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Studies on binuclear Schiff base derivatives having a Si—O—Sb (V) linkage

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Schiff base derivatives of the type $Ph_3Si—O—Sb(NO)Ph_3$ (where NO represents the donor system of a monobasic bidentate ligand) have been synthesized. These are obtained as coloured solids; they are non-electrolytes and monomeric in nature, and have been characterized by elemental analysis, IR and ^1H NMR. Spectral studies suggest that silicon and antimony atoms are in tetra- and hexa-coordinated states, respectively.

Keywords: Schiff base, antimony, silicon, complexes

INTRODUCTION

Binuclear derivatives having oxo- or μ-oxo-bridging constitute an important class of compounds due to their manifold applications ranging from thermoplastics, plastics stabilizers, catalysts, additives to lubricants and corrosion inhibitors to pesticides and pharmaceuticals.[1-4] Silicon complexes have found various uses in different fields.[5] Organoantimony complexes have also been used in various parasitic diseases.[6,7] Some polymeric derivatives having Si—O—Sb linkages have also been reported in the literature,[8,9] but no work so far has apparently been reported on chelated complexes having Si—O—Sb(V) linkages. Our continuing interest in chelated binuclear oxoderivatives[10,11] has led us to the synthesis and characterization of some Schiff base derivatives of the type $Ph_3Si—O—Sb(NO)Ph_3$ which are thermally stable.

EXPERIMENTAL

Reagents and instruments

Triphenylsilanol was obtained from Fluka. Triphenylantimony dichloride (Fluka; Ph_3SbCl_2) was used as supplied. Methanol was dried by refluxing over magnesium methoxide. Schiff bases (NOH) were prepared by the method reported earlier.[10] Nitrogen was estimated by Kjeldahl's method; silicon was estimated gravimetrically as silicon dioxide and antimony was estimated iodometrically. Carbon and hydrogen were determined in the microanalytical laboratory of this Department on a Colman analyzer 5612. Molecular weight determination carried out by the Rast camphor method. IR spectra were recorded for KBr pellets in the region 4000–200 cm^{-1}, using a Perkin–Elmer 577 grating spectrophotometer. Proton NMR spectra were recorded on a JEOL EX 90 spectrometer operating at 90 MHz in DMSO-d_6 using TMS as an internal reference.

Synthesis of binuclear complexes

These complexes were prepared by refluxing (for about 2 h) an equimolar mixture of triphenylantimony dichloride, the lithium salt of triphenylsilanol and the Schiff base in methanol (lithium salts were prepared *in situ* in methanol). The reactions can be represented by Eqns [1] and [2], in which NO represents the donor system of the monofunctional bidentate Schiff bases derived by

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Table 1 Physical properties and analytical data for binuclear Schiff base derivatives having the Si—O—Sb(V) linkage

Complex	Description	M.p. (°C)	Mol. wt: Found(Calcd)	Analysis[a]: Found (Calcd) (%) Si	Sb	N
1 $Ph_3Si-O-Sb(C_{13}H_9NO-F)Ph_3$	Light yellow solid	265 (d)[b]	840	3.30	14.41	1.65
			(841)	(3.32)	(14.45)	(1.66)
2 $Ph_3Si-O-Sb(C_{13}H_9NO-Cl)Ph_3$	Dark yellow solid	270 (d)	860	3.23	14.16	1.66
			(858)	(3.26)	(14.18)	(1.63)
3 $Ph_3Si-O-Sb(C_{13}H_9NO-Br)Ph_3$	Dark yellow solid	290 (d)	900	3.08	13.42	1.51
			(902)	(3.10)	(13.48)	(1.55)
4 $Ph_3Si-O-Sb(C_{13}H_9NO-NO_2)Ph_3$	Orange-red solid	280 (d)	865	3.18	13.97	3.20
			(868)	(3.22)	(14.00)	(3.22)
5 $Ph_3Si-O-Sb(C_{17}H_{11}NO-F)Ph_3$	Dark yellow solid	275 (d)	895	3.11	13.61	1.58
			(991)	(3.14)	(13.64)	(1.57)
6 $Ph_3Si-O-Sb(C_{17}H_{11}NO-Cl)Ph_3$	Dark yellow solid	290 (d)	900	3.05	13.61	1.51
			(908)	(3.08)	(13.39)	(1.54)
7 $Ph_3Si-O-Sb(C_{17}H_{11}NO-Br)Ph_3$	Dark yellow solid	285 (d)	—	2.90	12.70	1.43
			(952)	(2.93)	(12.74)	(1.46)
8 $Ph_3Si-O-Sb\ (C_{17}H_{11}NO-NO_2)Ph_3$	Brick-red solid	300 (d)	—	3.01	13.20	3.00
				(3.04)	(13.24)	(3.04)

[a] Satisfactory C and H analyses were found. [b] d, with decomposition.

the condensation of saliscyl aldehyde or 2-hydroxy-1-naphthaldehyde with different *para*-substituted (fluoro-, chloro-, bromo- or nitro-) anilines.[10]

$$Ph_3SiOLi + Cl_2SbPh_3 \rightarrow Ph_3Si-O-SbClPh_3 + LiCl \tag{1}$$

$$Ph_3Si-O-SbClPh_3 + LiON \rightarrow Ph_3Si-O-Sb(NO)Ph_3 + LiCl \tag{2}$$

RESULTS AND DISCUSSION

These complexes are insoluble in common organic solvents but soluble in DMSO and DMF and show a tendency to decompose on heating. Their physical and analytical data are recorded in Table 1.

IR spectra

A comparison of the IR spectra of the Si—O—Sb type of complexes with the corresponding ligands

Table 2 ^1H NMR data (δ, ppm) of ligands and complexes

Ligand or complex	—OH	—CH	Aromatic protons[a]
$HOC_6H_4 \cdot CH{:}N \cdot C_6H_4F$	12.90	8.60	7.20
$HOC_6H_4 \cdot CH{:}N \cdot C_6H_4Cl$	12.85	8.25	7.16
$HOC_{10}H_6 \cdot CH{:}N \cdot C_6H_4F$	12.60	8.70	7.50
$HOC_{10}H_6 \cdot CH{:}N \cdot C_6H_4Cl$	12.40	8.50	7.70
$Ph_3Si-O-Sb(OC_6H_4 \cdot CH{:}N \cdot C_6H_4F)Ph_3$ (Complex **1**)	—	8.85	7.26
$Ph_3Si-O-Sb(OC_6H_4 \cdot CH{:}N \cdot C_6H_4Cl)Ph_3$ (Complex **2**)	—	8.40	7.18
$Ph_3Si-O-Sb(OC_{10}H_6 \cdot CH{:}N \cdot C_6H_4F)Ph_3$ (Complex **5**)	—	8.80	7.50
$Ph_3Si-O-Sb(OC_{10}H_6 \cdot CH{:}N \cdot C_6H_4Cl)Ph_3$ (Complex **6**)	—	8.55	7.80

[a] Centre of multiplets.

provides the following useful information regarding the mode of bonding in these complexes.

(1) The bands in the region 3400–2850 cm^{-1} in the free ligand (Schiff base) are assigned to ν(OH). The ν(OH) in triphenylsilanol appears at approx. 3400 cm^{-1}. The IR spectra of the corresponding binuclear Schiff base complexes do not show these bands, indicating complexation via deprotonation of OH groups.

(2) The C═N mode in the Schiff bases appears at approx. 1610 ± 5 cm^{-1}, and shifts to higher wave number in the corresponding Si—O—Sb derivatives, indicating coordination of an azomethine nitrogen to an antimony atom. This is further confirmed by the presence of a band at approx. 270 cm^{-1} in all the complexes which is assigned to ν(Sb—N).[12, 14]

(3) In the Schiff base Si—O—Sb complexes, new bands in the region 415–400 cm^{-1} and 980–940 cm^{-1} have been observed and these may be assigned to the ν(Sb—O)[12, 13] stretching frequency and ν(Si—O—Sb)[8, 9] modes.

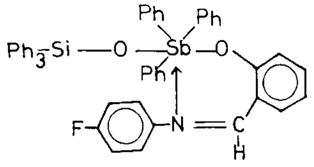
¹H NMR spectra

To confirm the mode of bonding in these complexes as indicated above, the PMR spectra of some representative compounds have been recorded and the data are given in Table 2 from which the following facts emerge.

(1) In the ligand *N*-(*p*-fluorophenyl)salicylaldimine, the hydrogen-bonded phenolic OH proton signal at δ 12.9 ppm disappears in the corresponding Schiff base Si—O—Sb(V) complex, indicating the chelation of the phenolic oxygen of the ligand moiety to the antimony atom after deprotonation. The azomethine proton signal at δ 8.6 ppm in the ligand shifts downfield in the corresponding complex and is observed at δ 8.85 ppm, supporting the IR evidence that the azomethine nitrogen coordinates with the antimony atom and gives an octahedral environment for the antimony atom.

(2) In the ligand *N*-(*p*-fluorophenyl)-2-hydroxy-1-naphthaldimine, the hydrogen-bonded phenolic OH proton signal at δ 12.6 ppm disappears in the corresponding binuclear complex, indicating chelation of the phenolic oxygen of the ligand moiety to the antimony atom. The downfield shift in the azomethine proton signal which is observed in the ligand at δ 8.7 ppm is indicative of the coordination of the azomethine nitrogen to the antimony atom, giving rise to a hexa-coordinated state for antimony.

Thus, on the basis of the spectral evidence, the following structure for complex **1** may be proposed, in which the silicon atom is in the usual tetravalent state and the antimony atom is in a hexa-coordinated state. Hexa-coordinated Sb(V) is reported to be quite stable.[14, 15].



Structure 1

CONCLUSION

New Schiff base complexes of the type $Ph_3SiOSb(NO)Ph_3$ have been synthesized and characterized.

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