Synthesis, spectral and antimicrobial studies of mixed-ligand complexes of antimony (III) with [3(2'-hydroxyphenyl)-5-(4-subsituted phenyl) pyrazolines] and 2-(N-salicylidine)-5-chlorobenzophenone

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ABSTRACT

Mixed-ligand complexes of antimony(III) of the types $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$ [where $C_{15}H_{12}N_2O.X$ = 3(2'-hydroxyphenyl)-5-(4-X-phenyl)pyrazoline {where X = H, $-CH_3$, $-OCH_3$ & –Cl} and $C_{20}H_{13}ClNO_2$ = 2-(N-salicylidine)-5-chlorobenzophenone] have been synthesized by the reaction of dichloroantimony(III) pyrazolines and chloroantimony(III) dipyrazolines with sodium salt of 2-(N-salicylidine)-5-chlorobenzophenone in 1:1 molar ratio in anhydrous benzene at elevated temperature. These newly synthesized derivatives have been characterized by elemental analysis (C, H, N, Cl, and Sb), molecular weight measurement, UV-Visible spectroscopy and spectral studies [near and far IR , multinuclear NMR (^1H & ^{13}C) and FAB mass]. The bonding mode of pyrazolines and coordination no. of antimony(III) in these derivatives are discussed. Antibacterial and antifungal potential of dichloroantimony(III) pyrazolines, chloroantimony(III) dipyrazolines and these newly synthesized derivatives are also discussed.

Keywords: Antimony(III), Pyrazolinates, Antimicrobial activity, Schiff base, specific optical rotation.

1. INTRODUCTION

Antimony (III) complexes are very interesting due to their fascinating structure /1], bonding variations /2/ and potential applicability as biocides and carcinostatics /3/. The antimony (III) complexes also exhibit potential antibacterial and antifungal activities /4/. The pyrazolines are an important class of heterocyclic

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compounds, which are used in industries as dyes, antioxidants, in lubricating oils /5/ and in agriculture as catalyst for decarboxylation reactions as well as inhibitors for plant growth /6-8/. In day-to-day life pyrazolines are extensively used in photography /9/. Reports are also available for a large number of other hydroxy phenyl substituted heterocycles, which are used as agrochemical fungicides /10/ and anticonvulsant agents /11/. Complexation behavior of 3(2'-hydroxyphenyl)-5-(4'-X-phenylpyrazoline and substituted pyrazolines with arsenic, antimony & bismuth have been investigated in our laboratories /12-14/. We have also investigated the complexation behavior and antimicrobial potential of 3(2'-hydroxyphenyl)-5-(4'-X-phenylpyrazoline and substituted pyrazolines with tin(IV), organotin(IV), diorganotin(IV) and triorganotin(IV) /15-19/.

In the continuation to our previous work, it was thought worthwhile to study the complexation behavior of arsenic(III), antimony(III) and bismuth(III) with 3(2'-hydroxyphenyl)-5-(4-substituted phenyl)pyrazoline and 2-(N-salicylidine)-5-chlorobenzophenone.

In the present paper we describe the synthesis, spectral and antimicrobial studies of mixed-ligand complexes of antimony(III) with 3(2'-hydroxyphenyl)-5-(4-X-phenyl)pyrazoline and 2-(N-salicylidine)-5-chlorobenzophenone.

2. MATERIALS AND METHODS

Solvents (benzene, acetone and alcohol) were rigorously dried and purified by standard methods before use /20/. All the chemicals used were of analytical grade quality. Antimony trichlriode (E.Merck) was used. Dichloroantimony(III) [3(2'-hydroxyphenyl)-5-(4-subsitutedphenyl) pyrazolines] and chloroantimony(III) di[3(2'-hydroxyphenyl)-5-(4-subsituted phenyl) pyrazolines] were prepared by the reported procedures /12/. 2-(N-salicylidine)-5-chlorobenzophenone was synthesized by the reported method /21/.

2.1 Synthesis of $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$

The new mixed-ligand complexes of antimony(III) of the general formula $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ were prepared by the reaction of dichloroantimony(III) pyrazolinates and the sodium salt of 2-(N-salicylidine)-5-chlorobenzophenone in 1:1 molar ratio.

$SbCl_2(C_{15}H_{12}N_2OX) + Na(C_{20}H_{13}ClNO_2) \rightarrow SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2) + NaCl$
[Where X = -H, $-CH_3$, $-OCH_3$ and –Cl]

Synthesis of $SbCl(C_{15}H_{13}N_2O)(C_{20}H_{13}ClNO_2)$

Freshly cut pieces of sodium (0.125 gm; 5.45 mmol) were taken in a flask with excess of isopropanol and refluxed for ~30 min., till a clear solution of sodium isopropoxide was obtained. The solution of 2-(N-salicylidine)-5-chlorobenzophenone (1.830 gm; 5.45 mmol) in anhydrous benzene was then added and the reaction mixture was further refluxed for ~1 hour, giving a yellow colour solution. The reaction mixture was cooled to room temperature and then benzene solution of dichloroantimony(III) pyrazolinates (3.437 gm; 5.45 mmol) was added to it with constant stirring. The reaction mixture was further stirred at room temperature for ~ 4 hours, till the color of the reaction mixture underwent a change. Reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate. The reddish brown coloured solid thus obtained was dissolved in a small amount of acetone. The solution was kept for three days at room temperature. The reddish brown coloured solid thus precipitated was filtered and dried in vacuum. 4.37 gm of $SbCl(C_{15}H_{13}N_2O)(C_{20}H_{13}ClNO_2)$ was obtained. Compounds no. 2, 3 & 4 were prepared by the same method. The analytical results are presented in **Table 1.**

2.2 Synthesis of $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$

The new mixed-ligand complexes of antimony(III) of the general formula $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$ were prepared by the reaction of chloroantimony(III) dipyrazolinates and the sodium salt of 2-(N-salicylidine)-5-chlorobenzophenone in 1:1 molar ratio.

$$SbCl(C_{15}H_{12}N_2OX)_2 + Na(C_{20}H_{13}ClNO_2) \rightarrow Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2) + NaCl$$

[Where X = -H, $-CH_3$, $-OCH_3$ and –Cl]

Synthesis of $Sb(C_{15}H_{13}N_2O)_2(C_{20}H_{13}ClNO_2)$

Freshly cut pieces of sodium (0.0569 gm; 2.4 mmol) were taken in a flask with excess of isopropanol and refluxed for ~30 min., till a clear solution of sodium isopropoxide was obtained. The solution of 2-(N-salicylidine)-5-chlorobenzophenone (0.5240 gm; 2.4 mmol) in anhydrous benzene was then added and the reaction mixture was further refluxed for ~1hour, giving a yellow coloured solution. The reaction mixture was cooled to room temperature and then benzene solution of chloroantimony(III) dipyrazolinates (1.568 gm; 2.4 mmol) was added to it with constant stirring. The reaction mixture was further stirred at room temperature for ~ 5 hours, till the colour of the reaction mixture underwent a change. Reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate. The reddish brown coloured solid thus obtained was dissolved in small amount of acetone. The solution was kept for three days at room temperature. The reddish brown coloured solid thus precipitated was filtered and dried in vacuum. 4.70 gram of $Sb(C_{15}H_{13}N_2O)_2(C_{20}H_{13}ClNO_2)$ was obtained . Compound no. 6,7 & 8 were prepared by the same method . The analytical results are presented in **Table 1.**

2.3 Physical measurements

Chlorine was estimated by Volhard's method /22/ and antimony was estimated iodometrically /22/. Infrared spectra were recorded on Varian 3100 FT-IR spectrophotometer in the range 4000-200 cm^{-1}. The ^1H NMR spectra and proton-decoupled ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on JEOL AL 300 FT NMR spectrometer, operated at 300.1 and 74.45 MHz, using TMS (tetramethylsilane) as internal standard. The elemental analysis (C, H & N) was obtained by using a Coleman CHN analyzer. The specific

Table 1

Synthetic analytical and data for $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$

Comp. No.	Compound	Yield (%)	M. P. (^0C)	Analysis Found (Calcd.) (in %)					Mol. Wt. Found (Calcd.)
				C	H	N	Sb	Cl	
1	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	89	140	57.74 (57.63)	3.58 (3.56)	5.78 (5.76)	16.92 (16.70)	9.72 (9.74)	720 (729.26)
2	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	82	154	58.04 (58.08)	3.74 (3.76)	5.63 (5.64)	16.24 (16.30)	9.50 (9.54)	741 (743.29)
3	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	86	160	56.80 (56.86)	3.67 (3.68)	5.50 (5.52)	16.20 (16.00)	9.35 (9.34)	754 (759.29)
4	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	90	152	55.60 (55.02)	3.26 (3.27)	5.48 (5.50)	15.80 (15.90)	13.90 (13.95)	761 (763.71)
5	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	75	159	64.40 (64.49)	4.80 (4.83)	7.50 (7.52)	13.04 (13.08)	3.80 (3.81)	928 (931.09)
6	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	80	164	65.04 (65.11)	4.46 (4.48)	7.28 (7.30)	12.69 (12.70)	3.68 (3.70)	957 (959.14)
7	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	75	167	62.84 (62.88)	4.30 (4.33)	7.03 (7.05)	12.26 (12.27)	3.54 (3.57)	992 (991.14)
8	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	79	157	60.03 (60.04)	3.69 (3.70)	7.01 (7.00)	12.14 (12.18)	10.63 (10.65)	995 (999.98)

Where X = H in 1 & 5; CH_3 in 2 & 6; OCH_3 in 3 & 7 and Cl in 4 & 8.

optical rotations were recorded at 25 ^{0}C in benzene on Perkin-Elmer polarimeter (model 341) using the sodium D line (λ = 589 nm). The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer. Electronic spectra were recorded in benzene solution on Hitachi U-2000 UV-Visible spectrophotometer.

2.4 Antimicrobial studies

Agar disc diffusion technique was used for screening in vitro antimicrobial activity /23/. Inoculums of bacteria were prepared in nutrient broth and fungi in potato dextrose agar slant. The cultures were inoculated and incubated for 48 hrs. in case of bacteria and 5 days for fungi. Molten Muller Hinton medium was poured in a sterile Petri dish (9 cm in diameter) to get a depth of 5 mm. The medium was left to solidify and then seeded with respective test organisms. For the purpose of seeding, 5 ml sterile water was added to agar slant culture of fungi. The culture was scraped to get a suspension of fungi spore. A sterile cotton swab was dipped in the culture/suspension and lightly rubbed over the solidified medium. The plate was left for a few minutes and then used for the test. 30 μm of each sample to be tested was dissolved in 1ml acetone. 5 mm discs of Whatman filter paper no. 40 were cut and sterilized. The filter paper discs were immersed in the solution of sample; after soaking, the disc was removed and left in a sterile Petri dish to permit the solvent to evaporate. After about 10 minutes the paper discs were transferred to seeded agar plate. Discs were kept on the seeded agar plates. Finally the dishes were incubated at 37 ^{0}C for 24 hrs (for bacteria) and at 30 ^{0}C for 72 hrs (for fungi), where clear or inhibition zones were detected around each disc.

A disc soaked in acetone alone was used as a control under the same conditions and there was no inhibition zone. Each distinct inhibition zone was measured as diameter in mm, both antibacterial and antifungal activity was calculated as a mean of three replicates.

3. RESULTS AND DISCUSSION

All the compounds are reddish brown colored solids, non-hygroscopic and stable at room temperature. These are soluble in common organic (benzene, chloroform, carbon tetrachloride and carbon disulfide) and coordinating (tetrahydrofuran, dimethylformamide and dimethylsulphoxide) solvents. The molecular weight measurements in dilute chloroform solution at 45 ^{0}C show monomeric nature of these compounds. The elemental analysis (C, H, N, Cl and Sb) data are in accordance with the stoichiometry proposed for the respective compounds.

We have already discussed the structural characteristics of dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates in our previous publication /12/. Therefore we will focus on the structural changes observed after coordination of 2-(N-salicylidine)-5-chlorobenzophenone to the antimony(III).

3.1 Specific optical rotation data

The specific optical rotation values of benzene solution of free pyrazolines and mixed-ligand complexes of antimony(III) are not measurable at the concentration of 1.00%, 0.50%, 0.10% and 0.05%. All the four pyrazolines show zero specific optical rotation at 0.02% concentration. Thus free pyrazolines are a racemic mixture. The specific optical rotation values for mixed-ligand complexes of antimony(III) in benzene solution at 0.02% concentration are also zero indicating that these are also existing as racemic mixture.

3.2 Infrared spectra

The infrared spectrum of the 2-(N-salicylidine)-5-chlorobenzophenone show three characteristic bands in the region 3380-3260, 1680 and 1607 cm^{-1} which are assigned to υ(O-H), υ(C=O) and υ(C=N) stretching vibrations respectively /21/. The infrared spectra of dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates have already been discussed in our previous publication /12/. The infrared spectral data of mixed-ligand complexes of antimony(III) are summarized in **Table 2**.

Table 2

IR spectral data (cm^{-1}) $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$
and $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$

Comp.No	v(N-H)	v(C=O)	v(C=N)	v(C-O)	v(Sb-O)	v(Sb-N)	v(Sb-Cl)
1	3330	1680	1622 1585	-	462 460	447 445	350
2	3322	1680	1628 1590	-	474 472	436 435	340
3	3325	1679	1620 1587	1014	486 481	448 446	338
4	3318	1680	1625 1589	-	470 466	441 439	345
5	3318	1685	1622 1586	-	466 462	442 440	-
6	3330	1694	1624 1588	-	475 468	438 436	-
7	3320	1686	1626 1585	1010	469 465	435 434	-
8	3322	1685	1621 1590	-	465 460	440 438	-

Where X = H in 1 & 5; CH_3 in 2 & 6; OCH_3 in 3 & 7 and Cl in 4 & 8.

The phenolic –OH group is found to be absent in spectra of the complexes, suggesting deprotonation of phenolic –OH and its subsequent involvement in co-ordination. The appearance of new bands (in comparison to free pyrazolines and Schiff base) in the regions 486-460 and 448-434 cm^{-1} have been assigned to υ(Sb-O) and υ(Sb-N) stretching vibrations respectively /12/. The signals due to υ(C=O) and υ(CH=N) stretching vibrations are observed in the regions 1694-1679 and 1605-1598 cm^{-1} respectively and suggesting the non-involvement of these groups in the coordination.

The bands present in the region 1628-1620 and 1590-1585 cm^{-1} may be assigned to υ(C=N) stretching vibrations of pyrazoline and Schiff base moieties. The signals of υ(C=N) stretching are shifted to lower wave number in comparison to the spectra of free ligands (at ~1654 cm^{-1} in free pyrazolines and at 1607 cm^{-1} in free Schiff base), suggesting the involvement of (C=N) group in coordination through nitrogen atom.

3.3 Multinuclear NMR spectroscopy

The ^1H NMR chemical shifts of these compounds are listed in **Table 3**. All the characteristic chemical shifts of pyrazoline moiety are present at their respective positions in the NMR spectra of mixed-ligand complexes of antimony(III) (**Table 3**).

The peak due to hydroxyl proton (originally present at $\delta \sim 11.00$ ppm in free pyrazoline and at $\delta \sim 11.30$ ppm in free 2-(N-salicylidine)-5-chlorobenzophenone) is absent from the spectra of complexes, suggesting the bonding through hydroxyl oxygen atom. The appearance of a peak at δ 5.5-5.1 ppm, as broad singlet, could be assigned to N-H group (originally present at δ 5.3-5.0 ppm in free pyrazolines) suggesting the non-involvement of N-H group in bond formation /12/. The chemical shifts of -CH and -CH_2 protons of heterocyclic five-membered ring are mentioned in **Table 3**. Since these groups do not contribute in coordination, it is not significant to describe their stereochemistry here.

The resonance due to CH=N group is observed in the region at δ 10.5-10.1 ppm (originally present at δ 9.3 ppm in free 2-(N-salicylidine)-5-chlorobenzophenone), suggesting the involvement of CH=N group in bond formation.

Aromatic protons of pyrazoline and 2-(N-salicylidine)-5-chlorobenzophenone moiety are present as a multiplet in the region, δ 7.9-6.5 ppm. Due to the presence of a large no. of peaks in the same region, it is difficult to assign individual aromatic protons.

The proton-decoupled ^{13}C NMR spectra (**Table 3**) of $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$ show the presence of all important signals with reference to pyrazolines and 2-(N-salicylidine)-5-chlorobenzophenone moieties.

The signal observed in the region δ 196.5-196.0 and δ 176.5-172.0 ppm could be assigned to carbon of C=O and CH=N groups respectively /24/. The signal of CH=N group is shifted downfield in comparison to the spectra of free 2-(N-salicylidine)-5-chlorobenzophenone (at ~ δ 161.5 ppm), suggesting the involvement of CH=N group in coordination.

The signal observed in the region δ 149.9-122.8 ppm as a multiplet could be assigned to aromatic carbon atoms. Due to the presence of a large no. of peaks in the same region, it is difficult to assign individual aromatic carbon atoms.

Table 3

^{1}H NMR and ^{13}C NMR Chemical shift (in δ ppm) for $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$

S. No.	Compound	^{1}H NMR Chemical shift (in δ ppm)	^{13}C NMR Chemical shift (in δ ppm)
1	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	10.5 (1H, s, CH=N) 7.9-6.9 (21H, m, Ar-H) 5.3 (1H, s, NH) 3.9 (1H, dd, CH) 2.8 (1H, dd, CH_2) 2.6 (1H, dd, CH_2)	196.3 (C=O) 176.5 (CH=N) 159.2 (C=N) 149.1-123.1 (Ar-C) 46.3 (CH) 28.4 (CH_2)
2	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	10.2 (1H, s, CH=N) 7.7-6.5 (20H, m, Ar-H) 5.1 (1H, s, NH) 4.1 (1H, dd, CH) 3.1 (1H, dd, CH_2) 2.9 (1H, dd, CH_2) 1.9 (3H, s, CH_3)	196.1 (C=O) 175.7 (CH=N) 158.5 (C=N) 148.8-123.3 (Ar-C) 47.1 (CH) 28.9 (CH_2) 13.5 (CH_3)
3	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	10.5 (1H, s, CH=N) 7.8-6.7 (20H, m, Ar-H) 5.1 (1H, s, NH) 3.8 (1H, dd, CH) 2.9 (1H, dd, CH_2) 2.7 (1H, dd, CH_2) 4.2 (3H, s, OCH_3)	196.5 (C=O) 176.3 (CH=N) 158.8 (C=N) 149.9-123.5 (Ar-C) 46.6 (CH) 28.7 (CH_2) 51.8 (OCH_3)
4	$SbCl(C_{15}H_{12}N_2OX)$ $(C_{20}H_{13}ClNO_2)$	10.1 (1H, s, CH=N) 7.8-6.3 (20H, m, Ar-H) 5.2 (1H, s, NH) 3.9 (1H, dd, CH) 2.8 (1H, dd, CH_2) 2.6 (1H, dd, CH_2)	196.1 (C=O) 176.1 (CH=N) 159.5 (C=N) 148.5-122.8 (Ar-C) 45.8 (CH) 28.2 (CH_2)
5	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	10.4 (1H, s, CH=N) 7.9-7.0 (30H, m, Ar-H) 5.4 (2H, s, NH) 3.8 (2H, dd, CH) 2.9 (2H, dd, CH_2) 2.7 (2H, dd, CH_2)	196.5 (C=O) 173.3 (CH=N) 158.5 (C=N) 148.9-123.6 (Ar-C) 46.5 (CH) 28.1 (CH_2)
6	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	10.2 (1H, s, CH=N) 7.7-6.9 (28H, m, Ar-H) 5.1 (2H, s, NH) 4.2 (2H, dd, CH) 3.1 (2H, dd, CH_2) 2.9 (2H, dd, CH_2) 1.9 (6H, s, CH_3)	196.0 (C=O) 172.0(CH=N) 159.1 (C=N) 149.1-123.3 (Ar-C) 47.5 (CH) 28.7 (CH_2) 13.8 (CH_3)
7	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	10.5 (1H, s, CH=N) 7.8-6.7 (28H, m, Ar-H) 5.5 (2H, s, NH) 4.0 (2H, dd, CH) 3.1 (2H, dd, CH_2) 2.9 (2H, dd, CH_2) 3.8 (6H,s,OCH_3)	196.3 (C=O) 173.5 (CH=N) 158.9 (C=N) 149.7-123.0 (Ar-C) 46.2 (CH) 28.1 (CH_2) 51.5 (OCH_3)
8	$Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$	10.1 (1H, s, CH=N) 7.8-6.3 (28H, m, Ar-H) 5.4 (2H, s, NH) 3.9 (2H, dd, CH) 2.9 (2H, dd, CH_2) 2.7 (2H, dd, CH_2)	196.2 (C=O) 173.3 (CH=N) 159.3 (C=N) 148.5-123.5 (Ar-C) 45.5 (CH) 28.5 (CH_2)

Where X = H in 1 & 5; CH_3 in 2 & 6; OCH_3 in 3 & 7 and Cl in 4 & 8

3.4 UV-Visible Spectra-

The electronic spectral data of the compound $[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$ and$[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$ in benzene solution are summarized in **Table 4**. These antimony(III) complexes show absorption bands in the regions 350-362 nm, 308-315 nm and 245-259 nm. The absorption band in the region 350-362 nm may be assigned to intraligand $n \rightarrow \pi^*$ transition of the C=N group of Schiff base /25/. The absorption band in the region 308-315 nm is attributed to ligand→d-orbital transition /26/.The bands in the region 248-258 nm may be assigned to intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition of the pyrazoline ring /27-28/.

Table 4

Electronic Spectral data for $[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$ and $[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$

S.No.	Compound	Electronic Spectral Studies	
		Assigment Charge transfer	Band (nm)
1.	$[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	360
		$L \rightarrow M$	315
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	254
2.	$[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	354
		$L \rightarrow M$	310
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	249
3.	$[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	356
		$L \rightarrow M$	311
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	250
4.	$[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	350
		$L \rightarrow M$	308
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	248
5.	$[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	352
		$L \rightarrow M$	310
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	249
6.	$[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	358
		$L \rightarrow M$	309
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	256
7.	$[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	359
		$L \rightarrow M$	312
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	251
8.	$[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$	$n \rightarrow \pi^*$	362
		$L \rightarrow M$	315
		$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	258

Where X = -H, $-CH_3$, $-OCH_3$ and –Cl; L = ligand , M = Metal

3.5 FAB mass spectra-

The FAB mass spectra have been recorded for $[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$ where X = H and $[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$ where X = OCH_3, i.e. compounds no. 1 & 7

The FAB mass spectrum of $[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$ where X = H shows
m/z (relative intensity)- 728(8.3%), 624(40.0%), 637(11.4%), 533(8.3%), 477(8.5%), 388(11.1%), 394(13.8%), 343(36.1%), 295(17.1%), 250(45.7%), 238(57.1%), 228(82.8%), 214(34.2%), 146(97.1%), 279(100%), 122(28.3%), 95(28.4%), 94(14.2%), 93(11.4%), 92(71.4%).

The FAB mass spectrum of $[SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)]$ where X =OCH_3 shows
m/z (relative intensity)- 758(7.6%), 654(40.1%), 667(10.2%), 553(8.8%), 507(9.4%), 424(16.0%), 388(11.1%), 329(55.5%), 295(17.1%), 268(57.1%), 250(45.7%), 228(82.8%), 214(34.1%), 146(100%), 122(29.9%), 95(10.9%), 94(14.2%), 93(19.3%), 92(62.2%).

The FAB mass spectrum of $[Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)]$ where X = OCH_3 shows
m/z (relative intensity)- 929(8.2%), 693(45.2%), 602(10.2%), 595(8.6%), 580(9.4%), 588(16.0%), 532(15.8%), 504(10.2%), 503(8.6%), 497(8.2%), 441(9.4%), 413(9.4%), 388(16.6%), 358(50.1%), 295(13.8%), 267(57.0%), 250(44.6%), 228(80.6%), 214(34.1%), 146(98.0%), 122(32.4%), 95(10.6%), 94(14.2%), 93(54.4%), 92(78.9%).

3.6 Microbial Assay

The antibacterial activities of dichloroantimony(III) pyrazolinates, chloroantimony(III) dipyrazolinates and two mixed-ligand complexes of antimony(III) were tested against the bacterial species *Staphylococcus aureus, Bacillus lichaniformis, Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa, and Vibrio spp.* and the antifungal activities were tested against *Aspergillus niger* and *Penicillium notatum.* The antimicrobial activity of some antibiotics were also tested and compared with dichloroantimony(III) pyrazolinates, chloroantimony(III) dipyrazolinates and two mixed-ligand complexes of antimony(III). The results are listed in **Table 5**.

Comparison of the antimicrobial activities of dichloroantimony(III) pyrazolinates, chloroantimony(III) dipyrazolinates and two mixed-ligand complexes of antimony(III) with some known antibiotics exhibit the following results :

1) The complexes $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$ exhibit greater antibacterial effect towards *Staphylococcus aureus* compared to dichloroantimony(III) pyrazolinates, chloroantimony(III) dipyrazolinates and chloramphenicol.
2) The complexes $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2$ $(C_{20}H_{13}ClNO_2)$ exhibit comparable effect towards *Klebsiella pneumoniae* and *Vibrio spp.* compared to dichloroantimony(III) pyrazolinates, chloroantimony(III) dipyrazolinates and chloramphenicol.

Table 5
Antimicrobial activity of the dichloroantimony(III) pyrazolinate, chloroantimony(III) dipyrazolinate, $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$

S. No.	Fungi		Gram (+ve) bacteria		Gram (–ve) bacteria			
	A. Niger	*P. notatum*	*S. aureus*	*B. lichaniformis*	*K. pneumoniae*	*Vibrio spp.*	*E. coli*	*P. aeruginosa*
1	+++	+++	+++	+++	+++	+++	++	+++
2	++	+++	+++	++	++	++	+	++
3	+++	++	+++	+++	+++	+++	++	+
4	++	+++	+++	++	+++	++	+	++
5	+++	+++	+++	+++	+++	+++	++	++

Inhibition values beyond control are + = 6–10 mm, ++ = 11–15 mm, +++ = 16–20 mm, ++++ = 21–25 mm (the values are including disc diameter).
The standards are in the form of sterile Hi-Disc cartridges, each disc containing 30 μm of the drug.
1 = Terbinafin (antifungal agent) and Kanamycinl (antibacterial agent)
2 = Dimethyl sulphoxide
3 = Chloroantimny (III) di[3(2'-hydroxyphenyl)-5-phenyl pyrazolinate],
4 = Compound no. 1 and 5 = compound no. 5

3) The complexes $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2 (C_{20}H_{13}ClNO_2)$ exhibit comparable antibacterial effect towards *Bacillus lichaniformis* compared to dichloroantimony(III) pyrazolinates, chloroantimony(III) dipyrazolinates and chloramphenicol .
4) The complexes $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2 (C_{20}H_{13}ClNO_2)$ exhibit comparable antifungal effect against *Aspergillus niger* and *Penicillium notatum* compared to dichloroantimony(III) pyrazolinates, chloroantimony(III) dipyrazolinates and terbinafin.

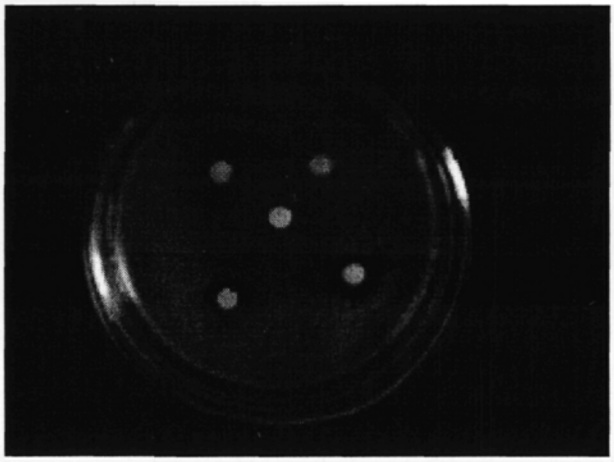

Fig. 1: Antibacterial activity against *Bacillus subtilis* , 1 = Kanamycin, 2 = [chloroantimony (III)dipyrazoline], 3 = Compound 1, and 4 = Compound 5.

It is difficult to make an exact structure and activity relationship between antimicrobial activity and the structure of these complexes. It can possibly be concluded that the complexation of substituted antimony(III) moiety with biologically active pyrazoline ligand results in increased activity of these complexes.

From the antimicrobial data presented in the **Table 5,** it appears that when chloride, in dichloroantimony(III) pyrazolinates is replaced by 2-(N-salicylidine)-5-chlorobenzophenone moiety, there is no significant change in antimicrobial activity. This further confirms that antimicrobial activity of these complexes arises from pyrazoline moiety but not from chloride or 2-(N-salicylidine)-5-chlorobenzophenone moiety. Further, 2-(N-salicylidine)-5-chlorobenzophenone moiety does not affect the antimicrobial potential of the pyrazoline ring.

Correlation between geometry around central atom in a complex and antimicrobial activity of the same complex is a further area of research.

4. CONCLUSIONS

The present study describes a series of mixed-ligand complexes of antimony(III) of the type $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$ and $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$.

Bulky size of pyrazoline and 2-(N-salicylidine)-5-chlorobenzophenone moieties causes steric repulsion between them and opposes the chelating linkage. Thus it is difficult to conclude about the exact bonding mode of ligands in these complexes. In addition to this, lone pair of electron in the valence shell of antimony(III) atom also affects the overall geometry around antimony(III) atom. On the basis of above discussion and available literature, the most plausible geometry around antimony(III) atom in these complexes is presented in **Figure 1** and **2**.

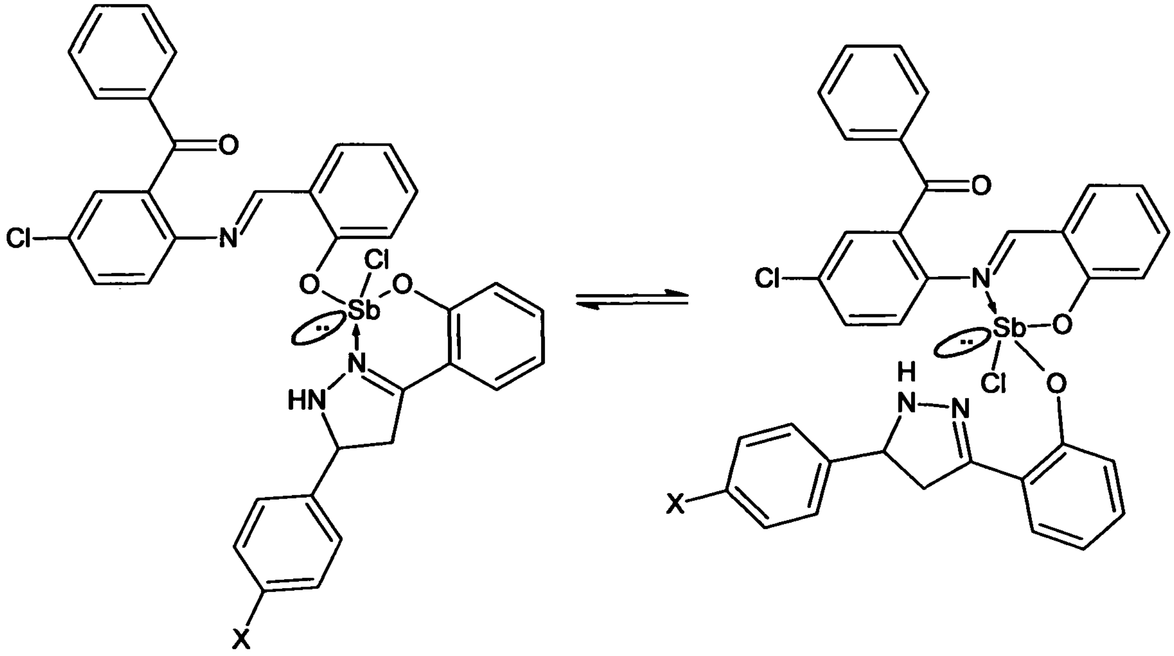

Fig. 2: Molecular structure of $SbCl(C_{15}H_{12}N_2OX)(C_{20}H_{13}ClNO_2)$
[where X = H, $-CH_3$, $-OCH_3$ & $-Cl$]

The most plausible geometry around the antimony(III) atom is distorted trigonal bipyramidal (**Figures 2 & 3**) /12, 29-32/. The central antimony(III) atom appears to acquire the coordination number four.

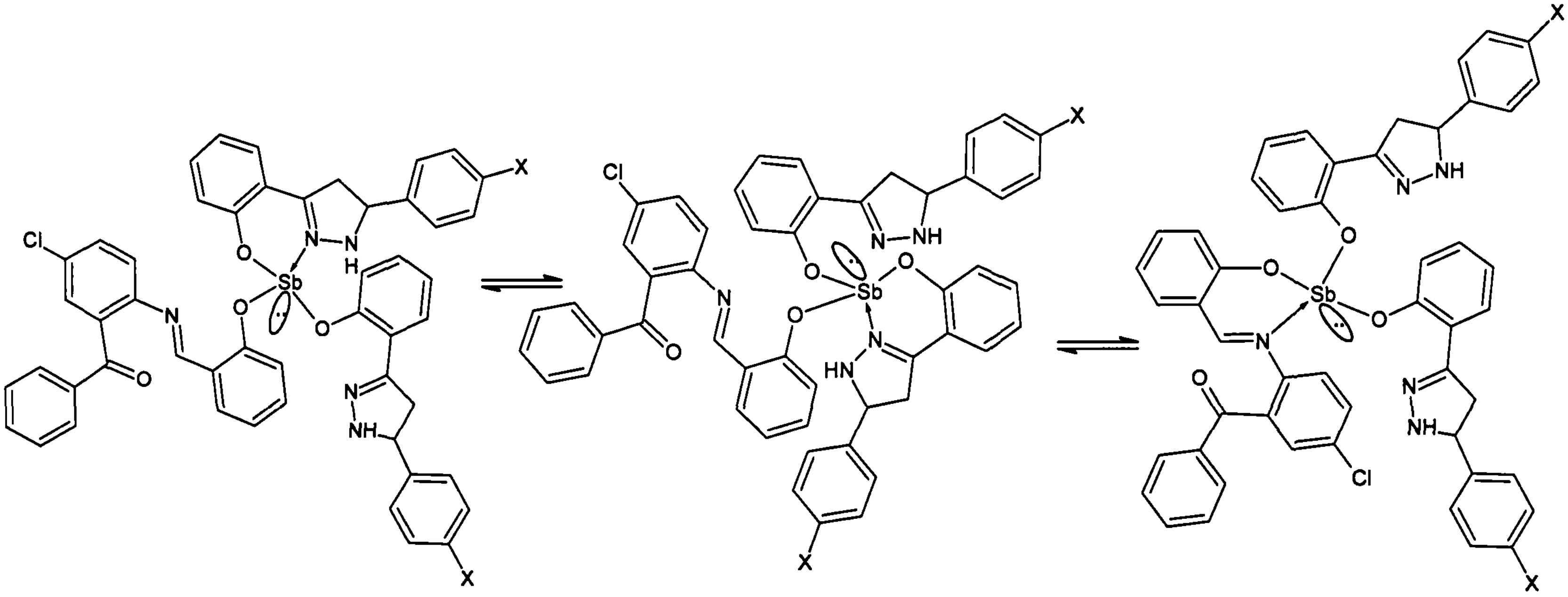

Fig. 3 : Molecular structure of $Sb(C_{15}H_{12}N_2OX)_2(C_{20}H_{13}ClNO_2)$
[where X = H, $-CH_3$, $-OCH_3$ & $-Cl$]

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