

Studies on some organotin(IV) complexes of azomethines derived from sulphad rugs

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Abstract. Equimolar reactions of Bu_2SnO and Ph_2SnO with azomethines derived by the condensation of salicylaldehyde with some well known sulphad rugs *viz.* sulphathiazole, sulphaphenazole, sulphadiazine, sulphaguanidine and 2-(*p*-aminobenzene sulphonamido)-4,5-dimethyl oxazole yield a new series of organotin(IV) complexes. The infrared and proton magnetic resonance spectral studies indicate coordination of phenolic oxygen and azomethine and secondary amino nitrogens providing a five coordinated environment at the tin atom.

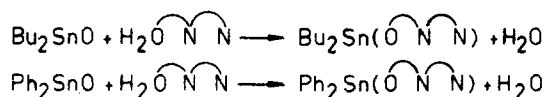
Keywords. Organotin(IV) complexes; azomethines; sulphad rugs; IR spectra; proton magnetic resonance spectra.

1. Introduction

In earlier publications from these laboratories, the syntheses of a variety of tin(II) and tin(IV) derivatives with different types of Schiff bases have been reported (Varshney and Tandon 1984a, b, c; Saxena *et al* 1982, 1984; Saxena and Tandon 1983). However, organotin(IV) complexes of azomethines derived from sulphad rugs have not been studied so far. In this paper, we report the synthesis and characterization of organotin(IV) derivatives with ligands derived by the condensation of salicylaldehyde with sulphathiazole, sulphaphenazole, sulphadiazine, sulphaguanidine and 2-(*p*-aminobenzene sulphonamido)-4,5-dimethyl oxazole.

2. Discussion

The reactions of dibutyltin oxide or diphenyltin oxide with the above mentioned azomethines, in benzene in 1:1 molar ratio, take place as follows:



All the newly synthesized complexes are coloured solids, insoluble in common organic solvents but soluble in DMSO and DMF.

The molar conductance measurements in anhydrous DMF at room temperature (6 to $8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) show that these complexes behave as non-electrolytes; the molecular weight determinations indicate their monomeric nature.

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2.1 Infrared spectra

In the IR spectra of complexes, no band in the region $3100\text{--}3450\text{ cm}^{-1}$ assignable to ν_{OH} and ν_{NH} could be observed due to their deprotonation on complex formation with the metal ion. A strong band in the region, $1595\text{--}1620\text{ cm}^{-1}$ may be assigned to $\nu_{\text{C=N}}$, which gets shifted to the lower range as compared to its position in the ligands, due to the coordination of azomethine nitrogen to the tin atom (Saxena *et al* 1982). A medium intensity band in the ligand at $\sim 1280\text{ cm}^{-1}$ due to the $\nu_{\text{C-O}}$ vibrations gets shifted to a higher frequency ($\sim 1300\text{ cm}^{-1}$) range in complexes indicating the participation of phenolic oxygen in coordination (Biradar and Kulkarni 1971). Besides these, several new and sharp to medium intensity bands are observed in the regions $510\text{--}530\text{ cm}^{-1}$ and $440\text{--}380\text{ cm}^{-1}$, due to $\nu_{\text{Sn-O}}$ (Saxena *et al* 1983) and $\nu_{\text{Sn-N}}$ (Kawakami and Okawara 1966) respectively, which are not observed in the spectra of azomethines.

2.2 NMR spectra

In the ^1H NMR spectra of salicylaldehyde sulphadiazine broad signals appear at $\delta 10.26$ and $\delta 12.50$ ppm due to the secondary amino (NH) and hydrogen bonded phenolic protons. These signals disappear in the spectra of tin(IV) complexes indicating the chelation of nitrogen and oxygen to tin. The azomethine proton signal (H-C=N) appearing at $\delta 8.80$ ppm in the ligand is shifted downfield on complexation. The complexes, however, show additional signals at $\delta 0.7\text{--}2.0$ ppm owing to the protons of the butyl group as mentioned in table 1.

Thus on the basis of the above evidences, the following structure can be assigned to these complexes:

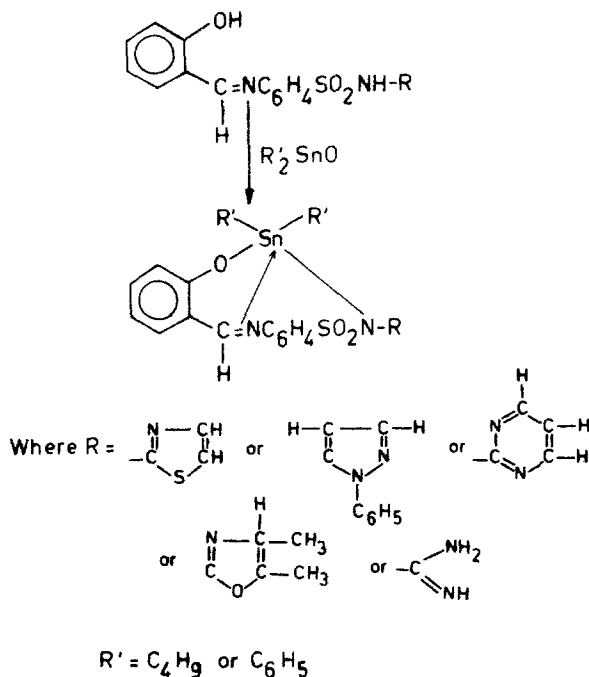
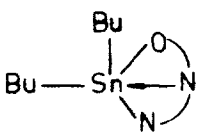
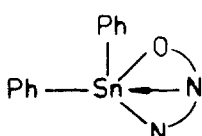


Table 1. ^1H NMR spectral data (δ ppm) of salicylaldehyde sulphadazine and its 1:1 tin(IV) complexes.

Compound	Aromatic protons	OH (H-bonded)	NH (SO ₂ NH)	CH (Azomethine)	Butyl protons
H ₂ ONN-4	6.50–7.80 m	12.50 bs	10.26 s	8.80 s	—
	6.65–7.90 m	—	—	8.9 s	0.70–2.0
	6.60–7.85 m	—	—	8.85 s	—

s = singlet, bs = broad singlet, m = complex multiplet.

3. Experimental

Glass apparatus fitted with quickfit interchangeable joints was used and the reactions were carried out under strictly anhydrous conditions. The fractionations were made on a column packed with Raschig rings and fitted to a ratiohead with a condenser.

3.1 Materials

The azomethines were synthesized by the condensation of salicylaldehyde with the respective sulphadugs in 95% ethanol. The solution was refluxed on a water-bath for 2–3 hours and then allowed to cool at room temperature (Dashora *et al* 1983). The ligands used in these studies are as follows:

- | | |
|---|----------------------|
| (1) Salicylaldehyde sulphathiazole
(C ₁₆ H ₁₃ N ₃ S ₂ O ₃) M.P. 222°C | H ₂ ONN-1 |
| (2) Salicylaldehyde sulphaphenazole
(C ₂₂ H ₁₈ N ₄ SO ₃) M.P. 185°C | H ₂ ONN-2 |
| (3) Salicylaldehyde sulphadiazine
(C ₁₇ H ₁₄ N ₄ SO ₃) M.P. 240°C | H ₂ ONN-3 |
| (4) Salicylaldehyde sulphaguanidine
(C ₁₄ H ₁₄ N ₄ SO ₃) M.P. 230°C | H ₂ ONN-4 |
| (5) 2-(<i>p</i> -amino benzene sulphonamide)-
4,5-dimethyloxazole
(C ₁₈ H ₁₇ N ₃ O ₄ S) M.P. 140°C | H ₂ ONN-5 |

3.2 Analytical methods and physical measurements

The complexes were analysed as reported earlier (Varshney and Tandon 1984b) and their molecular weights were determined by the Rast camphor method. The conduct-

Table 2. Characterisation data of Sn(IV) complexes of azomethines derived from sulphadrigs.

Tin compounds	Azomethines	Compound, colour and state	M.P. °C	Composition found (calcd.) %				Mol. Wt. found (calcd.)
				Sn	N	S	S	
Bu ₂ SnO	H ₂ ONN-1	Bu ₂ SnC ₁₆ H ₁₁ N ₃ S ₂ O ₃ (yellow powder)	225 s	19.93 (20.12)	6.86 (7.12)	10.24 (10.85)	548 (589.7)	
Bu ₂ SnO	H ₂ ONN-2	Bu ₂ SnC ₂₂ H ₁₆ N ₄ SO ₃ (yellow powder)	243 s	17.68 (18.19)	8.26 (8.63)	4.52 (4.93)	627 (648.7)	
Bu ₂ SnO	H ₂ ONN-3	Bu ₂ SnC ₁₇ H ₁₂ N ₄ SO ₃ (yellow powder)	210 s	19.62 (20.30)	9.02 (9.57)	5.12 (5.47)	560 (584.7)	
Bu ₂ SnO	H ₂ ONN-4	Bu ₂ SnC ₁₄ H ₁₂ N ₄ SO ₃ (dark yellow powder)	215 d	20.98 (21.63)	9.78 (10.20)	5.32 (5.83)	526 (548.7)	
Bu ₂ SnO	H ₂ ONN-5	Bu ₂ SnC ₁₈ H ₁₅ N ₃ O ₄ S (dark yellow powder)	160 s	18.96 (19.73)	6.34 (6.98)	4.92 (5.32)	574 (601.7)	
Ph ₂ SnO	H ₂ ONN-1	Ph ₂ SnC ₁₆ H ₁₁ N ₃ S ₂ O ₂ (light yellow powder)	200 d	18.68 (19.34)	6.32 (6.84)	10.05 (10.42)	584 (613.7)	
Ph ₂ SnO	H ₂ ONN-2	Ph ₂ SnC ₂₂ H ₁₆ N ₄ SO ₃ (light yellow powder)	230 d	16.35 (17.23)	7.84 (8.13)	4.16 (4.64)	664 (688.7)	
Ph ₂ SnO	H ₂ ONN-3	Ph ₂ SnC ₁₇ H ₁₂ N ₄ SO ₃ (dark yellow powder)	250 d	18.34 (19.00)	8.32 (8.96)	5.01 (5.12)	601 (624.7)	
Ph ₂ SnO	H ₂ ONN-4	Ph ₂ SnC ₁₄ H ₁₂ N ₄ SO ₃ (dark yellow powder)	280 d	19.68 (20.16)	9.12 (9.51)	4.86 (5.43)	566 (588.71)	
Ph ₂ SnO	H ₂ ONN-5	Ph ₂ SnC ₁₈ H ₁₅ N ₃ O ₄ S	170 s	17.82 (18.49)	6.03 (6.54)	4.26 (4.98)	613 (641.7)	

s = sharp, d = decompose, Calcd. = Calculated.

ance of 10^{-3} M solutions of the complexes was measured at $32 \pm 1^\circ\text{C}$ with a conductivity bridge. Infrared spectra were scanned in KBr pellets and NMR spectra in DMSO- d_6 or CDCl_3 using TMS as an internal standard at 60 MHz.

3.3 Synthesis of tin(IV) azomethine complexes

Ph_2SnO or Bu_2SnO was dissolved in dry benzene (30–40 ml) and the requisite amount of ligand was added. The contents were refluxed on a fractionating column for about 48 hrs. The water liberated in the reaction was removed azeotropically with benzene. On completion of the reactions, the resulting products were rendered free from the solvent and then washed repeatedly with dry cyclohexane. The products so formed were finally dried *in vacuo* at 60 to 70°C for 2–3 hrs. Their properties and analyses are recorded in table 2.

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