



SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF COPPER (II) AND PALLADIUM (II) COMPLEXES OF 2-((5-BROMOBENZO [D][1,3]-DIOXOL-4-YL) METHYLENE) HYDRAZINE-1-CARBOTHIOAMIDE

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ABSTRACT

Equimolar amounts of 5-bromo-1,3-benzodioxole-4-carbaldehyde and thiosemicarbazide were combined together and the 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide was prepared as a new bidentate complexing agent. The synthesized ligand was reacted with Copper (II) and Palladium (II) ions yielding air stable complexes. For quantification and characterization purposes; infrared spectra, electronic spectra, proton nuclear magnetic resonance spectra and mass spectral studies were carried out on the obtained ligand and its metal complexes. Thermo gravimetric analysis and magnetic susceptibility measurements were also used for characterization of metal complexes. The IR spectrum showed that the ligand acts as a bidentate coordinates to the metal ions through the nitrogen and Sulfur atoms. Measurements of magnetic susceptibility for Copper (II) and Palladium (II) complexes were found to be 2.59 and 0.0 B.M respectively, suggested the octahedral and square planar geometry respectively. The conductivity measurements revealed that the chelates are non-electrolytes and electrolytes respectively. An *in vitro* antimicrobial investigation was also carried out for the free ligand and its metal complexes against bacterial and fungal strains, to assess their antimicrobial properties by disc diffusion method. Antimicrobial activity of the prepared complexes showed higher activity than the free ligand.

Keywords: Preparation, 5-bromo-1,3-Benzodioxole-4-carboxaldehyde, thiosemicarbazone, Bidentate ligand, Antifungal activity, Antibacterial activity.

1. INTRODUCTION

The syntheses of transition metal complexes with thiosemicarbazone ligands have been receiving considerable attention due to the pharmacological properties of both ligands and complexes [1-3]. Also the Chemistry of Thiosemicarbazone has received considerable attention because of their variable bonding modes, promising biological implications, structural diversity, and ion-sensing ability [4-6]. The ligand based on semicarbazone and pyridoxal moieties (forms found in vitamin B6), has an enormous potential as a biologically active reagent as it has been demonstrated that transition metal complexes incorporating thiosemicarbazone and semicarbazones show biological activity. In particular, with regard to biological importance, nickel(II) complexes with thiosemicarbazone and semicarbazone ligands

show antibacterial activity [7], and copper(II) complexes containing semicarbazones have also displayed biological properties [8-11]. Additionally, several nickel(II) complexes with octadien thiosemicarbazone and semicarbazones exhibit strong inhibitory activity against *Staphylococcus aureus* and *Escherichia coli* [12]. In vitro anticancer studies of several nickel (II) complexes with naphthoquinone semicarbazone and thiosemicarbazone on MCF-7 human breast cancer cells reveal that semicarbazone derivative with nickel(II) complexes is more actively inhibiting cell proliferation than thiosemicarbazone analogues [13]. The present work is related to synthesized and characterization of Cu (II) and Pd (II) complexes of 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide. These compounds were screened antibacterial, and antifungal properties.

2. EXPERIMENTAL

2.1. Materials and measurements

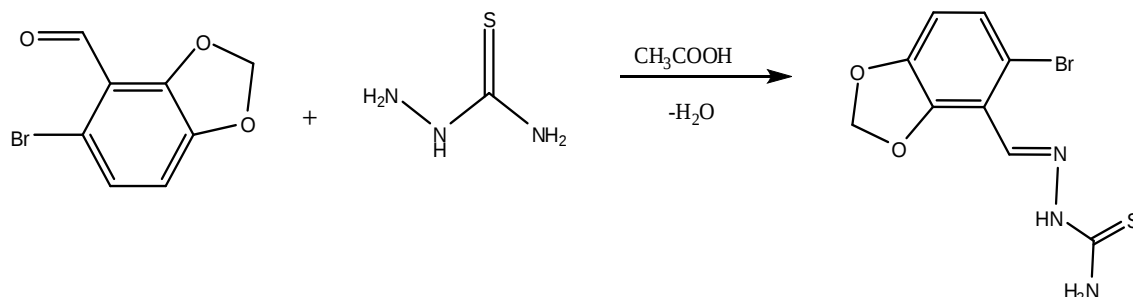
Organic solvents (absolute ethyl alcohol (Schar Lab.S.L, Spain), dimethyleformamide (DMF, LAB TECH Chemicals, Avishkar reagents), dimethylsulfoxide (DMSO, Sd FINE-CHEM LIMITED, SDFCL, India.), Acetonitrile HPLC grade (Scharlau)) were used without purification. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (East Anglia Chemicals, LRG), PdCl_2 99.99 % (Sigma Aldrich, USA), Thiosemicarbazide 99% (Sigma Aldrich, USA), Ammonia Solution, 5-bromo -1, 3-Benzodioxole-4-carboxaldehyde 96% (Sigma Aldrich), (Analar, England), Glacial acetic acid, (LOBA Chemie and Fine Chemicals, India) are of analytical grade and used as is. Double distilled water was used in all preparations.

2.2. Instrumentations

Infrared spectra were recorded on Shimadzu FT-IR.8400S type spectrometer in the wave-number region $(400\text{-}4000)\text{ cm}^{-1}$. The spectra of the solid samples were recorded as KBr pellets. Mass spectra were recorded on Agilent, 6420 Triple quad. ^1H NMR spectra were recorded on Shimadzu, Advance III 400 MHz FT- NMR spectrometer. The spectra were run at 400 MHz in deuterated dimethylsulfoxide (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 DMSO (10^{-3}M) solution were recorded using Shimadzu model 3101pc spectrophotometer. The magnetic susceptibility was measured on powdered samples using Sherwood balance. The electrical conductivity was measured using a Conductivity TDS Meter model 4510 JENWAY, (England).

2.3 Synthesis of the ligand 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide ($\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr}$)

0.916 g (0.004 mol) of 5-bromo-1, 3-benzodioxole-4- carbaldehyde was placed in 100 ml round bottomed flask. About 30 ml of absolute ethanol was added and the mixture was 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 of few drops of glacial acetic acid. The mixture was then refluxed on water bath for about two hours. On cooling, pale yellow crystals were precipitated. The precipitate was filtered, washed with ethanol and left to dry in air. The product was recrystallized from ethanol and weighed [14].



Scheme 1: Structure of 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide

2.4. Synthesis of complexes

2.4.1 Synthesis of [Cu(C₉H₈N₃O₂SBr)₂(Cl)₂].2H₂O

0.034 g (0.0002 mol) of CuCl₂.2H₂O was placed in 100 ml beaker and dissolved in about 30 ml warm absolute ethanol slowly added, with stirring to a solution containing 0.121 g (0.0004 mol) 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide dissolved in about 30 ml of dimethyleformamide. Then few drops of ammonia solution were added to the mixture. The mixture was refluxed for 1.5 hours. On partial evaporation of the solvent, pale yellow precipitate separated out, and then collected by filtration, washed with cold ethanol and left to dry in air and weighed.

2.4.2 Synthesis of [Pd (C₉H₈N₃O₂SBr)₂]Cl₂

0.035 g (0.0002 mol) of PdCl₂ was placed in 100 ml beaker and dissolved in about 30 ml acetonitrile added, with stirring to a solution containing 0.121 g (0.0004 mol) of 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide dissolved in about 30 ml of dimethyle formamide. Then few drops of ammonia solution were added to the mixture. The mixture was refluxed for two hours. On partial evaporation of the solvent, pale brownish precipitate separated out, and then collected by filtration, washed with cold ethanol and left to dry in air and weighed.

2.5. Biological activity

The Schiff base ligand and its metal complexes were tested for their antimicrobial activities at National Center for Research, Medicinal and Aromatic Plants Research Institute, Khartoum, Sudan.

2.5.1. Antibacterial screening

The antibacterial activity of the ligand and its metal complexes were tested by using disc diffusion method, against gram positive bacteria namely *Staphylococcus aureus* ATCC 25923 and *Bacillus cereus* NCTC 8236. The gram negative bacterial namely *Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 27853 [15]. The test compounds were dissolved in DMSO. Twenty five milliliters nutrient agar was placed in petri plates. After solidification, the test bacteria were spread over the medium using spreader. The discs of Whatman No.1 filter paper saturated with the test compounds were placed at four equidistant places from the center in the inoculated petri plates. Filter paper disc treated with DMSO served as control and Ciprofloxacin and Erythromycin were used as standard for assessing the antibacterial studies. The Petri dishes were kept in refrigerator for 24 hours for pre-diffusion and then incubated for 72 hours at 38°C and the inhibition zone around each disk was measured. The zone of inhibition was carefully calculated in millimeters [16].

2.5.2. Antifungal screening

The antifungal activity of the synthesized ligand and its metal complexes were tested *Candida albicans* 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 two tested fungi. Fifty milliliter of the medium was 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 tested compounds were done by dissolving appropriate amounts of each compound in 10mL. Equal volumes of DMSO containing diluted compounds were added to PDA to get series of different concentrations for each compound [17].

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 amended PDA plates with four replicate plates for each fungus. All plates were incubated at 25°C. A colony diameter (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 $100(C-T)/C$, 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 [18].

3. RESULTS AND DISCUSSION

3.1. Spectral studies

The analytical data of the ligand and its metal complexes was given in experimental section, coincide with empirical formula. The electronic impact mass spectrum of the ligand, shows molecular ion (M^+) peak at m/z 302.9 a.m.u, corresponding to the species $[C_9H_8N_3O_2SBr]^+$, confirming the empirical formula of the ligand. The spectrum also shows a series of peaks corresponding to the various fragments of the compound. The intensities of the peaks give an idea of the relative stability of the fragments [19].

IR spectral data of the ligand 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide, shows bands at 3411 cm^{-1} and 3253 cm^{-1} which are assignable to $\nu(NH_2)$. The band at 3151 cm^{-1} is assigned to $\nu(N-H)$. The band at 2977 cm^{-1} corresponds to $\nu(CH)$. The band at 1529 cm^{-1} corresponds to $\nu(C=N)$, carbon nitrogen double bond which confirms the formation of the ligand [20]. The strong absorption band at 838 cm^{-1} is attributed to $\nu(C=S)$ [21].

Further evidence for the formation of the ligand was obtained from 1H NMR. The 1H NMR spectrum of the ligand (HL) shows proton signal at δ 11.75 ppm assigned to (1H , NHCS), the signal at δ 8.45 ppm for (1H , CH=N) and δ (7.16 and 7.23) ppm assigned to (2H, NH_2). The proton signals for benzene ring are at δ (6.91 and 6.89) ppm. (Carmona et al, 2016).

In the IR spectrum of $[Cu(C_9H_8N_3O_2SBr)_2(Cl)_2] \cdot 2H_2O$ complex with the ligand 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide the absorption band at 1529 cm^{-1} assigned to $\nu(C=N)$ in the free ligand, is shifted to 1456 cm^{-1} in the complex $[Cu(C_9H_8N_3O_2SBr)_2(Cl)_2] \cdot 2H_2O$, indicating the involvement of azomethine nitrogen in coordination to the Cu(II) ion [22].

The Cu–N bond is detected by appearance of frequency in the region 516 cm^{-1} . Furthermore in the spectrum of the free ligand the $\nu(C=S)$ vibration observed at 838 cm^{-1} is shifted to 817 cm^{-1}

upon complexation, indicating the involvement of the thione sulphur in the bond formation to the Cu(II) ion [23]. This is confirmed by the presence of new bands at 418-472 cm^{-1} which can be assigned to ν (Cu-S) bond [24]. The band at 3151 cm^{-1} observed in the spectrum of the free ligand is ascribed to the ν (NH) vibration is shifted to 3095 cm^{-1} in the Cu(II) complex. The appearance of this band is an indication that bonding is through the sulfur atom, and not through the NH [25].

The reflectance electronic spectra data of Cu(II) complex with the ligand shows bands at 30487 cm^{-1} (328 nm), 35971 cm^{-1} (278 nm), 37453 cm^{-1} (267 nm), 38610 cm^{-1} (259 nm) and 40485 cm^{-1} (247 nm). While in DMSO solution shows bands at 29069 cm^{-1} (344 nm), 32679 cm^{-1} (306 nm) and 45662 cm^{-1} (219 nm). The electronic spectrum of Cu(II) complex consists of bands in the region 306-328 nm is assigned to $n \rightarrow \pi^*$ intraligand transitions [26]. The molar conductivity measurement recorded is (10.13 S cm^{-1}); this value indicates that the complex is non-electrolyte in nature [27]. The observed magnetic moment is 2.59 B.M. Based on conductivity data, together with spectral studies, for the Cu(II) complex suggested to have an octahedral geometry. From these observations, together with the results obtained from other analytical data, the suggested structure of Cu(II) complex with the ligand can be illustrated as follow:

In the IR spectrum of $[\text{Pd}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$ complex with the ligand 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide the absorption band at 1529 cm^{-1} assigned to ν (C=N) in the free ligand, is shifted to 1448 cm^{-1} in the complex $[\text{Pd}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$, indicating the involvement of azomethine nitrogen in coordination to the Pd(II) ion [22]. The Palladium–nitrogen bond was detected by appearance of frequencies in the region 518-568 cm^{-1} . Furthermore in the spectrum of the free ligand the ν (C=S) vibration observed at 838 cm^{-1} is shifted to 794 cm^{-1} upon complexation, indicating the involvement of the thione sulphur in the bond formation to the Pd(II) ion [23]. This is confirmed by the presence of new bands at 432-484 cm^{-1} which can be assigned to ν (Pd-S) bond [24]. The band at 3151 cm^{-1} observed in the spectrum of the free ligand is ascribed to the ν (NH) vibration is shifted to 3147 cm^{-1} in the Pd(II) complex. The appearance of this band is an indication that bonding is through the sulfur atom, and not through the NH [25].

The reflectance electronic spectral data of Pd(II) complex with the ligand consists of bands at 25000 cm^{-1} (400 nm), 30769 cm^{-1} (325 nm), 36101 cm^{-1} (277 nm), 37313 cm^{-1} (268 nm) and 38461 cm^{-1} (260 nm). While in DMSO solution, it shows bands at 33003 cm^{-1} (303 nm) and 39062 cm^{-1} (256 nm). The electronic spectrum of Pd(II) complex consists of bands in the region 325-303 nm is assigned to $n \rightarrow \pi^*$ intraligand transitions. The absorption bands at 400 nm in the spectrum of $[\text{Pd}(\text{HL})_2]\text{Cl}_2$ complex can be attributed to ligand-metal charge transfer [26]. The molar conductivity measurement recorded is (86.4 S cm^{-1}), and this indicates that the Pd(II) complex is electrolyte in nature [27]. The observed magnetic moment is zero. The electronic spectra of this complex indicates square planar geometry around the Pd(II) [28].

3.2. Thermogravimetric analysis of the complexes

Thermal decomposition data of metal complexes of the ligand 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide follows TGA and DSC techniques under nitrogen atmosphere measured at heating rate of 10 $^{\circ}\text{C min}^{-1}$. The weight loss was measured from the ambient temperature up to 1000 $^{\circ}\text{C}$. The weight losses for each compound are calculated within the corresponding temperature ranges. The curves show three decomposition steps for Cu(II) and Pd(II) complexes. The total % weight loss of the complexes corresponds to the loss of ligand after considering the transfer of one oxygen atom to the metal ion. The TGA

curve for the $[[\text{Cu}(\text{HL})_2(\text{Cl})_2] \cdot 2\text{H}_2\text{O}$ complex shows three decomposition steps within the temperature range 50-1000 °C. The first step of the decomposition within the temperature range 50-150 °C, corresponds to the loss of two water molecules of hydration ($2\text{H}_2\text{O}$), H_2S , HCl and part of the first ligand ($\text{C}_2\text{H}_2\text{N}_3$), the observed mass loss is equal to 18.72% (calculated 22.51%). The second step within the temperature range 150-300 °C, correspond to the loss of the remaining of the ligand molecule ($\text{C}_7\text{H}_4\text{O}_2\text{Br}$) and HCl with an estimated mass loss of 24.26% (calculated 30.51%). The third step within the temperature range 300-1000 °C with an estimated mass loss of 34.78% (calculated 36.64%), corresponds to removal of the part of second ligand molecule ($\text{C}_9\text{H}_6\text{N}_3\text{OSBr}$), leaving CuO as a residue at 1000 °C. The overall weight loss amount to 77.76% (calculated 89.66%). The complex gives endothermic and exothermic peaks within the temperature ranges of the decomposition, as shown by DSC results obtained during the thermal decomposition of the compound.

The thermogram of $[\text{Pd}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$ complex shows three decomposition steps within the temperature range 50-1000 °C. The first step of the decomposition is within the temperature range 50-250 °C, the observed mass loss is equal to 14.57% (calculated 16.38%) corresponds to the removal of the part of the first ligand ($\text{C}_3\text{H}_4\text{N}_4\text{S}$) and NH_3 at 250 °C. The second steps within the temperature range 250-450 °C with an estimated mass loss of 32.18% (calculated 38.02%), corresponds to removal of the remaining of the ligand molecule ($\text{C}_8\text{H}_2\text{O}_2\text{BrN}$) and 2HCl . The third step within the temperature range 450-1000 °C with an estimated mass loss of 21.74% (calculated 23.68%), corresponds to removal of the remaining the of second ligand molecule ($\text{C}_7\text{H}_5\text{OBr}$), leaving PdO as a residue. The overall weight loss amount to 68.49% (calculated 78.08%). The complex gives endothermic and exothermic peaks within the temperature ranges of the decomposition, as shown by DSC results obtained during the thermal decomposition of the compound.

3.3. Antimicrobial activity of the ligand and its Metal complexes

In vitro antibacterial activity of the free ligand and its $\text{Cu}(\text{II})$ and $\text{Pd}(\text{II})$ complexes were carried out using gram positive bacteria *Bacillus subtilis*, *Staphylococcus aureus* and as gram negative bacteria *Escherichia coli* *Pseudomonas aeruginosa*. The test was done by using the disc diffusion method. Ciprofloxacin (a) and Erythromycin (b) were used as standard drugs, and DMSO was used as negative control. The diameters of the inhibition zones for all tested compounds are presented in table (2). The ligand shows higher antibacterial activity against *Bacillus subtilis* as G(+) bacteria), *Escherichia coli* and *Pseudomonas aeruginosa* than Erythromycin (b) standard, but less activity than Ciprofloxacin (a). It's also shows less activity against *Staphylococcus aureus* as G(+) bacteria than Erythromycin (b) standard. The compound $[\text{Cu}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ shows more activity against all organisms than Erythromycin (b) standard. It's also shows more activity against *Escherichia coli* and *Staphylococcus aureus* than Ciprofloxacin (a) standard. On the other hand the $[\text{Cu}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ complex shows equal activity against *Bacillus subtilis* and *Pseudomonas aeruginosa* to the standard Ciprofloxacin (a). The $[\text{Pd}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2]\text{Cl}_2$ complex shows more activity against *Bacillus subtilis*, *Staphylococcus aureus* and *Escherichia coli* than Ciprofloxacin (a) and Erythromycin (b) standards, but less activity against *Pseudomonas aeruginosa* than Ciprofloxacin (a) standard. It's also shows more activity against *Pseudomonas aeruginosa* than Erythromycin (b) standard. A comparative study of the ligand and its $\text{Cu}(\text{II})$ and $\text{Pd}(\text{II})$ complexes as antibacterial activity indicates that the complexes exhibit more inhibitory effect than the parent ligand.

3.4. Antifungal activity 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide and its complexes

The compounds were evaluated for their in vitro antifungal activity against *Candida albicans* ATCC 7596, using disk diffusion technique. The screening results are given in table (3), where the activities of compounds were compared with Ketoconazole (a) and Itraconazole (b) as antifungal standards, the screening results show that the free ligand and its Pd (II) complex exhibit zero antifungal activity. The Cu complex exhibit significant activity against *Candida albicans* ATCC 7596 fungus, nearly equal to Itraconazole (b) standard, but less than the Ketoconazole (a) standard. Investigation of antifungal activity data indicates that Cu complex is more active than free ligand.

Table 1: Thermo analytical results (TGA and DSC) of complexes of the ligand 2-((5-bromobenzo [d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide

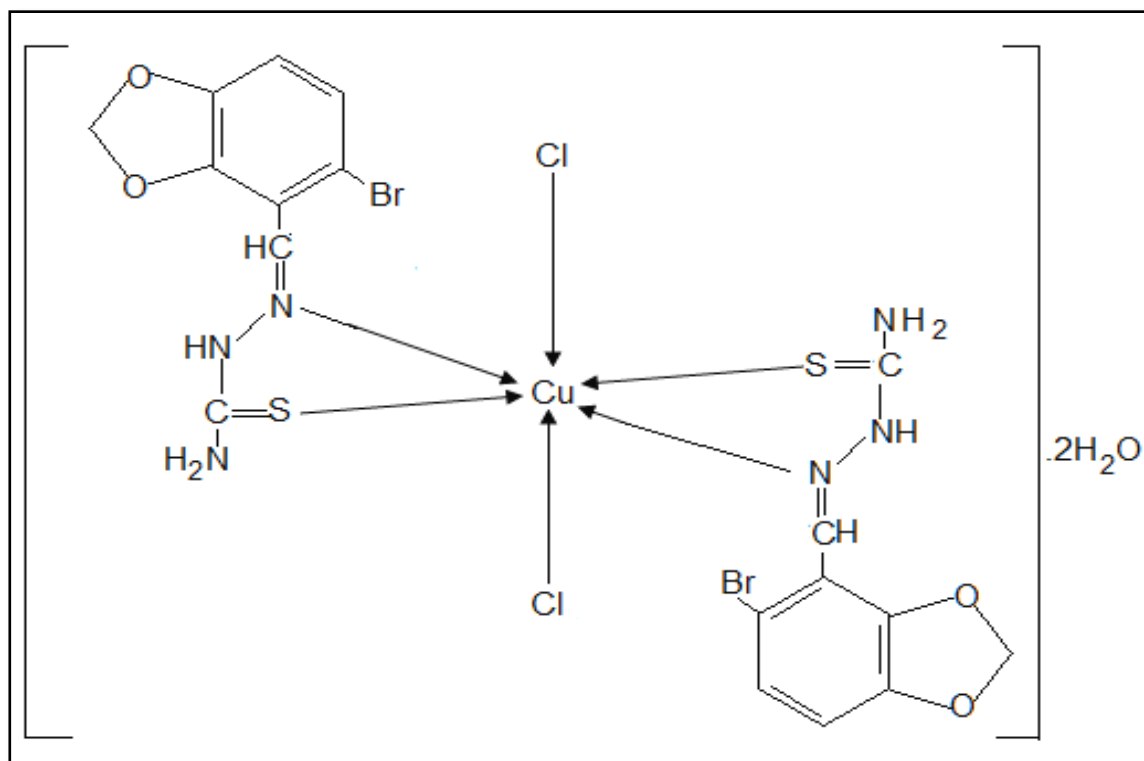
Complex	TGA range (°C)	DSC (°C)	No. of steps	Mass loss (%)	Total mass loss (%)	Assignment	Metallic residue
[Cu(C ₉ H ₈ N ₃ O ₂ SBr) ₂ (Cl) ₂].2H ₂ O	50-150 150-300 300-1000	77(-) 237(-), 182(+)	3	22.51 (Cal) , 18.72 (F) 30.51 (Cal) , 24.26 (F) 36.64 (Cal) , 34.78 (F)	89.66 cal 77.76(F)	Loss of 2H ₂ O , H ₂ S, HCl and C ₂ H ₂ N ₃ Loss of (C ₇ H ₄ O ₂ Br) and HCl Loss of (C ₉ H ₆ N ₃ OS Br)	CuO
[Pd(C ₉ H ₈ N ₃ O ₂ SBr) ₂ Cl ₂]	50- 250 250-450 450-1000	226(-), 161(+) 305(-)	3	16.38 (Cal), 14.57 (F) 38.02 (Cal), 32.18 (F) 23.68 (Cal), 21.74 (F)	78.08 cal 68.49(F)	Loss of C ₃ H ₄ N ₄ S and NH ₃ Loss of C ₈ H ₂ O ₂ BrN and 2HCl Loss of C ₇ H ₅ OBr	PdO

Table 2: Antibacterial activity of the ligand 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide and its Complexes

Compound	Inhibition zone diameter (mm/mg sample)							
	Gram positive bacteria				Gram negative bacteria			
	<i>Bs. Subtilis</i>		<i>Sa. aureus</i>		<i>E. coli</i>		<i>Ps. aeruginosa</i>	
	10mg/ml	20mg/ml	10mg/ml	20mg/ml	10mg/ml	20mg/ml	10mg/ml	20mg/ml
Ligand	11	12	10	11	13	15	13	14
[Cu(C ₉ H ₈ N ₃ O ₂ SBr) ₂ (Cl) ₂].2H ₂ O	20	20	20	22	18	19	17	20
[Pd(C ₉ H ₈ N ₃ O ₂ SBr) ₂]Cl ₂	23	24	22	23	17	18	15	18
Ciprofloxacin	20	22	16	17	13	13	18	20
Erythromycin	10	11	17	19	8	10	12	13
DMSO(Control)	0	0	0	0	0	0	0	0

Table 3: Antifungal activity of the ligand 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide and its Complexes

Compound	Inhibition zone diameter (mm/mg sample)		
	<i>Candida albicans</i>		
	5mg/ml	10mg/ml	20mg/ml
Ligand	0.0	0.0	0.0
[Cu(HL) ₂ (Cl) ₂].2H ₂ O	12	13	18
[Pd(HL) ₂]Cl ₂	0.0	0.0	0.0
Ketoconazole (Standard) (a)	14	15	16
Itraconazole (Standard) (b)	12	14	15
DMSO(Control)	0	0	0

**Fig 1: Suggested structure of [Cu(C₉H₈N₃O₂SBr)₂(Cl)₂].2H₂O complex.**

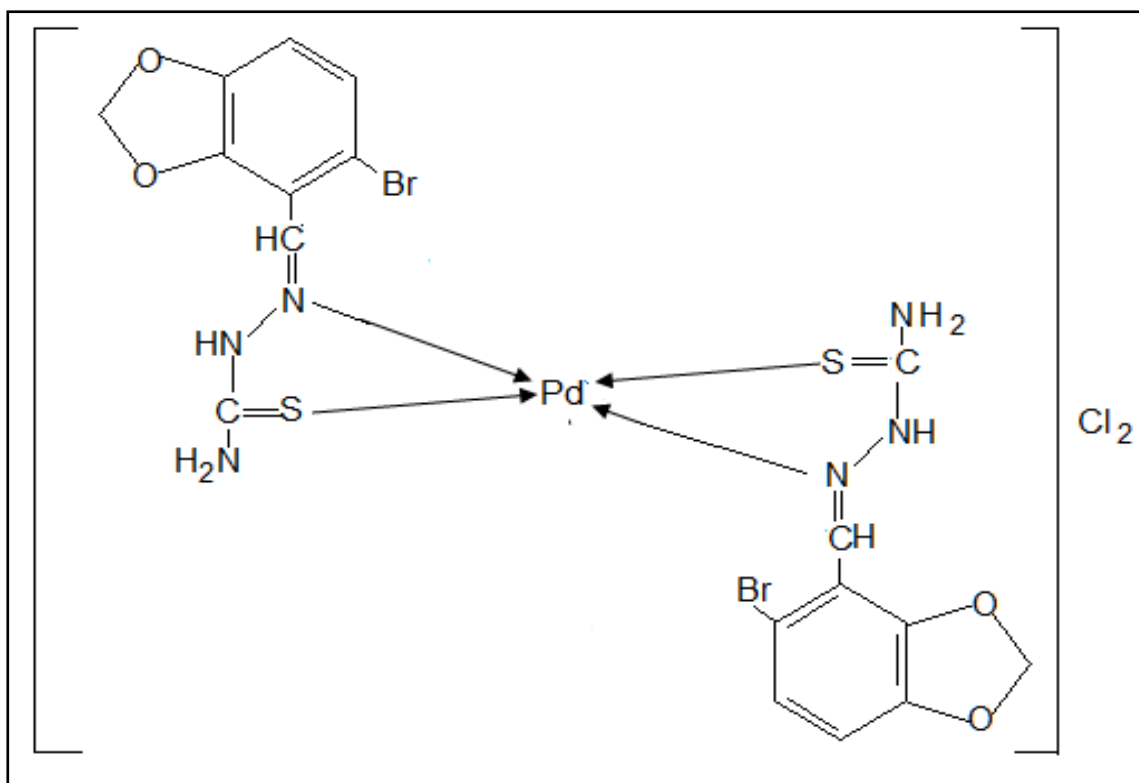


Fig 2: Suggested structure o $[Pd(C_9H_8N_3O_2SBr)_2]Cl_2$ complex.

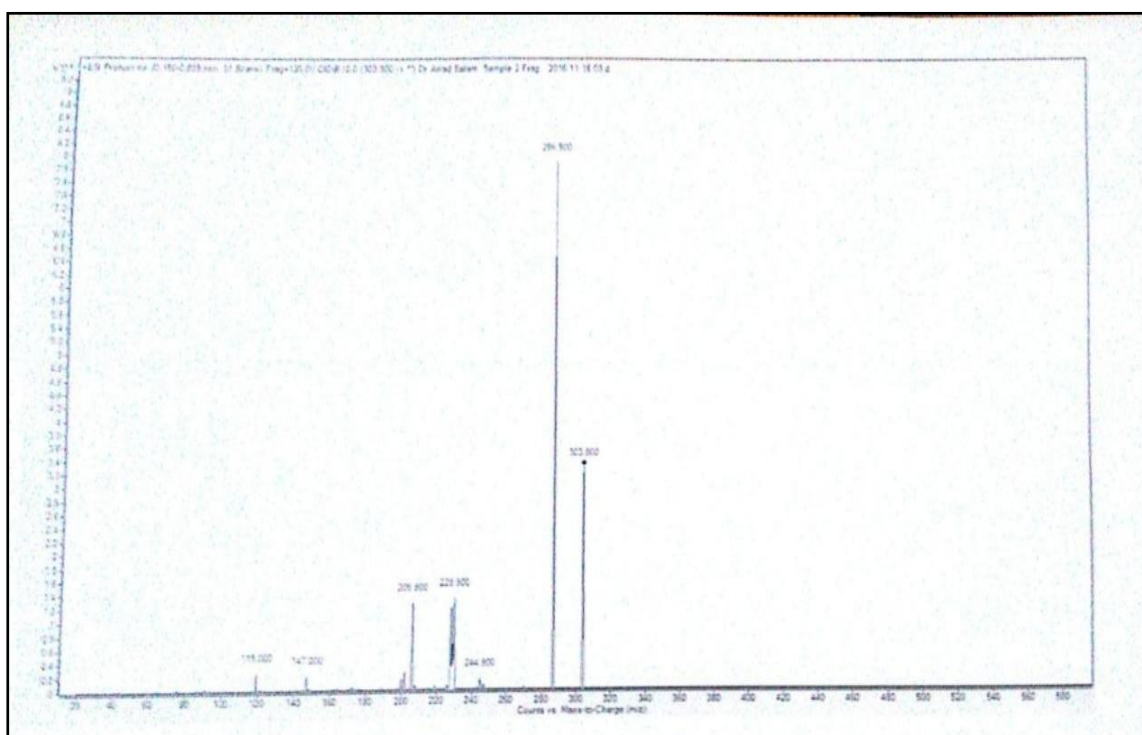


Fig 3: Mass spectrum of 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide

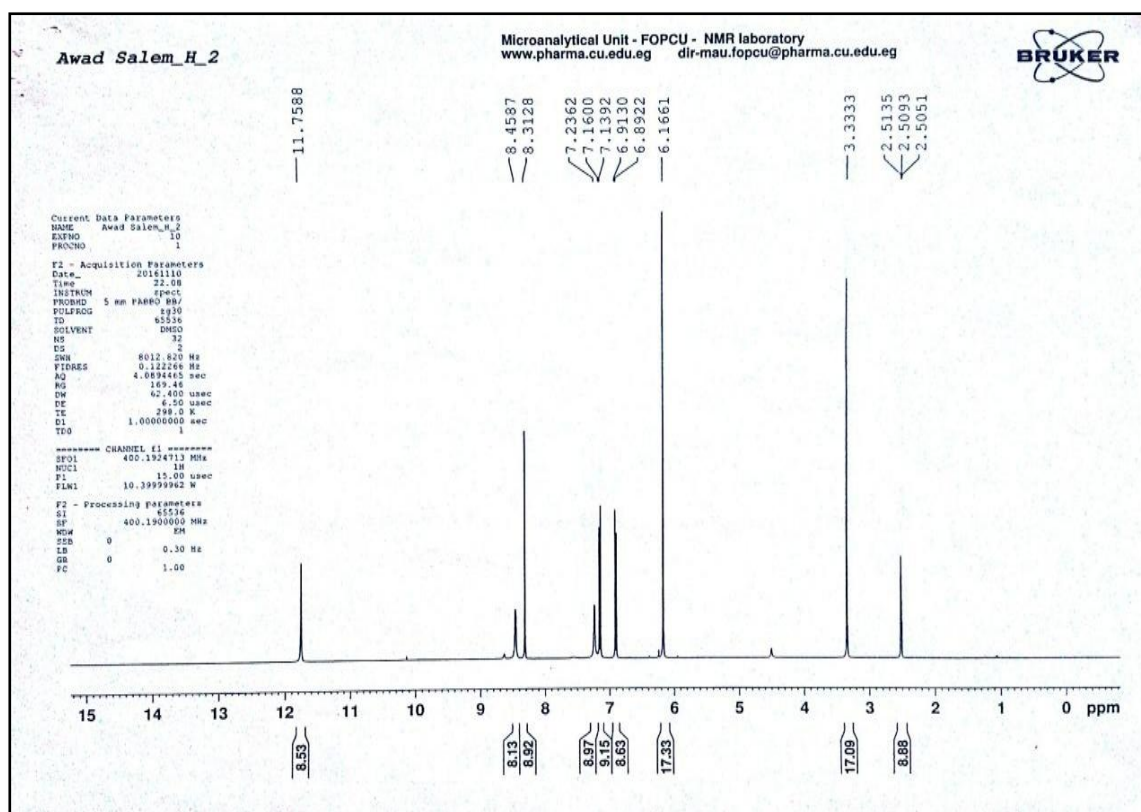


Fig 4: ^1H NMR spectrum of 2-((5-bromobenzo[d][1,3]-dioxol-4-yl)methylene) hydrazine-1-carbothioamide

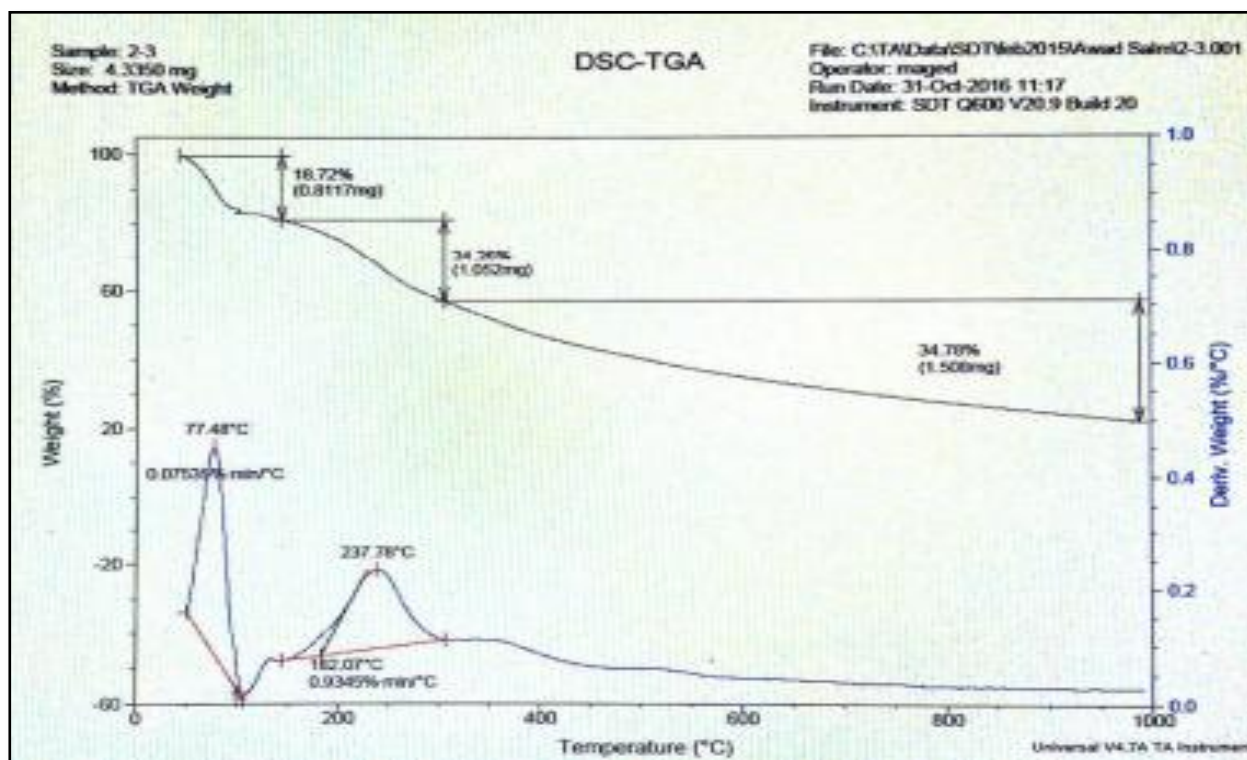


Fig 5: Thermogram of the complex $[\text{Cu}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2(\text{Cl})_2] \cdot 2\text{H}_2\text{O}$.

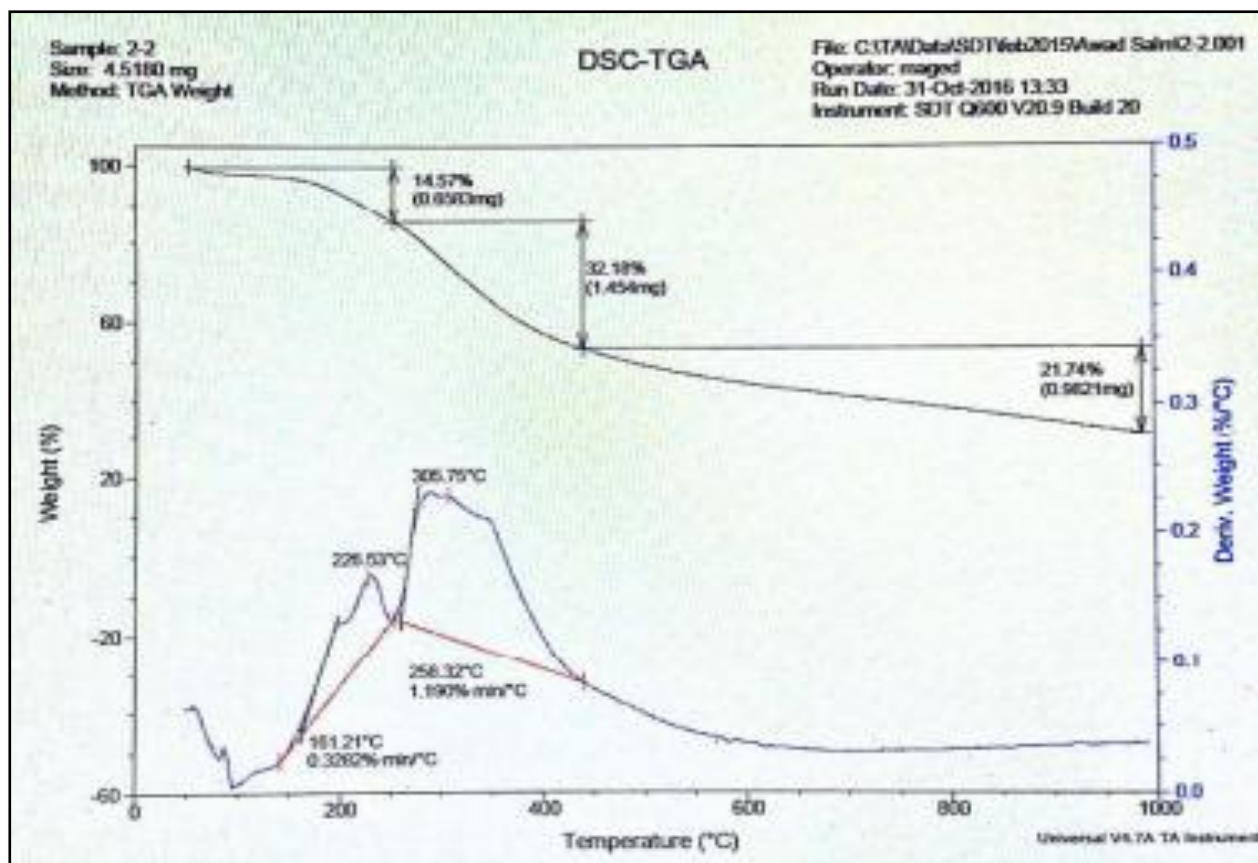


Fig 6: Thermogram of the complex $\text{Pd}(\text{C}_9\text{H}_8\text{N}_3\text{O}_2\text{SBr})_2\text{Cl}_2$

4. CONCLUSION

In conclusion, this study reports a new bidentate ligand from the reaction between 5-bromo-1,3-Benzodioxole-4-carboxaldehyde and thiosemicarbazide. Two stable colored metal ion complexes were synthesized from the reaction between the prepared ligand and two metal ions namely Cu(II) and Pd(II). The ligand and its metal complexes were characterized by using different spectroscopic analytical techniques such as MS, IR, UV-Vis and ^1H NMR spectra. *In vitro* antimicrobial potential of the ligand and complexes were also investigated. Higher antibacterial and antifungal activities were observed from the metal ion complexes compared to that of the free ligand.

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