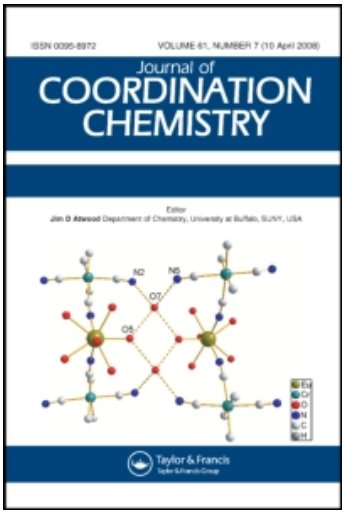


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# Synthesis, spectral study and antimicrobial activity of bismuth(III) 3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates

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Dichlorobismuth(III) pyrazolinates and chlorobismuth(III) dipyrazolinates of the type $BiCl_2(C_{15}H_{12}N_2OX)$ and $BiCl(C_{15}H_{12}N_2OX)_2$ have been synthesized in dry benzene by reaction of $BiCl_3$ and the sodium salt of pyrazoline in 1 : 1 and 1 : 2 molar ratios at elevated temperature [$C_{15}H_{12}N_2OX$ = 3(2′-hydroxyphenyl)-5-(4-X-substituted phenyl) pyrazoline and X = H in compounds **1**, **5**, $CH_3$ in **2**, **6**, $OCH_3$ in **3**, **7** and Cl in **4**, **8**, respectively]. These newly synthesized derivatives have been characterized by elemental analysis (C, H, N, Cl and Bi), molecular weight measurements and spectral (IR, $^1$H NMR, $^{13}$C NMR) studies. Selected compounds screened against different bacteria and fungi show potential antibacterial and antifungal activities.

*Keywords*: Bismuth trichloride; Pyrazolinates; Antimicrobial activity

## 1. Introduction

Bismuth compounds have been used in the treatment of gastrointestinal diseases for two centuries [1]. Compounds such as bismuth carbonates were at one time applied so carelessly that the intake of 10 g several times per day resulted in strong side effects, such as neurotoxicity, but side effects are not to be expected with small doses [2, 3]. Traditional bismuth therapy, carried out with pharmaceuticals in appropriate doses and formulations, is preferred over a combination of organic antibiotics and proton pump inhibitors [4]. Bismuth compounds do not require maintenance of a neutral stomach pH, which involves the risk of intestinal infections with other bacteria that are no longer destroyed by acidic gastric juice [5]. Colloidal bismuth sub citrate is the number one bismuth drug in the classical triple therapy [6–8]. J. Roderick published structural and spectroscopic data for bismuth(III) citrate compounds which are useful in treatment of peptic ulcers [9–11].

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Pyrazolines are an important class of heterocyclic compounds used in industries as dyes and lubricating oils, as antioxidants in agriculture, as catalysts for decarboxylation reactions and inhibitors for plant growth [12–14]. Derivatives of pyrazolines are used extensively in photography [15]. Metal complexes of 5(2′-hydroxyphenyl)-3-phenyl pyrazoline with Ni(II), Co(II) and Cu(II) have been prepared in our laboratory by extraction methods [16].

We have studied the synthesis, spectral characterization and antimicrobial activity of diorganotin(IV) dipyrazolinates [17] and synthesis, spectral and antimicrobial studies of triorganotin(IV) 3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates [18].

In the present article, we describe the syntheses, spectral study and antimicrobial activity of bismuth(III) 3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates.

The combination of bismuth(III) with biologically-active pyrazoline ligands provides complexes with high effectiveness against bacteria and fungi.



## 2. Experimental

Solvents (benzene, acetone and alcohol) were rigorously dried and purified by standard methods before use [19]. All chemicals used were of analytical grade. Bismuth trichloride (E. Merck), o-hydroxyacetophenone (CDH) and benzaldehydes (E. Merck) were used as received.

### 2.1. *Synthesis of* $(C_{15}H_{12}N_2OX)BiCl_2$

Ligands were prepared by the reported procedure [20]. New complexes of the type dichlorobismuth(III) pyrazolinates $(C_{15}H_{12}N_2OX)BiCl_2$ were prepared by the reaction of sodium salt of pyrazolinates and bismuth trichloride in 1 : 1 molar ratio at elevated temperature.

$$BiCl_3 + Na(C_{15}H_{12}N_2OX) \xrightarrow{\text{Dry benzene}} (C_{15}H_{12}N_2OX)BiCl_2 + NaCl$$

X = H in **1**, $CH_3$ in **2**, $OCH_3$ in **3** and Cl in **4**

Freshly cut pieces of sodium (0.4872 g, 2.11 mmol) were taken in a flask with excess isopropanol and refluxed ~30 min until a clear solution of sodium isopropoxide was obtained. The dry benzene solution of 3(2′-hydroxyphenyl)-5-(4-X-phenyl) pyrazoline (0.5 g, 2.11 mmol) was then added and the reaction mixture was further refluxed for 1 h, and a yellow color was obtained. The reaction mixture was cooled to room temperature and then $BiCl_3$ (0.6652 g, 2.11 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for ~6 h. The reaction mixture was filtered to remove precipitated NaCl and solvent was removed under reduced pressure giving a red brown solid. For purification the compound was dissolved in a small amount of chloroform (10 ml), the solution kept overnight and then dried in vacuum. Analytical results are presented in table 1. Compounds **1**, **2**, **3** and **4** were prepared by the same route.

Table 1. Analytical and physical data for $BiCl_2(C_{15}H_{12}N_2OX)$ and $BiCl(C_{15}H_{12}N_2OX)_2$ complexes.

| No. | Compound | Yield% | M. p (°C) | Analysis% (calculated) found C | H | N | Bi | Cl | M.W.(calc) Found |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $BiCl_2(C_{15}H_{12}N_2OX)$ | 80 | 126 | (34.95) | (2.52) | 5.43) | (40.58) | (13.59) | (514.98) |
| | | | | 35.15 | 2.52 | 5.46 | 40.81 | 13.67 | 512 |
| **2** | $BiCl_2(C_{15}H_{12}N_2OX)$ | 75 | 135 | (36.22) | 2.83) | (5.28) | (39.43) | (13.20) | (529.98) |
| | | | | 36.36 | 2.84 | 5.30 | 39.57 | 13.25 | 528 |
| **3** | $BiCl_2(C_{15}H_{12}N_2OX)$ | 88 | 158 | (35.16) | 2.74) | (5.12) | (38.27) | (12.82) | (545.98) |
| | | | | 35.29 | 2.75 | 5.14 | 38.41 | 12.86 | 544 |
| **4** | $BiCl_2(C_{15}H_{12}N_2OX)$ | 79 | 150 | (32.72) | 2.18) | (5.09) | (37.99) | (12.72) | (549.98) |
| | | | | 32.60 | 2.17 | 5.07 | 37.85 | 12.68 | 552 |
| **5** | $BiCl(C_{15}H_{12}N_2OX)_2$ | 77 | 168 | (59.11) | 4.26) | (9.19) | (34.42) | (5.74) | (608.98) |
| | | | | 59.21 | 4.26 | 9.24 | 34.48 | 5.77 | 606 |
| **6** | $BiCl(C_{15}H_{12}N_2OX)_2$ | 81 | 190 | (51.47) | 4.02) | (7.50) | (8.01) | (4.69) | (745.98) |
| | | | | 51.61 | 4.03 | 7.52 | 28.08 | 4.70 | 744 |
| **7** | $BiCl(C_{15}H_{12}N_2OX)_2$ | 93 | 186 | (49.35) | 3.85) | (7.19) | (26.86) | (4.490) | (777.98) |
| | | | | 49.61 | 3.87 | 7.23 | 27.00 | 4.52 | 774 |
| **8** | $BiCl(C_{15}H_{12}N_2OX)_2$ | 89 | 167 | (45.80) | 3.05) | (7.12) | (26.58) | (4.45) | (785.98) |
| | | | | 46.06 | 3.06 | 7.16 | 26.72 | 4.47 | 782 |



### 2.2. *Synthesis of $(C_{15}H_{12}N_2OX)_2BiCl$*

Complexes of the type $BiCl_2$ $(C_{15}H_{12}N_2OX)_2$ were prepared by reaction of bismuth trichloride with the sodium salt of pyrazolinates in 1 : 2 molar ratio at elevated temperature.

$$BiCl_3 + 2Na(C_{15}H_{12}N_2OX) \xrightarrow{\text{Dry benzene}} BiCl(C_{15}H_{12}N_2OX)_2 + 2NaCl$$

Pyrazolinate was prepared as in section 2.1. and then benzene solution of bismuth trichloride (00.3127 g, 2.11 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for ~8 h, filtered to remove precipitated NaCl and the solvent removed under reduced pressure. The red brown colored solid thus obtained was reprecipitated in acetone and dried in vacuum to get the purified product. Compounds **5**, **6**, **7** and **8** were prepared by the same route.

## 3. Physical measurements

Chlorine was estimated by Volhard's method and bismuth was estimated by direct titration with standard EDTA solution using xylonol orange as indicator [21]. Infrared spectra were recorded on a Perkin Elmer Model 557 FT-IR spectrophotometer using a CsI cell from 4000–200 $cm^{-1}$; NMR spectra were recorded at room temperature on a Bruker DRX-300 spectrometer operated at 300.1 and 75.45 MHz for $^1H$ and $^{13}C$ using TMS (tetramethylsilane) as internal standard. Molecular weights were determined on a Knauer Vapor pressure in $CHCl_3$ at 45°C. The elemental analyses (C, H and N) was estimated by Coleman CHN analyzer.

### 3.1. *Antimicrobial studies*

Agar disc diffusion technique was used for screening *in vitro* antimicrobial activity [22]. Inoculums of bacteria were prepared in nutrient broth and fungi in potato dextrose

agar slant. The cultures were inoculated and incubated for 48 h 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 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 1 ml acetone. article discs (5 mm discs of Whatmann filter article no. 42 cut and sterilized) were immersed in solution of sample, removed and left in a sterile Petri dish to permit the solvent to evaporate. After 10 min the article discs were transferred to seeded agar plates. The dishes were incubated at 37°C for 24 h (for bacteria) and at 30°C for 72 h (for fungi), where clear 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.



## 4. Results and discussion

All the compounds are red-brown solids, non-hygroscopic, stable at room temperature, soluble in common organic (chloroform, acetone carbontetrachloride) and coordinating (tetrahydrofuran, dimethylformamide and dimethylsulphoxide) solvents. Molecular weight measurements in dilute chloroform at 45°C show monomeric compounds. Elemental analyses (C, H, N, Cl and Bi) are in accord with stoichiometry proposed.

### 4.1. *IR spectral studies*

The infrared spectral data for these compounds are summarized in table 2. All compounds exhibit bands of medium intensity in the region 3328–3321 $cm^{-1}$ due to $\nu$(N–H) stretching and bands in the region 1626–1618 $cm^{-1}$ due to $\nu$(C=N). The $\nu$(C=N) is shifted to lower wavenumber in comparison to free pyrazolines (at ~1654 $cm^{-1}$), suggesting involvement of imino nitrogen in coordination. The signal due to $\nu$(O–H) (originally present at 3080 $cm^{-1}$ in free pyrazolines) is absent from the

Table 2. IR spectral data ($cm^{-1}$) for $(C_{15}H_{12}N_2OX)BiCl_2$ and $(C_{15}H_{12}N_2OX)_2BiCl$.

| No. | (N–H) | (C=N) | (C–O) | (Bi–O) | (Bi–N) | Bi–Cl |
|---|---|---|---|---|---|---|
| **1** | 3328 | 1618 | – | 520 | 465 | 315 |
| **2** | 3321 | 1620 | – | 517 | 464 | 315 |
| **3** | 3322 | 1618 | – | 518 | 467 | 312 |
| **4** | 3326 | 1618 | 1030 | 522 | 470 | 314 |
| **5** | 3328 | 1619 | – | 522 | 465 | 316 |
| **6** | 3323 | 1621 | – | 523 | 467 | 312 |
| **7** | 3327 | 1619 | – | 518 | 468 | 314 |
| **8** | 3326 | 1626 | – | 516 | 464 | 316 |

X = H in **1** and **5**, $CH_3$ in **2** and **6**, $OCH_3$ in **3** and **7** and Cl in **4** and **8**.

spectra of the complexes [15–18, 23, 24]. Bands at 1030 $cm^{-1}$ and 1032 $cm^{-1}$ in **3** and **7** may be assigned to $\nu$(C–O) of $-OCH_3$. Bands of medium intensity at 316–315 $cm^{-1}$ are due to $\nu$(Bi–Cl) [25]. New bands (in comparison to free pyrazolines) in the region 527–517 $cm^{-1}$ and 470–464 $cm^{-1}$ are assigned to $\nu$(Bi–O) and $\nu$(Bi–N), respectively [26]. The IR spectra suggest that pyrazoline is a monobasic bidentate ligand in all the complexes.

### 4.2. *Multinuclear NMR spectral studies*

$^1$H NMR spectra (table 3) show aromatic protons of bismuth(III) pyrazolinates as a multiplet in the region $\delta$ 7.9–6.3 ppm. The integration ratio indicates 8 protons in **2**–**4** and 16 protons for **6**–**8**. The peak due to hydroxyl proton (originally present at $\delta\sim$11.00 ppm in free pyrazolines) completely disappears from the spectra of compounds suggesting bonding through hydroxyl oxygen. The peak at $\delta$ 5.5–5.1 ppm as a broad singlet is assigned to N–H group (originally present at $\delta$ 5.2–5.0 ppm in free pyrazolines) suggesting non-involvement of N–H in bond formation. The skeletal protons of the five-membered ring observed at $\delta$ 3.7–3.3 ppm as a triplet and at $\delta$ 2.5–2.0 ppm as a doublet could be assigned to CH and $CH_2$, respectively [15–18, 23, 24].

The proton decoupled $^{13}$C NMR spectra (table 4) of bismuth(III) pyrazolinates show the presence of all important signals expected from free pyrazolines and assignments have been made on the basis of available literature along with the spectra of the free pyrazolines. The signal at $\delta$ 134.8–127.5 ppm as a multiplet could be assigned to aromatic carbons [15–18, 23, 24]. The signal at $\delta$ 165.5–161.5 ppm due to



Table 3. $^1$H NMR data for $(C_{15}H_{12}N_2OX)BiCl_2$ and $(C_{15}H_{12}N_2OX)_2BiCl$.

| No. | Chemical shift (in $\delta$ ppm) |
|---|---|
| **1** | 7.4–6.8 (9H, m, Ar–H), 5.1 (1H, s, NH), 3.6 (1H, t, CH), 2.1 (2H, d, $CH_2$) |
| **2** | 7.7–6.9 (8H, m, Ar–H), 5.3 (1H, s, NH), 3.5 (1H, t, CH), 2.0 (2H, d, $CH_2$), 1.2 (3H, s, $CH_3$) |
| **3** | 7.6–6.5 (8H, m, Ar–H), 5.1 (1H, s, NH), 3.3 (1H, t, CH), 2.5 (2H, d, $CH_2$), 3.9 (3H, s, $OCH_3$) |
| **4** | 7.7–6.8 (8H, m, Ar–H), 5.1 (1H, s, NH), 3.6 (1H, t, CH), 2.2 (2H, d, $CH_2$) |
| **5** | 7.9–6.9 (18H, m, Ar–H), 5.3 (2H, s, NH), 3.6 (2H, t, CH), 2.1 (4H, d, $CH_2$) |
| **6** | 7.9–6.5 (16H, m, Ar–H), 5.4 (2H, s, NH), 3.5 (2H, t, CH), 2.1 (4H, d, $CH_2$), 1.4 (6H, s, $CH_3$) |
| **7** | 7.6–6.7 (16H, m, Ar–H), 5.1 (2H, s, NH), 3.7 (2H, t, CH), 2.4 (4H, d, $CH_2$), 4.0 (6H, s, $OCH_3$) |
| **8** | 7.8–6.7 (16H, m, Ar–H), 5.3 (2H, s, NH), 3.3 (2H, t, CH), 2.2 (4H, d, $CH_2$) |

X = H in **1** and **5**, $CH_3$ in **2** and **6**, $OCH_3$ in **3** and **7** and Cl in **4** and **8**, m = multiplet, s = singlet, d = doublet, t = triplet.

Table 4. $^{13}$C NMR data (in $\delta$ ppm) for $(C_{15}H_{12}N_2OX)BiCl_2$ and $(C_{15}H_{12}N_2OX)_2BiCl$.

| No. | Chemical shift (in $\delta$ ppm) |
|---|---|
| **1** | 134.6–127.6 (Ar–C), 165.3 (C=N), 43.7 (CH), 26.4 ($CH_2$) |
| **2** | 134.8–127.5 (Ar–C), 165.5 (C=N), 43.3 (CH), 26.3 ($CH_2$), 13.5 ($CH_3$) |
| **3** | 134.8–127.8 (Ar–C), 161.5 (C=N), 43.8 (CH), 26.1 ($CH_2$), 51.8 ($OCH_3$) |
| **4** | 134.5–127.5 (Ar–C), 161.5 (C=N), 43.6 (CH), 26.5 ($CH_2$) |
| **5** | 133.7–129.9 (Ar–C), 162.8 (C=N), 43.5 (CH), 26.6 ($CH_2$) |
| **6** | 133.8–129.6 (Ar–C), 163.5 (C=N), 43.2 (CH), 26.8 ($CH_2$), 13.7 ($CH_3$) |
| **7** | 133.7–129.5 (Ar–C), 164.6 (C=N), 43.6 (CH), 26.3 ($CH_2$), 51.5 ($OCH_3$) |
| **8** | 133.8–129.5 (Ar–C), 162.3 (C=N), 43.3 (CH), 26.6 ($CH_2$) |

imino carbon of C=N group is shifted downfield in comparison to free pyrazolines (at $\delta$ 142.6–140.2 ppm) suggesting involvement of imino nitrogen in coordination. All other signals were found at their respective positions as in free pyrazolines.

### 4.3. *Structures*

The bidentate behavior of 3(2′-hydroxyphenyl)-5-phenyl pyrazoline in $(C_{15}H_{12}N_2OX)BiCl_2$ and $(C_{15}H_{12}N_2OX)_2BiCl$ is indicated by IR, $^1$H NMR and $^{13}$C NMR data [15–18, 21, 22]. In $(C_{15}H_{12}N_2OX)BiCl_2$ the bismuth(III) has coordination number four and most plausible geometry around the bismuth atom is Distorted trigonal bipyramidal [figure 1(a) including the lone pair]. In $(C_{15}H_{12}N_2OX)$ BiCl the bismuth(III) is five-coordinate distorted octahedral [figure 1(b)].

### 4.4. *Microbial assay*

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



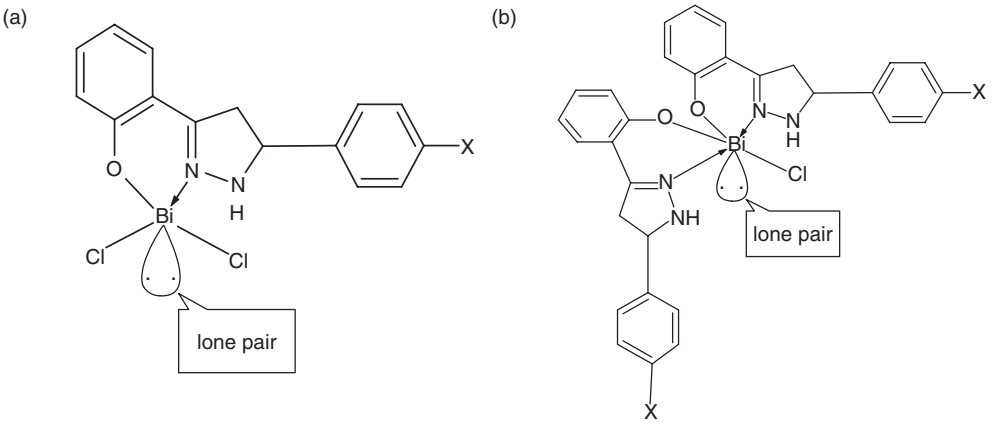


Figure 1. Structures of $(C_{15}H_{12}N_2OX)BiCl_2$ and $(C_{15}H_{12}N_2OX)_2BiCl$.

Table 5. Antimicrobial activity of the free pyrazoline and bismuth(III) pyrazolinates.

| | Fungi | | Gram (+ve) bacteria | | Gram (–ve) bacteria | | |
|---|---|---|---|---|---|---|---|
| Compd. No. | *A. niger* | *P. notatum* | *S. aureus* | *B. lichaniformis* | *K. pneumoniae* | *Vibrio spp.* | *E. coli* |
| **L** | + | + | + | ++ | ++ | + | – |
| **1** | ++ | ++ | +++ | ++ | ++ | ++ | ++ |
| **5** | ++ | +++ | ++++ | +++ | +++ | ++++ | ++ |
| **R** | +++ | +++ | +++ | +++ | +++ | +++ | +++ |

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

*Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, and *Vibrio Spp*., and the antifungal activities were tested against *Aspergillus niger* and *Penicillium notatum*. The antimicrobial activity of antibiotics were also tested and compared with free pyrazoline and its bismuth complexes (table 5). The antibacterial studies exhibited that the bismuth(III) pyrazolinates have greater activity towards all tested bacteria and antifungal than free pyrazoline (Supplementary Material) and are comparable to the standard antibiotics.

## 5. Conclusions

$(C_{15}H_{12}N_2OH)BiCl_2$ and $(C_{15}H_{12}N_2OH)_2BiCl$ exhibited higher antibacterial and antifungal effect than the free pyrazoline. Chlorobismuth(III) dipyrazolinates $(C_{15}H_{12}N_2OH)_2BiCl$ exhibited higher antimicrobial and antifungal activity compared to free pyrazolines as well as chloramphenicol and antifungal agent terbinafin.

Chlorobismuth(III) dipyrazolinates with distorted octahedral structures around bismuth(III) atom are more effective antimicrobial agents than those with trigonal bipyramidal geometry [28–30]. When Cl in dichlorobismuth(III) pyrazolinate is replaced by another pyrazoline, there is significant change in antimicrobial activity, further confirming that antimicrobial activities of these complexes arise from pyrazoline, not from chloride [11, 12].



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