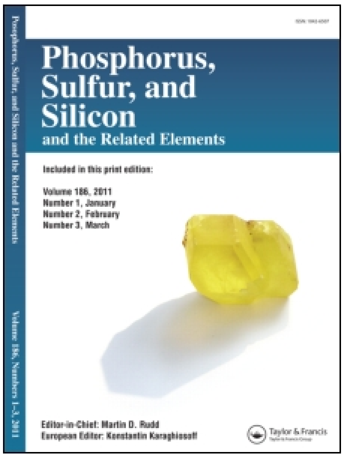

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND CHARACTERISATION OF DIORGANOANTIMONY(III) COMPLEXES OF THIOSEMICARBAZONES

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To cite this Article Gupta, R. , Singh, Y. P. and Rai, A. K.(1990) 'SYNTHESIS AND CHARACTERISATION OF DIORGANOANTIMONY(III) COMPLEXES OF THIOSEMICARBAZONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 53: 1, 397 — 401

To link to this Article: DOI: 10.1080/10426509008038049

URL: http://dx.doi.org/10.1080/10426509008038049

Phosphorus, Sulfur, and Silicon, 1990, Vol. 53, pp. 397–401
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SYNTHESIS AND CHARACTERISATION OF DIORGANOANTIMONY(III) COMPLEXES OF THIOSEMICARBAZONES

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(Received October 30, 1989; in final form February 7, 1990)

The interaction of the sodium salts of thiosemicarbazones with diphenylantimony chloride in 1:1 molar ratio in benzene solution lead to the formation of derivatives, $Ph_2Sb[SC(NH_2)NN:C(R)R']$ where $R = H$; $R' = C_6H_5$, $CH_3OC_6H_4$, $C_6H_5CH{=}CH$, and $R = CH_3$; $R' = C_6H_5$, $CH_3OC_6H_4$, $C_6H_4CH_3$, respectively. The resulting complexes have been characterised on the basis of elemental analyses and molecular weight determination. The mode of bonding of the ligands with the metal atom has been proposed on the basis of I.R., ^1H and ^{13}C NMR studies. All these ligands are found to behave as monofunctional bidentate moiety in these complexes.

Key words: Thiosemicarbazone; diorganoantimony(III); IR and NMR spectra; bidentate ligands.

INTRODUCTION

Although, the coordination chemistry of organoantimony(V)[1] and antimony(III)[2] has been studied with various sulphur and nitrogen containing ligands, reports on the corresponding organoantimony(III) compounds are scanty.

In continuation to our work on diorganoantimony(III) complexes with N, S and O containing ligands,[3–6] in the present communication we report the synthesis and spectral studies of some analogous thiosemicarbazone complexes.

RESULTS AND DISCUSSION

The reactions of diphenylantimony(III) chloride with the sodium salts of thiosemicarbazones in 1:1 molar ratio in benzene solution yield the corresponding diorganoantimony derivatives:

$$Ph_2SbCl + R'(R)C{:}NN(Na)SCNH_2 \xrightarrow{C_6H_6} Ph_2Sb[SC(NH_2)NN{:}C(R)R'] + NaCl$$

where

$$R = H;\ R' = C_6H_5,\ CH_3OC_6H_4,\ C_6H_5CH{=}CH$$
$$R = CH_3;\ R' = C_6H_5,\ CH_3C_6H_4,\ CH_3OC_6H_4$$

All these complexes are light yellow coloured solids and have sharp melting points. Osmometric molecular weight determination in chloroform solution show their monomeric nature.

TABLE I

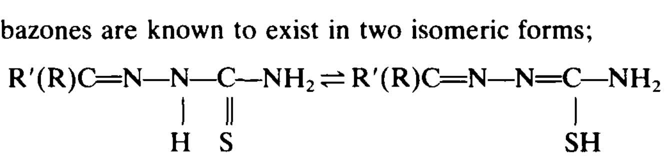
Analytical data of diphenylantimony(III) complexes of thiosemicarbazones

Reactants (gms)							
Na	Ligand $R'(R)C{:}NN(H)SCNH_2$	Ph_2SbCl	Product, % yield*	Sb% found (calcd)	N% found (calcd)	S% found (calcd)	Mol. wt. found (calcd)
0.14	$R = H$, $R' = C_6H_5$ (1.09)	1.89	$Ph_2Sb(C_8H_8N_3S)$ 81	26.62 (26.83)	9.01 (9.25)	6.90 (7.05)	420 (453.7)
0.11	$R = H$, $R' = C_6H_5CH{:}CH$ (1.03)	1.57	$Ph_2Sb(C_{10}H_{10}N_3S)$ 85	24.95 (25.37)	8.59 (8.75)	6.41 (6.67)	460 (479.7)
0.14	$R = H$, $R' = CH_3OC_6H_4$ (1.31)	1.95	$Ph_2Sb(C_9H_{10}N_3SO)$ 79	25.00 (25.16)	8.52 (8.67)	6.42 (6.61)	500 (483.9)
0.10	$R = CH_3$, $R' = C_6H_5$ (0.85)	1.37	$Ph_2Sb(C_9H_{10}N_3S)$ 80	25.95 (26.02)	8.89 (8.97)	6.54 (6.84)	450 (467.7)
0.22	$R = CH_3$, $R' = C_6H_4CH_3$ (2.06)	3.06	$Ph_2Sb(C_{10}H_{12}N_3S)$ 76	25.00 (25.27)	8.62 (8.71)	6.31 (6.64)	510 (481.7)
0.12	$R = CH_3$, $R' = CH_3OC_6H_4$ (1.21)	1.70	$Ph_2Sb(C_{10}H_{12}N_3SO)$ 81	23.98 (24.46)	8.21 (8.43)	6.12 (6.42)	475 (497.7)

ecrystallised product.

I.R. SPECTRA

Thiosemicarbazones are known to exist in two isomeric forms;



$$R'(R)C{=}N{-}\underset{\displaystyle H}{\underset{|}{N}}{-}\underset{\displaystyle S}{\underset{\|}{C}}{-}NH_2 \rightleftharpoons R'(R)C{=}N{-}N{=}\underset{\displaystyle SH}{\underset{|}{C}}{-}NH_2$$

The I.R. spectra of the ligands show a band in the region 2500–3200 cm^{-1} due to ν NH and ν SH modes, indicating the presence of both the forms. Disappearance of these bands and appearance of a new absorption band in the region 355–372 cm^{-1}, which may be assigned to ν Sb—S,[7] confirm the formation of antimony sulphur bond. The positions of the two bands at ~3400 cm^{-1} and ~3300 cm^{-1}, which may be assigned to ν_{asym} NH_2 and ν_{sym} NH_2 modes, respectively[8] in the ligands remain unchanged in the spectra of their complexes. The bands due to ν C=N and ν C=S are observed in the range 1520–1570 cm^{-1} and 962–1026 cm^{-1}, respectively. The position of these bands is shifted towards lower wave number in comparison to their position in the free ligand, suggesting the involvement of the nitrogen of azomethine moiety and sulphur of C—S group in the bonding. This has been further supported by the presence of an absorption band in the region 405–421 cm^{-1}, which may be assigned to ν Sb—N vibrations. A medium intensity band observed at 454–495 cm^{-1} is basically a phenyl deformation mode incorporating some Sb—C deformation.[9,10]

^{1}H NMR SPECTRA

The proton NMR spectra of ligands and their corresponding diphenylantimony(III) complexes have been recorded in $CDCl_3$ and the position of the signals along with their plausible assignments have been tabulated in Table II.

Two sharp signals which have been observed at δ 8.6–10.0 ppm and 1.5 to 1.7 ppm in the ligands, assigned for —NH and —SH protons, respectively, are found to be missing in the spectra of the complexes. A shift of ~2 ppm has been observed for $>$HC=N— as compared to their position in the corresponding ligands. A multiplet observed at δ 6.0–7.8 ppm in the ligands due to phenyl

TABLE II

^{1}H NMR data (in δ ppm) of diphenylantimony(III) complexes of thiosemicarbazones

S. No.	Complex $Ph_2Sb[SC(NH_2)NN:C(R)R']$	NH_2	CH	CH_3	Phenyl
1.	$R = H, R' = C_6H_5$	6.74(b)	8.04(s)	—	7.10–7.82(m)
2.	$R = H, R' = C_6H_5CH:CH$	6.57(b)	6.88(d)	—	7.06–8.04(m)
3.	$R = H, R' = CH_3OC_6H_4$	6.52(b)	7.95(s)	3.84(s)	6.79–7.73(m)
4.	$R = CH_3, R' = C_6H_5$	6.99(b)	—	2.27(s)	7.24–7.68(m)
5.	$R = CH_3, R' = C_6H_4CH_3$	6.61(b)	—	2.32(s)	7.19–7.77(m)
6.	$R = CH_3, R' = CH_3OC_6H_4$	6.52(b)	—	2.45(s) 1.96(s) 2.72(s)	6.79–7.86(m)

s = singlet, d = doublet, m = multiplet, b = broad.

protons, show a slight downfield shift in the complexes. However, NH_2 signal observed at δ 6.3–6.6 ppm in the ligands do not show any significant shift in the complexes indicating its non-participation in the bonding.

^{13}C NMR SPECTRA

A comparison of ^{13}C NMR spectra of the metal derivatives (Table III) with those of the corresponding ligands show a slight upfield shift for C=S and C=N carbon atoms. This shift is due to the change in the electronic environment in the quasi-aromatic ring formed on complexation.[11] The signals for phenyl carbons, attached to antimony are observed in the range of δ 125.6–144.5 ppm. The appearance of only one set of signals for these carbons indicates the equivalent nature of the two phenyl groups. The corrected chemical shift values δ′,[12,13] defined as $\delta' = \delta$ Cp–δ Cm (where δ Cp and δ Cm are the chemical shift values of para and meta carbon atoms of phenyl rings, respectively) are negative for these complexes. These values have been related to Hammet–Taft constant (σ R°)[14] by the relation $\delta' = 22.06\,\sigma R^\circ$. The values of σ R° are found to be in the range of −0.06 to −0.34 ppm. These negative δ′ and σ R° values are an indication of an electron release from antimony atom towards phenyl ring through pπ–pπ conjugation and poor donor capability of antimony atom in these complexes, respectively.

EXPERIMENTAL

All the reactions were carried out under anhydrous conditions. The chemicals used were of reagent grade. Diphenylantimony chloride was synthesized by reported method.[15] Thiosemicarbazones were prepared[16] by the condensation of aldehyde or ketone with thiosemicarbazide in 1:1 molar ratio in ethanol and were recrystallised from the same solvent. Antimony, sulphur and nitrogen were estimated by iodometric, gravimetric and Kjeldahl method, respectively.[17] Molecular weights were determined on Knauer Vapour Pressure Osmometer in $CHCl_3$ solutions at 45°C. I.R. spectra were recorded on Perkin Elmer 577 spectrophotometer using KBr films. NMR spectra (^1H and ^{13}C) were recorded on JEOL FX-90Q. 90 MHz spectrometer in $CDCl_3$ solutions using TMS as an internal standard.

TABLE III

^{13}C NMR data (in δ ppm) of diphenylantimony(III) complexes of thiosemicarbazones

S. No.	Complexes $Ph_2Sb[SC(NH_2)NN:C(R)R']$	CH_3	C=S	HC—N	Sb—C_6H_5*	δ′	σ R°
1.	$R = H, R' = C_6H_5$	—	177.5	144.1	141.4, 136.1, 135.0, 128.7	−7.7	−0.34
2.	$R = H, R' = CH_3OC_6H_4$	55.1	177.0	161.4	144.5, 135.3, 128.9, 125.6	−3.3	−0.14
3.	$R = CH_3, R' = C_6H_5$	13.7	178.7	148.2	137.0, 134.9, 129.7, 128.3	−1.4	−0.06
4.	$R = CH_3, R' = C_6H_4CH_3$	20.8 13.2	179.6	150.1	140.4, 136.6, 129.1, 126.9	−2.2	−0.09

* = Values are given in order of i, o, m and p carbons, respectively.

Synthesis of $Ph_2Sb[C_6H_5CH:NNCS(NH_2)]$

A weighed amount of sodium (0.14 g, 6.08 mM) was dissolved in methanol and the calculated amount of thiosemicarbazone $C_6H_5CHNNHCSNH_2$ (1.09 g, 6.08 mM) was added. After refluxing the reaction mixture for about 3 hours, the benzene suspension of diphenylantimony chloride (1.89 g, 6.07 mM) was added. The reaction mixture was further refluxed for about 6 hours. After completion of the reaction, the precipitated sodium chloride was filtered off. The excess of the solvent was removed from the filtrate by evaporation under reduced pressure. A light yellow solid product was obtained. The product was recrystallized from $CHCl_3$/pet. ether solution (in ~80% yield). Anal; found., Sb = 26.62, S = 6.95, N = 9.01, Calcd for $Ph_2Sb[C_6H_5CH:NNCS(NH_2)]$: Sb = 26.83, S = 7.05, N = 9.25%, respectively. The other complexes have been synthesised by similar route and therefore for brevity the results are being summarised in Table I.

ACKNOWLEDGEMENT

One of the authors, Rita Gupta, is thankful to CSIR, New Delhi for financial assistance.

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