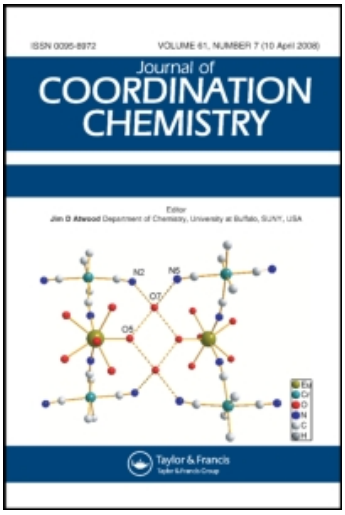

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Synthesis, spectral and antimicrobial studies of chloroantimony(III)di[3(2'-hydroxyphenyl)-5-(4-substitutedphenyl)pyrazolinates]

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Synthesis, spectral and antimicrobial studies of chloroantimony(III)di[3(2′-hydroxyphenyl)-5-(4-substitutedphenyl)pyrazolinates]

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Dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates of the type $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$ [where $C_{15}H_{12}N_2OX = 3(2'$-hydroxyphenyl)-5-(4-X-phenyl)pyrazoline, X=H in **1** and **5**; $-CH_3$ in **2** and **6**; $-OCH_3$ in **3** and **7** and –Cl in **4** and **8**] have been synthesized by reaction of $SbCl_3$ and sodium salt of pyrazolines in 1 : 1 and 1 : 2 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 and spectral studies [IR and ^1H and ^{13}C NMR]. The free pyrazoline and some dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates have been screened for antibacterial and antifungal activities, with some dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates exhibiting higher antibacterial and antifungal effects than free pyrazoline and some antibiotics.

Keywords: Antimony(III); Pyrazolinates; Antimicrobial activity

1. Introduction

Pyrazolines are an important class of heterocyclic compounds used in industries as dyes, lubricating oils, antioxidants and in agriculture as catalysts for decarboxylation, as well as inhibitors for plant growth [1–3]. Complexation behavior of 3(2′-hydroxy phenyl)-5-phenylpyrazoline with Ni(II), Co(II) and Cu(II) have been investigated in our laboratories [4]. We have also investigated the complexation behavior and antimicrobial potential of 3(2′-hydroxyphenyl)-5-phenylpyrazoline and substituted pyrazolines with tin(IV), organotin(IV), diorganotin(IV) and triorganotin(IV) [5–9]. Perusal of the literature shows no pyrazolinate derivatives of arsenic(III), antimony(III) or bismuth(III).

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Some diphenylantimony(III) derivatives have been reported to exhibit both *in vitro* and *in vivo* antitumor activity [10–12]. Structure characterization along with antitumor activity of substituted triorganoantimony(V) disalicylates, $\{5\text{-Y-2(OH)–}C_6H_3COO\}_2SbR_3$ (where Y=H, Me and OMe), have been studied by Silvestru *et al*. [13]. Antimony(III) complexes also exhibit potential antibacterial and antifungal activities [14].

In continuation of our previous work, where we studied the synthesis, spectra and antimicrobial activity of bismuth(III) 3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates [15], in the present article we describe synthesis, spectral and antimicrobial studies of dichloroantimony(III) 3(2′-hydroxyphenyl)-5-(4-substituted-phenyl)pyrazolinates and chloroantimony(III)di[3(2′-hydroxyphenyl)-5-(4-substitutedphenyl)pyrazolinates].

2. Experimental

Solvents (benzene, acetone and alcohol) were rigorously dried and purified by standard methods before use [16]. Chemicals used were of analytical grade. Antimony trichloride (E. Merck), O-hydroxy acetophenone (CDH) and benzaldehydes (E. Merck) were used as received. Ligands were prepared by the reported procedure [17].

2.1. *Synthesis of $SbCl_2(C_{15}H_{12}N_2OX)$*

Dichloroantimony(III) pyrazolinates of general formula $SbCl_2(C_{15}H_{12}N_2OX)$ were prepared by reaction of antimony trichloride and the sodium salt of pyrazolinate in 1 : 1 molar ratio:

$$SbCl_3 + Na(C_15H_{12}N_2OX) \xrightarrow[\text{benzene}]{\text{Anhydrous}} SbCl_2(C_{15}H_{12}N_2OX) + NaCl$$

$$[X = H,\ CH_3,\ OCH_3 \text{ and } Cl]$$

2.1.1. Synthesis of $SbCl_2(C_{15}H_{13}N_2O)$. Freshly cut pieces of sodium (0.112 g; 4.9 mmol) were taken in a flask with excess isopropanol and refluxed ~1/2 h until a clear solution of sodium isopropoxide was obtained. The solution of 3(2′-hydroxyphenyl)-5-phenyl pyrazoline (1.17 g; 4.9 mmol) in anhydrous benzene was then added and the reaction mixture was further refluxed for ~1 h, giving a yellow solution. The reaction mixture was cooled to room temperature and then a benzene solution of anhydrous $SbCl_3$ (1.12 g; 4.9 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for ~2 h, when the color of the reaction mixture changed. Reaction mixture was filtered to remove precipitated NaCl and the solvent was removed under reduced pressure from the filtrate. The light yellow solid thus obtained was dissolved in a small amount of chloroform and acetone (10.0 mL). The solution was kept for three days at room temperature. The light yellow solid thus precipitated was filtered and dried in vacuum; 1.60 g of $SbCl_2(C_{15}H_{13}N_2O)$ was obtained.

Table 1. Synthetic analytical data for $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$.

Comp. No.	Compound	Yield (%)	M.P. (°C)	Analysis Found (Calcd) (in%) C	H	N	Sb	Cl	Mol. Wt. Found (Calcd)
1	$SbCl_2(C_{15}H_{12}N_2OH)$	76	130	41.18 (42.05)	3.02 (3.02)	6.51 (6.54)	28.33 (28.44)	16.20 (16.35)	428 (429.50)
2	$SbCl_2(C_{15}H_{12}N_2OCH_3)$	85	165	43.36 (43.36)	3.38 (3.95)	6.32 (6.36)	27.49 (27.67)	15.81 (15.90)	440 (442.75)
3	$SbCl_2(C_{15}H_{12}N_2OCH_3)$	88	156	41.85 (42.10)	3.26 (3.28)	6.10 (6.14)	26.53 (26.69)	15.25 (15.35)	456 (458.75)
4	$SbCl_2(C_{15}H_{12}N_2OCl)$	82	175	38.89 (39.13)	2.59 (2.60)	6.05 (6.08)	26.31 (26.43)	22.69 (22.82)	460 (462.75)
5	$SbCl(C_{15}H_{12}N_2OH)_2$	79	167	57.07 (57.73)	4.12 (4.14)	8.87 (8.91)	19.30 (19.38)	5.54 (5.57)	628 (630.75)
6	$SbCl(C_{15}H_{12}N_2OCH_3)_2$	80	189	58.29 (58.71)	4.55 (4.58)	8.50 (8.56)	18.48 (18.61)	5.31 (5.35)	688 (690.75)
7	$SbCl(C_{15}H_{12}N_2OCH_3)_2$	89	167	55.59 (55.81)	4.34 (4.36)	8.10 (7.84)	17.62 (17.69)	5.06 (5.0)	656 (658.75)
8	$SbCl(C_{15}H_{12}N_2OCl)_2$	93	190	51.55 (51.72)	3.43 (3.44)	8.01 (7.75)	17.42 (17.479)	15.02 (15.08)	696 (698.75)

Compounds **2**, **3** and **4** were prepared by the same method. The analytical results are presented in table 1.

2.2. *Synthesis of $SbCl(C_{15}H_{12}N_2OX)_2$*

The chloroantimony(III) dipyrazolinates of general formula $SbCl(C_{15}H_{12}N_2OX)_2$ were prepared by reaction of antimony trichloride and sodium salt of pyrazolinate in 1 : 2 molar ratio:

$$SbCl_3 + 2Na(C_15H_{12}N_2OX) \xrightarrow[\text{benzene}]{\text{Anhydrous}} SbCl(C_15H_{12}N_2OX)_2 + 2NaCl$$

[X = H, CH_3, OCH_3 and Cl]

2.2.1. Synthesis of $SbCl_2(C_{15}H_{13}N_2O)$. A clear solution of sodium isopropoxide was obtained as above. Solution of 3(2′-hydroxyphenyl)-5-phenyl pyrazoline (1.17 g; 4.9 mmol) in anhydrous benzene was then added and the reaction mixture was further refluxed for ~1 h, giving a yellow solution. The reaction mixture was cooled to room temperature and a benzene solution of anhydrous $SbCl_3$ (0.56 g; 2.45 mmol) was added with constant stirring. The reaction mixture was stirred at room temperature for ~3 h, when the color of the reaction mixture changed. Reaction was filtered to remove precipitated NaCl and the solvent removed under reduced pressure from the filtrate. The light yellow solid thus obtained was dissolved in a small amount of chloroform and acetone (10.0 mL) and kept for three days at room temperature. The light yellow solid thus precipitated was filtered and dried in vacuum giving 1.20 g of $SbCl(C_{15}H_{13}N_2O)_2$.

Compounds **6**, **7** and **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 and antimony was estimated iodometrically [18]. Infrared spectra were recorded as nujol mulls using CsI discs on a Perkin–Elmer Model 557 FT-IR spectrophotometer in the range 4000–200 cm^{-1}. ^{1}H NMR spectra and proton decoupled ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker DRX-300 spectrometer, operated at 300.1 and 75.45 MHz for ^{1}H and ^{13}C, using TMS (tetramethylsilane) as internal standard. Molecular weights were determined on a Knoauer Vapour Pressure osmometer in $CHCl_3$ at 45°C. The elemental analyses (C, H and N) were obtained by using a Coleman CHN analyzer.

2.4. *Antimicrobial studies*

Agar disk diffusion technique was used for screening *in vitro* antimicrobial activity [19]. Inoculums of bacteria were prepared in nutrient broth and fungi in potato dextrose agar slant. The cultures were inoculated and incubated for 48 h for bacteria and 5 days for fungi. The molten Muller Hinton medium was poured in a sterile Petri dish (9 cm in diameter) to a depth of 5 mm. The medium was left to solidify and then it was seeded with 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 suspension of fungi spore. A sterile cotton swab was dipped in the culture/suspension, 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 were dissolved in 1 mL of acetone. 5 mm discs of Whatman filter article no. 40 were cut and sterilized. The filter article 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 min, the article discs were transferred to seeded agar plates and the dishes incubated at 37°C for 24 h (for bacteria) and at 30°C for 72 h (for fungi), where inhibition zones were detected around each disc.

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

3. Results and discussion

All compounds are light yellow solids, non-hygroscopic, stable at room temperature and soluble in common organic (chloroform and acetone) and coordinating (tetrahydrofuran, dimethylformamide and dimethylsulphoxide) solvents. The molecular weight measurement in dilute chloroform at 45°C shows monomers. The elemental analyses (C, H, N, Cl and Sb) agree with stoichiometry proposed for the compounds.

3.1. *Infrared spectra*

Infrared spectral data of these compounds are summarized in table 2. All compounds exhibit bands of medium intensity in the region 3332–3320 cm^{-1} due to ν(N–H) and

Table 2. IR spectral data (cm^{-1}) for $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$.

S. No.	ν(N–H)	ν(C=N)	ν(C–O)	ν(Sb–O)	ν(Sb–N)	ν(Sb–Cl)
1	3330	1620	–	460	447	350
2	3321	1630	–	475	435	340
3	3327	1620	1014	484	450	335
4	3318	1606	–	466	440	345
5	3332	1620	–	466	440	338
6	3322	1624	–	468	438	340
7	3320	1621	1008	470	435	335
8	3321	1623	–	464	437	337

bands in the region 1630–1606 cm^{-1} due to ν(C=N) [5–9, 15, 20]. The band in the region 1014–1008 cm^{-1} in **3** and **7** may be assigned to ν(C–O) from OCH_3 [5–9, 15, 20]. The signal due to ν(O–H) (originally present at ~3085 cm^{-1} in free pyrazolines) disappears from the spectra of complexes. All compounds exhibit bands of medium intensity in the region 350–335 cm^{-1} due to ν(Sb–Cl) stretching vibrations [21–27].

The appearance of two new bands (in comparison to free pyrazolines) in the region 484–460 cm^{-1} and 450–435 cm^{-1} are assigned to ν(Sb–O) and ν(Sb–N) stretching vibrations, respectively [21–27]. The appearance of these two new bands and absence of hydroxyl band suggests that the pyrazoline is monobasic bidentate in these compounds.

3.2. *Multinuclear NMR spectroscopy*

In ^1H NMR spectra (Supplementary Material), the aromatic protons of $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$ were observed as multiplets in the region δ 7.8–6.3 ppm [5–9, 15, 20]. The peak due to hydroxyl proton (originally present at δ ~ 11.00 ppm in free pyrazolines) is absent from the spectra of the complexes, suggesting bonding through hydroxyl oxygen [5–9, 15, 20]. A peak at δ 5.5–5.1 ppm, as a broad singlet, could be assigned to N–H (originally present at δ 5.3–5.0 ppm in free pyrazolines), suggesting non-involvement of N–H in bond formation [5–9, 15, 20]. The skeletal protons of the five-member ring are observed at δ 3.7–3.2 ppm as a triplet and at δ 2.5–2.0 ppm as a doublet, assigned to CH and CH_2, respectively [5–9, 15, 20].

The proton decoupled ^{13}C NMR spectra (Supplementary Material) of $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$ show all important signals with reference to free pyrazolines. The assignments have been made on the basis of available literature along with the spectra of the free pyrazolines. The signal observed in the region δ 145.9–122.1 ppm as multiplets is assigned to aromatic carbon [5–9, 15, 20]. The signal observed at δ 160.4–156.1 ppm due to imino carbon of C=N group is shifted downfield in comparison to the spectra of free pyrazolines (at δ 143.5–142.8 ppm) suggesting imino nitrogen coordination [5–9, 15, 20].

The most plausible geometries around antimony(III) in these complexes are shown in figures 1 and 2 [19, 20, 22, 28–30].

3.3. *Microbial assay*

The antibacterial activity of a free ligand and two complexes were tested against the bacterial species *Staphylococcus aureus*, *Bacillus lichaniformis*, *Escherichia coli*,

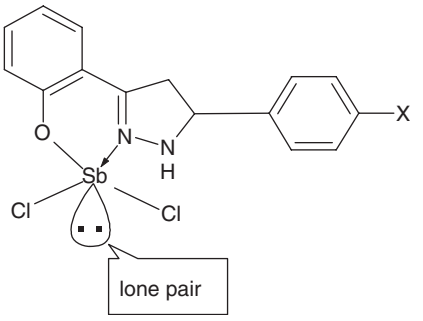

Figure 1. Molecular structure of $SbCl_2(C_{15}H_{12}N_2OX)$. (X=H, CH_3, OCH_3 and Cl).

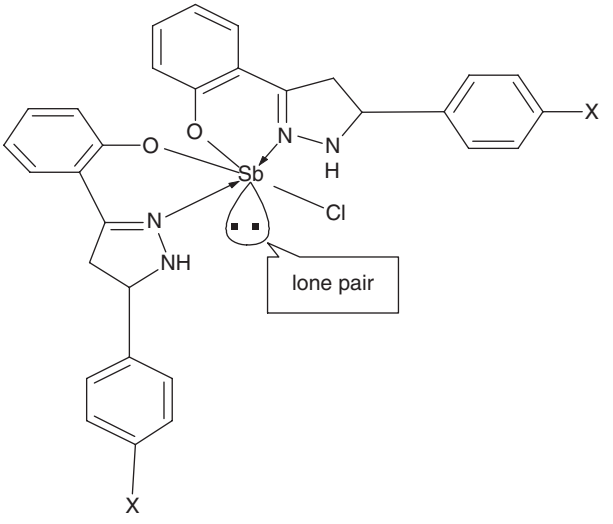

Figure 2. Molecular structure of $SbCl(C_{15}H_{12}N_2OX)_2$. (X=H, CH_3, OCH_3 and Cl).

Klebsiella pneumoniae, *Pseudomonas aeruginosa*, and *Vibrio spp*. and the fungi *Aspergillus niger* and *Penicillium notatum*. The antimicrobial activity of antibiotics were also tested and compared with free pyrazoline and complexes (table 3).

The antibacterial studies show that the dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates have greater activity towards all tested bacteria than free pyrazoline. The dichloroantimony(III)pyrazolinates and chloroantimony(III) pyrazolinates also exhibited greater antifungal activity towards all tested fungi than free pyrazoline (figure 3).

Comparison of the antimicrobial activities of the free pyrazoline and antimony(III) complexes with known antibiotics exhibit the following results: (1) $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$ exhibit greater antibacterial effect towards *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Vibrio spp*. compared to free pyrazoline and chloramphenicol. (2) $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$ exhibit comparable effects toward *Bacillus lichaniformis* compared to free pyrazoline and chloramphenicol. (3) $SbCl_2(C_{15}H_{12}N_2OX)$ and $SbCl(C_{15}H_{12}N_2OX)_2$ exhibit

Table 3. Antimicrobial activity of the free pyrazoline, dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates.

	Fungi		Gram (+ve) bacteria		Gram (–ve) bacteria			
Compound	*A.niger*	*P.notatum*	*S.aureus*	*B.lichaniformis*	*K.pneumoniae*	*Vibriospp.*	*E.coli*	*P.aeruginosa*
a	++	++	++	++	+	++	–	++
b	+++	+++	+++	+++	+++	+++	++	+++
1	+++	+++	+++	++	+++	+++	+	++
5	+++	++	++++	+++	++++	++++	++	+

Inhibition values beyond control are + = 6–10 mm, ++ = 11–15 mm, +++ = 16–20 mm, ++++ = 21–25 mm (the values include disc diameter).
The standards are in the form of sterile Hi-Disc cartridges, each disc containing 30 µm of the drug. *a* = 3(2′-hydroxyphenyl)-5-phenyl pyrazoline.
b = Terbinafin (antifungal agent) and chloramphenicol (antibacterial agent).

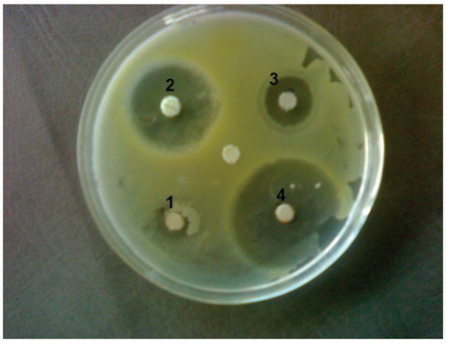

Figure 3. Antibacterial activity against *Staphylococcus aureus*, 1 = free pyrazoline [3(2′-hydroxyphenyl)-5-phenyl pyrazoline], 2 = chloramphenicol, 3 = compound **1** and 4 = compound **5**.

comparable antifungal effects toward *Aspergillus niger* and *Penicillium notatum* compared to free pyrazoline and terbinafin.

Complexation of antimony(III) with biologically active pyrazoline ligand results in increased activity of these complexes.

Chloroantimony(III) dipyrazolinates, $SbCl(C_{15}H_{12}N_2OX)_2$, exhibited higher antimicrobial and antifungal activity compared to free pyrazolines and dichloroantimony(III) pyrazolinates, $SbCl_2(C_{15}H_{12}N_2OX)$. Evidently, distorted octahedral structure around antimony(III) gives more potent antimicrobial agents [31–33]. From the antimicrobial data presented in table 3, it appears that when chloride in dichloroantimony(III) pyrazolinates is replaced by another pyrazoline, there is significant change in antimicrobial activity. This further confirms that antimicrobial activity of these complexes arises from pyrazoline moiety but not from chloride.

Correlation between geometry around the central atom in a complex and antimicrobial activity needs further research.

4. Conclusions

The present study describes a series of dichloroantimony(III) pyrazolinates and chloroantimony(III) dipyrazolinates. Bidentate pyrazoline ligands have been confirmed

by IR, ^{1}H NMR and ^{13}C NMR data. In dichloroantimony(III) pyrazolinates [$SbCl_2(C_{15}H_{12}N_2OX)$], the antimony(III) appears to be four coordinate and most plausible geometry around the antimony(III) atom is distorted trigonal bipyramidal (including the lone pair, figure 1) [14, 28, 29].

In chloroantimony(III) dipyrazolinates [$SbCl(C_{15}H_{12}N_2OX)_2$], the antimony(III) is five coordinate square pyramidal (figure 2) [28–30].

The dichloroantimony(III) pyrazolinates and chloroantimony(III) pyrazolinates exhibit higher antibacterial and antifungal activity than the free pyrazoline and chloramphenicol and terbinafin, respectively. Chloroantimony(III) dipyrazolinates have greater antimicrobial activity than dichloroantimony(III) pyrazolinates.

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