



Synthesis, Characterization and Antimicrobial Activity of Cobalt (II) and Nickel(II) Complexes of 5-Bromo-1,3-Benzodioxole-4-Carbaldehyde Thiosemicarbazone

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Abstract: The aim of the present work is to synthesize the ligand with sulfur and nitrogen as donor atoms and its complexes with (M^{+2}) metal ions, characterize them and check their microbial activity. 5-bromo-1,3-Benzodioxole-4-carbaldehyde was prepared by reacting of equimolar amounts of thiosemicarbazide with the 5-bromo-1,3-Benzodioxole-4-carbaldehyde. The synthesized ligand was reacted with metal ions namely, Cobalt(II) and Nickel(II), stable complexes were obtained. The synthesized ligand and its complexes were subjected to partial elemental analyses, and infra-red spectra, proton nuclear magnetic resonance, electronic spectra, and mass spectral of ligand was studied. Magnetic susceptibility measurements were studied. Infrared spectra of the ligand appeared the band at ν (1529 cm^{-1}) attributed to $\nu(\text{HC}=\text{N})$ and in all complexes these band shifted to ($1440\text{-}15415\text{ cm}^{-1}$) to elucidate the coordinate ion of the azomethine nitrogen $\nu(\text{HC}=\text{N})$ to metal ions. ^1H NMR spectrum appear signal protons at δ (8.75 ppm) to indicate $^1\text{H}(\text{HC}=\text{N})$ for the ligand. Magnetic susceptibility measurements for the Cobalt (II) and Nickel(II) complexes were found 3.59, 3.08 M.B respectively in the normal range of the octahedral geometry. The results of electronic absorption spectra in dimethylsulfoxide 10^{-3} M indicate the transition of ligand to metal charge transfer. On partial elemental analysis, the ligand coordinate to metal ion by 2:1(ligand -Metal) molar ratio. The conductivity measurements revealed that metal chelates are non-electrolytes in (10^{-3} M) DMSO. The free ligand and its metal complexes were checked in vitro against a number of microorganisms, to evaluate their antimicrobial activity by disk diffusion method. Antimicrobial screening of the complexes against *Bacillus subtilis* NCTC 8236(G+), *Staphylococcus aureus* ATCC 25923(G+), *Escherichia coli* ATCC 25922(G-) and *Pseudomonas aeruginosa* ATCC 2785(G-) Bacteria and *Candida albicans* ATCC 7596 fungus showed higher activity. The studied compounds are higher biologically active.

Keywords: Preparation, Antimicrobial activity, Structural characterization, Co(II) and Ni(II) complexes, Carbothiomide derivative, Bidentate ligand

I. Introduction

Thiosemicarbazones have been a subject of interest to researchers of different profiles. In view of the fact that these compounds form complexes with many metals and diverse chemical, physical and structural characteristics, they are of special interest to coordination chemists [1]. Sulfur containing ligands such as thiosemicarbazones and their transition metal complexes have received more attention in the area of medicinal chemistry, due to their pharmacological properties, such as antiviral [2], antibacterial [3,4], antifungal [5], antiparasitic [6], and antitumor activities [7]. Thiosemicarbazones have received great interest because of their bonding modes, biological implications, structural diversity, and ion-sensing ability [8,9]. Thiosemicarbazone compounds are also applicable in fields of inorganic chemistry. Moreover, metal complexes of thiosemicarbazones often display enhanced activities when compared to the uncomplexed thiosemicarbazones.

In this manuscript, the preparation and characterization of 5-bromo-1,3-Benzodioxole-4-carbaldehyde and its cobalt (II) and nickel (II) complexes were carried out. The obtained compounds were subjected to different analytical techniques, such as elemental analysis, IR, UV-Vis, ^1H NMR spectra, magnetic susceptibility measurements. Antimicrobial activities of the synthesized ligand and its cobalt (II) and nickel (II) complexes were also investigated.

II. Experimental

Materials

Organic solvents (absolute Ethanol (Schar Lab.S.L, Spain), Dimethylformamide (DMF), (LAB TECH Chemicals, Avishkar reagents), Dimethylsulfoxide A.R.(DMSO), (Sd FINE-CHEM LIMITED, SDFCL, India), Acetonitrile HPLC grade (Scharlau). Were used without purification. CoCl_2 (anhydrous) 97% (Sigma Aldrich, USA), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (BURGOYNE, India), Thiosemicarbazide 99% (Sigma Aldrich, USA), 5-bromo-1, 3-Benzodioxole-4-carboxaldehyde 96% (Sigma Aldrich), Ammonia Solution, (Analar, England), Glacial acetic acid, (LOBA Chemie and Fine Chemicals, India). All chemicals were commercially obtained in their purest form and were used without further purification.

Instrumentations

Infrared spectra of the synthesized ligand and its complexes were recorded on Shimadzu model FT-IR.8400S spectrometer in the wave number region $(400\text{--}4000)\text{ cm}^{-1}$. Elemental analysis of the ligand and its complexes were recorded on HEKA. Mass spectra of the solid samples were recorded as KBr pellets. Mass spectra were recorded on Agilent, model 6420 Triple quad. Proton nuclear magnetic resonance spectra of ligand were recorded on Shimadzu, Advance III 400MHz the spectra were run at 400 MHz in deuterated dimethyl sulfoxide (DMSO-d_6). Chemical shifts are quoted in δ and were related to that of the solvent. The UV-Vis electronic absorption spectra of the complexes in dimethyl sulfoxide (10^{-3}M) solution were recorded using Shimadzu model 3101pc spectrophotometer. The electrical conductivity was measured using Conductivity. The magnetic susceptibility was measured on powdered samples using Sherwood Scientific Magnetic Susceptibility balance.

Synthesis of the ligand 5-bromo-1,3-Benzodioxole-4-carbaldehyde.

To a 250 mL round bottomed flask containing 0.916 g (0.004 mol) of 5-bromo-1, 3-benzodioxole-4-carbaldehyde. About 30 mL of absolute ethanol was added, then heated until the dissolution was completed. To this solution 0.365g (0.004mol) of thiosemicarbazide dissolved in about 30 mL of hot absolute ethanol was added, followed by addition dropwise of glacial acetic acid. The content was then refluxed on water bath for about 2 hours. Pale yellow crystals were filtered off and washed with ethanol and left to dry in air. The product was recrystallized from ethanol and weighed. The melting point of the product was obtained using melting point apparatus (Scheme 1) [10].

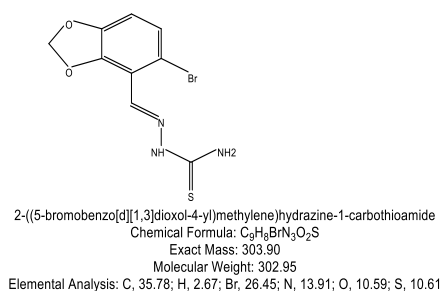


Figure 1. 5-bromo-1,3-Benzodioxole-4-carbaldehyde

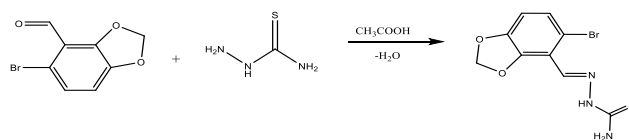
Color: Pale yellow

Yield: 88.27%.

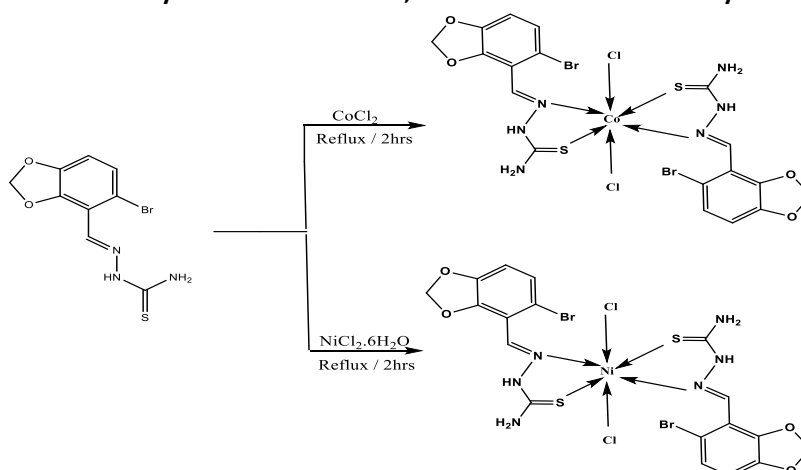
M.p: 256-260 °C.

FT-IR (KBr, ν , cm^{-1}): 3411- 3253 (NH_2), 3151 (NH), 2977 (CH), 1529 ($\text{C}=\text{N}$), 838 ($\text{C}=\text{S}$).

^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 11.76 (s, 1H, NHCS), 8.46 (s, 1H, $\text{CH}=\text{N}$), 7.16-7.23 (s, 2H, NH_2), 6.91-6.89 (s, C_6H_6).



Scheme 1. Synthesis of 5-bromo-1,3-Benzodioxole-4-carbaldehyde



Scheme 2. Synthesis of 5-bromo-1,3-Benzodioxole-4-carbaldehyde with cobalt(II) and nickel(II) complexes.

Synthesis of $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$ and $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ complexes

A 100 mL round bottom flask (RBF), 0.0004 mol each of $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$ and $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$ 0.026 g (0.0002 mol) and 0.055g (0.0002 mol) respectively were dissolved in 30mL warm absolute ethanol slowly added, with stirring to a solution containing 0.121g (0.0004 mol) of 5-bromo-1,3-benzodioxole-4-carbaldehyde thiosemicarbazone, dissolved in about 30 mL of dimethyleformamide, then dropwise of ammonia solution were added to the mixture. The mixture was refluxed for two hours. After evaporation of the solvent, the pale black precipitate separated out, washed with cold ethanol and left to dry in air and weighed.

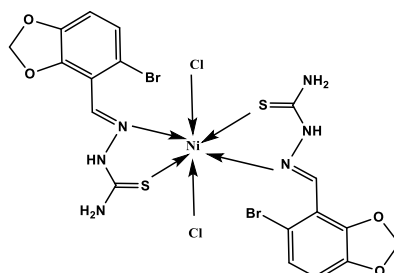
Colour: Pale black

Yield: 76.27%.

M.p: 198-202 °C.

FT-IR (KBr, ν , cm^{-1}): 3130 (NH), 1440 cm^{-1} (C=N), 806 (C=S), 543-565 ν (M-N), 462-499 ν (M-S).

Figure 2. Suggested structure of $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$



Chemical formula: $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$
 Elemental analysis: C, 25.68 H, 2.00 N, 9.98

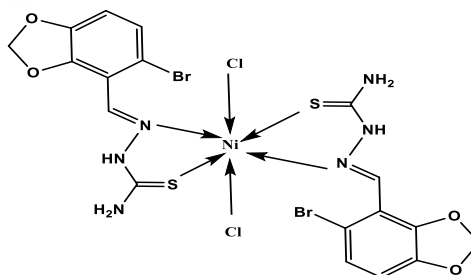
Color: Pale black.

Yield: 73.45%.

M.p: 217-220°C.

FT-IR (KBr, ν , cm^{-1}): 3151 (NH), 1541(C=N), 792 (C=S), 503-516 ν (M-N), 418-445 ν (M-S).

Figure3. Suggested structure of $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$.



Chemical formula: $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$
 Elemental analysis: C, 25.68 H, 2.00 N, 9.98

Antimicrobial activity

The synthesized ligand and its metal compounds were checked for their antimicrobial activities at National Center for Research, Medicinal and Aromatic Plants Research Institute, Ministry of Higher Education and Scientific Research, Khartoum, Sudan. The antimicrobial activity of the compounds was studied by disc diffusion method against certain pathogenic organisms, and performed by using Mueller Hinton agar (MHA). The experiment was carried out according to the National Committee for Clinical Laboratory Standards Guidelines (NCCLS, 1999). Bacterial suspension was diluted with sterile physiological solution to 108cfu/ ml (turbidity = McFarland standard 0.5). One hundred microliters of bacterial suspension were swabbed uniformly on surface of MHA and the inoculum was allowed to dry for 5 minutes. Sterilized filter paper discs (Whatman No.1, 6 mm in diameter) were placed on the surface of the MHA and soaked with 20 μl of a solution of each compound .The inoculated plates were incubated at 37 ° C for 24h, in the inverted position. The diameters (mm) of the inhibition zones were measured. The antibacterial activity of synthesized compounds (20 mg/ml using DMSO as a solvent) was studied against gram positive bacteria namely Staphylococcus aureus ATCC 25923 and Bacillus cereus NCTC 8236. The gram negative bacterial screened were Escherichia coli ATCC 25922 and Pseudomonas aeruginosa ATCC 27853. Ciprofloxacin, 40 mg/ml and Erythromycin 40 mg/ml were used as standard for assessing the antibacterial studies. The fungus was grown on subouraud dextrose agar (Hi media) plates. The inoculated plates were incubated at 26°C for 72-96 hr. The antifungal activity of synthesized compounds (20 mg/ml using DMSO as solvent) was studied against Candida albicans ATCC 7596. Ketaconazole

40 mg/ml and Itraconazole 40 mg/ml were used as standard for assessing the antifungal studies. The antibacterial and antifungal activity results were expressed in term of the diameter of zone of inhibition and < 9 mm zone was considered as inactive; 9-12 mm as partially active; while 13-18 mm as active and > 18 mm as very active [12].

Antifungal activity

The antifungal activity of the synthesized ligand and its Cobalt(II) and Nickel(II) compounds were checked against *Candida albicans* (ATCC7596) by serial dilution method. Potato-dextrose agar (PDA) was used to evaluate the effect of the compound under investigation on the mycelia linear growth of the tested fungi. Fifty milliliters of the medium were poured into 100 mL conical flask and autoclaved at 121°C for 20 minutes. Three drops of lactic acid were added to prevent bacterial contamination. Dilutions for each of the checked compounds were done by dissolving appropriate amounts of each compound in 10 mL. Equal volumes of dimethylsulfoxide containing diluted compounds were added to PDA to get series of different concentrations for each compound. Zero concentration treatment was prepared for fungus which contains equivalent volume of DMSO only and used as control. Compounds amended PDA was dispensed aseptically into 9 cm diameter petri dish, plugs of mycelium were cut from the margins of actively growing culture of the fungus and placed in the center of compound amended and unamended PDA plates with four replicate plates for each fungus. All plates were incubated at 25 °C. Colony diameters (in mm) was measured after three days. The growth inhibition percentage diameter was calculated on the basis of the average diameter of the fungal colony, percentage inhibition is equal to $\left(\frac{C-T}{C}\right) \times 100$ where C is the diameter of the fungus colony in the control plate after three days and T is the diameter of the fungus colony in the tested plates after the same period of time [13].

III. Results and discussion

The mass spectra data of the ligand in figure 1. shows molecular ion (M⁺) peak at m/z = 303.90 a.m.u corresponding to the species $[C_9H_8N_3O_2SBr]^+$, this identify with empirical formulae. Infrared spectral data of the ligand demonstrate bands at 3411 cm⁻¹ and 3253 cm⁻¹ which are assignable to ν (NH₂). The band at 3151 cm⁻¹ is assigned to ν (N-H). The band at 2977 cm⁻¹ corresponds to ν (CH). The band at 1529 cm⁻¹ corresponds to ν (C=N) [14]. The strong absorption band at 838 cm⁻¹ is attributed to ν (C=S) [15].

The ¹H NMR spectrum of the ligand shows proton signal at δ 11.75 ppm is attributed to the (1H, NHCS), the signal at δ 8.45 ppm for (1H, CH=N) and The peaks at δ (7.16 and 7.23) ppm due to (2H, NH₂). Whereas the proton signals for benzene ring are at peaks δ (6.91 and 6.89) ppm.

The infrared spectral data of $[Co(C_9H_8N_3O_2SBr)_2(Cl)_2]$, complex reported sharp band at 1529 cm⁻¹ assigned to (C=N) in the free ligand, is shifted to 1440 cm⁻¹ in the $[Co(C_9H_8N_3O_2SBr)_2(Cl)_2]$, complex, after coordination. This result indicates the coordination of the azomethine nitrogen to the Co(II) ion [16]. The (Co-N) bond was detected by appearance of frequencies in the region 543-565 cm⁻¹. Furthermore, in the free ligand the ν (C=S) vibration observed at 838 cm⁻¹ is shifted to 806 cm⁻¹ upon complexation, indicating the involvement of the thione sulphur in the bond formation to the Co(II) ion [17]. This is confirmed by the presence of new bands at 462-499 cm⁻¹ which can be assigned to ν (Co-S) bond [18]. From the IR spectral data, the $[Co(C_9H_8N_3O_2SBr)_2(Cl)_2]$ complex showed the bands in the region 640 cm⁻¹ and 655 cm⁻¹ not originally found in the spectrum of the free ligand confirming the presence of chloride ion. The band at 3130 cm⁻¹ is described to the ν (NH) vibration in the $[Co(C_9H_8N_3O_2SBr)_2Cl_2]$ complex. The appearance of this band is an indication that bonding is through the sulfur atom, and not through the NH [19]. The band at 3411 cm⁻¹ in the free ligand due to ν (NH₂) [20]. This band is disappearance on complexation.

The diffuse reflectance spectrum of $[Co(C_9H_8N_3O_2SBr)_2Cl_2]$ complex shows bands at 29940 cm⁻¹ (334 nm), 36496 cm⁻¹ (274 nm), 38314 cm⁻¹ (261 nm) and 41493 cm⁻¹ (241 nm). While in DMSO solution, it shows bands at 24752 cm⁻¹ (404 nm), 25575 cm⁻¹ (391 nm), 29239 cm⁻¹ (342 nm), 34482 cm⁻¹ (290 nm) and 39062 cm⁻¹ (256 nm).

The electronic spectrum of $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ complex consists of bands in the region 334-391 nm is assigned to $n \rightarrow \pi^*$ intraligand transitions [21]. The absorption bands at 404 nm in the spectrum of $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ complex can be attributed to ligand-metal charge transfer this is in agreement with that reported by reference [22].

The magnetic moment value for the $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ complex is 3.59 B.M, corresponds to three unpaired electrons. The molar conductance value of the $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ complex is $30.30 \text{ S}\mu\text{cm}^{-1}$ indicates that this complex is non- electrolyte in nature this result is in agreement with pervious reported studies [23]. Based on conductivity data, together with spectral studies, for the $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ complex with the ligand suggested having an octahedral geometry [24]. In the IR spectrum of $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ complex with the ligand. These complex showed absorption band at 1529 cm^{-1} assigned to $\nu(\text{C}=\text{N})$ in the free ligand is shifted to 1541 cm^{-1} in the complex $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$, after coordination. This result denotes the coordination of the azomethine nitrogen to the Ni(II) ion [16]. The $\nu(\text{Ni}-\text{N})$ bond is detected by appearance of frequencies in the region $503-516 \text{ cm}^{-1}$. thus, in free ligand the $\nu(\text{C}=\text{S})$ vibration observed at 838 cm^{-1} is shifted to 792 cm^{-1} upon complexation, indicating the involvement of the thione Sulphur in the bond formation to the Ni(II) ion [14]. This is confirmed by the presence of new bands at $418-445 \text{ cm}^{-1}$ which can be assigned to $\nu(\text{Ni}-\text{S})$ bond [18]. The band at 3151 cm^{-1} observed in the spectrum of the free ligand is ascribed to the $\nu(\text{NH})$ vibration, this band remained unaltered on complexation 3151 cm^{-1} in the Ni(II) complex.

The reflectance electronic spectra data of $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$, complex shows bands at 30395 cm^{-1} (329 nm), 31948 cm^{-1} (313 nm), 36496 cm^{-1} (274 nm), 37735 cm^{-1} (265 nm), 39062 cm^{-1} (256 nm) and 41493 cm^{-1} (241 nm). While in DMSO solution shows bands at 30395 cm^{-1} (329 nm) and 39062 cm^{-1} (256 nm). The electronic spectrum of $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ complex consists of bands in the region 313- 329 nm is assigned to $n \rightarrow \pi^*$ intraligand transitions [21]. The magnetic moment value for the $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ complex is 3.08 B.M. The molar conductance of the complex is $(17.82 \text{ S}\mu\text{cm}^{-1})$. This value indicates that this complex is non- electrolyte in nature [25].

The results of elemental analysis in figures (1,2 and 3) shows all the synthesized ligand and its cobalt (II) and nickel (II) complexes were in good agreement with their structure. All findings found % in agreed with the outcome (calculated %).

Antibacterial activity of the ligand 5-bromo-1,3-Benzodioxole-4-carbaldehyde and its complexes

In vitro antibacterial activity of the free ligand 5-bromo-1,3-Benzodioxole-4-carbaldehyde thiosemicarbazone and its $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ and $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ complexes were carried out using the culture of *Bacillus subtilis* NCTC 8236, *Staphylococcus aureus* as gram positive bacteria and *Escherichia Coli* *Pseudomonas aeruginosa*, as gram negative bacteria. The test was done using the disk diffusion technique. Ciprofloxacin (a) and Erythromycin (b) were used as standard drugs, and dimethyleformamide was used as negative control. The diameters of the inhibition zones for all tested compounds are presented in table (1). Where, the activities of compounds were compared with Ciprofloxacin (a) and Erythromycin (b) as antibacterial standards, the ligand 5-bromo-1,3-Benzodioxole-4-carbaldehyde shows more antibacterial activity against *Bacillus subtilis* (G (+) bacteria), *Escherichia coli* (G (-) bacteria) and *Pseudomonas aeruginosa* than Erythromycin (b) standard, but less than Ciprofloxacin (a) (Table 1). It's also shows less activity against *Staphylococcus aureus* (G (+) bacteria) than Erythromycin (b) standard.

The $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ complex shows high activity against *Escherichia coli* and *Pseudomonas aeruginosa* than Erythromycin (b), but less than Ciprofloxacin (a). It's also shows less activity against *Staphylococcus aureus* ATCC 25923 than Erythromycin (b) standard; on the flip side, the $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ complex shows equal activity against *Bacillus subtilis* to the standard Erythromycin (b). The $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ shows more antibacterial potency against all organisms than Erythromycin (b) standard, and more activity against

Escherichia coli and *Staphylococcus aureus* than Ciprofloxacin (a) standard. It's also shows less activity against *Pseudomonas aeruginosa* than Ciprofloxacin (a) standard.

A comparative study of the ligand 5-bromo-1,3-Benzodioxole-4-carbaldehyde and its $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ and $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ complexes as antibacterial activity indicates that the complexes exhibit more inhibitory effect than the parent ligand 5-bromo-1,3-Benzodioxole-4-carbaldehyde. The reason why for this difference might be due to chelation which reduces the polarity of the central metal atom because of the partial sharing of its partial positive charge with donor groups and possible Π -electron delocalization within the whole chelating ring. As a result of this, the lipophilic nature of the central metal atom increases, which favours the permeation of the complexes through the lipid layer of the cell membrane [26].

Antifungal activity of the ligand 5-bromo-1,3-Benzodioxole-4-carbaldehyde and its complexes

The synthesized ligand and its complexes were checked *in vitro* against *Candida albicans*, [28]. Table 2 reported below. the activities of compounds were compared with Ketoconazole (a) and Itraconazole (b) as antifungal standards, the results showed that the ligand exhibit zero antifungal activity. The compounds $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ and $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ are partially active against the tested fungus, but less than Ketoconazole (a) and Itraconazole (b) standards. Investigation of antifungal activity data indicates that the $[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$ and $[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ complexes are more active than free ligand. However, the ligand and its compounds exhibit more inhibitory effect against the selected bacteria species rather than *Candida albicans* fungus.

Table 1. the results of antibacterial activity of the synthesized ligand and its complexes.

Sample	Inhibition zone diameter in (mm)											
	Gram-positive bacteria						Gram-negative bacteria					
	<i>B. subtilis</i>			<i>S. aureus</i>			<i>E. coli</i>			<i>P. aeruginosa</i>		
	5 mg/mL	10 mg/mL	20 mg/mL	5 mg/mL	10 mg/mL	20 mg/mL	5 mg/mL	10 mg/mL	20 mg/mL	5 mg/mL	10 mg/mL	20 mg/mL
DMSO (Control)	0	0	0	0	0	0	0	0	0	0	0	0
Ciprofloxacin (Standard)	18	20	22	15	16	17	12	13	13	15	18	20
Erythromycin (Standard)	8	10	11	14	17	19	7	8	10	10	12	13
$\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr}$	10	11	12	7	10	11	12	13	15	12	13	14
$[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$	9	10	11	11	14	15	12	15	16	13	15	16
$[\text{Ni}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$	10	20	25	20	20	28	13	14	15	14	15	16

Table 2. the results of antifungal activity of the synthesized ligand and it is complexes.

Sample	Inhibition zone diameter in (mm)		
	<i>Candida albicans</i>		
	5 mg/mL	10 mg/mL	20 mg/mL
DMSO (Control)	0	0	0
Ketoconazole (Standard) (a)	14	15	16
Itraconazole (Standard) (b)	12	14	15
$\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr}$	0.0	0.0	0.0
$[\text{Co}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2]$	0.0	8	10

IV. Conclusion

In conclusion, this study reports a new ligand, 5-bromo-1, 3-benzodioxole-4-carbaldehyde and thiosemicarbazide and two stable colored metals complexes were synthesized from the reaction between the prepared ligand and metal ions namely, Co(II) and Ni(II). The ligand was characterized by using different spectroscopic analytical techniques such as MS, IR, and 1H NMR spectra and elemental analysis whereas, the complexes were subjected to infrared spectra, elemental analysis in addition to UV-Vis. As well as *in vitro* antimicrobial activity of the ligand and its complexes were also checked. Higher antibacterial and antifungal activities were observed in the metals complexes compared to that of the free ligand.

V. Acknowledgments

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Supporting information

In the text (experimental and preparation methods) and supplementary section.

CRediT authorship contribution statement

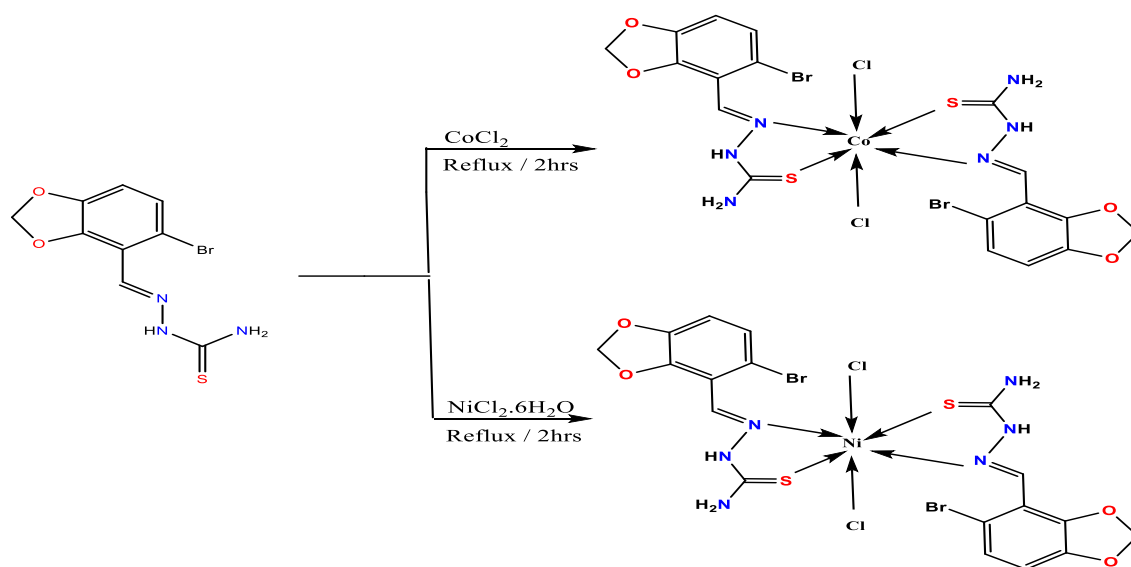
Conceptualization, Awad Salim Ibrahim and Abdalla Gobara Habieballa.; methodology, Abdalla Gobara Habieballa; software, Awad Salim Ibrahim and Mohammed Bahreldin Hussein.; validation, Awad Salim Ibrahim, and Abdalla Gobara Habieballa; formal analysis, Slaheldeen Homida Ahamed Abdrazig, investigation, Awad Salim Ibrahim and Mohammed Bahreldin Hussein; writing—original draft preparation, Awad Salim Ibrahim and Mohammed Bahreldin Hussein; writing—review and editing, Abdalla Gobara Habieballa. and Slaheldeen Homida Ahamed Abdrazig; visualization, Abdalla Gobara Habieballa and Awad Salim Ibrahim; supervision, Awad Salim Ibrahim.; project administration, Awad Salim Ibrahim.; Funding acquisition

VI. References

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Graphical Abstract



Supplementary Materials section

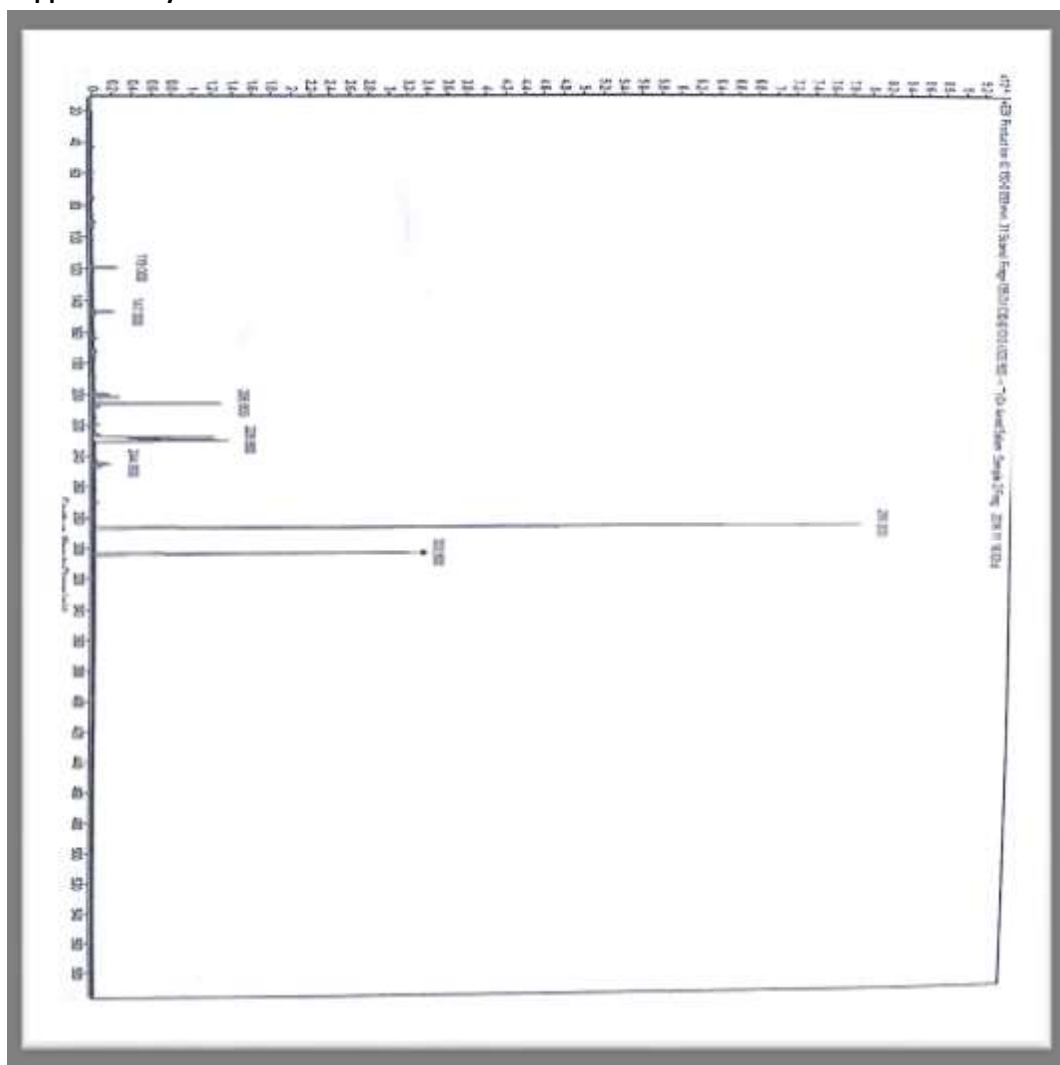


Figure 1. Mass spectrum of compound **2-((5-bromobenzo[d][1,3]dioxol-4-yl)methylene)hydrazine-1-carbothioamide**

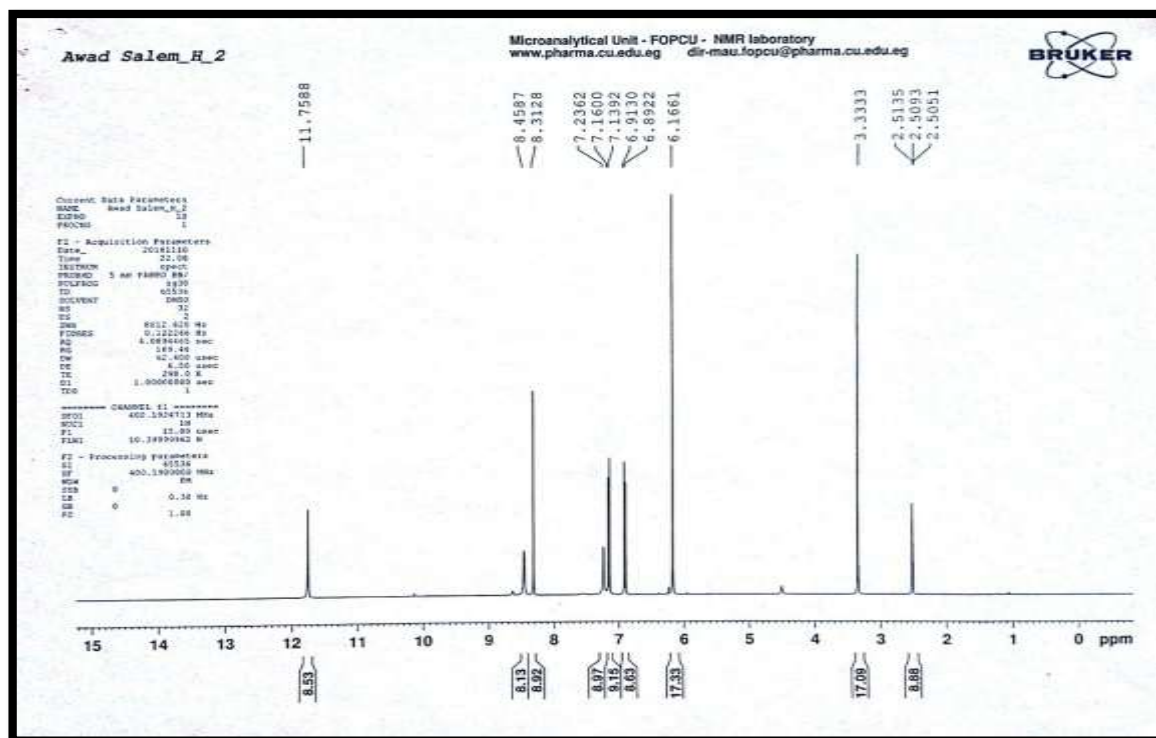


Figure 2. ^1H NMR spectrum of the ligand **2-((5-bromobenzo[d][1,3]dioxol-4-yl)methylene)hydrazine-1-carbothioamide**

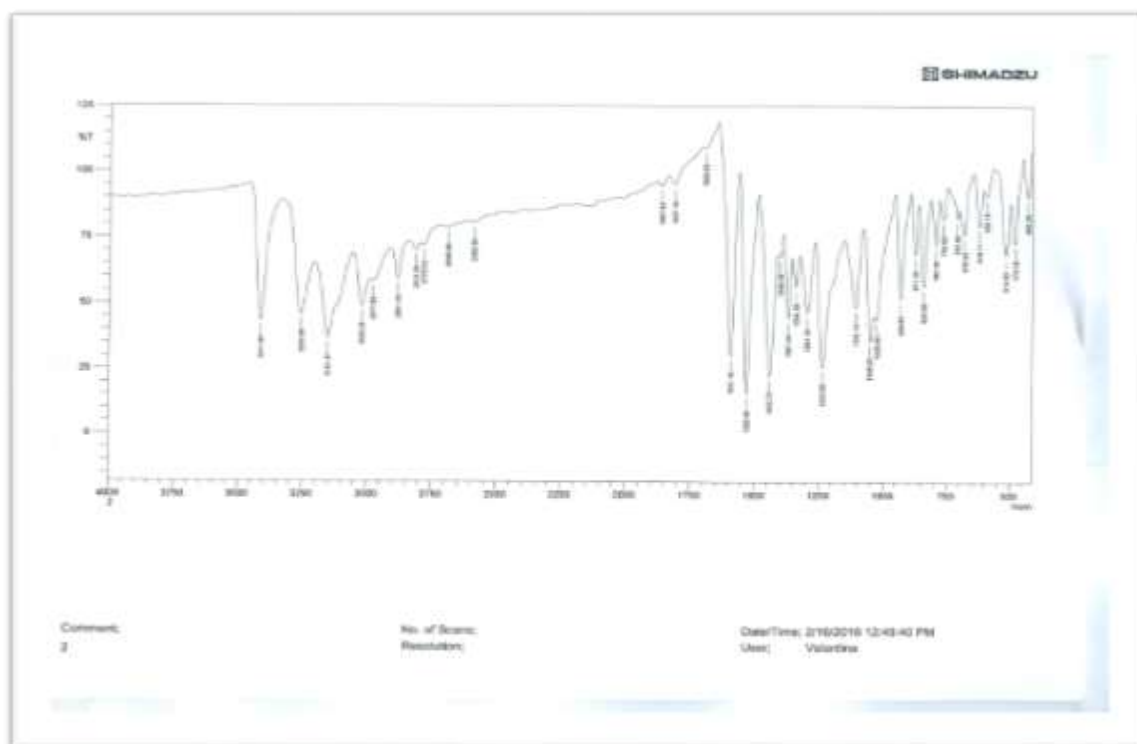


Figure 3. IR spectrum of the ligand **2-((5-bromobenzo[d][1,3]dioxol-4-yl)methylene)hydrazine-1-carbothioamid**

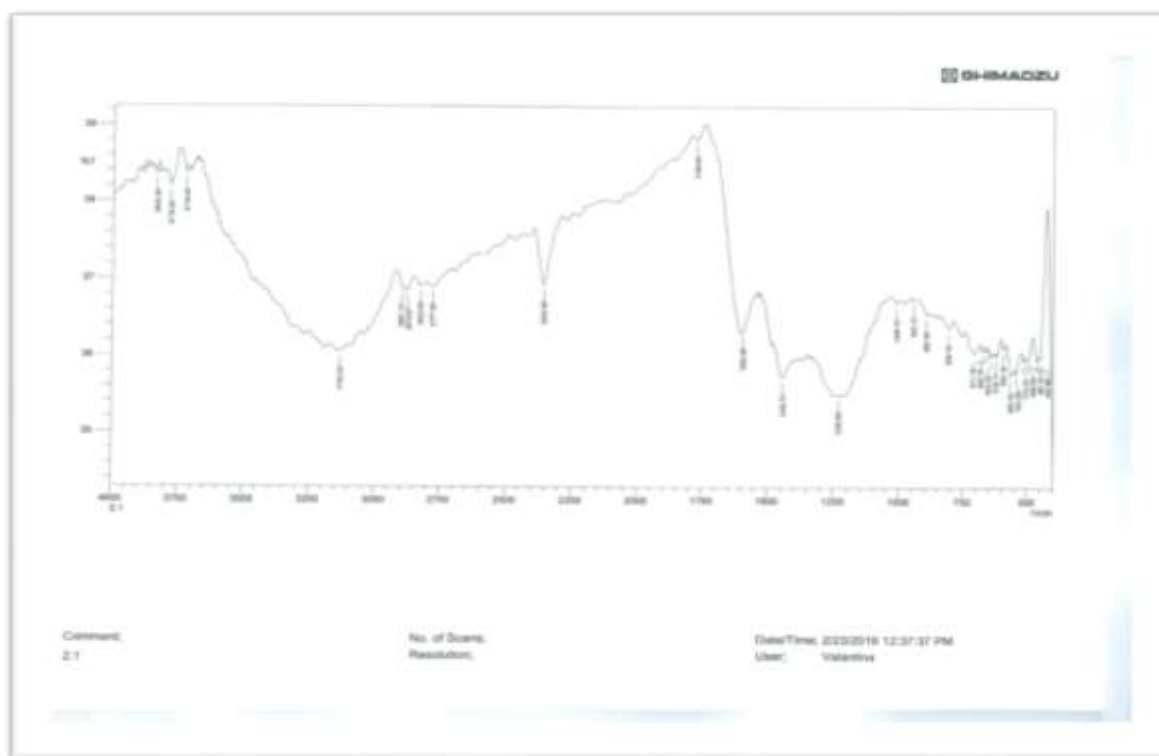


Figure 4. IR spectrum of the $[Co(C_9H_8N_3O_2SBr)_2]Cl_2$

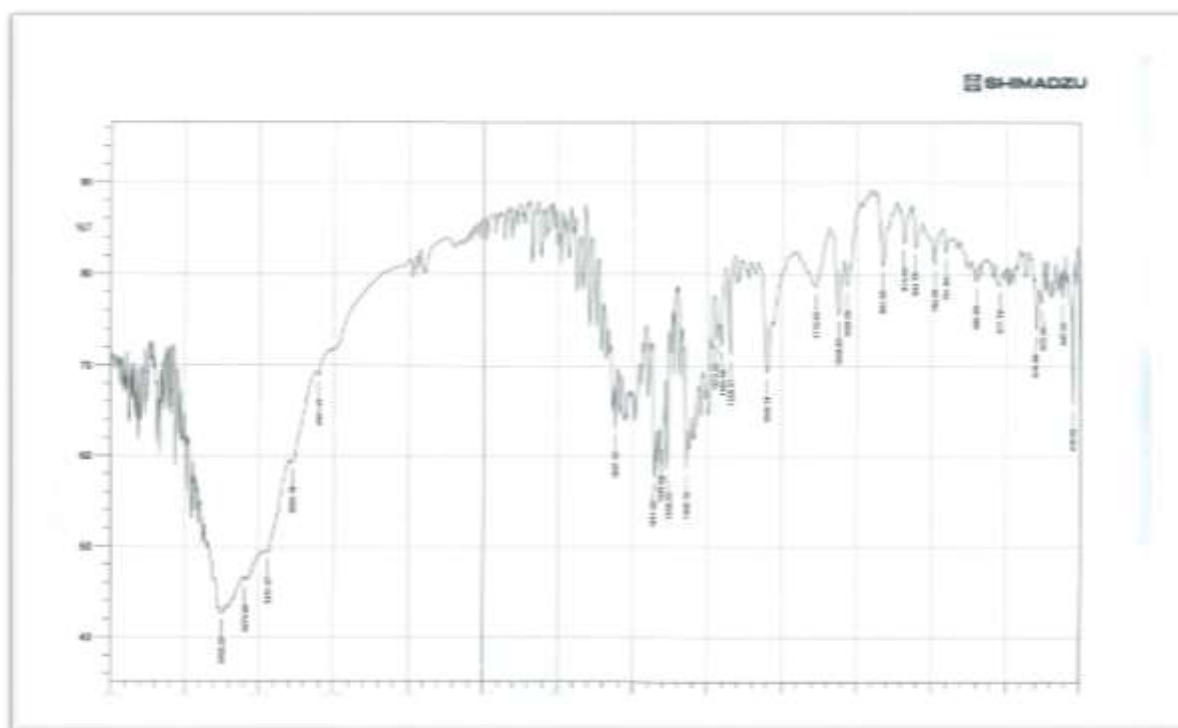


Figure 5. IR spectrum of the $[Ni(C_9H_8N_3O_2SBr)_2](Cl)_2 \cdot 6H_2O$.