SYNTHESIS AND CHARACTERIZATION OF MONOHALO-DIORGANOANTIMONY(V) SCHIFF BASE COMPLEXES

Pankaj Sharma*, Noé Rosas, Ramashankar and Armando Cabrera*

Instituto De Quimica UNAM, Circuito exterior, Ciudad Universitaria, Coyoacan, 04510 Mexico D.F.

Abstract

Monohalodiorganoantimony(V) Schiff base complexes of the type R_2SbXL, where R = Ph, p-tolyl or methyl and H_2L are potentially tetradentate Schiff base ligands with ONNO donors, have been synthesized and characterized. The Schiff bases obtained by the condensation of ethylenediamine with salicyladehyde ($SalenH_2$) and o-aminophenol with glyoxal ($GbapH_2$). Molecular weight-determination in benzene reveals the monomeric nature of these complexes. IR and NMR data suggest the presence of seven coordinated antimony in these complexes.

Introduction

There are a number of reports on the synthesis and structural studies of novel complexes by $R_3Sb(V)$ moieties (R = Ph or Me) with polydentate ligands [1-4]. In some of these complexes the antimony atom attains the coordination number seven. We thought it worthwhile to extend our studies to the corresponding complexes of $R_2Sb(V)$ with tetradentate bianionic Schiff base ligands having ONNO donor atoms. As such, there are a number of reports [2-5] on the complexes of $R_3Sb(V)$ moiety with tetradentate Schiff bases compared to only one report [6] of $R_2Sb(V)$ with tetradentate schiff base. Further, it was also expected that $R_2Sb(V)$ moiety may form stronger complexes because of its better acceptor property [7-8] than that of $R_3Sb(V)$.

Experimental

Materials. R_2SbBr_3 and R_2SbCl_3 where R = Methyl , Phenyl or p-Tolyl were prepared and purified by reported methods[9,10]. The Schiff bases were obtained by condensation of appropriate aldehyde with amine in alcohol as previously reported [11-13]. Solvents and other materials were dried and purified before use. All the reactions were performed in an inert atmosphere.

Measurements. Molecular weights of the compounds soluble in benzene were determined using a Knaver vapour pressure osmometer. IR spectra in the range 4000-400cm^{-1} were reported in KBr on a Nicolet (5-DX) FT-IR spectrometer. The far IR spectra (700-30 cm^{-1}) of the compounds were recorded on a Perkin Elmer 1700X-far IR FT spectrometer. The PMR spectra were recorded in $CDCl_3$ on a Jeol NM FX100 NMR spectrometer using TMS as an internal standard.

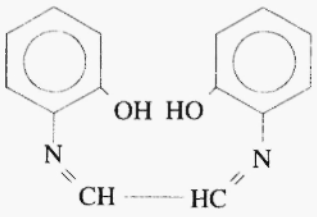
Analysis. Antimony was determined volumetrically by a reported method [14]. Elemental analysis were done on a Perkin-Elmer 240C elemental analyser. Halogen was determined by Volhard's method

Preparation.

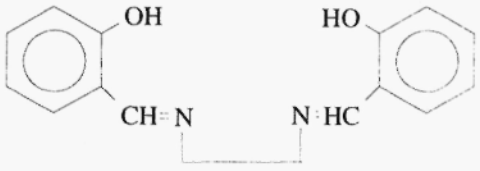
All the complexes were prepared by addition of a solution of sodium salt of the ligand, Na_2L [prepared from H_2L + NaOMe (5 mmol: 10 mmol)] in benzene-methanol (35:15 ml) to a stirred solution of R_2SbBr_3 (5 mmol in 50 ml benzene). The mixture was refluxed at 60°C for 2 hr. The resultant solution was then concentrated to dryness and 20 ml benzene were added to it. Sodium bromide or sodium chloride separated which was filtered off. The filtrate was concentrated and the complexes were precipitated by adding dry hexane to the concentrate. Recrystallization from chloroform-hexane or benzene-hexane mixtures gave crystalline solids, with yields ranging from 53-67%.

Results and discussion

The structures of potentially tetradentate dianionic Schiff bases of the type ONNO used for this work are shown below:



$GbapH_2$



$SalenH_2$

The diorganoantimony(V) chelates were prepared by the interaction of diarylorganoantimony trihalide with sodium salt of the Schiff base in dry benzene according to the following equation:

Table.1. Analytical Data, Melting Points and Molecular Weights of Schiff Bases H_2L and of R_2SbXL Complexes

Compound	formula	%yield/ colour	m. p.	%C	%H	%N	%Sb	%X	Mol.Wt
$SalenH_2$	$C_{16}H_{16}N_2O_2$	79/yellow	121-122	71.02 (71.63)	5.76 (6.01)	10.31 (10.44)			254 (268.2)
$Ph_2SbBr(Salen)$	$C_{28}H_{24}SbBrN_2O_2$	63/yellow	139-141	53.91 (54.06)	3.89 (3.89)	4.44 (4.5)	20.7 (19.58)	13.12 (12.84)	610 (622)
$Ph_2SbCl(Salen)$	$C_{28}H_{24}SbClN_2O_2$	65/yellow	192	57.17 (58.22)	4.12 (4.18)	4.00 (4.85)	21.13 (21.08)	6.33 (6.14)	561 (577.6)
$Me_2SbBr(Salen)$	$C_{18}H_{20}SbBrN_2O_2$	59/yellow	133	43.10 (43.41)	3.93 (4.05)	5.15 (5.63)	25.13 (24.44)	16.92 (16.05)	483 (497.9)
$(Tolyl)_2SbCl(Salen)$	$C_{30}H_{30}SbClN_2O_2$	61/yellow	160-161	55.27 (55.35)	4.38 (4.97)	4.07 (4.62)	20.19 (20.03)	6.34 (5.85)	590.0 (607.5)
$(Tolyl)_2SbBr(Salen)$	$C_{30}H_{30}SbBrN_2O_2$	61/yellow	169	59.93 (59.27)	4.47 (4.60)	4.10 (4.30)	19.09 (18.58)	12.94 (12.28)	632 (651)
$GbapH_2$	$C_{14}H_{12}N_2O_2$	78/white	203-205	69.48 (70.00)	4.94 (5.09)	10.89 (11.66)	-	-	232 (240)
$Me_2SbBr(Gbap)$	$C_{16}H_{16}SbBrN_2O_2$	67/brown	112(d)	39.87 (40.89)	3.34 (3.43)	5.20 (5.97)	26.17 (25.91)	18.00 (17.00)	452 (469.9)
$Ph_2SbBr(Gbap)$	$C_{26}H_{20}SbBrN_2O_2$	63/brown	98(d)	52.47 (52.57)	3.21 (3.39)	4.17 (4.72)	21.30 (20.49)	14.01 (13.45)	581 (594)

$$R_2SbX_3 + Na_2L \xrightarrow{\text{Benzene + methanol}} R_2SbLX + 2NaBr$$

Analytical data, melting points and molecular weight determination results for these complexes are given in Table 1.

All the complexes are microcrystalline in nature and are stable towards atmospheric oxygen but are sensitive to moisture to varying extents. They are soluble in most organic solvents like benzene, chloroform, acetonitrile but sparingly soluble in CCl_4 . The elemental analyses correspond to the stoichiometry R_2SbLBr or R_2SbLCl with the bases present in dianionic form. Molecular weight determination of the complexes showed that they are non-dissociating monomers in benzene. Conductance measurement in acetonitrile showed the complexes to be non-conducting.

IR and far IR spectra

A weak and broad IR band in the region 2635-2910 cm^{-1} in the ligands which may be assigned to the intramolecularly hydrogen bonded -OH is not observed in the IR spectra of the complexes indicating the absence of -OH proton [1, 3,5,15-17].

`The phenolic C-O stretching vibrations appearing at 1280 cm^{-1} in the Schiff bases undergo a shift towards higher frequency in the complexes which confirms the participation of oxygen in C-O-Sb bonding. A strong band found around 1620 cm^{-1} in the ligands is attributed to the -C=N stretch. This band in the complexes shows a shift of 25 cm^{-1} indicating sensitivity of this band to chelation; such an observation has also been reported earlier [4-6, 18-20].

In the far IR spectra of the complexes there are some additional peaks which were not present in the ligands or in the starting organoantimony compounds. A new band present in the region 428-443 cm^{-1} may be attributed to the Sb-O stretching vibration [1,3,6,21,22]. These vibrations are at higher wave-number (12 cm^{-1}) than those in $Ph_3Sb(V)$ (ONNO) complexes. This increase may be attributed to the replacement at antimony of the organic group R by the more electron-withdrawing halogen atom. It may be further observed that Sb-O vibration is at higher wavenumber in chlorocomplexes than in bromocomplexes. In all the complexes a band is observed (271-280cm^{-1}) suggesting chelation through nitrogen. However, Sb-Ph vibration is also observed in the same region and, hence, unequivocal assignment of the νSb-N cannot be made except in the case of Me_2SbBr (Salen) and Me_2SbBr(Gbap) [1,6].

The observed decrease in the Sb-X absorption frequencies in R_2SbXL (Sb-Br 151-168 cm^{-1} and Sb-Cl 260-269 cm^{-1}) in comparison to R_2SbX_3 can be interpreted in

terms of increased ionicity of the Sb-X bond. Further, the absorption frequencies of (Sb-X) in R_2SbXL are similar to the values in the related complexes $R_2SbCl(Trid)$[where Trid are tridentate bianionic (ONO type) Schiff base ligands] reported earlier [6-7]. This decrease may also be due to increase in coordination number of antimony on complexation[23,24].

PMR spectra

The PMR spectra of all the compounds in $CDCl_3$ were recorded at room temperature and the positions of the important resonance signals are compiled in Table 2. The spectra of the complexes containing $Me_2Sb(V)$ and $(p\text{-tolyl})_2Sb(V)$ moieties were more useful from a structural point of view than those of the containing $Ph_2Sb(V)$ moiety because of the presence of the distinguishable methyl groups.

Table. 2. PMR Data of Schiff Bases H_2L and of R_2SbXL Complexes.

Compound	-OH	-CH=N	-CH_2-CH_2 ppm)	-Me	Aromatic protons
$SalenH_2$	13.13	8.34(s,2H)	3.85(s,4H)	-	7.14-7.66(m,8H)
Ph_2SbBr(Salen)	-	8.36(s,2H)	3.84(s,4H)		7.26-7.83(m,18H)
Ph_2SbCl(Salen)	-	8.41(s,2H)	3.85(s,4H)		7.24-7.92(m,18H)
Me_2SbBr(Salen)	-	8.36(s,2H)	3.86(s,4H)	1.57(s,3H),1.38(s,3H)	7.18-7.71(m,8H)
$(Tolyl)_2SbBr$(Salen)	-	8.38(s,2H)	3.85(s,4H)	2.12(s,3H),2.30(s,3H)	7.25-7.91(m,16H)
$(Tolyl)_2SbCl$(Salen)	-	8.41(s,2H)	3.86(s,4H)	2.05(s,3H),2.14(s,3H)	7.21-7.89(m,16H)
$GbapH_2$	4.78 (s,2H)	5.26 (s,2H)			6.61-7.23(m,8H)
Ph_2SbBr(Gbap)	-	5.38(s,2H)			6.72-7.45(m,18H)
Me_2SbBr(Gbap)	-	5.45(s,2H)		1.76(s,3H),1.60(s,3H)	6.78-7.52(m,8H)

The chemical shift observed for the -OH protons in the schiff bases were not observed in the complexes indicate the absence of -OH protons.

The PMR spectra show a downfield shift of the peak for the CH=N proton as compared to that in the free Schiff base, $GbapH_2$ and $SalenH_2$ indicating the coordination of the azomethine nitrogen with the antimony atom. The downfield shifts of azomethine protons on complexation have been reported [1,3-7]

The PMR spectrum of Me_2SbBr(Salen) and Me_2SbBr(Gbap) exhibits two equally intense signals for methyl protons at 1.57 ppm and 1.38 ppm and 1.76 and 1.60 ppm respectively indicating that the two methyl groups are in different environments. Similarly, the two tolyl groups in $(tolyl)_2SbBr$(Salen) and $(tolyl)_2SbCl$(Salen) are also in different environments as indicated by the appearance of two equally intense peaks due to

two types of methyl protons at 2.12ppm and 2.30 ppm and 2.05 ppm and 2.14 ppm respectively. No such distinction, however, can be made in the case of complexes with the Ph_2Sb moiety.

Taking into consideration the above facts, it is tentatively proposed that the complexes of these ligands have a pentagonal-bipyramidal structure in which antimony is seven coordinated and in sp^3d^3 hybridization state as shown in (figure I).

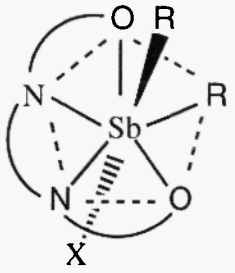


Fig. I

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