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Synthesis and Structural Studies of Complexes of Sb(III) and Bi(III) with Thiosemicarbazones

Kiran Singh[1,*] and **Jagdish P. Tandon**[2]

[1] Department of Chemistry, Kurukshetra University, Kurukshetra-132 119, India
[2] Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

Summary. Several new complexes of Sb(III) and Bi(III) with thiosemicarbazones of furfuraldehyde, thiophene-2-carbaldehyde, indol-3-carbaldehyde and pyridine-2-carbaldehyde have been prepared and characterized by elemental analysis, conductivity, molecular weight determination and IR, ^{1}H- and ^{13}C-NMR spectral studies. The ligands form complexes of the type $MX_3L[M=$ Sb(III) or Bi(III); $X=$ chloride; $L=$ ligand] which are found to be non-electrolytes in *DMF*. Spectral data indicate that the thiosemicarbazones act as bidentate ligands through the azomethine nitrogen and sulphur.

Keywords. Thiosemicarbazones; Heterocyclic aldehydes; Metal complexes.

Synthese und Strukturuntersuchungen an Komplexen von Sb(III) and Bi(III) mit Thiosemicarbazonen

Zusammenfassung. Es wurden einige neue Komplexe von Sb(III) und Bi(III) mit Tiosemicarbazonen von Furfural, Thiophen-2-carbaldehyd, Indol-3-carbaldehyd und Pyridin-2-carbaldehyd hergestellt und mittels Elementaranalyse, Leitfähigkeitsmessungen, Molekulargewichtsbestimmungen und IR-, ^{1}H- bzw. ^{13}C-NMR-Spektroskopie charakterisiert. Die Komplexe sind vom Typ $MX_3L[M=$ Sb(III) oder Bi(III); $X=$ Chlorid; $L=$ Ligand] und sind in *DMF* Nichtelektrolyten. Die spektroskopischen Daten zeigen, daß die Thiosemicarbazone als zweizähnige Liganden über den Azomethin-Stickstoff und Schwefel wirken.

Introduction

Thiosemicarbazones usually behave as chelating ligands towards transition and non-transition metal ions bonding through sulphur and nitrogen atoms, although in a few cases they act as unidentate ligands with sulphur as the binding atom. After Domagk's et al. original report [1] on the antitubercular activity of thiosemicarbazones, the number of papers on the pharmacology of these compounds have increased steadily. Thiosemicarbazones have also been found to be active against influenza [2], protozoa [3], small pox [4] and certain kinds of tumour [5] and have been suggested as having pesticidal [6] and fungicidal [7] properties. Their activity has frequently been thought to be due to their ability to chelate trace metals. Prompted from this, a few non-transition metal complexes with these potential S and N donor atoms containing ligands have been prepared and studied.

Experimental Part

Chemicals and solvents used were dried and purified by standard methods. Moisture was excluded from the glass apparatus using $CaCl_2$ guard tubes. The ligands were prepared by reported methods [8, 9]. The complexes were analysed by the methods described in Refs. [10, 11]. The molecular weights of some representative complexes were determined by Rast's camphor method. IR spectra were recorded on a Perkin Elmer 577 grating spectrophotometer using KBr optics. PMR spectra were recorded on a Jeol Fx-90 spectrometer in *DMSO-d*$_6$ at 89.55 MHz. ^{13}C-NMR spectra were recorded in *DMSO-d*$_6$ at 22.49 MHz.

Synthesis of Sb(III) *and* Bi(III) *Complexes*

The requisite amount of antimony trichloride and bismuthtrichloride were added to the calculated amount of ligand in equimolar ratio in dry methanol. The reaction started immediately as indicated by a colour change of the contents. To ensure completion of the reaction, the contents were stirred on a magnetic stirrer for 8 h. The excess of the solvent was decanted off and the solid derivatives so obtained were dried in vacuo. The compounds were then repeatedly washed with cyclohexane and again dried in vacuum. The purity was checked by TLC. The analytical data of the resulting products are compiled in Table 1.

Results and Discussion

The reactions of antimony trichloride and bismuth trichloride with thiosemicarbazones have been carried out in 1 : 1 molar ratio in methanol:

$$SbCl_3 + HN\text{-}S \xrightarrow[MeOH]{1:1} SbCl_3NH\text{-}S$$

$$BiCl_3 + HN\text{-}S \xrightarrow[MeOH]{1:1} BiCl_3NH\text{-}S$$

The stoichiometry of the resulting complexes have been confirmed by analytical data (Table 1). The compounds are coloured solids and insoluble in all common organic solvents except *DMF* and *DMSO*. The molar conductance values of 10^{-3} *M* solutions of the complexes ($10 - 15\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$) in *DMF* showed them to be non-electrolytes. The monomeric nature of these complexes was confirmed by their molecular weight measurements.

In the IR spectra of the ligands, NH stretching vibrations were observed at ~3 300 − 2 800 cm^{-1} which are slightly shifted towards higher frequency; they are observed at ~3 360 cm^{-1} in the spectra of the complexes. Two sharp bands are observed at ~3 310 and 3 420 cm^{-1} in the spectra of the ligands due to symmetric and asymmetric modes of the NH_2 group; these bands remain unchanged in the complexes, indicating the non-involvement of this group in the complexes.

A strong absorption band at ~1 620 cm^{-1} in the IR spectra of the ligands has been attributed to the presence of the azomethine (C=N) group. This band shifts towards the lower frequency side in the spectra of the resulting compounds and thus indicates the coordination of the azomethine nitrogen to the metal atom.

Several new bands in the complexes at ~410, 350 and 300 cm^{-1} are due to $\nu(Sb \leftarrow N)$[12], $\nu(Sb \leftarrow S)$[13] and $\nu(Sb-Cl)$[14] respectively and in case of the bismuth complexes new bands at ~428, 280 and 254 cm^{-1} are due to $\nu(Bi \leftarrow N)$[15], ν(Bi

Table 1. Synthetic and physical data for the Sb(III) and Bi(III) complexes

Compounds Colour and state	Yield %	M. p. °C	Analyses (%)						M. w. found (calcd.)
			found (calcd.) C	found (calcd.) H	found (calcd.) Cl	found (calcd.) N	found (calcd.) S	found (calcd.) Sb/Bi	
$SbCl_3(C_6H_7N_3SO)$ Pink solid	83	217	17.78 (18.09)	1.52 (1.76)	26.32 (26.74)	10.05 (10.55)	8.00 (8.04)	30.37 (30.57)	373 (398)
$SbCl_3(C_7H_8N_4S_2)$ Dark yellow solid	85	230	20.12 (20.53)	1.62 (1.96)	25.82 (26.02)	13.35 (13.68)	7.42 (7.82)	29.42 (29.75)	389 (409)
$SbCl_3(C_{10}H_{10}N_4S)$ Dark red solid	88	82	26.44 (26.85)	2.00 (2.23)	23.41 (23.81)	12.02 (12.52)	7.00 (7.15)	27.00 (27.22)	425 (447)
$SbCl_3(C_{10}H_{11}N_3S)$ Yellow solid	86	73	28.22 (28.50)	2.25 (2.61)	25.00 (25.28)	9.56 (9.97)	7.34 (7.59)	28.56 (28.90)	445 (421)
$BiCl_3(C_6H_7N_3SO)$ Light yellow solid	91	270 (dec.)	14.52 (14.87)	1.21 (1.45)	21.54 (21.98)	8.35 (8.67)	6.21 (6.61)	43.00 (43.13)	449 (484)
$BiCl_3(C_7H_8N_4S_2)$ Yellow solid	93	246 (dec.)	16.54 (16.97)	1.26 (1.62)	21.18 (21.49)	11.00 (11.30)	6.15 (6.46)	42.00 (42.18)	465 (495)
$BiCl_3(C_{10}H_{10}N_4S)$ Red solid	92	170	22.20 (22.51)	1.43 (1.88)	19.46 (19.96)	10.00 (10.49)	5.64 (6.15)	39.00 (39.17)	506 (533)
$BiCl_3(C_{10}H_{11}N_3S)$ Dark yellow solid	95	78	22.78 (23.07)	2.00 (2.12)	20.14 (20.46)	7.97 (8.06)	5.85 (6.15)	40.00 (40.15)	489 (520)

Table 2. ^{1}H-NMR spectral data (δ, ppm) of thiosemicarbazones of furfural and pyridine-2-carbaldehyde and their Sb(III) and Bi(III) complexes (δ/ppm)

Ligands and Compounds	Aromatic	-NH	Azomethine	$-NH_2$
$C_4H_3OCH{:}N.NHC.S.NH_2$	7.68 – 6.60 m	11.40 s(b)	8.00 s	2.40 s(b)
$SbCl_3(C_4H_3OCH{:}N.NH.C.S.NH_2)$	8.08 – 6.68 m	11.68 s(b)	8.48 s	2.80 s(b)
$BiCl_3(C_4H_3OCH{:}N.NH.C.S.NH_2)$	8.00 – 6.96 m	11.84 s	8.56 s	2.88 s(b)
$C_5H_4NCH{:}N.NH.C.S.NH_2$	8.48 – 7.52 m	11.76 s(b)	8.64 s	2.94 s(b)
$SbCl_3(C_5H_4NCH{:}N.NH.C.S.NH_2)$	8.64 – 7.76 m	12.00 s(b)	8.96 s	2.96 s(b)
$BiCl_3(C_5H_4NCH{:}N.NH.C.S.NH_2)$	8.32 – 7.68 m	12.00 s(b)	8.84 s	2.80 s(b)

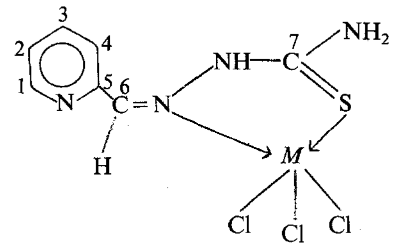
← S)[16] and ν(Bi – Cl)[17] respectively; these bands are absent in the spectra of the ligands which supports the proposed coordination in these complexes.

The participation of both N and S atoms of the ligands in bonding is further supported by ^{1}H- and ^{13}C-NMR spectral studies.

^{1}H and ^{13}C-NMR

The ^{1}H-NMR spectral data of the ligands and their antimony and bismuth complexes are given in Table 2.

A sharp singlet is observed for -NH at δ = 11.40 and 11.76 ppm. This signal shifts downfield in the adducts indicating the involvement of sulphur in bonding with Sb and Bi. The signals at 8.00 and 8.64 ppm are observed in the ligands due to the proton attached to the > C = N group. The signals shift downfield in the spectra of adducts in comparison to their original position in the ligands indicating the coordination of azomethine nitrogen to the metal atom.



M = Sb or Bi

The involvement of thiolic sulphur and azomethine nitrogen in complexation is further confirmed by the ^{13}C NMR spectral data.

Table 3. ^{13}C-NMR spectral data of pyridine-2-aldehyde thiosemicarbazone and its Sb complex (chemical shift in ppm, for the numbering see the formula of the complex)

C-No.	1	2	3	4	5	6	7
Ligand	142.12	123.36	119.46	135.70	148.40	152.2	176.99
Complex	139.30	123.80	120.65	137.90	146.87	146.77	167.54

The ^{13}C-NMR spectral data of $C_5H_4NCH{:}NNHC{:}SNH_2$ and $SbCl_3(C_5H_4NCH{:}NNHC{:}SNH_2)$ are summarized in Table 3. The chemical shifts of the carbon atoms attached to azomethine nitrogen and thiolic sulphur clearly show the involvement of these atoms in the complexation.

On the basis of spectral evidences the following tentative structures may be proposed:

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