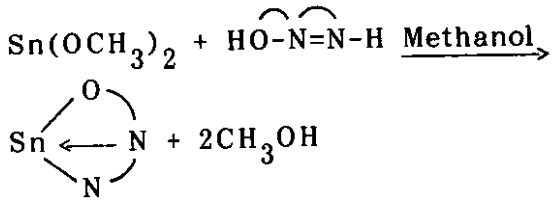
^{119}Sn Mossbauer spectra were recorded with $Ba^{119}SnO_3$ source at 77K. The isomer shift values are relative to SnO_2. Electronic spectra were recorded in methanol on a Pye Unicam SP8-100 spectrophotometer and the IR spectra on a Perkin Elmer 577 grating spectrophotometer in KBr pellets. NMR spectral measurements were carried out as a Perkin Elmer R-12B spectrometer in DMSO-d^6 using TMS as an internal standard at 60 MHz. Conductance of 10^{-3}M solutions of complexes soluble in DMF was measured at 30 ± 1°C with a conductivity bridge (type 305, Systronics). Molecular weights were determined by the Rast Camphor method.

Synthesis of Sn(II) Schiff Base Complexes:

The requisite amount of tin(II) methoxide 0.235-0.823g was added to the calculated amount 0.467-1.502g of the ligand in presence of methanol while maintaining a nitrogen atmosphere. Immediately, the colour of the solution changed and it was then stirred magnetically for 2 hours. The excess of the solvent was removed and the compound finally dried in Vacuo at a bath temperature of 45 ± 5°C after being repeatedly washed with dry cyclohexane.

Results and Discussion

Tin(II) methoxide reacts with these azomethine in equimolar ratio as shown below:



$$Sn(OCH_3)_2 + HO\overset{\frown}{-}N\overset{\frown}{=}N-H \xrightarrow{\text{Methanol}} Sn\begin{matrix}O\\ \leftarrow N\\ N\end{matrix} + 2CH_3OH$$

On stirring magnetically for about 2 hours, the resulting complexes are obtained as coloured solids. These are monomeric and non-electrolyte in nature. The physical characteristics of these complexes are recorded in Table-1.

The electronic spectrum of the salicylaldehyde sulphathiazole show a maximum at 249 nm due to the $\pi-\pi^*$ (benzenoid) transitions, which gets shifted towards the lower energy region ($\sim$ 269 nm) in the complexes. This may be attributed to an increase in the availability of electrons on the auxochromic oxygen in the absence of hydrogen bonding, which is present initially in the ligand molecule.

In the complexes, two intense maxima are observed at $\sim$ 335 and $\sim$ 380 nm and which are due to the $\pi-\pi^*$ and M-π^* transitions of the C=N chromophore. The appreciable shifting observed in the former case ($\sim$ 365 nm) is due to the polarisation in the C=N bond caused by tin-ligand electron interaction.

In the IR spectra of the ligands, medium intensity bands, appearing at $\sim$ 3350 and 2750 cm^{-1} may be assigned to the hydrogen bonded ν OH/νNH vibrations, which disappear in the resulting 1:1 tin complexes suggesting the possible deprotonation on complexation and formation of new Sn-O and Sn-N bonds.

A sharp band observed at $\sim$ 1620 cm^{-1} in the ligands gets shifted

Table-1: Synthesis and Characteristics of Tin(II) Complexes.

Sl. No.	Reactants (g) Tin compound	Ligand	Yield %	Product & characteristic (colour and state)	M.p. °C Found (Calcd.)	Analysis % Sn Found (Calcd.)	N Found (Calcd.)	S (Calcd.)	Mol.Wt. Found
1	$Sn(OCH_3)_2$	$C_{16}H_{13}N_3S_2O_3$(I)	76	$SnC_{16}H_{11}N_3S_2O_3$	220	24.0	8.2	12.8	440
	0.235	0.467		(yellow solid)		(24.9)	(8.8)	(13.4)	(476)
2	$Sn(OCH_3)_2$	$C_{22}H_{18}N_4SO_3$(II)	73	$SnC_{22}H_{16}N_4SO_3$	230	21.8	7.2	5.4	510
	0.625	1.446		(yellow solid)		(22.2)	(7.8)	(6.0)	(535)
3	$Sn(OCH_3)_2$	$C_{17}H_{14}N_4SO_3$(III)	74	$SnC_{17}H_{12}N_4SO_3$	215d	24.9	11.2	6.1	450
	0.723	1.416		(Dark Yellow solid)		(25.2)	(11.9)	(6.8)	(471)
4	$Sn(OCH_3)_2$	$C_{14}H_{14}N_4SO_3$ (IV)	75	$SnC_{14}H_{12}N_4SO_3$	160	26.9	12.1	6.9	420
	0.823	1.448		(yellow solid)		(27.3)	(12.9)	(7.3)	(435)
5	$Sn(OCH_3)_2$	$C_{18}H_{17}N_3O_4S$(V)	73	$SnC_{18}H_{15}N_3O_4S$	240d	23.8	8.1	6.0	470
	0.732	1.502		(yellow solid)		(24.6)	(8.6)	(6.5)	(488)
6	$Sn(OCH_3)_2$	$C_{18}H_{15}N_3O_3S$(VI)	75	$SnC_{18}H_{13}N_3O_3S$	180	24.8	8.3	6.2	440
	0.624	1.218		(orange solid)		(25.7)	(8.9)	(6.8)	(470)
7	$Sn(OCH_3)_2$	$C_{18}H_{17}BN_3O_3S$(VII)	76	$SnC_{18}H_{15}N_3O_3S$	170d	24.7	8.3	6.2	450
	0.470	0.923		(yellow solid)		(25.2)	(8.9)	(6.8)	(472)

d = decompose.

towards higher energy region ($\sim$ 10 cm^{-1}) and this indicates the coordination of azomethine nitrogen to the tin atom in the resulting complexes.

Few new and sharp intensity bands observed only in the complexes at $\sim$ 540 cm^{-1} and 430 cm^{-1} are due to the ν Sn $\leftarrow$ N and ν Sn - O respectively.

The ^1H NMR spectra of the ligands show a signal at δ 12.50-13.50 ppm for the hydrogen bonded phenolic protons, which disappears completely in the resulting complexes suggesting thereby chelation of the tin atom through the phenolic oxygen after its deprotonation. The ligands also exhibit the -NH proton signal at δ10.10-10.50 ppm, which disappears in the tin complexes.

The azomethine proton signal appearing at 8.85 ppm in the ligand is shifted downfield (δ 8.96) after complexation. The complex multiplet CH_2-S centered at δ 7.50-7.56 ppm is due to the aromatic protons, which remain almost unchanged in the resulting derivatives.

The conclusions drawn from electronic, IR and ^1H NMR studies get further support by the ^{119}Sn Mossbauer data. The isomer shift values have been measured with respect to $BaSnO_3$ at the liquid nitrogen temperature and the Mossbauer parameters have been enlised in Table-2.

The Mosabauer isomer shift values (δ) lie in the range (2.5-4.5 mm s^{-1}) prescribed for tin(II) compounds and these values are lower than the value of tin(II) chloride (4.15 mm s^{-1}). The decrease in the isomer shift value is probably on account of the interaction between the tin and the donor atom of the ligands [10,11].

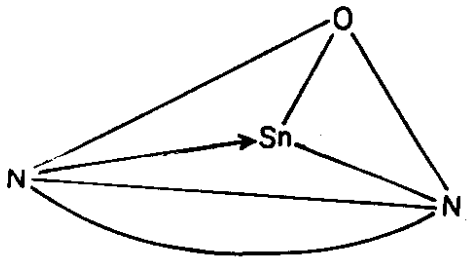
The appearance of a relatively large resolvable quadrupole splitting (Δ Eq) for the tin(II) complexes may

Table-2

Sl.No.	Compound	IS δ mm sec^{-1}	Q.S. Δ Eq mm sec^{-1}
1.	$SnC_{16}H_{11}N_3S_2O_3$	3.18	1.83
2.	$SnC_{22}H_{16}N_4SO_3$	3.17	1.86

be due to the distortion arising mainly out of an imbalance of p-electrons in the lone pair orbital with trigonal pyramidal geometry around tin [12].

On the basis of the above evidences, the following tentative structure can be assigned to these newly synthesized derivatives.



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