

Some new tin(II) complexes of Schiff bases derived from S-benzyl-dithiocarbazate

ANIL VARSHNEY and J P TANDON*

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

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Abstract. Some new derivatives of tin(II) have been synthesised by the reactions of anhydrous tin(II) chloride with biologically active monofunctional bidentate and bifunctional tridentate thio-Schiff bases in oxygen-free nitrogen atmosphere using tetrahydrofuran as the reaction medium. The ligands used in these studies are the condensation products of S-benzyl dithiocarbazate with various aldehydes and ketones. An attempt has been made to probe their structures by elemental analyses, molecular weight determination, conductivity measurement and UV, IR and ^1H NMR spectral studies.

Keywords. Tin(II) complexes; dithiocarbazate derivatives; Schiff bases; UV spectra, ^1H NMR spectra; IR spectra.

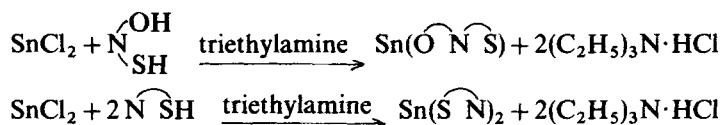
1. Introduction

Extensive work has been carried out on the coordination chemistry of inorganic and organometallic tin(IV) derivatives; but only a few papers have been published on the tin(II) Schiff base complexes (Hobday and Smith 1971; Stocco *et al* 1974; Ewings *et al* 1976). It has now evoked considerable interest and an exhaustive review on the subject has recently appeared (Veith and Recktenwald 1982).

However, the preparation of pure tin(II) compounds presents difficulties on account of its ease of oxidation in aqueous solution (Latimer 1952), but it is usually possible to prevent this by carrying out synthesis in a deaerated solution in a non-oxidising atmosphere. Compounds containing S bonds have been reported to be fairly stable. It was, therefore, considered worthwhile to synthesize and characterize tin(II) complexes with the Schiff bases derived from the condensation of S-benzyl dithiocarbazate with aldehydes and ketones and the results of these studies are reported in this paper.

2. Discussion

The monofunctional bidentate and bifunctional tridentate thio-Schiff bases react with tin(II) chloride in the following manner:



* To whom all correspondence should be addressed.

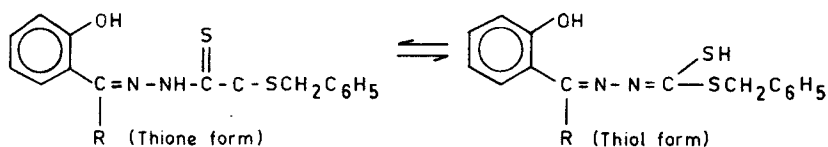
These reactions were quite facile in the presence of triethylamine and could be completed in 1 to 2 hr of stirring. The HCl liberated in the reactions was conveniently removed as $\text{Et}_3\text{N} \cdot \text{HCl}$, which could be precipitated out instantaneously. The resulting complexes are coloured solids and soluble in methanol, DMF and DMSO. Their monomeric nature is shown by the molecular weight determination. These are, however, susceptible to moisture and aerial oxidation. A list of complexes prepared and other data about them are given in table 1.

2.1 UV spectra

In the electronic spectra of the Schiff bases, a band is observed at *ca* 216 nm, which may be assigned to the '1B' band of the phenyl ring (Pardley *et al* 1980). This undergoes a bathochromic shift due to complexation and is observed at *ca* 220 nm in the complexes. Similarly, the ligand chromophore $\text{C}=\text{N}$, which absorbs at *ca* 290 nm, shifts to higher wavelengths and is observed at 296 nm. The band in the spectrum of the ligand at *ca* 340 nm is likely to be the secondary band of the benzene red shifted owing to the chromophore, $\text{>C}=\text{N}-\text{N}=\text{C}<$ and this shifts to 370 nm in the complexes possibly due to the polarization of $\text{C}=\text{N}$ bond caused by metal-ligand interaction.

2.2 IR spectra

The IR spectra of the ligands show a broad and strong band in the region, $3450\text{--}2900\text{ cm}^{-1}$ attributable to $\nu(\text{OH})$ and $\nu(\text{NH})$ modes, while no peak is observed at *ca* 2570 cm^{-1} showing the absence of $\nu(\text{SH})$ (Ali and Bose 1977). However, the latter band appears in the solution spectra with the disappearance of $\nu(\text{NH})$ and $\nu(\text{C}=\text{S})$ bonds. This spectral evidence suggests the existence of a tautomeric equilibrium between two forms of the ligand as shown in figure 1 (Ali *et al* 1972).



In the IR spectra of complexes, no band in the region, $3450\text{--}2900\text{ cm}^{-1}$ assignable to $\nu(\text{OH})$ and $\nu(\text{NH})$ could be observed due to their deprotonation on complex formation with the metal ion. A strong band in the region $1605\text{--}1620\text{ cm}^{-1}$, may be assigned to $\nu(\text{C}=\text{N})$, which is shifted to the higher side as compared to its position in the ligands due to the coordination of the azomethine nitrogen to the metal atom. A shift towards higher wavenumbers has been reported earlier also (Busch *et al* 1956), which has been attributed to the donation of an unshared pair of electrons from nitrogen to the metal atom, causing an increase in the carbon-nitrogen bond order. A medium intensity band at *ca* 1310 cm^{-1} due to the $\nu(\text{C}=\text{S})$ vibration splits on complexation suggesting the participation of the thiolic sulphur in coordination (Silverstein *et al* 1974).

Besides these, several new bands observed at *ca* 656 cm^{-1} , 430 and 360 cm^{-1} may be assigned to $\nu(\text{Sn}-\text{O})$, $\nu(\text{Sn}-\text{N})$ (Saxena *et al* 1982) and $\nu(\text{Sn}-\text{S})$ (Cusack *et al* 1980) respectively, thus lending support to the proposed coordination in the complexes.

Table 1. Synthesis and characteristics of tin(II) complexes.

Tin compound	Reactants (g)		Product obtained theoretical		M. P. °C	Analysis %				Mol. wt. observed (theoretical)
	Ligand	Molar ratio	Yield (g)	Colour and state		Sn Observed	N Observed	S	S	
SnCl ₂ (0-696)	C ₁₅ H ₁₄ N ₂ S ₂ O (0-726)	1:1	SnC ₁₅ H ₁₄ N ₂ S ₂ O 1-234 (1-5036)	Yellow solid	225s	27-962 (28-350)	6-032 (6-687)	14-962 (15-285)	430 (418-7)	
SnCl ₂ (0-346)	C ₁₉ H ₁₆ N ₂ S ₂ O (0-642)	1:1	SnC ₁₉ H ₁₆ N ₂ S ₂ O 0-734 (0-854)	Yellow solid	220s	24-834 (25-325)	5-633 (5-973)	13-236 (13-654)	445 (468-7)	
SnCl ₂ (0-436)	C ₁₆ H ₁₆ N ₂ S ₂ O (0-726)	1:1	SnC ₁₆ H ₁₆ N ₂ S ₂ O 0-723 (0-994)	Greenish yellow solid	190s	26-805 (27-432)	6-264 (6-470)	14-624 (14-790)	416 (432-7)	
SnCl ₂ (0-523)	C ₁₃ H ₁₆ N ₂ S ₂ O (0-772)	1:1	SnC ₁₃ H ₁₆ N ₂ S ₂ O 0-803 (1-093)	Yellow solid	130s	29-323 (29-920)	6-902 (7-058)	15-823 (16-133)	882 (396-7)	
SnCl ₂ (0-456)	C ₁₈ H ₁₇ N ₂ S ₂ O (0-820)	1:1	SnC ₁₈ H ₁₇ N ₂ S ₂ O 0-843 (1-100)	Yellow solid	230s	25-528 (25-934)	5-392 (6-117)	13-486 (13-982)	470 (457-7)	
SnCl ₂ (0-327)	C ₁₅ H ₁₄ N ₂ S ₂ (1-172)	1:2	Sn(C ₁₅ H ₁₃ N ₂ S ₂) 0-869 (1-187)	Yellow solid	140s	16-623 (17-235)	7-873 (8-130)	17-825 (18-585)	710 (688-7)	
SnCl ₂ (0-526)	C ₁₅ H ₁₄ N ₂ S ₂ (0-793)	1:1	SnCl(C ₁₅ H ₁₃ N ₂ S ₂) 1-021 (1-217)	Yellow solid	150d	26-743 (27-026)	6-108 (6-375)	14-023 (14-570)	450 (439-2)	
SnCl ₂ (0-382)	C ₁₂ H ₁₆ N ₂ S ₂ (1-014)	1:2	Sn(C ₁₂ H ₁₃ N ₂ S ₂) ₂ 0-927 (1-250)	Brown semi-solid	—	18-923 (19-123)	8-960 (9-020)	19-963 (20-620)	632 (620-7)	
SnCl ₂ (0-472)	C ₁₂ H ₁₆ N ₂ S ₂ (0-626)	1:1	SnCl(C ₁₂ H ₁₃ N ₂ S ₂) 0-870 (1-008)	Brown semi-solid	—	28-923 (29-294)	6-523 (6-910)	15-236 (15-794)	387 (405-2)	
SnCl ₂ (0-296)	C ₁₆ H ₁₆ N ₂ S ₂ (0-936)	1:2	Sn(C ₁₆ H ₁₅ N ₂ S ₂) ₂ 0-924 (1-118)	Orange solid	142s	16-072 (16-562)	7-620 (7-813)	17-256 (17-860)	701 (716-7)	
SnCl ₂ (0-378)	C ₁₆ H ₁₆ N ₂ S ₂ (0-597)	1:1	SnCl(C ₁₆ H ₁₅ N ₂ S ₂) 0-764 (0-903)	Orange solid	148d	25-821 (26-191)	6-023 (6-178)	13-983 (14-120)	438 (453-2)	
SnCl ₂ (0-493)	C ₂₁ H ₁₈ N ₂ S ₂ (1-881)	1:2	Sn(C ₂₁ H ₁₇ N ₂ S ₂) ₂ 1-864 (2-184)	Yellow solid	138s	13-635 (14-119)	6-426 (6-66)	15-023 (15-225)	825 (840-7)	
SnCl ₂ (0-721)	C ₂₁ H ₁₈ N ₂ S ₂ (1-375)	1:1	SnCl(C ₂₁ H ₁₇ N ₂ S ₂) 1-723 (1-958)	Yellow solid	145d	22-867 (23-040)	5-270 (5-430)	12-047 (12-420)	496 (515-2)	
SnCl ₂ (0-642)	C ₁₇ H ₂₆ N ₂ S ₂ (2-179)	1:2	Sn(C ₁₇ H ₂₅ N ₂ S ₂) ₂ 2-236 (2-574)	Dark brown semi-solid	—	14-828 (15-604)	7-264 (7-361)	16-238 (16-826)	734 (760-7)	
SnCl ₂ (0-582)	C ₁₇ H ₂₆ N ₂ S ₂ (0-987)	1:1	SnCl(C ₁₇ H ₂₅ N ₂ S ₂) 1-235 (1-457)	Dark brown semi-solid	—	24-624 (24-978)	5-426 (5-892)	13-003 (13-470)	462 (475-2)	

s = sharp; d = decomposition

2.3 NMR spectra

In the NMR spectrum of 2-hydroxy-1-naphthaldehyde-S-benzyl dithiocarbazate, a broad signal is observed at δ 7.70–6.90 ppm (table 2). This is due to the phenyl and benzyl protons; it gets slightly shifted in the complex. A sharp signal observed at δ 4.35 ppm is attributable to the $-\text{CH}_2$ protons of the benzyl group. In the ligand, broad signals due to the NH proton at δ 10.80 ppm and the hydrogen bonded phenolic proton also appear at δ 13.20 ppm (Dashora *et al* 1983). However, in the complexes these two signals are not observed on account of their deprotonation as a result of complex formation.

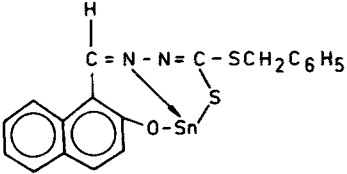
Further, a signal at δ 9.1 ppm appears owing to the $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{N}$ proton and this is shifted downfield due to the coordination of the azomethine nitrogen to the metal atom.

2.4 Mössbauer spectra

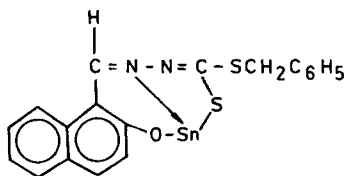
The Mössbauer spectrum of one of the samples ($\text{SnC}_{19}\text{H}_{14}\text{N}_2\text{S}_2\text{O}$) was recorded at 80°K for about 24 hr with a ^{119}Sn isotope in BaSnO_3 matrix. The spectrum shows absorption corresponding to two different isomer shifts (I.S. 3.17 ± 0.2 and 0.9 ± 0.2 mm/sec.). This may be assigned to the existence of both the oxidation states *i.e.* Sn(II) and Sn(IV), as on keeping the sample *ca* 20% of the Sn(II) probably gets oxidized to Sn(IV) state as reported earlier (Cassidy *et al* 1970).

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

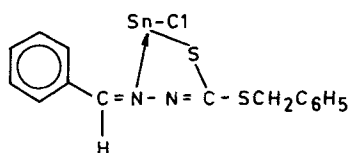
Table 2. ^1H NMR spectral data (δ , ppm) of 2-hydroxy-1-naphthaldehyde-S-benzyl dithiocarbazate and its 1:1 tin(II) complex.

No.	Compound	Aromatic	$-\text{OH}$ (Hydrogen bonded)	$-\text{NH}$	Azomethine ($\text{CH}-$)	$-\text{CH}_2$
(i)	$2\text{-OH} \cdot \text{C}_{10}\text{H}_6\text{CH:NNHC:SSCH}_2\text{C}_6\text{H}_5$	7.70–6.90 m	13.20 bs	10.80 bs	9.05 s	4.35 s
(ii)		7.80–6.95 m	—	—	9.25 s	4.50 s

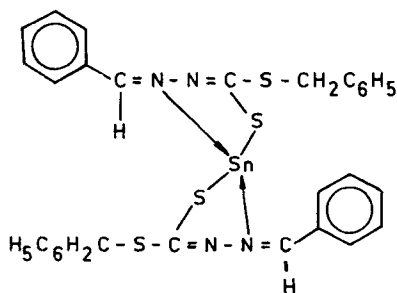
s = singlet, bs = broad singlet and m = complex multiplet.



1:1, Sn(II) derivative of 2-OH-naphthaldehyde-S-benzyl dithiocarbazate



1:1, Sn(II) derivative of benzaldehyde-S-benzyl dithiocarbazate



1:2, Sn(II) derivatives of benzaldehyde-S-benzyl dithiocarbazate

3. Experimental

All the reactions were carried out under anhydrous and oxygen-free nitrogen atmosphere.

3.1 Materials

Stannous chloride was dehydrated by dissolving in acetic anhydride (Gell and Zeldin 1975). S-benzyl dithiocarbazate was prepared as reported earlier (Sandstrom 1963). To prepare the Schiff bases, a weighed amount of S-benzyl dithiocarbazate was dissolved in ethanol and mixed with an equimolar amount of aldehyde or ketone (ethanolic solution). The reaction mixture was kept over a water bath for about 10 min and left overnight at room temperature. The crystals, which separated out, were filtered off and recrystallized from the same solvent. The ligands used are listed in table 3.

Table 3. Ligands used in complex-formation.

Ligand used	Formula	M. P (°C)
Salicylaldehyde-S-benzyl dithiocarbazate	C ₁₅ H ₁₄ N ₂ S ₂ O	186
2-hydroxy-1-naphthaldehyde-S-benzyl dithiocarbazate	C ₁₉ H ₁₆ N ₂ S ₂ O	205
2-hydroxy-acetophenone-S-benzyl dithiocarbazate	C ₁₆ H ₁₆ N ₂ S ₂ O	132
2,4-pentanedione-S-benzyl dithiocarbazate	C ₁₃ H ₁₆ N ₂ S ₂ O	60
1-phenyl-1,3-butanedione-S-benzyl dithiocarbazate	C ₁₈ H ₁₇ N ₂ S ₂ O	80
Benzaldehyde-S-benzyl-dithiocarbazate	C ₁₅ H ₁₄ N ₂ S ₂	159
Ethyl methyl ketone-S-benzyl dithiocarbazate	C ₁₂ H ₁₆ N ₂ S ₂	67
Acetophenone-S-benzyl dithiocarbazate	C ₁₆ H ₁₆ N ₂ S ₂	124
Benzophenone-S-benzyl dithiocarbazate	C ₂₁ H ₁₈ N ₂ S ₂	130
Diisobutyl ketone-S-benzyl dithiocarbazate	C ₁₇ H ₂₆ N ₂ S ₂	72

3.2 Analytical methods and physical measurements

Tin was estimated gravimetrically as tin oxide. Nitrogen was estimated by Kjeldahl's method and sulphur as BaSO₄ by Messenger's method.

The Mössbauer spectrum was obtained on a conventional spectrometer at 80 K. Electronic spectra were recorded in methanol on a Pye Unicam SP-8-100 spectrophotometer and the IR spectra on a Perkin Elmer 577 grating spectrophotometer in KBr pellets. NMR spectra were recorded on a Perkin Elmer RB-12 spectrometer in DMSO-d⁶ 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.

3.3 Synthesis of Sn(II) Schiff base complexes

To a weighed amount of tin(II) chloride was added the calculated amount of the ligand and triethylamine in 1:1:2 or 1:2:2 molar ratio, using dry THF as the reaction medium in an oxygen-free nitrogen atmosphere. The colour of the contents immediately changed with the precipitation of triethylamine hydrochloride. The solution was stirred on a magnetic stirrer for about one hour. The precipitate of triethylaminehydrochloride was filtered off and rejected. Excess solvent was removed from the filtrate and the compound was finally dried in vacuum, at a bath temperature of 35 ± 5°C, after being repeatedly washed with dry cyclohexane.

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