SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF ORGANOANTIMONY(III) COMPLEXES

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ABSTRACT

Some new complexes of diphenylantimony (III) with the monobasic bidentate semicarbazones and thiosemicarbazones derived from 2-fluorobenzaldehyde and (2-fluorophenyl) acetone have been synthesized and characterized by elemental analysis, molecular weight determination; IR, ^{1}H and ^{13}C NMR spectral studies. The complexes are monomeric and non-electrolytes. A probable tetra-coordinated environment around the antimony atom has been assigned. The results of fungicidal and bactericidal tests are also reported. It has been attempted to correlate the results with the structures of the compounds.

INTRODUCTION

The chemistry of the metal complexes of main group elements with various nitrogen and oxygen donor ligands is the subject of increasing interest due to the striking structural features exhibited by this class of compounds and on account of their biological significance [1-4]. Despite extensive preparative and spectroscopic investigations on organodervatives of tin, lead, silicon and titanium with Schiff bases [5-8] containing NO donor system, comparatively fewer studies have been made on the organoantimony (III) derivatives [9-10]. So there is a considerable scope for undertaking systematic studies of coordination compounds of orgnoantimony (III) with a variety of chelating agents.

The focus of our present communication is the exploration of the studies on synthetic, structural and biological aspects of diorganoantimony (III) complexes derived from fluorine containing semi-and thiosemicarbazones.

EXPERIMENTAL

All the chemicals and solvents used were dried and purified by standard methods and moisture was excluded from glass apparatus using fused $CaCl_2$ guard tubes. The diphenylantimony chloride was prepared by the standard method. [11] The semi and thiosemicarbazones were prepared by the procedure reported earlier[12] and analysed before use.

1. O-fluorobenzaldehyde semicarbazone ($C_8H_8N_3OF$), white crystalline solid, m.p. 218°C.
2. O-fluorobenzaldehyde thiosemicarbazone ($C_8H_8N_3SF$), white solid m.p. 190°C.
3. (2-fluorophenyl) acetone semicarbazone ($C_{10}H_{12}N_3OF$), white crystalline solid, m.p. 165°C.
4. (2-fluorophenyl) acetone thiosemicarbazone ($C_{10}H_{12}N_3SF$), white crystalline solid, m.p. 140°C.

The complexes were analysed by the standard method[13]. Molecular weights were determined by Rast-camphor method. IR spectra with KBr optics were obtained using a Perkin-Elmer 577 grating spectophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer in DMSO-d_6 and dry DMSO, respectively using T.M.S. as an internal reference. The antifungal and antibacterial activities of the ligands and their corresponding antimony (III) complexes were ascertained by the methods reported earlier [14-15].

SYTHESIS OF DIORGANOANTIMONY (III) COMPLEXES : GENERAL METHOD

The diorganoantimony (III) complexes were synthesized by reacting the diphenylantimony chloride with the potassium salt of the ligand in 1:1 molar ratio. The contents were refluxed for 6-7 hours over a fractionating column with dry methanol as the reaction medium and the potassium chloride so precipitated was filtered off. The excess of the solvent was removed and the product dried under vacuo. The solids so obtained were repeatedly washed with pet. eher (40-60°C). These were purified by recrystallization in methanol and benzene and finally dried under reduced pressure. The analytical and physical data of these compounds are given in Table-I.

Table I :

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF ORGANOANTIMONY (III) COMPLEXES.

No.	Compound	Colour	M.P.	Yield %	Analyses (%) Found (Calcd.) N	S	Sb	M.Wt. Found (Calcd.)
5.	$Ph_2Sb(C_8H_8N_3OF)$	Off White	149	77	9.02 (9.20)	- -	24.44 (26.68)	470.56 (456.12)
6.	$Ph_2Sb(C_{10}H_{12}N_3OF)$	Light Yellow	207	70	8.87 (8.69)	- -	23.35 (25.14)	502.66 (486.18)
7.	$Ph_2Sb(C_8H_8N_3SF)$	Light Yellow	166	75	8.57 (8,85)	6.48 (6.79)	25,42 (25.78)	468.28 (472.19)
8.	$Ph_2Sb(C_{10}H_{12}N_3SF)$	Creamish	184	80	8.74 (8.40)	6.22 (6.41)	24.07 (24.34)	512.86 (500.24)

RESULTS AND DISCUSSION

The diphenylantimony (III) derivatives of monofunctional bidentate semicarbazones and thiosemicarbazones have been prepared by the substitution reactions of diphenylantimony chloride with the potassium salt of the ligand in 1:1 molar ratio in the medium of dry methanol. The reactions proceed with the precipitation of potassium chloride, which is removed by filtration.

$$Ph_2SbCl + LK \longrightarrow Ph_2SbL + KCl$$

(where LK =potassium salt)

All the resulting products are solids and partially soluble in common organic solvents. Molecular weight determinations showed that all the compounds are monomers. The low values of molar conductance (below 12 $ohm^{-1}\ cm^2\ mol^{-1}$) indicate their non-electrolytic nature.

SPECTROSCOPIC STUDIES

IR Spectra

The IR spectra of Semi- and Thiosemi-carbazones show a strong band around 3300 and 2700 cm^{-1} due to (NH)/(OH) and (SH) groups, respectively. In the IR spectra of the complexes the NH/SH bands are absent showing the bonding of oxygen or thiolic sulfur to the metal after the deprotonation of the functional groups. A band of medium intensity at ca. 1640 cm^{-1} in these complexes as compared to one at ca. 1615 cm^{-1} in the ligands may be assigned to (C =N) vibrations. The shifting of this band to higher frequency is probably due to an increase in the (>C = N) bond order after the coordination of nitrogen with metal atom[9]. Besides this, new bands are also observed in the spectra of complexes at ca. 515, 450 and 410 cm^{-1} which are not present in the spectra of free ligands. These may be assigned to υ(Sb-0)[10], υ(Sb-S) and υ(Sb←N)[16] respectively and thus leading suport to the complex formation. Further, the sharp band observed in the region 450-440 cm^{-1} may be assigned to (Sb-C)[17].

1H NMR Spectra

The ^1H NMR spectra of ligands and their complexes have also been recorded in Table-II. The disappearance of NH proton signals from the ^1H NMR specta of organoantimony (III) complexes in comparison to the spectra of the free ligands, clearly indicates the bond formation of oxygen and sulfur with the antimony atom. The aromatic protons have been observed in the range of δ 6.50-8.98 ppm in ligands as well as in their metal complexes. The aromatic protons signal was found to be merged with the aromatic protons in the case of some ligands and their metal chelates, whereas , in

the remaining complexes a downfield shifting was observed in the position of this signal as compared to its position in the ligands. This is an additional evidence that the nitrogen of the azomethine group is coordinated to the antimony atom.

TABLE II : ^{1}H NMR DATA FOR COMPOUNDS 1-8.

Compunds	-NH	-NH2	-C=H	Aromatic
1.	11.67	2.35	8.42	7.68-6.65
2.	11.10	2.25	8.26	7.28-6.55
3.	11.24	2.16	8.33	7.78-6.70
4.	11.56	2.20	*	8.18-6.50
5.	--	2.39	8.71	8.51-6.74
6.	--	2.30	8.58	8.25-6.70
7.	--	2.18	8.60	8.42-6.83
8.	--	2.23	*	8.98-6.65

*merged with aromatic protons

^{13}C NMR Spectra

In the metal complexes, the bonding occuring through nitrogen and oxygen/sulfur is further supported by the ^{13}C NMR spectral data (Table-III). The noticeable shifts in the resonances of the carbon atoms attached to N and O/S in the complexes as compared to those of the ligands is indicative of bonding of the ligand through nitrogen and oxygen or sulfur as discussed earlier. The signals for phenyl carbons attached to antimony are observed in the range of δ142-143 ppm. Further only one set of signals for the carbons of two phenyl groups attached to to central antimony atom has been observed which indicates that the two phenyl groups are chemically equivalent.

On the basis of the above observation, the structures I and II may tentatively be proposed for the monomeric diorganoantimony (III) complexes.

Biocidal Activity

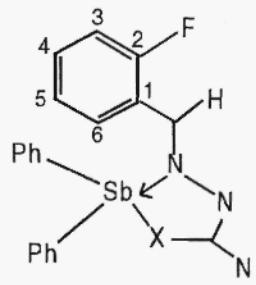
It is clear from the fungicidal and bactericidal screening data given in Tables IV and V that all the metal complexes are more toxic than the parent ligand. The increased biocidal properties after complexation may be due to the effect of metal ions in the normal cell process. The antimicrobial activity of these ligands and their complexes can be ascribed to hydrogen bond formation between the nitrogen (>C=N) atom of the compounds and some bioreceptors in the cells of fungi and bacteria, which in turn blocks the synthesis of proteins by inhibiting the movement of ribosomes along RNA. This also inhibits the synthesis of DNA in the cell nucleus. The greater toxicity of the metal chelates than the ligand can also be explained by the greater lipophilic character of the complexes so that they can pass through the lipoid layers of the cell membrane and thus interfere in the normal cellular processes. [18,19] Further, it has also been observed that lower concentration of the compounds can check the sporunlation in the fungi and the higher concentration inhibits the growth of organisms completely.

Table IV :ANTI FUNGAL SCREENING DATA OF COMPUNDS 1-8.

Compound	Average percentage inhibition after 7 days					
	Alternaria alternata		Alternaria tenues		Fusarium oxysporum	
	Conc. (ppm)		Conc. (ppm)		Conc. (ppm)	
	200	400	200	400	200	400
1.	30	45	22	38	28	49
2.	30	47	24	40	32	56
3.	32	48	25	44	31	53
4.	33	50	26	47	35	60
5.	58	80	55	78	60	81
6.	60	83	58	83	62	86
7.	64	85	57	80	65	90
8.	65	88	60	86	65	93

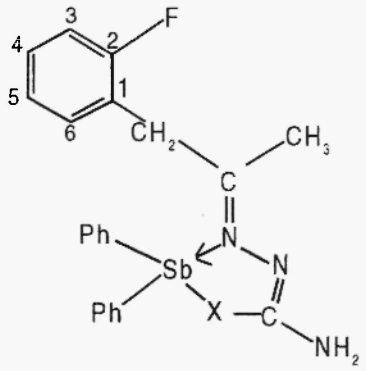
TABLE III : ^{13}C NMR DATA FOR COMPOUNDS 1-8

Compound	C = N	C-NH_2	C_1	C_2	C_3	C_4	C_5	C_6	Sb-C_6H_5	
1.	160.2	175.2	144.1	129.3	128.2	128.8	127.6	125.0	--------	--------
2.	158.2	178.1	142.6	130.5	129.1	128.3	127.3	126.4	--------	--------
3.	157.4	179.5	143.6	127.8	126.5	123.3	122.1	125.5	--------	--------
4.	162.2	177.3	143.0	127.4	126.0	124.1	123.6	126.4	--------	--------
5.	156.7	170.3	145.2	130.4	129.0	129.6	128.1	125.8	135.5	136.8
									139.7	141.5
6.	153.8	172.7	144.4	131.1	130.8	129.2	128.5	127.0	132.4	134.5
									136.7	138.1
7.	150.2	168.0	144.2	128.1	126.8	124.5	123.6	126.0	136.2	137.8
									139.4	140.5
8.	155.8	169.2	143.8	128.1	126.8	124.9	124.1	126.6	134.1	136.5
									140.6	142.0



Structure-I

X = O or S



Structure-II

Table : V : ANTIBACTERIAL ACTIVITY OF COMPOUND 1-8.

Compound	Diameter of inhibition zone (mm) at 1000 ppm conc.		
	E.coli	B.subtilis	S.aureus
1.	10	15	11
2.	12	17	13
3.	13	19	14
4.	16	20	15
5.	12	30	22
6.	25	28	26
7.	18	21	25
8.	27	30	28

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REFERENCES

1. R.R. Holmes, Acc. Chem. Res. ; 22(1989), 190.
2. K. Singh, R.V. Singh and J.P. Tandon, *Inorg. Chim. Acta* ; 151 (1988), 179.
3. A. Saxena and F. Huber ; *Coored. Chem. Rev.*, 95 (1989) 109.
4. A Saxena and J.P. Tandon, *Polyhedron* ; 3 (1984), 661.
5. A. Saxena ; Appl. *Organomet. Chem.* 1 (1987), 39.
6. P. Dixit and J.P. Tandon, *Phosphororus, Sulfur and Silicon*; 53 (1990), 389.
7. D. Singh and R.V. Singh, *Main group met. Chem.* ; 13 (1990), 19.
8. T.A.K. All-Allaf, R.H.Al -Bayati and S.H. Khalaf, *Appl. Organomet. Chem.* 7 (1993), 635.
9. V.K. Jain, R.Bohra and R.C. Mehrotra, *J. Indian Chem. Soc.*, 57 (1989), 408.
10. T.B. Brill and N.C. Compbell, *Inorg. Chem.;* 12 (1973), 1884.
11. M.Nunn, D.B. Sowerby and D.M. Wesolek, *J. Organomet. Chem.*; 251 (1983) C-45.
12. A. Kumari, J.P. Tandon and R.V. Singh ; *Appl. Organomet. Chem.* ; 7 (1993) 655.
13. A.I. Vogel, Quantitative Inorganic Analysis. The ELBS and Longmans Green and Co. Ltd., 1978.
14. J.G. Hosfall, *Bot. Rev.,* 11 (1945), 357.
15. V.P. Singh, R.V. Singh and J.P. Tandon, *J. Inorg. Biochem,* 39 (1990), 237.
16. J.Otera and R. Okawara, *J. Organomet Chem.* ; 11(1968), 299.
17. R. Bally, *Acta Cryst.* ; 23 (1967), 295.
18. J.G. Horsfall, "Fungicides and their action." Chronica Botanica, Waltham, massachusetts (1945)
19. H. Singh, L.D.S. Yadav and S.B.S. Mishra, *J. Inorg. Nucl. Chem.*, 43 (1981)

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