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Hexacoordinated Complexes of Antimony(V)

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Hexacoordinated complexes of antimony with ligands obtained by the condensation of various mono- and diamines with salicylaldehyde and o-vanillin have been synthesized. The complexes were characterized by elemental analyses, molecular weight determinations, conductivity measurements and spectral results. The monoamine complexes exhibited a 1:2 (metal:chelate) stoichiometry while the diamine complexes have a 1:1 (metal:chelate) stoichiometry. All complexes have shown a 1:1 electrolytic behavior in solutions of DMF.

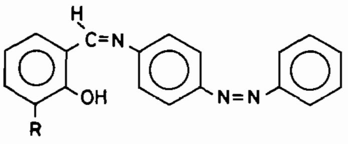
Introduction

A wide range of tetradentate Schiff bases has been reported in the literature [1, 2], among these, the tetradentate Schiff bases containing two acidic groups and two azomethine nitrogens [3–9]. In recent years a number of papers have appeared in the literature [10–12] dealing with metal complexes of ligands derived from the condensation of mono- and diamines with *o*-hydroxy aldehydes. However, none of these ligands were complexed with antimony(V). This provided a stimulus to synthesize antimony(V) complexes of ligands containing O, N and O, N, N, O sequences. These complexes were characterized by elemental analyses, conductivity measurements, infrared (IR) and nuclear magnetic resonance (NMR) spectral data.

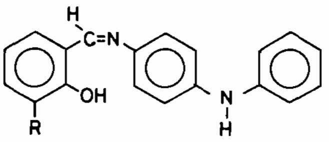
Experimental

The chemicals used in this work were reagent grade and used without further purification. Schiff bases derived from monoamines have been prepared according to a previously published procedure [13]. Equimolar proportions of the monoamines and the respective aldehyde were refluxed in alcohol for approximately two hours. The reaction mixture was allowed to cool and the crystals of Schiff base which formed were recrystallized in ethanol. The Schiff bases derived from diamines were prepared by refluxing a mixture of 0.01 mol diamine and 0.02 mol aldehyde in methanol for 30 minutes. After cooling, crystals of Schiff base were separated and recrystallized from methanol. The ligands which were prepared are:

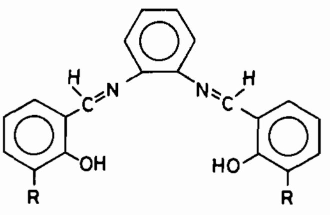
	R
A.	-H
B.	-OCH$_3$



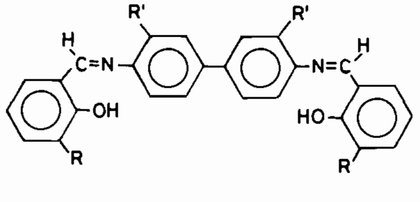
	R
C.	-H
D.	-OCH$_3$



	R
E.	-H
F.	-OCH$_3$



	R	R'
G.	-H	-H
H.	-OCH$_3$	-H
I.	-H	-OCH$_3$
J.	-OCH$_3$	-OCH$_3$



Complexes I–X were prepared by reacting antimony(V) chloride (0.01 mol) with the Schiff base (0.02 mol) in dry benzene with vigorous shaking. The resulting mixture was allowed to react overnight,

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TABLE I. Analytical and Physical Data for Antimony(V) Schiff Base Complexes.

Ligand	Complex Number	Empirical Formula of Complex	% Sb[a]	% N[a]	% Cl[a]	Mol. Wt.	Molar Cond., ohm^{-1} cm^2 mol^{-1}
A	**I**	$(C_{19}H_{15}ON_3)_2SbCl_5$	13.50	9.50	19.72	875.9	106.23
			(13.53)	(9.31)	(19.68)	(901.5)	
B	**II**	$(C_{21}H_{19}O_3N_3)_2SbCl_5$	11.89	8.30	17.40	990.2	121.01
			(11.94)	(8.22)	(17.37)	(1021.5)	
C	**III**	$(C_{19}H_{16}ON_2)_2SbCl_5$	13.96	6.43	20.25	839.7	102.70
			(13.93)	(6.39)	(20.27)	(875.5)	
D	**IV**	$(C_{21}H_{20}O_3N_2)_2SbCl_5$	12.30	5.60	17.81	978.1	109.83
			(12.25)	(5.62)	(17.83)	(995.5)	
E	**V**	$(C_{20}H_{16}O_2N_2)SbCl_5$	20.01	4.53	28.75	587.4	93.86
			(19.82)	(4.55)	(28.83)	(615.5)	
F	**VI**	$(C_{22}H_{20}O_4N_2)SbCl_5$	18.09	4.17	26.22	647.9	95.22
			(18.06)	(4.14)	(26.27)	(675.5)	
G	**VII**	$(C_{26}H_{20}O_2N_2)SbCl_5$	17.75	4.08	25.63	667.2	111.45
			(17.71)	(4.04)	(25.66)	(691.5)	
H	**VIII**	$(C_{28}H_{24}O_4N_2)SbCl_5$	16.30	3.75	23.55	701.9	98.73
			(16.23)	(3.72)	(23.61)	(751.5)	
I	**IX**	$(C_{28}H_{24}O_4N_2)SbCl_5$	16.26	3.81	23.60	726.6	103.66
			(16.23)	(3.72)	(23.61)	(751.5)	
J	**X**	$(C_{30}H_{28}O_6N_2)SbCl_5$	15.71	3.51	21.73	777.3	109.08
			(15.63)	(3.45)	(21.87)	(811.5)	

[a] Values in the parentheses are theoretical values.

filtered, and washed thoroughly with dry benzene. The product was dried in vacuum over P_2O_5.

Elemental analyses were carried out by a procedure discussed elsewhere [14]. Antimony was determined as its azide by a direct ignition method. Chlorine was determined as the silver chloride precipitate. Nitrogen was determined by the Kjeldahl method.

The conductivities of the complexes were measured in dimethylformamide (DMF) using an Elico-CM-82 conductivity bridge with a cell having a cell constant of 0.829 cm^{-1}. All measurements were performed at room temperature using 10^{-3} *M* solutions of the complex.

The infrared (IR) spectral results (4000 to 200 cm^{-1}) were obtained from KBr pellets using a Perkin-Elmer 180 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded using a S-60-C NMR instrument with deuterated dimethylsulfoxide (d_6-DMSO) as a solvent and $CDCl_3$ as the internal standard. The molecular weights were determined by the cryoscopic method using nitrobenzene as solvent.

Results and Discussion

Analytical Data

All complexes are colored and amorphous in nature and are soluble in nitrobenzene, pyridine, DMF and DMSO. The elemental analyses show (Table I) that the complexes with monoamines exhibit a 1:2 (metal:chelate) stoichiometry while the diamine complexes have a 1:1 stoichiometry. The molar conductivities are in the range of 80–110 ohm^{-1} cm^2 mol^{-1} suggesting a 1:1 electrolytic behavior in solution. The molecular weights in nitrobenzene were obtained by cryoscopic method, and agree well with the theoretical values suggesting the purity of the complexes.

Infrared Spectra

The infrared spectra of ligands and complexes together with their assignments are available upon request from the author to whom all correspondence should be addressed.

A comparison of spectra of ligands and complexes clearly shows a band at 2700 cm^{-1} due to a hydrogen bonded OH group which did not change position, suggesting the nonreactivity of the *o*-hydroxy group in coordination. This is further confirmed by the unchanged position of the phenolic C–O stretch (approximately 1280 cm^{-1}) in both ligands and complexes. A strong band at 1640–1600 cm^{-1} can be attributed to the C=N stretch and the nonconjugated C=N is found at 1690–1670 cm^{-1}. Conjugation with the aromatic rings and hydrogen bonding lowers the frequency [15] to 1600 cm^{-1} [8, 16]. For ligands A and B, this band is broad and split slightly. This may be due to the mixture of ν(C=N), ν(Sb–N) and aromatic ν(C=C) vibrations. The spectra of complexes, however, show a consistent shift of the azomethine band to the higher

TABLE II. Nuclear Magnetic Resonance Chemical Shifts (in ppm) of Schiff Base Ligands and Complexes.

Ligand	(Complex)	$-OH^a$	$-CH$	$-C_6H_5$	$-OCH_3$	$-NH$
A	**I**	13.20(13.20)	8.39(9.60)	6.80–7.80(6.8–7.8)	–	–
B	**II**	13.15(13.16)	8.36(9.66)	7.0–8.0(6.8–7.8)	3.89(3.66) (3.81)	–
C	**III**	13.29(13.30)	8.62(9.76)	6.9–8.0(7.0–8.0)	–	5.07(5.09)
D	**IV**	13.30(13.30)	8.90(9.79)	7.0–8.0(6.9–8.0)	3.98(3.71) (3.92)	5.21(5.20)
E	**V**	13.90(13.20)	8.43(9.63)	6.9–7.9(7.0–8.0)	–	–
F	**VI**	12.96(12.95)	8.37(9.57)	6.8–7.7(6.7–8.1)	4.01(3.96)	–
G	**VII**	13.3(13.30)	8.46(9.63)	6.9–7.9(7.0–8.1)	–	–
H	**VIII**	13.2(13.22)	8.40(9.58)	7.1–8.0(6.8–7.8)	3.79(3.80)	–
I	**IX**	13.26(13.29)	8.75(9.79)	7.2–8.1(6.9–8.1)	–	–
J	**X**	13.29(13.30)	8.89(9.80)	6.8–7.8(7.0–8.0)	3.88(3.9)	–

[a] Values in parentheses are shifts for the complexes.

frequency (from 1600 to 1640 cm^{-1}). This shift indicates the possible coordination of azomethine nitrogen to the central metal atom.

In complexes **I** and **II**, bands observed at 1650 cm^{-1} and 1615 cm^{-1} are assigned to C=N and N=N stretching vibrations respectively. The stationary position of the band due to N=N frequency suggests that the nitrogen of the azo group is not involved in coordination. The proof that the secondary amine groups in ligands C and D are not involved in coordination is shown in the infrared frequency of the NH group. The position of the band due to NH stretching (at approximately 3400 cm^{-1}) is unchanged in the complexes.

In accordance with previously reported data [17–21] the two bands appearing at 570 cm^{-1} and 530 cm^{-1} are assigned to the ν(Sb–N) vibrations. This suggests the possible *trans* configuration for two ligand molecules around antimony(V) in complexes **I** to **IV**. In complexes **V** to **X**, however, a band is found at approximately 530 cm^{-1} which characterizes the *cis* environment. A band found at 350 cm^{-1} is attributed to the ν(Sb–Cl) stretching vibrations [22–25].

Nuclear Magnetic Resonance Spectra

The proton signals of the Schiff base ligands and complexes are presented in Table II. The ligand spectra are characterized by three signals at 13.2, 8.4, and 6.7–7.8 ppm, which are attributable to the intramolecularly hydrogen bonded hydroxyl proton, azomethine proton and the phenyl protons respectively. In ligands C and D an additional peak at 5.00 ppm is attributed to the NH proton resonance. However, in the vanillydene Schiff bases an extra proton signal due to m-OCH_3 group is observed near 4.0 ppm.

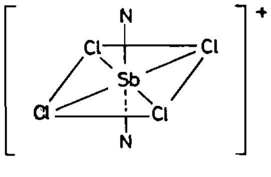
In the complexes, the signal at 13.2 ppm is unchanged which indicates adduct formation. The coordination through the azomethine nitrogen to antimony(V) is evidenced by the shift of the peak from 8.4 ppm (azomethine proton) to approximately 9.6 ppm. Upon complexation the phenyl protons did not change their positions, and the signal at 5 ppm remained in its original position, signifying the nonreactivity of the NH protons. In complexes **II** and **IV** however, the peak due to m-OCH_3 protons is observed at 3.6 ppm and 3.8 ppm indicating a *trans* geometry for the antimony complexes with monoamine Schiff bases. With complexes **VI**, **VIII** and **X** only one signal at 3.9 ppm (due to m-OCH_3) is observed suggesting a *cis* configuration for these diamine complexes with antimony.

Conclusions

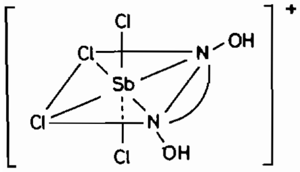
Ten complexes of antimony with ligands obtained by the condensation of various mono- and diamines with salicylaldehyde and o-vanillin have been synthesized. These complexes were characterized by elemental analyses, molecular weight determinations, conductance measurements, and infrared and nuclear magnetic resonance spectral data. The spectral data indicate that the coordination may occur through the azomethine nitrogen and that the o-hydroxyl groups do not participate. A stoichiometry of 1:1 for the diamine complexes and 1:2 for the monoamine complexes is observed, with all complexes behaving as 1:1 electrolytes.

Correlation of these observations has led to the proposal of the following stereochemical models for these complexes.

1) Monoamine Complexes



2) Diamine Complexes



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