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Some Schiff's Base Complexes of Antimony(III)

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Some Schiff's base complexes of antimony(III) have been prepared using antimony trichloride and triiodide separately. The Schiff's base ligands have been obtained by condensation of salicylaldehyde with amines (ethylamine, aniline, *o*-toluidine), amides (acetamide, benzamide) and ureas (urea, thiourea). It has been observed that the complexes are readily formed just on slight warming. In case of antimony triiodide, two iodines are readily attacked but in case of antimony trichloride all the three chlorines are attacked. The complexes with urea and thiourea involve macrocyclic Schiff's base ligands.

INTRODUCTION

It has been observed that Ti(IV), Cu(II) and Ni(II) can act as matrices for the formation of Schiff's base macrocyclic ligands which coordinate to the metal through nitrogen and oxygen forming chelates[1, 2]. These systems are of interest, since some of them are models for investigating many biological processes. Cu(II), Ni(II), Pd(II) and VO(IV) ions facilitate the condensation of salicylaldehyde with carbazones and amino acids; it is observed that the condensation takes place more rapidly for the Ni(II) ion[3–6]. It was thought proper to seek this condensation facility in presence of normal elemental salts; $SbCl_3$ and SbI_3 were used for the synthesis of Schiff's base macrocylic ligand complexes with Sb(III). The complexes have been characterized by elemental analysis, conductivity measurements, magnetic data, infrared and electronic spectra.

EXPERIMENTAL

All the reactions were carried out in warm chloroform in dry atmosphere. Analar grade chemicals were used in synthesis and analytical estimations. Carbon, hydrogen and nitrogen were semimicroanalytically estimated. Antimony was estimated iodometrically. Chlorine and iodine were determined as AgCl and AgI respectively and sulphur as $BaSO_4$.

Preparation of Sb(III) Schiff's base complexes from $SbCl_3$

A warm solution of amine (ethylamine, aniline, *o*-toluidine) or amides (acetamide, benzamide) (0.012 mol) and salicylaldehyde (0.012 mol) was prepared in 30 mL chloroform. A warm solution of $SbCl_3$, 0.912 g (0.001 mol), in chloroform was slowly added to the above solution with constant shaking. The mixture was kept at *ca.* 45°C for 2–3 h. Cream to deep red solids separated out which were filtered, washed with petroleum ether and dried. The products were recrystallized from hot THF.

In case of urea and thiourea Schiff's bases the amounts of urea or thiourea, salicylaldehyde and $SbCl_3$ were taken in molar ratios 2 : 1 : 1. The analytical data and other physical constants are given in Table-1.

Preparation of Sb(III) Schiff's base complexes from SbI_3

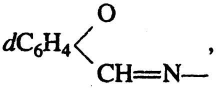
A similar procedure as above was used with SbI_3, but the ratios of the reactants were different. For amine-salicylaldehyde Schiff's base complexes the molar ratio of SbI_3, salicylaldehyde and amine were 1 : 2 : 2, but for urea and thiourea Schiff's base complexes the molar ratios were 1 : 2 : 1.

Deep red to dark brown solids were obtained which were filtered, washed with ether and dried. The complexes were recrystallized from alcohol-THF mixture (1:2). The analytical data and physical constants are given in Table-1.

All the complexes are quite stable under room temperature and atmospheric pressure. They start decomposing before melting points in the range 130–160°C ($SbCl_3$-complexes) and 100–130°C (SbI_3-complexes). The complexes are readily soluble in DMF. They are decomposed by hot acids and alkalies.

RESULTS AND DISCUSSIONS

The cryoscopically determined molecular weights determined cryoscopically of the complexes indicated their monomeric nature. Conductance studies in DMF (λ_M 5–20 ohm^{-1} cm^2 mol^{-1}) proved them to be esentially non-electrolytes. The magnetic susceptibilities measured at room temperature using copper sulphate as calibrant are very low (*ca.* 0.02 BM) indicating that all the complexes are diamagnetic.

In all these complexes the salicylaldoxime residue,  $dC_6H_4\left\langle\begin{matrix}O\\ CH{=}N{-}\end{matrix}\right.$, is a common structural feature, which is indicated by the following absorption peaks in their IR spectra. The disappearance of ν(OH) shows that the phenolic OH has entered into combination. A band at *ca.* 1560 cm^{-1} is assigned to ν(C═N), lowered due to coordination to antimony through nitrogen. The phenolic ν(C—O) has been assigned at *ca.* 1315 cm^{-1}. The bands at ca. 3030, 1590, 1500, 1410, 1150, 1040 and 930 cm^{-1} are assigned to ν(C—H) of a 1,2-substituted benzene ring and the band *ca.* 750 cm^{-1} is assigned to π(C—H). The aldehydic ν(C—H) are assigned as two bands at *ca.* 2900 and 2720 cm^{-1}; the δ(C—H) at *ca.* 900 cm^{-1} and C—H skeletal vibrations[8,9] at *ca.* 1390, 1280 and 1210 cm^{-1}.

The ethylamine based Schiff's base complex IR spectra showed no bands at *ca.* 3500 cm^{-1} indicating the absence of N—H bonds. A band at *ca.*1075 cm^{-1} could be assigned to ν(C—N) somewhat lowered due to coordination of N to antimony[10]. The CH_3—CH_2— group frequencies are assigned as ν(C—H) at *ca.* 2950 and 2860 cm^{-1}. The ν_{asym}(C—H) bending and ν_{sym}(C—H) bending at *ca.* 1440 and 1370 cm^{-1} respectively, (—CH_2—) scissoring at *ca.*1450 cm^{-1} and

TABLE-1

PHYSICAL AND ANALYTICAL DATA OF SOME SCHIFF'S BASE COMPLEXES OF ANTIMONY (III)

Compound (ligand used)	Mol. wt. Found (Calcd.)	Colour (Dec. temp) (°C)	Elemental analysis (%) Found/(Calcd.)		
			Sb	N	Cl/I
$[C_6H_4OCH(NC_2H_5)]_3Sb$	570.3	Light pink	21.31	7.32	—
(Ethylamine-salicylaldehyde)	(565.7)	(131)	(21.51)	(7.42)	
$[C_6H_4OCH(NC_6H_5)]_3Sb$	702.1	Mustard yellow	17.30	6.11	—
(Aniline-salicylaldehyde)	(709.7)	(145)	(17.15)	(5.92)	
$[C_6H_4OCH(NC_6H_4CH_3)]_3Sb$	757.3	Green brown	16.27	5.72	—
(*o*-Toluidine-salicylaldehyde)	(751.7)	(141)	(16.19)	(5.59)	
$[C_6H_4OCH(NCOCH_3)]_3Sb$	611.2	Red	20.15	6.82	—
(Acetamide-salicylaldehyde)	(607.7)	(140)	(20.03)	(6.91)	
$[C_6H_4OCH(NCOC_6H_5)]_3Sb$	790.2	Red brown	15.24	5.34	—
(Benzamide-salicylaldehyde)	(793.7)	(148)	(15.33)	(5.29)	
$[(C_6H_4OCH)_2(NCON)]SbCl$	425.7	Cream	28.52	6.73	8.53
(Urea-salicylaldehyde)	(423.2)	(155)	(28.16)	(6.48)	(8.21)
$[(C_6H_4OCH)_2(NCSN)]SbCl$	442.3	Brick red	27.48	6.21	8.31
(Thiourea-salicylaldehyde)	(439.2)	(158)	(27.71)	(6.37)	(8.08)
$[C_6H_4OCH(NC_2H_5)]_2SbI$	539.3	Brick red	22.03	5.32	23.42
(Ethylamine-salicylaldehyde)	(544.7)	(102)	(22.34)	(5.14)	(23.31)
$[C_6H_4OCH(NC_6H_5)]_2SbI$	634.7	Yellow brown	18.74	4.13	19.57
(Aniline-salicylaldehyde)	(640.7)	(124)	(18.99)	(4.37)	(19.82)
$[C_6H_4OCH(NC_6H_4CH_3)]_2SbI$	670.8	Brown	18.32	4.01	18.80
(*o*-Toluidine-salicylaldehyde)	(668.7)	(120)	(18.20)	(4.19)	(18.99)
$[C_6H_4OCH(NCOCH_3)]_2SbI$	567.7	Red brown	21.45	4.67	22.32
(Acetamide-salicylaldehyde)	(572.7)	(107)	(21.25)	(4.89)	(22.17)
$[C_6H_4OCH(NCOC_6H_5)]_2SbI$	702.3	Dark brown	17.31	4.19	18.41
(Benzamide-salicylaldehyde)	(696.7)	(126)	(17.47)	(4.02)	(18.23)
$[(C_6H_4OCH)_2(NCON)]SbI$	519.3	Orange	23.29	5.23	24.79
(Urea-salicylaldehyde)	(514.7)	(127)	(23.64)	(5.44)	(24.67)
$[(C_6H_4OCH)_2(NCSN)]SbI$	536.8	Brown	22.72	5.43	24.21
(Thiourea-salicylaldehyde)	(530.7)	(128)	(22.93)	(5.28)	(23.93)

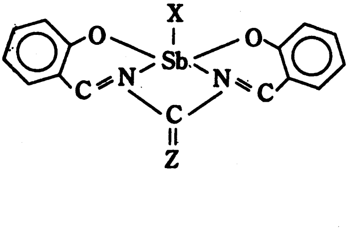
the ρ(CH_3—C) at *ca.* 1100 cm^{-1}. The aniline based schiff's base complex did not show any N—H absorption modes. The ν(C—N) appeared at *ca.* 1280 cm^{-1}, lowered due to coordination to antimony through nitrogen[10]. The aromatic ν(C—H) are assigned at *ca.* 3100, 1865, 1720 cm^{-1}, the δ(C—H) at *ca.* 1130, 1080 and 1020 cm^{-1}, the π(C—H) at *ca.* 750 cm^{-1}. The ring skeletal vibrations appeared at *ca.* 1610, 1570 and 1480 cm^{-1}. In the IR spectra of *o*-toluidine based Schiff's base complex no bands were observed due to ν(N—H). The ν(C—N) is assigned at *ca.* 1270 cm^{-1} lowered due to coordination through nitrogen. The ν(C—H) are assigned at *ca.*2810, 1590, 1500, 1110 and 1020 cm^{-1}, π(C—H) at *ca.* 740 cm^{-1}, δ(C—H) of the CH_3—C group at *ca.* 1360 cm^{-1}, and ρ_r of CH_3—C group at *ca.* 920 cm^{-1}.[11]

No absorption bands are present due the ν(N—H) in the IR spectra of acetamide, benzamide and urea based Schiff's base complexes. The ν(C═O) appeared at *ca.* 1760 cm^{-1} for benzamide and 1700 and 1680 cm^{-1} for acetamide. The ν(C—N) appeared at *ca.* 1275 cm^{-1}, somewhat lowered due to coordination of nitrogen to antimony. The benzamide based complexes showed bands at *ca.* 3015, 1610, 1575, 1525 and 1400 cm^{-1} due to aromatic ring ν(C—H), the π(C—H) are assigned at *ca.* 730 cm^{-1}, while the bands at *ca.* 1260, 1080 and 1020 cm^{-1} may be due to δ(C—H). The δ(CH_3) bands in the acetamide complexes appear at *ca.* 1510 and 1455 cm^{-1}. In the thiourea based Schiff's base complexes the IR spectra showed bands at *ca.* 1460 and 1310 cm^{-1} due to ν(C—N) and at *ca.* 1030 cm^{-1} due to ν(C═S). The lowering of ν(C—N) suggested nitrogen coordination to antimony. The band at *ca.* 720 cm^{-1} may be assigned to ν(C═S) and some contributions from δ(NCS).

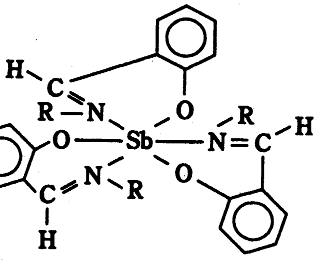
The lower region IR spectra of the complexes showed bands at *ca.* 425, 400, 320, 225 and 170 cm^{-1} which may be assigned to composite bands of ν(Sb—N), ν(Sb—O) and ν(Sb—Cl) or ν(Sb—I).[12-14]

The bands in the range 310–400 nm in the electronic spectra of these complexes have intensities comparable to those of the ligands indicating them to be ligands → metal charge transfer transitions. The red shift and the splitting of intralignad bands are good evidences for chelation[15].

On the basis of foregoing studies, the proposed structures for the complexes are:



X = Cl, I; Z = O, S



R = C_2H_5, C_6H_5, $CH_3C_6H_4$—, CH_3CO, C_6H_5CO

REFERENCES

1. S.R. Safia, S. Kushnev, L.M. Bravcone and Y. Subbaraw, *J. Org. Chem.*, **13**, 924 (1948).
2. D.H. Busch, *Uspekshi Khim.*, **28**, 822 (1969).
3. Y. Nakao, K. Sakurai and A.N. Akitsugu, *Bull. Chem. Soc., Japan*, **40**, 1536 (1967).
4. L.J. Nunej and Eichhorn, *J. Am. Chem. Soc.*, **84**, 901 (1962).
5. N.M. Samus and R.G. Abu Al-Magd, *Zh. Neorg. Khim.*, **24**, 482 (1979).
6. N.M. Samus, R.G. Abu Al-Magd and V.G. Bodyu, *Russ. J. Inorg. Chem.*, **25**, 1032 (1980).
7. D. Hadzi and N. Sheppard, *Trans. Faraday Soc.*, **50**, 911 (1954).
8. (a) K. Burger and I. Egyed, *J. Inorg. Nucl. Chem.*, **27**, 2361 (1965); (b) K. Burger, F. Ruff, I. Ruff and I. Egyed, *Acta Chim.*, **46**, 1 (1967).
9. K.K. Ramaswami, C.I. Jose and D.N. Sen, *Indian J. Chem.*, **5**, 156 (1967).
10. J.E. Stewart, *J. Chem. Phys.*, **30**, 1259 (1959).
11. L.L. Ingraham, J. Corse, G.G. Bailey and F. Stitt, *J. Am. Chem. Soc.*, **74**, 2297 (1952).
12. Y.M. Bosworth and R.J.M. Clark, *J. Chem. Soc. Dalton*, 1749 (1974).
13. R.E. Hester and R.A. Plane, *Inorg. Chem.*, **3**, 573 (1964).
14. R.J.H. Clark and Rippon, *J. Mol. Spectrosc.*, **52**, 58 (1974).
15. M.K. Rastogi, R.C. Sharma and A.C. Gupta, *Indian J. Chem.*, **21A**, 190 (1982).

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