

Synthesis and Spectroscopic Studies of Sb(III) and Bi(III) Complexes of Semicarbazones

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Summary. New complexes of Sb(III) and Bi(III) with semicarbazones of the general formulae $SbCl_3L$ and $BiCl_3L$ (where L = semicarbazones) have been prepared and characterized by IR, 1H - and ^{13}C -NMR spectral measurements. The results of the spectroscopic studies indicate that the semicarbazone ligands act as bidentate in all the complexes. All complexes are non-electrolytes in *DMF* solution. The molecular weight determinations indicate that the compounds are monomeric.

Keywords. Heterocyclic aldehydes; Semicarbazones; Metal complexes.

Synthese und spektroskopische Untersuchungen von Sb(III)- und Bi(III)-Komplexen mit Semicarbazonen

Zusammenfassung. Es wurden neue Komplexe von Sb(III) und Bi(III) mit Semicarbazonen von der allgemeinen Formel $SbCl_3L$ und $BiCl_3L$ (L = verschiedene Semicarbazone) dargestellt und mittels IR, 1H - und ^{13}C -NMR charakterisiert. Die spektroskopischen Untersuchungen zeigten, daß die Semicarbazon-Liganden in allen Komplexen zweizählig agieren. Molekulargewichtsbestimmungen zeigten die monomere Natur der Verbindungen an.

Introduction

Semicarbazones of hetrocyclic aldehydes have attracted much interest amongst the N, O donor ligands as their metal complexes show a remarkable diversity in the coordination behaviour depending upon the nature of the central metal atom [1–7]. Besides, their metal complexes exhibit significant biological activity.

An exhaustive survey of literature reveals that only limited studies have been carried out on the addition reactions of Sb(III) and Bi(III).

Prompted from this, it was considered worthwhile to synthesize the Sb(III) and Bi(III) complexes with the ligands of the type $RCH = NNHC = ONH_2$ ($R = C_5H_4N$, C_4H_3O , C_8H_6N , and C_8H_7).

Experimental

Chemicals and solvents used were dried and purified by the standard methods. Moisture was excluded from the glass apparatus using $CaCl_2$ guard tubes. The ligands were prepared by reported methods

Table 1. Physical data and elemental analyses of antimony and bismuth complexes

Compounds colour and state	Yield %	M. p. °C	Analyses (%)					M. w. found (calcd.)
			C found (calcd.)	H found (calcd.)	Cl found (calcd.)	N found (calcd.)	Sb/Bi found (calcd.)	
SbCl ₃ (C ₆ H ₇ N ₃ O ₂) Dark brown solid	82	140	18.64 (18.84)	1.40 (1.83)	27.55 (27.86)	10.66 (10.99)	31.44 (31.87)	403 (382)
SbCl ₃ (C ₇ H ₈ N ₄ O) White solid	84	201	21.00 (21.37)	1.72 (2.04)	27.00 (27.08)	14.00 (14.24)	30.63 (30.97)	369 (393)
SbCl ₃ (C ₁₀ H ₁₀ N ₄ O) Dark orange solid	81	90	27.53 (27.84)	1.90 (2.32)	24.29 (24.69)	12.63 (12.99)	28.00 (28.24)	410 (431)
SbCl ₃ (C ₁₀ H ₁₁ N ₃ O) Dark yellow solid	85	65	28.35 (28.78)	2.41 (2.63)	25.08 (25.54)	10.00 (10.07)	28.00 (28.19)	393 (417)
BiCl ₃ (C ₆ H ₇ N ₃ O ₂) Yellow solid	89	244	15.15 (15.38)	1.10 (1.49)	22.23 (22.75)	8.55 (8.97)	44.21 (44.63)	444 (468)
BiCl ₃ (C ₇ H ₈ N ₄ O) Light yellow solid	87	235	17.21 (17.53)	1.45 (1.67)	22.00 (22.21)	11.25 (11.68)	43.35 (43.61)	455 (479)
BiCl ₃ (C ₁₀ H ₁₀ N ₄ O) Orange solid	85	95	23.00 (23.21)	1.48 (1.93)	20.18 (20.58)	10.41 (10.82)	40.00 (40.40)	495 (517)
BiCl ₃ (C ₁₀ H ₁₁ N ₃ O) Brown solid	88	120	23.38 (23.80)	1.81 (2.18)	20.86 (21.16)	8.00 (8.33)	41.11 (41.44)	474 (504)

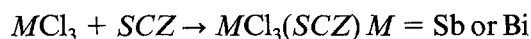
[1, 2]. The complexes were analysed by methods reported in earlier publications [5, 6]. The molecular weights of the complexes were determined by Rast's comphor method. IR spectra were recorded on a Perkin Elmer 577 grating spectrophotometer using KBr optics. PMR spectra were recorded on a Jeol Fx90 spectrometer in *DMSO* at 89.55 MHz. ¹³C-NMR spectra were recorded in *DMSO* at 22.49 MHz.

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

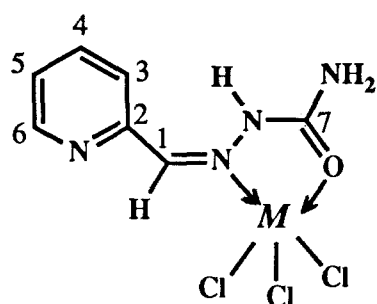
The requisite amount of antimony trichloride and bismuth trichloride were added to the calculated amount of ligand in equimolar ratio in dry methanol. The reaction started immediately as indicated by the colour change of the contents. To ensure completion of the reaction, the contents were stirred on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

Results and Discussion

Reactions of antimony(III) chloride and bismuth(III) chloride with bidentate ligands have been carried out in 1:1 molar ratio in dry methanol:



The resulting derivatives are coloured solids, insoluble in benzene, methanol, chloroform, and carbontetrachloride, but soluble in *DMF* and *DMSO*. The molar



(numbering refers to Table 3)

conductance values of $10^{-3} M$ solutions ($10-15 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in *DMF* show them to be nonelectrolytes. The monomeric nature of these complexes was confirmed by molecular weight determinations.

In the IR spectra of the ligands a strong band observed at $3300-2800 \text{ cm}^{-1}$ may be ascribed to the $\nu\text{NH/OH}$ mode. This band is slightly shifted towards higher frequency and is observed at 3360 cm^{-1} in the IR spectra of the adducts.

Two sharp bands are observed in the ligand spectra at 3225 and 3440 cm^{-1} which may be attributed to the symmetric and asymmetric stretching modes of the NH_2 group. No significant shift has been observed for these bands in the spectra of metal complexes, showing the non-involvement of the NH_2 group in complexation. A sharp band at $1600 \pm 5 \text{ cm}^{-1}$ in the complexes, compared to the one at $\sim 1620 \text{ cm}^{-1}$ in the ligand, may be assigned to $\nu(\text{C}=\text{N})$; its shifting to lower values is probably due to a decrease in the bond order showing the coordination of the azomethine nitrogen to the metal atom [8, 9]. Further, in the spectra of complexes some new bands have been observed in the far IR region at $\sim 520, 410, \text{ and } 300 \text{ cm}^{-1}$

Table 2. $^1\text{H-NMR}$ spectral data (δ , ppm) of semicarbazones of furfuraldehyde and pyridine-2-aldehyde and their antimony(III) and bismuth(III) complexes

Ligands and compounds	Aromatic	-NH	Azomethine	-NH ₂
$\text{C}_4\text{H}_3\text{OCH}=\text{N-NH-CO-NH}_2$	6.80-6.32m	10.68 br.s	7.75 s	2.55 br.s
$\text{SbCl}_3(\text{C}_4\text{H}_3\text{OCH}=\text{N-NH-CO-NH}_2)$	7.12-6.88 m	10.96 s	8.00 s	2.88 br.s
$\text{BiCl}_3(\text{C}_4\text{H}_3\text{OCH}=\text{N-NH-CO-NH}_2)$	7.20-6.72 m	10.80 br.s	8.24 s	2.88 br.s
$\text{C}_5\text{H}_4\text{NCH}=\text{N-NH-CO-NH}_2$	7.48-6.20m	10.87 br.s	7.92 s	2.44 br.s
$\text{SbCl}_3(\text{C}_5\text{H}_4\text{NCH}=\text{N-NH-CO-NH}_2)$	8.00-7.20m	11.36 br.s	8.56 s	2.80 br.s
$\text{BiCl}_3(\text{C}_5\text{H}_4\text{NCH}=\text{N-NH-CO-NH}_2)$	7.68-7.12 m	11.00 br.s	8.88 s	2.72 br.s

Table 3. $^{13}\text{C-NMR}$ spectral data of pyridine-2-aldehyde semicarbazones and the corresponding Bi complex (δ/ppm , the numbers refer to the formula scheme)

Proton No.	1	2	3	4	5	6	7
Ligand	153.40	149.34	138.83	122.79	124.96	140.13	159.63
Complex 2	150.00	148.10	138.11	121.50	123.15	138.50	155.54

due to $\nu(\text{Sb} \leftarrow \text{O})^{10}$, $\nu(\text{Sb} \leftarrow \text{N})^{11}$, and $\nu(\text{Sb}-\text{Cl})^{12}$ modes of vibrations. In case of bismuth complexes new bands at ~ 430 , 428 , and 254 cm^{-1} have been assigned to $\nu(\text{Bi} \leftarrow \text{O})^{13}$, $\nu(\text{Bi} \leftarrow \text{N})^{14}$, and $\nu(\text{Bi}-\text{Cl})^{15}$, respectively and these bands further support the proposed coordination in these complexes.

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

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

A sharp singlet is observed for the -NH proton at $\delta 10.68$ and 10.87 ppm. This signal shifts downfield in the adducts indicating the involvement of oxygen in bonding with Sb and Bi. The signals at $\delta 7.75$ and 7.92 ppm are observed in the ligands due to the proton attached with the $>\text{C}=\text{N}$ group. The signals shift downfield in the spectra of the adducts in comparison to their original position in the ligands, indicating the coordination of azomethine nitrogen to the metal atom.

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

The ^{13}C -NMR spectral data of one ligand and its bismuth complex $\text{C}_5\text{H}_4\text{NCH}=\text{NNHC}=\text{ONH}_2$ and $\text{BiCl}_3(\text{C}_5\text{H}_4\text{NCH}=\text{NNHCONH}_2)$ have been recorded in *DMSO* (see Table 3).

The chemical shifts of the carbon atoms attached to the azomethine nitrogen and the alcoholic oxygen show clearly the involvement of these atoms in complexation.

On the basis of the spectral evidences, the tentative structures shown in the formula scheme may be proposed.

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