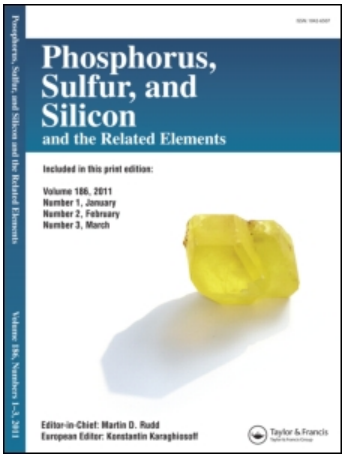

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Jeeven S. Solanki[a]; U. N. Tripathi[b]; Arpan Bhardwaj[c]; Vinod K. Jena[d]
[a] School of Studies in Chemistry, Vikram University, Ujjain, India [b] School of Studies in Chemistry, DDU University, Gorakhpur, India [c] Madhav Science Collage, Vikram Universities, Ujjain, India [d] School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India

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Synthesis, Spectral Studies, and Antimicrobial Evaluation of Antimony(III) Tri[3(2′-hydroxyphenyl)-5-(4-substituted Aryl]pyrazolinate

Jeeven S. Solanki,[1] U. N. Tripathi,[2] Arpan Bhardwaj,[3] and Vinod K. Jena[4]

[1]School of Studies in Chemistry, Vikram University, Ujjain, India
[2]School of Studies in Chemistry, DDU University, Gorakhpur, India
[3]Madhav Science Collage, Vikram Universities, Ujjain, India
[4]School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India

*The synthesis and structure of antimony(III) tripyrazolinates complexes with bidentate N,O, Schiff base pyrazoline ligands are reported. Four new coordination complexes incorporating antimony have been synthesized and characterized by spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR), molecular weight, and elemental analysis. Novel complexes of the type $Sb(C_{15}H_{12}N_2OX)_3$ have been synthesized in dry benzene by the reaction of $SbCl_3$ and the sodium salt of pyrazoline, $NaC_{15}H_{12}N_2OX$, [where X = H (1), CH_3 (2), OCH_3 (3), and Cl (4)] in 1:3 molar ratio. The 3(2′-hydroxyphenyl)-5-(4-substituted aryl) pyrazoline behaves as a bidentate ligand and coordinates to antimony through oxygen and nitrogen atoms, leading to distorted pentagonal bipyramidal structure. The antimicrobial properties of antimony are greatly enhanced when antimony is combined with this pyrazoline ligand. Compounds were screened against different bacteria (*B. licheniformis *and* K. pneumonia*) and fungi (*Aspergillus niger *and* Penicillium notatum*), and show potential activities.*

Keywords Antimony trichloride; bacteria; fungus; pyrazolinates and antimicrobial activity

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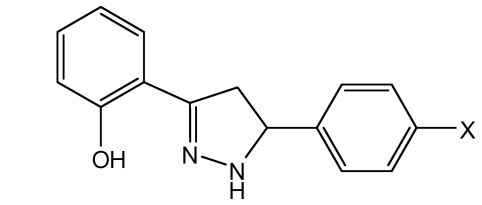
Address correspondence to Jeeven S. Solanki, School of Studies in Chemistry, Vikram University, Ujjain (M.P.), 456010, India. E-mail: solankijeevan8@gmail.com

INTRODUCTION

The medicinal and cosmetic use of antimony complexes dates back at least two centuries.[1] Potassium antimony tartrate and sodium antimony(V) gluconate are useful for treatment of various bacterial diseases. Recently, the use of antimony complexes in cancer chemotherapy has become a topic of interest.[2] Our interest in synthesizing and studying pyrazoline complexes has increased because of their possible use as therapeutic agents, cosmetic, dyes, lubricating oils, and as catalysts for decarboxylation reactions as well as inhibitors for plant growth.[3–5] The 3(2-hydroxyphenyl)-5-(4-X-substituted phenyl) pyrazoline ligands (Scheme 1) are known to exhibit remarkable diversity in their



X = H, CH_3, OCH_3, Cl

SCHEME 1

coordination patterns with transition metals as well as main group metals.[4–5] In most cases these ligands behave as chelating bidentate moieties.[4–9] We have recently published the synthesis, spectral study, and antimicrobial activity of chloro antimony(III) dipyrazolinates and bismuth(III) dipyrazolinates.[10–11] Many of the main-group compounds have pronounced antimicrobial activity and were once widely used in the treatment of syphilis and yaw before the era of antibiotics.[12–14]

Silvrestru et al. documented the highly efficient antitumor activity of antimony complexes, i.e., diphenyl antimony(III) derivatives both in vitro and in vivo.[15] Antimony(III) complexes also show potential as antibacterial and antifungal activities.[16] In the present research article, we describe the results of the syntheses, spectral studies, and antimicrobial activity of antimony(III) tri-3(2′ -hydroxyphenyl)-5-(4-substituted aryl) pyrazolinate.

RESULTS AND DISCUSSION

The novel complexes $Sb(C_{15}H_{12}N_2OX)_3$ have been prepared by the reaction of antimony trichloride and the sodium salt of pyrazolinates in

a 1:3 molar ratio at an elevated temperature.

$$SbCl_3 + Na(C_{15}H_{12}N_2OX) \xrightarrow{\text{Dry benzene}} SbCl_2(C_{15}H_{12}N_2OX) + NaCl$$

Where X = H (1), CH_3 (2), OCH_3 (3) and Cl (4).

All the compounds are yellow colored solids, and are hygroscopic and unstable at room temperature. These are insoluble in common organic solvents such as benzene and hexane but are soluble in chloroform, acetone, and methanol. Molecular weight measurements in dilute chloroform solution at 45°C show the monomeric nature of these compounds. The elemental analysis (C, H, N) data is in accordance with stoichiometry proposed for the new compounds.

Infrared Spectra

The infrared spectral data of these compounds are summarized in Table I. All compounds display bands of medium intensity in the region 3322–3317 cm^{-1} due to ν (N-H) stretching vibrations and bands in the region 1626–1618 cm^{-1} due to ν (C=N) stretching vibrations.[6–7] In all compounds, ν (C=N) stretching is shifted to lower wave number in comparison to the spectra of free pyrazolines (at ~1654 cm^{-1}), suggesting the participation of the imino nitrogen upon coordination. The band present in the region 1012 cm^{-1} in compound **3** may be assigned to ν (C-O) stretching, demonstrating the presence of $-OCH_3$ group. The signal due to ν (O-H) originally the present at ~3080 cm^{-1} in the free pyrazoline ligand is completely absent from the spectra of the complexes. All compounds display bands of medium intensity in the region 469–462 cm^{-1} and 444–435 cm^{-1}, which may be assigned to v(Sb-O) and v(Sb-N) stretching vibration respectively[17–21] The appearance of these two new bands and the disappearance of the hydroxyl band suggest that the pyrazoline behaves as a monobasic bidentate ligand.

TABLE I IR Spectral Data (cm^{-1}) for Antimony(III) Tripyrazolinates

S. No	Compound	ν (N-H)	ν (C=N)	ν (C-O)	ν (Sb-O)	ν (Sb-N)
1	$Sb(C_{15}H_{12}N_2OH)_3$	3318	1624	—	464	442
2	$Sb(C_{15}H_{12}N_2OCH_3)_3$	3317	1617	—	462	435
3	$Sb(C_{15}H_{12}N_2O_2CH_3)_3$	3320	1624	1012	469	444
4	$Sb(C_{15}H_{12}N_2OCl)_3$	3322	1618	—	465	443

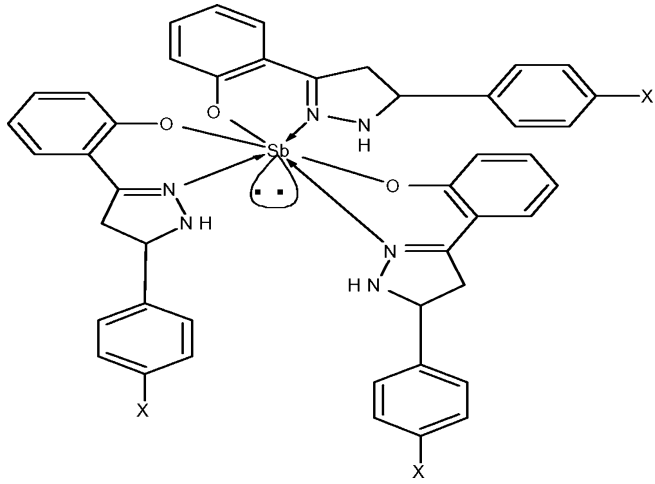


FIGURE 1 Proposed structure of $[C_{15}H_{12}N_2OX)_3Sb]$.

Multinuclear NMR Spectral Studies

The ^1H NMR chemical shifts of these compounds are listed in Table II. In the ^1H NMR spectra, the aromatic protons of antimony(III) tripyrazolinates were observed as a multiplet in the region δ 8.5–6.4 ppm. The peak due to the hydroxyl proton originally present at $\delta \sim 11.00$ppm in the free pyrazolines ligand is completely absent from the spectra of the compounds, suggesting bonding through the hydroxyl oxygen atom. The appearance of a peak at δ 5.5–5.2 ppm as a broad singlet could be assigned to N-H group (originally present at δ 5.4–5.0 ppm in the free pyrazolines ligand) suggesting the noninvolvement of the N-H group in bond formation. The skeletal protons of the five-membered ring are observed at δ 3.6–3.1 ppm as a triplet, and at δ 2.4–1.9 ppm as a doublet could be assigned to CH and CH_2 groups, respectively.[6–7] The proton decoupled ^{13}C NMR spectral data are listed in Table II. The peak observed in the region δ 146.9–122.4 ppm as multiplet could be assigned to aromatic carbon. The signal observed at δ 165.5–162.8 ppm due to imino carbon of C=N group is shifted to down field in comparison to the spectra of free pyrazolines (at δ 143.5–142.8 ppm) suggesting the participation of imino nitrogen in coordination.[6–7] All other peaks were found at their particular positions as in the free pyrazolines.

Microbial Assay

The antibacterial activity of a free ligand and complexes was tested against the bacteria, *Bacillus lichanforimis* (Gram +) and *Klebsiella*

TABLE II ^{1}H NMR and ^{13}C NMR Data (in δ ppm) for Antimony(III) Tripyrazolinates

	^{1}H NMR Chemical shift (in δ ppm)		^{13}CNMR		Chemical shift (in δ)	
	^{1}H NMR data	C=N	CH	CH_2	C-C_6H_4O	C-C_6H_4X
1	7.8-6.5(27H, m, Ar-H) 5.3 (3H, s, NH) 3.6 (3H, t, CH) (J=6.5) 2.2 (6H, d, CH_2) (J=7.4)	163.7	42.8	27.6	140.8 (1) 128.9 (2) 123.2 (3) 122.4 (4) 125.9 (5) 128.1 (6)	129.9 (1) 127.8 (2) 122.4 (3) 125.9 (4) 122.5 (5) 129.1 (6)
2	8.3-7.7 (24 H, m, Ar-H) 5.4 (3H,s,NH 3.7(3H,t,CH) (J=6.2) 2.0(6H,d,CH_2)(J=7.2) 0.8 (CH_3)	165.2	43.7	27.9	139.8 (1) 128.9 (2) 123.2 (3) 122.4(4) 125.9 (5) 128.1 (6)	129.9 (1) 127.8 (2) 122.4 (3) 129.9 (4) 122.5 (5) 129.1 (6)
3	8.5-7.4 (24H, m, Ar-H) 5.1 (3H, s, NH) 3.3 (3H, t, CH)(J=6.3) 2.5 (6H, d, CH_2) (J=7.3) 4.2 (9H, s, OCH_3)	162.9	43.6	27.4	139.8 (1) 129.9 (2) 124.2 (3) 122.6 (4) 125.8 (5) 128.2 (6)	129.9 (1) 128.8 (2) 122.5 (3) 143.1 (4) 122.6 (5) 129.4 (6)
4	7.9-6.4 (24H, m, Ar-H) 5.5 (3H, s, NH) 3.6 (3H, t, CH) (J=6.3) 2.6 (6H, d, CH_2) (J=7.4 Hz)	164.1	43.7	23.3	140.9 (1) 128.7 (2) 123.3 (3) 122.7 (4) 124.9 (5) 128.6 (6)	129.9 (1) 127.8 (2) 122.4 (3) 146.9 (4) 122.8 (5) 129.1 (6)

pneumoniae (Gram −), and the antifungal activity was tested against *Aspergillus niger* and *Penicillium notatum*. The antimicrobial activity of some antibiotics was also tested and compared with free pyrazoline and its antimony(III) complexes. The results are listed in Table III). The $(C_{15}H_{12}N_2OX)_3Sb$ complexes exhibited higher antibacterial and antifungal effect than the free pyrazoline.

Structural Elucidations

In the corresponding IR spectra, the (C=N) stretching vibrations ranging from 1654 cm^{-1} in the free pyrazoline ligand are shifted toward

TABLE III Antimicrobial Activity of the Free Pyrazoline and Antimony(III) Tripyrazolinates Complexes

Comp.	Fungi		Gram (+) bacteria		Gram (–) bacteria	
No	*A. niger*	*P. notatum*	*S. aureus*	*B. lichaniformis*	*K. pneumoniae*	*Vibrio spp.*
L	+	++	+	++	+	++
(**1**)	++	++	+++	+++	+++	+++
(**2**)	+++	+++	++	++	+	+
(3)	+++	+++	++	+++	++	—
(4)	++	++	–	+	++	
R	+++	++	+++	++++	++++	+++

Inhibition values beyond control are + = 6–10 mm, ++ = 11–15 mm, +++ = 16–20 mm, ++++ = 21–25 mm and – = not active (the values are including disc diameter).

L = ($C_{15}H_{12}N_2OH$).

1, 2, 3, 4 = compounds.

R = Terbinafin (antifungal agent) and chloramphenicol (antibacterial agent).

The standards are in the form of sterile Hi-Disc cartridges, each disc containing $30_{\mu m}$ of sample.

lower frequencies by ~29 cm^{-1} and are present in the range 1626–1618 cm^{-1}, indicating weakening of C=N bond due to the coordination of the imino nitrogen atom to antimony. The signal due to ν (O-H) originally present at ~3080 cm^{-1} in free ligand) is completely absent from the spectra of complexes and presence new bands in the range 469–462 cm^{-1} and 444–435 cm^{-1}. The presences of these new bands and disappearance of hydroxyl band suggests that the pyrazoline behaves as monobasic bidentate ligand.[4–7] This has been further confirmed by ^{13}CNMR. The signal observed at δ 165.5–162.8 ppm due to imino carbon of C=N group is shifted to downfield in comparison to the spectra of free pyrazolines at δ 143.5–142.8 ppm, suggesting the involvement of imino nitrogen in coordination. On the basis of the above spectral studies, it may be concluded that the 3(2′-hydroxyphenyl)-5-(4-X-substituted phenyl) pyrazoline ligand behaves in a bidentate mode of attachment to the antimony, in all these derivatives thus leading to the six-coordinated distorted pentagonal bipyramidal geometry of around the antimony(III) atom.

EXPERIMENTAL

Solvents (benzene, acetone, and alcohol) were rigorously dried and purified by standard methods before use.[23] The other chemicals used were of analytical grade quality. Antimony chlorides (E. Merck) were used

as received. O-hydroxy acetophenone (CDH) and benzaldehydes (E. Merck) were used as received.

Physical Measurements

Chlorine was estimated by Volhard's method, and antimony was estimated iodometrically.[23] Infrared spectra were recorded on Perkin Elmer Model 557 FT-IR spectrophotometer using KBr cell in the range 4000–400 cm^{-1}. NMR spectra were recorded at room temperature on a Bruker DRX-300 spectrometer operated at 300.1 and 75.45 MHz for ^{1}H NMR and ^{13}C NMR using TMS as internal standard, respectively. Molecular weights were determined on a Knauer Vapour Pressure in $CHCl_3$ at 45°C. The elemental analysis (C, H, and N) was estimated using a Coleman CHN analyzer.

Antimicrobial Studies

An agar disc diffusion technique was used for the screening of in vitro antimicrobial activity.[24] 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 for 5 days for fungi. The molten Muller Hinton medium was poured in a sterile Petri dish (9 cm in diameter) to obtain a depth of 5 mm. The medium was left to solidify. Thereafter it was seeded with the respective test organisms. For the purpose of seeding, 5 mL sterile water was added to the agar slant culture of fungi. The culture was scrips to get 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 μ m of each sample to be tested was dissolved in 1 mL of acetone solvent. 5 mm discs of Whatman filter paper no.42 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 min, the paper discs were transferred to the seeded agar plate. Discs were kept on the seeded agar plates. Finally the discs were incubated at 37°C for 24 h (for bacteria) and at 30 °C for 72 h (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 no inhibition zone was observed for acetone. Each distinct inhibition zone was measured as diameter in mm; both antibacterial and antifungal activity can be calculated as a mean of three replicates.

TABLE IV Synthetic, Physical, and Analytical Data for Antimony(III) Tripyrazolinates

S, No.	Reactant in gm			Molar ratio	Product in gm	Yield (%)	Mp (°C)	M.w. found (calcd)	Analysis % (caculated) found			
	$SbCl_3$	Sodium	Ligand						C	H	N	Sb
1.	0.3202	0.0974	1	1:3:3	$(C_{15}H_{12}N_2OX)_3Sb$ 2.9 gm	85	157	(832.75)	(64.48)	(4.68)	(10.1)	(14.62)
	1.4mm	4.2 mm	4.2 mm					830	65.06	4.69	10.1	14.66
2.	0.3008	0.091	1	1:3:3	$(C_{15}H_{12}N_2OX)_3Sb$ 2.7 gm	77	160	(874.75)	(65.64)	(5.14)	(9.60)	(13.91)
	1.3 mm	3.9 mm	3.9 mm					872	66.05	4.47	9.63	13.96
3.	0.2830	0.0861	1	1:3:3	$(C_{15}H_{12}N_2OX)_3Sb$ 2.9 gm	84	155	(922.75)	(62.42)	(4.876)	(9.10)	(13.19)
	1.2 mm	3.7 mm	3.7 mm					920	62.60	4.89	9.13	13.23
4.	0.2789	0.0848	1	1:3:3	$(C_{15}H_{12}N_2OX)_3Sb$ 3.00 gm	87	186	(934.75)	(57.76)	(3.83)	(8.98)	(13.02)
	1.2 mm	3.6 mm	3.6 mm					930	58.06	3.87	9.03	13.09

Where X= H in **1**, CH_3 in **2**, OCH_3 in **3,** and Cl in **4** compound.

Synthesis of $(C_{15}H_{12}N_2OX)_3$ Sb

Ligands were prepared by the reported procedure. Antimony(III) tripyrazolinates of the general formula $(C_{15}H_{12}N_2OX)_3$ Sb were prepared by the following procedure:

$$SbCl_3 + Na\,(C_{15}H_{12}N_2OX) \xrightarrow{\text{Dry benzene}} SbCl_2(C_{15}H_{12}N_2OX) + NaCl$$

Freshly cut pieces of sodium (0.0974 g, 4.2 mmol) were taken in a flask with an excess of isopropanol (30 mL) and refluxed for 30 min, until a clear solution of sodium isopropoxide was obtained. A benzene solution of 3(2′-hydroxyphenyl)-5(4-X-phenyl) pyrazoline (1.0 g; 4.2 mmol) was then added, and the reaction mixture was further refluxed for ~1 h, whereby a constant yellow color was obtained. The reaction mixture was cooled to room temperature, and then a benzene (10 mL) solution of antimony trichloride (0.320 g; 1.411 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for ~8 h, until the color of the reaction mixture underwent a change. The reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate. A light yellow colored solid was obtained. For purification, the compound was dissolved in a small amount of chloroform and acetone, and the solution was kept overnight and dried in vacuum. All compounds **1–4**, whose properties are summarized in Table IV, were prepared by the same route.

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