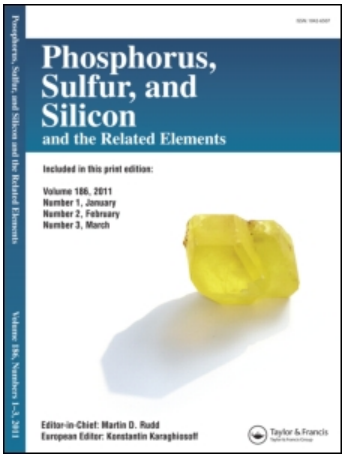

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Kumari, Anita , Sharma, Neelam , Singh, R. V. and Tandon, J. P.(1992) 'SYNTHETIC, STEREOCHEMICAL AND BIOLOGICAL ASPECTS OF ORGANOANTIMONY(III) DERIVATIVES OF THIO-IMINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 71: 1, 225 — 229
To link to this Article: DOI: 10.1080/10426509208034515
URL: http://dx.doi.org/10.1080/10426509208034515

Phosphorus, Sulfur, and Silicon, 1992, Vol. 71, pp. 225–229
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SYNTHETIC, STEREOCHEMICAL AND BIOLOGICAL ASPECTS OF ORGANOANTIMONY(III) DERIVATIVES OF THIO-IMINES

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(Received February 8, 1992; in final form April 29, 1992)

Diphenylantimony(III) derivatives of monobasic bidentate thiosemicarbazones derived from heterocyclic aldehydes and ketones have been synthesized and characterized by elemental analyses, molecular weight determinations and conductance measurements. The stereochemical features of these newly synthesized complexes have been discussed in terms of IR, ^{1}H NMR and ^{13}C NMR spectral data. Some representative ligands and their metal chelates have also been screened for their antifungal activity.

INTRODUCTION

The azomethine ligands containing NS donor system are known to exhibit a remarkable diversity of coordination patterns.[1,2] It is only recently that their derivatives with the main group and related organometallics have been investigated.[3,4] However, little information on the bonding, structural and biological properties is available for organoantimony(III) derivatives of such ligands. In view of this, in the present communication, the synthesis and antifungal activity of diphenylantimony(III) complexes of heterocyclic thiosemicarbazones are reported.

RESULTS AND DISCUSSION

The diphenylantimony(III) derivatives of heterocyclic thiosemicarbazones have been prepared by the substitution reactions of diphenylantimony chloride and the potassium salt of the ligand in 1:1 molar ratio. The resulting $Ph_2Sb(NS)$ products are solids, partially soluble in common organic solvents, monomers and nonelectrolytic in nature.

In the IR spectra of thiosemicarbazonato complexes of diorganoantimony(III), the band associated with the NH group of the free ligand in the region 3300–3100 cm^{-1} does not appear. A sharp and strong band is observed at ca. 1590 cm^{-1} in all the complexes and which may be assigned to the (C=N) stretching vibrations. The position of this band is lower than the corresponding one in the free ligand, which strongly suggests that the nitrogen of the azomethine group is coordinated to antimony.[5] The two bands, observed at ca. 3420 and 3310 cm^{-1} due to the symmetric and antisymmetric modes of primary amino group in the ligands are observed at the same positions in the complexes.

Several new bands at ca. 420, 360 cm^{-1} and 445 cm^{-1} are due to ν(Sb ← N),[6] ν(Sb—S)[7] and ν(Ph—Sb)[8] modes of vibrations, respectively.

TABLE I

^{1}H NMR Spectral data (δ, ppm) of thiosemicarbazones and their corresponding diorganoantimony(III) complexes

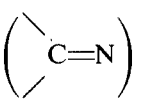
Compound	-NH	$-NH_2$	$-CH_3$	Aromatic
2-AcPyd.TsczH	10.64	2.84	1.80	8.92-7.48
Ph_2Sb(2-AcPyd.Tscz)	-	2.94	2.15	8.81-7.69
2-AcFur.TsczH	10.90	2.83	1.80	7.93-7.11
Ph_2Sb(2-AcFur.Tscz)	-	2.96	2.46	8.68-7.16
2-AcThiop.TsczH	10.68	2.81	1.68	8.69-7.38
Ph_2Sb(2-AcThiop.Tscz)	-	2.74	2.22	8.84-7.61
3-AcIndol.TsczH	10.87	2.36	1.99	8.75-7.68
Ph_2Sb(3-AcIndol.Tscz)	-	2.75	2.36	8.86-7.76

TABLE II

Antifungal screening data of ligands and their organoantimony(III) complexes

Compound	Average percentage inhibition after 7 days					
	Alternaria brassicae		Alternaria tenuis		Aspergillus niger	
	conc.(ppm)		Conc.(ppm)		Conc.(ppm)	
	200	400	200	400	200	400
2-AcFur.TsczH	24	31	21	28	32	37
2-AcPyd.TsczH	30	36	29	34	37	44
2-AcThiop.TsczH	35	39	31	38	41	47
Ph_2Sb(2-AcFur.Tscz)	68	72	77	83	61	64
Ph_2Sb(2-AcPyd.Tscz)	71	76	80	88	65	81
Ph_2Sb(2-AcThiop.Tscz)	79	87	86	91	74	82

In the ^{1}H NMR spectra of the complexes studied (Table I), the NH proton signals of the free ligands are found to be absent indicating the formation of a covalent bond between antimony and thiolo sulphur after deprotonation of the SH group. The signal due to the protons of $-CH_3$ group attached to the azomethine group undergoes a down field shifting in the complexes as compared to its position in the free ligand and this is further evidence that the nitrogen of



group is coordinated to antimony.

Further, the bonding pattern in these complexes gets substantiated by the ^{13}C NMR spectral studies. In the spectra of complexes, the chemical shifts of carbons

TABLE III

Physical and analytical data of diorganoantimony(III) derivatives of hetereocyclic thiosemicarbazones

Compound	Yield (%)	M.P. (°C)	Elemental analysis %					Mol. wt.
			C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)	Sb Found (Calcd.)	Found (Calcd.)
Ph_2Sb(Pyd.Tscz)	72	165	50.43 (50.14)	3.52 (3.76)	12.05 (12.31)	7.31 (7.04)	26.47 (26.75)	476.24 (455.12)
Ph_2Sb(Fur.Tscz)	81	204	48.39 (48.68)	3.50 (3.63)	9.27 (9.46)	7.48 (7.22)	27.25 (27.41)	462.00 (444.16)
Ph_2Sb(Thiop.Tscz)	86	d	46.71 (46.98)	3.28 (3.50)	9.35 (9.13)	13.66 (13.93)	22.29 (26.45)	451.16 (460.20)
Ph_2Sb(Indol.Tscz)	74	105	53.42 (53.57)	3.63 (3.88)	11.09 (11.36)	6.76 (6.50)	24.43 (24.68)	477.56 (493.24)
Ph_2Sb(2-AcPyd.Tscz)	70	140	51.36 (51.19)	4.30 (4.08)	11.75 (11.94)	6.69 (6.83)	25.67 (25.95)	456.22 (469.21)
Ph_2Sb(2-AcFur.Tscz)	80	185	49.63 (49.80)	3.48 (3.96)	9.39 (9.17)	6.73 (6.99)	26.81 (26.57)	442.20 (458.18)
Ph_2Sb(2-AcThiop.Tscz)	75	215	48.33 (48.12)	3.64 (3.83)	8.71 (8.86)	13.40 (13.52)	25.52 (25.67)	490.53 (474.24)
Ph_2Sb(3-AcIndol.Tscz)	77	112	54.21 (54.46)	4.84 (4.70)	11.27 (11.05)	6.19 (6.32)	24.32 (24.00)	522.31 (507.26)

attached to the nitrogen (δ 156.20, 155.47 and 150.25 ppm) and sulphur (δ 179.19, 179.86 and 177.98 ppm) atoms in 2-AcPyd. TsczH, 2-AcFur. TsczH and 3-AcIndol. TsczH, respectively, appear further downfield, which clearly indicate the involvement of both azomethine nitrogen and thiolic sulphur in complex formation.

On the basis of the foregoing structural evidences and the monomeric behaviour of the complexes, a tetracoordinated state may tentatively be proposed for the metal atom in the synthesized complexes.

FUNGICIDAL ACTIVITY

In order to ascertain the fungitoxicity of the complexes, a few representative ligands and their antimony complexes have been screened against some pathogenic fungi (Table II). All the complexes show significant activity against these fungi and it may be explained on the basis of chelation theory.[4]

EXPERIMENTAL

All the chemicals used were dried and distilled before use. The ligands and diphenylantimony chloride were prepared by the literature method.[9,10] The following ligands have been used in the present communication:

Furfuraldehyde thiosemicarbazone (Fur. TsczH)
2-Thiophene-carboxaldehyde thiosemicarbazone (Thiop. TsczH)
2-Pyridine-carboxaldehyde thiosemicarbazone (Pyd. TsczH)
3-Indole-carboxaldehyde thiosemicarbazone (Indol. TsczH)
2-Acetylfuran thiosemicarbazone (2-AcFur. TsczH)
2-Acetylthiophene thiosemicarbazone (2-AcThiop. TsczH)
2-Acetylpyridine thiosemicarbazone (2-AcPyd. TsczH)
3-Acetylindole thiosemicarbazone (3-AcIndol. TsczH)

Preparation of the complexes. The methanolic solution of diphenylantimony chloride was added to the methanolic solution of potassium salt of thiosemicarbazone ligand in 1:1 molar ratio. To ensure the completion of the reaction the reaction mixture was refluxed over a fractionating column for ca. 6–7 h resulting in the precipitation of potassium chloride. The mother liquor after KCl filtration is concentrated to give the product. The product was then washed with methanol and pet. ether and finally dried under reduced pressure. The physical properties and analytical data of these complexes are enlisted in Table III.

Analytical methods and physical measurements. Antimony and sulphur were estimated by the standard methods.[11] Other details are same as reported elsewhere.[2]

ACKNOWLEDGEMENT

Authors are thankful to the U.G.C., New Delhi for financial assistance and to Prof. D. Singh, Department of Botany, University of Rajasthan, Jaipur for providing necessary laboratory facilities for the biocidal activity.

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