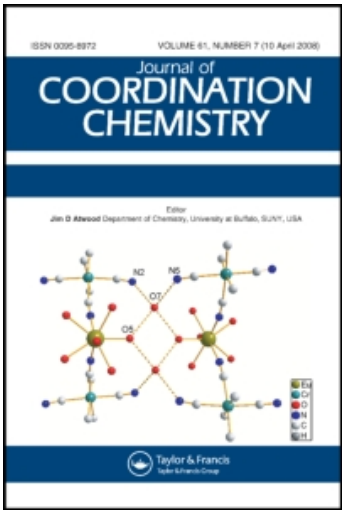


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# Synthesis, structural characterization, and *in vitro* antimicrobial properties of salicylate and pyrazoline complexes of bismuth(III)

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Displacement reactions of dichlorobismuth(III)pyrazolinates with oxygen donors such as sodium salicylate and acetate in 1 : 1 and 1 : 2 molar ratio in refluxing anhydrous benzene yields $(C_{12}H_{15}N_2OX)Bi(C_6H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ [$C_{12}H_{15}N_2OX$ = 3(2′-hydroxyphenyl)-5-(4-X-substituted phenyl) pyrazoline X = H in **1**,**5**,**9**, $CH_3$ in **2**,**6**,**10**, $OCH_3$ in **3**,**7**,**11**, and Cl in **4**,**8**,**12**, respectively, ($C_6H_4O_3$) = salicylate and ($CH_3COO$) = acetate]. Newly synthesized derivatives are brown solids, soluble in organic solvents like benzene, chloroform, and acetone. The compounds have been characterized by elemental analyses (C, H, N, Cl, and Bi), molecular weight measurements, and spectral (IR, $^1$H NMR, $^{13}$C NMR) studies. The ($C_{12}H_{15}N_2OX$) and ($C_6H_4O_3$) are bidentate while ($CH_3COO$) is monodentate to bismuth(III), leading to a distorted trigonal bipyramidal structure. The complexes were screened against different bacteria and fungi showing potential antibacterial and antifungal activities.

*Keywords*: Dichlorobismuth(III)pyrazolinates; Pyrazoline; Salicylate; Carboxylate; Antimicrobial

## 1. Introduction

Bismuth compounds, such as bismuth carbonates, have been used in the treatment of gastrointestinal diseases for two centuries [1–9]. The application of bismuth complexes is widespread due to bismuth's antiseptic, antisecretory, antacid, and gastrointestinal properties [10–13]. Special attention has been placed recently on the use of bismuth for duodenal ulcers and peptic disease [2–8]. Colloidal bismuth subcitrate (CBS) is the number one bismuth drug in the classical triple therapy [14, 15]. The recent discovery that CBS is useful in treating peptic ulcers has increased interest in bismuth compounds. Roderick published structural and spectroscopic data for bismuth(III) citrate

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compounds which are useful in the treatment of peptic ulcers and are now used clinically [16–18]. Pyrazolines are an important class of heterocyclic compounds [19, 20], used as ligands in metal complexes for the treatment of various diseases [21–24]. Bismuth complexes with bidentate pyrazoline have potential as antimicrobial and antifungal agents [25, 26]. Therefore, we decided to focus our attention on the syntheses of mixed ligand complexes containing pyrazoline and salicylate or acetate.

## 2. Experimental

Solvents (benzene, acetone, and alcohol) were rigorously dried and purified by standard methods before use [27, 28]. All chemicals used were analytical grade. Bismuth trichloride (E. Merck), *o*-hydroxyacetophenone (CDH) and benzaldehydes (E. Merck), salicylic acid and sodium acetate were used as received. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 557 FT-IR spectrophotometer using a CsI cell from 4000 to 200 $cm^{-1}$. NMR spectra were recorded at room temperature on a Bruker DRX-300 spectrometer operated at 300.1 (1H) and 75.45 (13C) MHz containing tetramethylsilane (TMS) as an internal standard. Molecular weights were determined on a Knauer vapor pressure apparatus in $CHCl_3$ at 45°C. Elemental analyses (C, H, and N) were measured with a Coleman CHN analyzer. Chlorine was measured by Volhard's method and bismuth was measured by direct titration with a standard EDTA solution using xylonol orange as indicator.



### 2.1. *Synthesis*

**2.1.1. Synthesis of mixed complexes of $(C_{12}H_{15}N_2OX)Bi(C_6H_4O_3)$.** $(C_{12}H_{15}N_2OX)BiCl_2$ was prepared by our previously reported procedure [25, 26]. Sodium (0.1664 g, 7.23 mmol) and isopropanol (20 mL) were refluxed for 20–35 min until a clear solution of sodium isopropoxide was obtained. Salicylic acid (0.5 g, 3.62 mmol) was added and the reaction mixture was refluxed for a further ~45 min to 1 h, forming a light yellow solution. An acetone solution of $(C_{12}H_{15}N_2OX)BiCl_2$ (0.1.871 g, 3.62 mmol) was added dropwise with constant stirring. The resulting brown reaction mixtures undergo a change in 4–6 h. The reaction mixture was filtered and solvent removed from the filtrate under reduced pressure yielding a brown solid. The brown solid was further purified by crystallization from acetone and chloroform and dried in vacuum to get 1.8 g of purified products. Compounds **1**–**4** (table 1) were prepared by the same procedure.

$$BiCl_2(C_{15}H_{12}N_2OX) + Na_2(C_7H_4O_3) \xrightarrow{\text{Dry acetone}} (C_{15}H_{12}N_2OX)Bi(C_7H_4O_3) + 2NaCl$$

**2.1.2. Synthesis of $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$.** To an acetone solution of $(C_{12}H_{15}N_2OX)BiCl_2$ (1.618 g, 3.048 mmol), a methanol solution of sodium acetate (0.25 g, 3.048 mmole) was added dropwise. The resulting dark brown reaction mixtures undergo a change in 3–4 h. The reaction mixture was filtered to remove the precipitated NaCl. The solvent was removed under reduced

Table 1. Synthesis and physical data for $(C_{12}H_{15}N_2OX)Bi(C_6H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$.

| No. | Formula of product | Yield (%) | m.p. | M.W. (Calcd) found | Analysis (Calcd) found (%) C | H | N | Bi |
|---|---|---|---|---|---|---|---|---|
| **1** | $(C_6H_4O_3)Bi(C_{15}H_{12}N_2OX)$ | 85 | 133 | (584.1) | (45.19) | (3.25) | (4.79) | (35.77) |
| | | | | 582 | 45.36 | 3.26 | 4.81 | 35.90 |
| **2** | $(C_6H_4O_3)Bi(C_{15}H_{12}N_2OX)$ | 83 | 149 | (598.1) | (46.14) | (3.51) | (4.68) | (34.93) |
| | | | | 596 | 46.30 | 3.52 | 4.69 | 35.06 |
| **3** | $(C_6H_4O_3)Bi(C_{15}H_{12}N_2OX)$ | 85 | 143 | (614.1) | (44.94) | (3.41) | (4.55) | (34.03) |
| | | | | 610 | 45.24 | 3.44 | 4.59 | 34.25 |
| **4** | $(C_6H_4O_3)Bi(C_{15}H_{12}N_2OX)$ | 84 | 134 | (619.55) | (42.61) | (2.90) | (4.51) | (33.73) |
| | | | | 616 | 42.85 | 2.92 | 4.54 | 33.92 |
| **5** | $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ | 81 | 167 | (563.43) | (36.20) | (2.83) | (4.96) | (37.11) |
| | | | | 560 | 36.42 | 2.85 | 5.00 | 37.31 |
| **6** | $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ | 86 | 178 | (577.43) | (37.40) | (3.11) | (4.84 | (36.19) |
| | | | | 576 | 37.5 | 3.12 | 4.71 | 36.25 |
| **7** | $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ | 66 | 187 | (593.43) | (36.39) | (3.03) | (4.71) | (35.21) |
| | | | | 590 | 36.61 | 3.05 | 4.74 | 35.42 |
| **8** | $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ | 77 | 196 | (597.88) | (34.12) | (2.50) | (4.68) | (34.95) |
| | | | | 594 | 34.12 | 2.52 | 4.71 | 35.17 |
| **9** | $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ | 75 | 204 | (609.98) | (37.37) | (3.11) | (4.59) | (34.26) |
| | | | | 606 | 37.62 | 3.13 | 4.62 | 34.48 |
| **10** | $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ | 82 | 218 | (623.98) | (38.46) | (3.84) | (4.48) | (33.49) |
| | | | | 620 | 38.7 | 3.87 | 4.51 | 33.70 |
| **11** | $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ | 87 | 222 | (639.98) | (37.50) | (3.28) | (4.37) | (32.65) |
| | | | | 636 | 37.73 | 3.30 | 4.40 | 32.85 |
| **12** | $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ | 86 | 201 | (644.43) | (35.31) | (2.79) | (4.34) | (32.42) |
| | | | | 640 | 35.62 | 2.81 | 4.37 | 32.65 |

$[C_{12}H_{15}N_2OX = 3(2'$-hydroxyphenyl)-5-(4-X-substitutedphenyl) pyrazoline; X = H in **1**,**5**,**9**; X = $CH_3$ in **2**,**6**,**10**; X = $OCH_3$ in **3**,**7**,**11**; X = Cl in **4**,**8**,**12**; $(C_6H_4O_3)$ = salicylate and $(CH_3COO)$ = carboxylate.



pressure from the filtrate giving a brown solid. The brown solid was further purified by crystallization from acetone and chloroform and dried in vacuum to get 1.5 g $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$. Compounds **5**–**12** were prepared by the same procedure.

$$(C_{15}H_{12}N_2OX)BiCl_2 + CH_3COONa \xrightarrow{\text{Dry acetone}} (C_{15}H_{12}N_2OX)BiCl(Ac) + NaCl$$

## 2.2. *Antimicrobial studies*

Agar disk diffusion was used for the screening of *in vitro* antimicrobial activity [29]. 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 into a sterile Petri dish (9 cm in diameter) to a depth of 5 mm. The medium was left to solidify before it was seeded with the respective test organisms. For seeding, 5 mL sterile water was added to agar slant culture of fungi. The culture was script 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. Thirty micrometer of each sample to be tested was dissolved in 1 mL of acetone. Disks (5 mm)

Table 2. Antimicrobial activity of $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$.

| | Zone of inhibition by bacteria (in mm) | | | | |
|---|---|---|---|---|---|
| Bacteria | $(C_{15}H_{12}N_2OX)$ | $(C_{15}H_{12}N_2OX)$ $Bi(C_7H_4O_3)$ | $(C_{15}H_{12}N_2OX)$ $BiCl(CH_3COO)$ | $(C_{15}H_{12}N_2OX)$ $Bi(CH_3COO)_2$ | *R* |
| *Staphylococcus aureus* | 15.00 | 32.00 | 28.00 | 21.00 | 24.00 |
| *Bacillus lichaniformis* | 14.00 | 34.00 | 29.00 | 18.00 | 25.00 |
| *Klebsiella pneumoniae* | 16.00 | 34.00 | 28.00 | 20.00 | 24.00 |
| *Vibrio* ssp. | 12.00 | 30.00 | 28.00 | 18.00 | 24.00 |
| *Pseudomonas aeruginosa* | 12.00 | 28.00 | 22.00 | 19.00 | 24.00 |
| *Escherichia coli* | 13.00 | 30.00 | 20.00 | 22.00 | 26.00 |

Table 3. Antifungal activity of $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$.

| | Zone inhibition by fungi (in mm) | | | | |
|---|---|---|---|---|---|
| Fungi | $(C_{15}H_{12}N_2OX)$ | $(C_{15}H_{12}N_2OX)$ $Bi(C_7H_4O_3)$ | $(C_{15}H_{12}N_2OX)$ $BiCl(CH_3COO)$ | $(C_{15}H_{12}N_2OX)$ $Bi(CH_3COO)_2$ | *R* |
| *Aspergillus niger* | 14.00 | 29.00 | 22.00 | 25.00 | 25.00 |
| *Penicillium notatum* | 15.00 | 28.00 | 21.00 | 22.00 | 24.00 |



of Whatman filter paper no. 40 were cut and sterilized and then immersed in solution of sample. After soaking, the disk was removed and left in a sterile Petri dish to permit the solvent to evaporate. After about 10 min the paper disks 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), afterward clear or inhibition zones were detected around each disk. A disk soaked in acetone alone was used as a control under the same conditions and no inhibition zone was observed. The diameter of each distinct inhibition zone was measured in millimeter, both antibacterial and antifungal activities were calculated as a mean of three replicates (tables 2 and 3).

## 3. Results and discussion

Complexes, $(C_{12}H_{15}N_2OX)Bi(C_6H_4O_3)$ (**1–4**), have been synthesized by the reaction of dichlorobismuth(III)pyrazolinates with sodium salts of salicylic acid in a 1 : 1 mole ratio. Acetate complexes of the type $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ (**5–8**) and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ (**9–12**) were synthesized by the reaction of dichlorobismuth(III)pyrazolinates with sodium acetate in 1 : 1 and 1 : 2 mole ratios at elevated temperature. Compounds **1–4** are dark brown solids, non-hygroscopic, stable at room temperature, and soluble in common organic solvents (benzene, chloroform, acetone and dimethylsulphoxide). The acetate mixed ligand complexes $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ are also brown solids, non-hygroscopic, stable at room temperature and soluble in benzene, acetone, chloroform and methanol, DMSO, and THF. The molecular weight measurements in dilute

Table 4. IR spectral data for $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$.

| No. | $\nu$(N–H) | $\nu$(C=N) | $\nu$(C–O) | $\nu_{sy}$(COO) | $\nu_{as}$(COO) | $\nu$(Bi–O) | $\nu$(Bi–N) |
|---|---|---|---|---|---|---|---|
| **1** | 3312 | 1624 | 1230 | 1340 | 1645 | 560 | 456 |
| **2** | 3320 | 1626 | 1228 | 1345 | 1657 | 562 | 460 |
| **3** | 3309 | 1618 | 1228 (1026) | 1344 | 1659 | 557 | 462 |
| **4** | 3312 | 1620 | 1222 | 1350 | 1654 | 556 | 461 |
| **5** | 3314 | 1626 | – | 1330 | 1658 | 568 | 428 |
| **6** | 3309 | 1618 | – | 1340 | 1648 | 570 | 440 |
| **7** | 3320 | 1624 | 1022 | 1345 | 1656 | 565 | 432 |
| **8** | 3316 | 1620 | – | 1342 | 1645 | 566 | 446 |
| **9** | 3311 | 1619 | – | 1339 | 1656 | 568 | 428 |
| **10** | 3316 | 1618 | – | 1340 | 1666 | 570 | 448 |
| **11** | 3320 | 1624 | 1026 | 1345 | 1657 | 565 | 432 |
| **12** | 3314 | 1626 | – | 1342 | 1658 | 566 | 440 |

chloroform at 45°C show the monomeric nature of these compounds. The elemental analysis (C, H, N) data (table 1) are in accord with the proposed stoichiometry.



### 3.1. *IR spectra*

Absorptions in IR spectra of $(C_{12}H_{15}N_2OX)Bi(C_6H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ (table 4) were assigned by comparisons with the spectra of starting materials and literature data [25, 26, 30–35]. All compounds showed strong absorptions at 3332–3320 $cm^{-1}$ due to –(N–H) stretching vibrations and at 1630–1606 $cm^{-1}$ due to –(C=N) stretching vibrations. The bands at 1230–1228 $cm^{-1}$ in **1**–**4** may be assigned to aromatic –(C–O) stretches and the band at 1026 $cm^{-1}$ in **3**, **7**, and **11** indicates the presence of $–OCH_3$. The signal due to –(O–H) originally present at ~3050 $cm^{-1}$ in free pyrazolines and the broad signal due to –(COOH) originally present at ~3150 $cm^{-1}$ in salicylic acid and the broad signal at 3245 $cm^{-1}$ in the carboxylate completely disappear from the spectra of the complexes. All compounds showed strong absorptions at 1666–1645 and 1345–1330 $cm^{-1}$. The –(C–O) bands shift to higher wavenumbers, indicating a single bond between each salicylate and carboxylate and bismuth, through one oxygen of COO. This correlates with the appearance of new bands at 562–557 $cm^{-1}$ assigned to Bi–O stretching vibrations. All compounds showed bands of medium intensity at 462–456 $cm^{-1}$ due to –(Bi–N) stretches. The appearance of these two new bands and the absence of hydroxyl and carboxylic bands suggest that the pyrazoline is a monobasic bidentate ligand, salicylate bidentate, and acetate monodentate.

### 3.2. *$^1$H and $^{13}$C NMR spectroscopy*

$^1$H data for **1**–**12** are listed in the "Supplementary material". The assignment of resonances was made by comparison with the spectra of previously reported chlorobismuth(III)dipyrazolinates and dichloroantimony(III)pyrazolinates [25, 26]. The aromatic protons were multiplets at 7.9–6.3 ppm. The integrated intensities of the resonances indicate the presence of 12 protons in **2**–**4**, **6**–**8**, and **10**–**12**. A peak

at 5.5–5.1 ppm as a broad singlet is assigned to N–H originally present at 5.4–5.0 ppm in chlorobismuth(III)dipyrazolinates suggesting the non-involvement of N–H in bonding to bismuth. The skeletal protons of the five-membered ring are observed as a triplet at 3.7–3.3 ppm and as a doublet at −2.5 to 2.0 ppm assigned to CH and $CH_2$, respectively. In **5**–**12**, the singlet at 3.9 ppm is assigned to $CH_3$.

The proton decoupled $^{13}C$ NMR spectra of **1**–**12** show all requisite signals by comparison to the spectra of dichlorobismuth(III)pyrazolinates (Supplementary Material). Assignments have been made on the basis of available data along with the spectra of the ligands. The signals observed at −133.8 to 122.6 ppm as multiplets are assigned to aromatic carbons. Signals between −164.8 to 166.9 ppm are due to the imino carbon of C=N. In all compounds signals due to the carbon of C=N are shifted downfield in comparison to the spectra of free pyrazolines (at −143.5 to 142.8 ppm) suggesting the involvement of imino nitrogen in coordination. All other signals were at comparable chemical shifts to those in free pyrazolines.



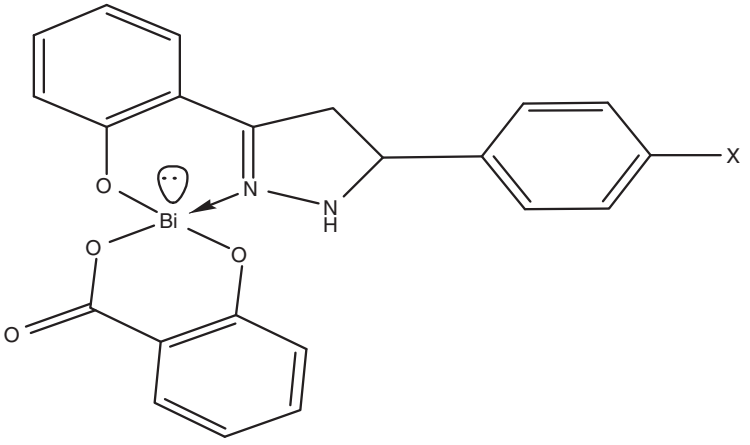


Figure 1. Proposed structure of $(C_{15}H_{12}N_2OX)Bi(C_6H_4O_3)$.

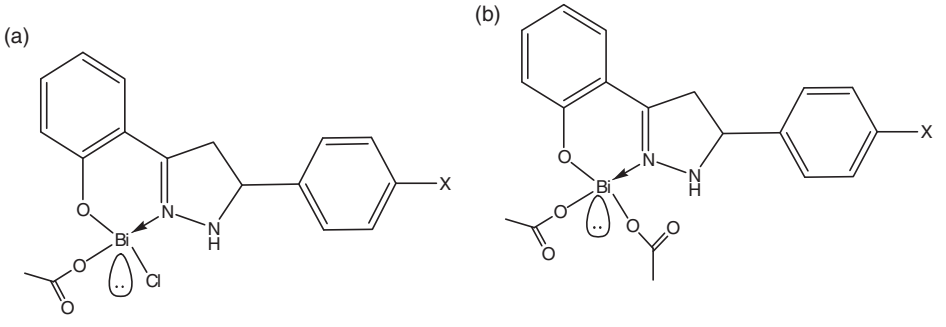


Figure 2. Proposed structure of (a) $(C_{15}H_{12}N_2OX)BiCl(CH_3COO)$ and (b) $(C_{15}H_{12}N_2OX)Bi(CH_3COO)_2$.

### 3.3. *Microbial assay*

The antibacterial activity of a free ligand and three $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ complexes were tested against *Staphylococcus aureus*, *Bacillus lichaniformis*, *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, and *Vibrio* spp. The antifungal activity was tested against *Aspergillus niger* and *Penicillium notatum*. The antimicrobial activity of some antibiotics were also tested and compared with free pyrazoline and mixed bismuth(III) complexes. The results are listed in table 2. Comparison of antimicrobial activities of free pyrazoline and its mixed ligand bismuth(III) complexes with known antibiotics exhibit the following results: $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$, $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$, and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ exhibit a comparable antibacterial effect toward *S. aureus*, *K. pneumoniae*, *B. lichaniformis* and comparable antifungal activity toward *A. niger* relative to free pyrazoline chloramphenicol and terbinafin.

The antimicrobial and antifungal data presented in tables 2 and 3 show that $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$ has greater antimicrobial activity compared to $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$. It appears that when Cl is replaced by a second acetate group, there is no significant change in the antimicrobial activity. Therefore, we conclude that the antimicrobial activity of $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$ is due to the pyrazoline and salicylate. Since bismuth salicylate (sub salicylate) is also a potential antimicrobial agent, the observation that $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$ shows greater activity as compared to free pyrazoline as well as $(CH_3COO)BiCl(C_{15}H_{12}N_2OX)$ and $(CH_3COO)_2Bi(C_{15}H_{12}N_2OX)$ is not surprising. The latter also have greater activity compared to antibiotics such as chloramphenicol, tetracycline, and antifungal agent terbinafin.



## 4. Conclusions

The bidentate coordination of pyrazoline and salicylate and the monodentate behavior of acetate in $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$, $(C_{15}H_{12}N_2OX)BiCl(Ac)$, and $(C_{15}H_{12}N_2OX)Bi(Ac)_2$ complexes have been confirmed by IR, $^1H$ NMR, and $^{13}C$ NMR data (figures 1 and 2). The salicylate is bidentate in **1**–**4** while acetate is monodentate in **5**–**12**. In all 12 complexes the bismuth(III) appears to be four-coordinate with the most plausible geometry around bismuth being distorted trigonal pyramidal [33–35]. $(C_{15}H_{12}N_2OX)Bi(C_7H_4O_3)$ show greater activity compared to free pyrazoline, $(C_{15}H_{12}N_2OX)BiCl(Ac)$, and $(C_{15}H_{12}N_2OX)Bi(Ac)_2$ as antimicrobial and antifungal agents. These complexes also show greater activity compared to chloramphenicol, tetracycline, and the antifungal agent terbinafin.

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