

SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME TRANSITION METAL COMPLEXES OF 2-(5-NITRO-1H-BENZIMIDAZOL-2-YL)-4-BROMOPHENOL

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ABSTRACT. MnCl₂, FeCl₃, Ru(DMSO)₄Cl₂, CoCl₂, NiCl₂, PdCl₂, CuCl₂, AgNO₃, CdCl₂ and HgCl₂ complexes of 2-(5-nitro-1H-benzimidazol-2-yl)-4-bromophenol (**HL**) were synthesized and characterized. The structures of the complexes were confirmed on the basis of elemental analysis, TGA, molar conductivity and magnetic moment measurements, FT-IR, far-IR, FT-Raman, UV-Visible, NMR and fluorescence spectroscopy. According to the analytical and spectral data, the ligand acted as bidentate, via the imine nitrogen and the phenolate oxygen atoms towards the metal ions except the Ag(I). The complexes were screened for *in vitro* antibacterial activities against *S. aureus*, *S. epidermidis*, *E. coli*, *K. pneumoniae*, *P. aeruginosa*, *P. mirabilis* and for antifungal activity against *C. albicans*. Ciprofloxacin and fluconazole were used as reference for antibacterial and antifungal activities of the complexes, respectively. In most cases, the complexes tested showed considerable activity on *S. aureus* especially, which is a Gram positive bacterium. In addition, the Hg(II) and Ag(I) complexes were found to have superior activity toward all of the microorganisms whereas the Pd(II) and Cd(II) complexes showed considerably antimicrobial effect on *S. aureus* and *C. albicans* selectively.

KEY WORDS: Benzimidazole, Bromophenol, Transition metal complexes, Antibacterial, Antifungal

INTRODUCTION

It is known that biological metal ions play key roles in the structural organization and activation of certain enzymes, which are involved in the transfer of genetic information from DNA, leading to the synthesis of specific proteins. Transition metal complexes have attracted attentions of inorganic, metallo-organic as well as bio-inorganic chemists because of their extensive applications in wide ranging areas from material to biological sciences [1].

Antimicrobial activity of some 2-(1H-benzimidazol-2-yl)-phenol derivatives and their metal complexes were investigated in detail against some microorganisms. In our previous studies, we found that various benzimidazolyl-phenol derivatives and some of their complexes showed antimicrobial activity against several microorganisms [2-6]. For instance, 2-(5-H/Me/Cl/NO₂-1H-benzimidazol-2-yl)-4-Br/NO₂-phenols were effective especially on *S. aureus*; their Ag(I) and Hg(II) complexes showed high antimicrobial activity toward six bacteria in the study [2]. The Fe(III) complexes of 2-(5-H/Me-1H-benzimidazol-2-yl)-4-Br/NO₂-phenols exhibited considerable activity against *S. aureus* and *S. epidermidis* [3]. 2-(5-H/Me/Cl-1H-benzimidazol-2-yl)-phenols and their Fe(III) complexes showed considerable activity on some bacteria and fungi [4]. It was reported that the Co(II) and Ni(II) chelates of 2-(1H-benzimidazol-2-yl)-phenol have antifungal activity against *A. alternata* and *A. niger* [5, 6].

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2-Methoxy-6-(5-H/Me/Cl/NO₂-1*H*-benzimidazol-2-yl)-phenols and their some transition metal complexes were synthesized and characterized. Some ligands and Cu(II) and Zn(II) complexes showed antibacterial activity against Gram positive bacteria [7]. It was reported that 4-methoxy-2-(1*H*-benzimidazol-2-yl)-phenol and its Ag(I) and Cu(II) complexes are effective on *S. epidermidis*, *S. aureus* and *B. subtilis*. Also, 4-methoxy-2-(5-methyl/chloro-1*H*-benzimidazol-2-yl)-phenols showed antibacterial activity toward *S. aureus* [8]. Ag(I) and Zn(II) complexes of 2-methyl-6-(1*H*-benzimidazol-2-yl)-phenol showed antibacterial effect toward *K. pneumoniae*, *S. epidermidis* and *S. aureus* bacteria whereas the ligand itself had no any activity [9]. 2-(5-H/Me/F/Cl/NO₂-1*H*-benzimidazol-2-yl)-benzene-1,4-diols (HL_x: x = 1-5) and HL₁ complexes with Fe(NO₃)₃, Co(NO₃)₂, Ni(NO₃)₂, Cu(NO₃)₂, Zn(NO₃)₂ showed considerable antimicrobial activity [10]. Pd(II), Ag(I) and Au(III) complexes of 4-(1*H*-benzimidazol-2-yl)-benzene-1,3-diol showed considerable antibacterial and antifungal activity whereas the ligand itself has no any activity [11].

Spectral characterizations and antibacterial effect of 2-(5-H/Cl/Me/NO₂-1*H*-benzimidazol-2-yl)-4-Me/Br-phenols (HL₁–HL₅) and their some transition metal complexes were reported by us: while HL₁ ligand has considerable antibacterial activity on *B. cereus* only; it's Ag(I) complex show antibacterial effect toward almost to the all bacteria. HL₅ and [Zn(L₅)₂]·HClO₄ exhibit considerable high antibacterial activity toward *K. pneumoniae*, *B. cereus*, *S. epidermidis* and *B. subtilis* [12].

3-(5-H/Me/Cl/NO₂-1*H*-benzimidazol-2-yl)-benzene-1,2-diols (HL_x: x = 1-4) ligands and HL₃ complexes with Fe(NO₃)₃, Cu(NO₃)₂, Co(NO₃)₂, Zn(NO₃)₂ have been synthesized and characterized. HL₁, HL₂, HL₃ and [Cu(L₃)₂]·(H₂O)₂ show considerable antimicrobial activity toward *S. epidermidis* and *C. albicans* [13].

Coordination compounds exhibit different characteristic properties depend on the metal ion that they are bonded [14]. These metal complexes have extensive applications in various fields of human interest on the basis of nature of the metal as well as the type of ligand [15, 16]. Chelation or complexation shows more potent antibacterial effect against some microorganisms than the respective drug [17-19]. We reported that 2-(5-nitro-1*H*-benzimidazol-2-yl)-4-bromophenol (**HL**) ligand and its Zn(NO₃)₂, Fe(NO₃)₃ and Cu(NO₃)₂ complexes showed strong antibacterial activity toward *S. aureus* and *S. epidermidis* [20, 21]. In this study, we aimed to synthesize the new transition metal complexes of **HL** (Figure 1) with MnCl₂, FeCl₃, Ru(DMSO)₄Cl₂, CoCl₂, NiCl₂, PdCl₂, CuCl₂, AgNO₃, CdCl₂ and HgCl₂ and to investigate their structural characteristics and antimicrobial activities toward six bacteria and one fungi, *C. albicans*.

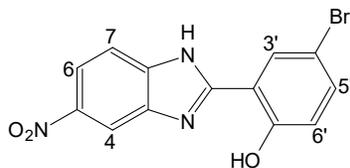


Figure 1. Structure of the ligand.

EXPERIMENTAL

Chemistry and apparatus

All chemicals and solvents were of reagent grade from Sigma-Aldrich, Merck, Alfa Easer, Carlo Erba and Acros Organics and they were used without further purification.

Analytical data were obtained with a Thermo Finnigan Flash EA 1112 analyzer. Melting points were determined using an Electrothermal melting-point apparatus. Molar conductivity of the complexes was measured on a WTW Cond315i conductivity meter in DMF at 25 °C. ¹H-NMR spectra were run on a Varian Unity Inova 500 NMR spectrometer. The residual DMSO-d₆

signal was also used as an internal reference. FT mid-IR and far-IR spectra were recorded on a Bruker Optics Vertex 70 spectrometer using Attenuated Total Reflection (ATR) techniques between 100 and 4000 cm^{-1} . The FT-Raman spectra were also recorded in the same instrument with a R100/R RAMII Raman module equipped with Nd:YAG laser source operating at 1064 nm line with 200 mW power and a spectral resolution of $\pm 2 \text{ cm}^{-1}$. UV-Visible spectra was performed on a Perkin Elmer Lambda 25 UV/Visible Spectrometer in MeOH. Fluorescence spectra were performed on a Shimadzu RF-5301 PC Spectrofluorophotometer. Thermogravimetric studies were made on a TG-60WS Shimadzu, with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and air flowing at the rate of 50 mL/min. Magnetic measurements of the paramagnetic complexes were carried out on MK1 Sherwood Scientific apparatus at room temperature by Gouy's method. Diamagnetic corrections were made using Pascal's constants.

Synthesis of the ligand

The ligand was prepared according to the literature procedures [22, 23]. 2-Hydroxy-5-bromobenzaldehyde (2.01 g, 10 mmol) reacted with an equivalent amount of NaHSO_3 (1.04 g, 10 mmol) in ethanol (25 mL) at room temperature for 4 h. The mixture was treated with 4-nitro-1,2-phenylenediamine (1.53 g, 10 mmol) in dimethylformamide (15 mL) and gently refluxed for 2 h. The reaction mixture was then poured into iced water (500 mL) and then a precipitate was formed. It was filtered and crystallized from ethanol. Yield: 2.04 g (61%).

Synthesis of the complexes

The metal complexes were synthesized by treating an ethanolic solution of the ligand with an equimolar amount of metal salts under reflux about 2 h except the Ag(I) complex.

$[\text{Mn}(\mathbf{L})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$. Equimolar amount of the ligand (167 mg, 0.5 mmol) and $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ (117 mg, 0.5 mmol) were mixed in ethanol (20 mL). This mixture was refluxed for 2 h and then filtered. After 2 days, a brown precipitate was formed in the filtrate. It was filtered and dried at room temperature. Yield: 155 mg (65%).

$[\text{Fe}(\mathbf{L})_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$. 135 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) were added to the ligand (167 mg, 0.5 mmol) solution in ethanol (20 mL). The black mixture was refluxed for 2 h and then filtered. In the filtrate, a black precipitate was formed after 3-4 days staying at room temperature. It was filtered and dried at room temperature. Yield: 156 mg (68%).

$[\text{Ru}(\mathbf{L})_2(\text{DMSO})_2\text{Cl}] \cdot 4\text{H}_2\text{O}$. 242 mg of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ (0.5 mmol) were added to the ligand (167 mg, 0.5 mmol) solution in ethanol (20 mL). The black mixture was refluxed for 2 h and then filtered. In the filtrate, a black precipitate was formed after a week staying at room temperature. It was filtered and dried at room temperature. Yield: 180 mg (68%).

$[\text{Co}(\mathbf{HL})\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$. 119 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) were added to the ligand (167 mg, 0.5 mmol) solution in ethanol (20 mL). The mixture was refluxed for 2 h, and a slightly turbid solution was formed. It was filtered after cooling and left at room temperature. A brown precipitate was obtained from the filtrate after 2 days. It was filtered and dried at room temperature. Yield: 185 mg (69%).

$[\text{Ni}(\mathbf{HL})\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$. 120 mg of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (~0.5 mmol) were added to the ligand (167 mg, 0.5 mmol) solution in ethanol (20 mL). The mixture was refluxed for 2 h, and a slightly turbid solution was formed as in the Co(II) complex. The brown colored precipitate formed in the filtrate after 3 days was filtered and dried at room temperature. Yield: 175 mg (70%).

$[Pd(HL)_2Cl_2]$. 88.5 mg of $PdCl_2$ (0.5 mmol) and 74.6 mg of KCl (1.0 mmol) were dissolved in ethanol (5 mL) and this solution was added to the ligand (167 mg, 0.5 mmol) solution in ethanol (15 mL). The mixture was refluxed for 2 h and filtered after cooling to room temperature. The claret red precipitate was filtered off, dried at room temperature. Yield: 195 mg (75%).

$[Cu(L)_2(EtOH)_2] \cdot H_2O$. 86 mg of $CuCl_2 \cdot 2H_2O$ (0.5 mmol) were added to the ligand (167 mg, 0.5 mmol) solution in ethanol (20 mL). The mixture was refluxed for 2 h and a slightly turbid solution was obtained. The brown colored precipitate formed in the filtrate in 2 days was filtered and dried at room temperature. Yield: 160 mg (74%).

$[Ag(HL)(L)] \cdot H_2O$. 85 mg of $AgNO_3$ (0.5 mmol) were added to the equimolar ligand solution in ethanol (20 mL). The mixture was stirred overnight at room temperature. A slightly turbid solution was formed and filtered. The filtrate was stayed at room temperature. After 2 days a dirty white precipitate was formed. It was filtered and dried at room temperature. Yield: 121 mg (64%).

$[Cd(HL)(L)Cl] \cdot H_2O$. 101 mg of $CdCl_2 \cdot H_2O$ (0.5 mmol) were added to the equimolar ligand solution in ethanol (20 mL). The mixture was refluxed for 2 h, and a slightly turbid solution was formed. It was filtered after cooling. The dirty white crystals were formed in the filtrate after 3 days at room temperature. It was filtered and dried at room temperature. Yield: 165 mg (67%).

$[Hg(HL)Cl_2] \cdot 2H_2O$. This complex was prepared in a similar manner to $[Cd(L)_2] \cdot H_2O$ complex. 136 mg of $HgCl_2$ (0.5 mmol) was added to the equimolar ligand solution. Yield: 275 mg (63%).

The analytical and physicochemical data of the complexes are presented in Table 1.

Determination of antimicrobial activity

Antimicrobial activity against *Staphylococcus aureus* ATCC 6538, *Staphylococcus epidermidis* ATCC 12228, *Escherichia coli* ATCC 8739, *Klebsiella pneumoniae* ATCC 4352, *Pseudomonas aeruginosa* ATCC 27853, *Proteus mirabilis* ATCC 14153 and *Candida albicans* ATCC 10231 were determined by the microbroth dilutions technique following the Clinical and Laboratory Standards Institute (CLSI) recommendations [24, 25]. Mueller-Hinton broth (MHB) (Difco, Detroit, MI, USA) for bacteria, RPMI-1640 medium buffered to pH 7.0 with MOPS (Sigma, St. Louis, MO, USA) for yeast strain was used as the test medium. Serial two-fold dilutions ranging from 5000 $\mu\text{g/mL}$ to 2.4 $\mu\text{g/mL}$ were prepared in MHB. The inoculum was prepared using a 4–6 h broth culture of each bacteria and 24 culture of yeast strains adjusted to a turbidity equivalent to a 0.5 McFarland standard, diluted in broth media to give a final concentration of 5×10^5 cfu/mL for bacteria and 0.5×10^3 to 2.5×10^3 cfu/mL for yeast in the test tray. The trays were covered and placed in plastic bags to prevent evaporation. The trays containing MHB were incubated at 35 °C for 18–20 h and the trays containing RPMI-1640 medium were incubated at 35 °C for 46–50 h. The minimum inhibitory concentrations (MIC) were defined as the lowest concentration of compound giving complete inhibition of visible growth. As control, antimicrobial effects of dimethylsulfoxide (DMSO) were investigated against test microorganisms. Ciprofloxacin and fluconazole were used to verify the standardization of the micro-dilution test procedure as reference antimicrobials for bacteria and yeast, respectively. According to values of the controls, the results were evaluated. The MIC values of the ciprofloxacin and fluconazole are within the accuracy range in CLSI throughout the study [26]. The experiments were performed in duplicate.

RESULTS AND DISCUSSION

The analytical data and physical properties of the complexes are summarized in Table 1.

Table 1. The analytical data and physical properties of the ligand and the complexes.

Compound	Elemental analysis: found (calcd) %			m.p. °C	M	Λ	Color
	C	H	N				
HL C ₁₃ H ₈ BrN ₃ O ₃	46.41 (46.73)	2.62 (2.46)	12.81 (12.66)	277	0	-	Dark yellow
[Mn(L) ₂ (H ₂ O)]·H ₂ O C ₂₆ H ₁₈ Br ₂ N ₆ O ₃ Mn	40.74 (41.24)	2.56 (2.40)	10.35 (11.10)	>35 0	4.00	58	Brown
[Fe(L) ₂ (OH)(H ₂ O)]·2H ₂ O C ₂₆ H ₂₁ Br ₂ N ₆ O ₁₀ Fe	39.48 (39.37)	3.01 (2.67)	10.14 (10.60)	>35 0	5.80	43	Black
[Ru(L) ₂ (DMSO) ₂ Cl]·4H ₂ O ¹ C ₃₀ H ₃₄ Br ₂ ClN ₆ O ₁₂ S ₂ Ru	35.09 (34.95)	3.13 (3.32)	7.87 (8.15)	>35 0	1.42	13	Black
[Co(HL)Cl ₂ (H ₂ O) ₂]·2H ₂ O C ₁₃ H ₁₆ BrCl ₂ CoN ₃ O ₇	29.42 (29.13)	2.71 (3.01)	7.42 (7.84)	>35 0	4.66	36	Dark brown
[Ni(HL)Cl ₂ (H ₂ O) ₂]·4H ₂ O ² C ₁₃ H ₂₀ BrCl ₂ N ₃ O ₉ Ni	26.12 (27.31)	3.94 (3.53)	6.85 (7.35)	>35 0	3.14	123	Dark brown
[Pd(HL) ₂ Cl ₂] C ₂₆ H ₁₆ Br ₂ Cl ₂ N ₆ O ₆ Pd	37.27 (36.93)	2.11 (1.91)	9.67 (9.94)	>35 0	0	18	Claret red
[Cu(L) ₂ (EtOH) ₂]·H ₂ O C ₂₈ H ₂₂ Br ₂ N ₆ O ₄ Cu	41.99 (42.36)	3.18 (2.79)	10.73 (10.59)	>35 0	1.75	52	Brown
[Ag(HL)(L)]·H ₂ O C ₂₆ H ₁₇ Br ₂ N ₆ O ₇ Ag	38.96 (39.37)	2.38 (2.16)	10.25 (10.60)	158	0	67	Dirty white
[Cd(HL)(L)Cl]·H ₂ O C ₂₆ H ₁₇ Br ₂ ClN ₆ O ₇ Cd	38.41 (37.48)	2.26 (2.06)	10.22 (10.09)	292	0	10	Dirty white
[Hg(HL)Cl ₂]·2H ₂ O C ₁₃ H ₁₂ BrCl ₂ N ₃ O ₃ Hg	23.92 (24.33)	1.73 (1.89)	6.27 (6.55)	221	0	31	Dirty white

M, magnetic moment, BM; Λ, molar conductivity, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ($25\pm 1^\circ\text{C}$) in DMF. ¹S%: 6.09 (6.22). ²Ni%: 7.89 (7.35).

General properties

HL is a bidentate, monodeprotonable and chelating ligand. Spectral characterization of **HL** and its Fe(NO₃)₃, Cu(NO₃)₂ and Zn(NO₃)₂ complexes were reported in previous studies [12, 13]. In this study, MnCl₂, FeCl₃, Ru(DMSO)₄Cl₂, CoCl₂, NiCl₂, PdCl₂, CuCl₂, AgNO₃, CdCl₂ and HgCl₂ complexes of the ligand (**HL**) were synthesized and characterized. Mn(II) Fe(III), Ru(III), Pd(II), Cu(II), Ag(I) and Cd(II) complexes have 1:1 M:L ratio whereas the Co(II), Ni(II) and Hg(II) complexes are 1:2 (bis-type).

According to the analytical data, the ligand is monodeprotonated through the phenolic OH hydrogen atom in most of the complexes. Molar conductivity data shows that the MnCl₂, FeCl₃, Ru(DMSO)₄Cl₂, CoCl₂, CuCl₂, CdCl₂ and HgCl₂ complexes are non-ionic (molar conductivities are in the 10-58 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ range). The Ag(I) complex is a 1:1 ionic complex (67 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) while the Ni(II) complex has 1:2 ionic character (123 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) [27].

The room temperature effective magnetic moment value of the Fe(III) complex, 5.80 BM, can be considered as indicating stabilization of the species having high ferric spin ($s = 5/2$) state. The magnetic moment value of the Cu(II) complex (1.75 BM) are very closer to the expected value (1.73 BM) for a simple mononuclear Cu(II) complex. The magnetic moment value of Mn(II) complex, 4.00 BM, may be accepted indicating stabilization of the species having intermediate spin ($s = 3/2$) state for d⁵ ion and can be taken into account as an indication for a five-coordinated structure and square pyramidal geometry due to theoretical magnetic moment value of three unpaired electrons is 3.88 BM (d⁵ ion in square pyramidal environment: $d_{xz}^2 d_{yz}^1 d_{xy}^1 d_{z^2}^1$) [28, 29].

The magnetic moment value of Co(II) complex, 4.66 BM, is in the expected range for octahedral complexes having high-spin state [30]. The magnetic moment value of the Ni(II)

complex (3.14 BM) can be considered as evidence showing a distorted octahedral geometry for $[\text{Ni}(\mathbf{HL})\text{Cl}_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ [31, 32].

Surprisingly, the ruthenium complex shows paramagnetic characteristic with a magnetic moment value 1.42 BM, although Ru(II), is a d^6 system, was used for complex preparation. This can be interpreted that ruthenium undergoes a one-electron oxidation during the course of the complexation reaction and in view of the ruthenium(III)/ruthenium(II) reduction potential displayed by this complex, aerial oxygen appears to have served as the oxidant. It can be interpreted that the magnetic moment value of Ru(III) complex corresponds to one unpaired electron for d^5 electronic configuration despite it is lower than the expected value (1.71 BM) [33]. It can be proposed capped octahedron or pentagonal bipyramid geometry for Ru(III) complex.

Thermal analysis

The major features of the thermal analysis of the complexes are summarized in Table 2. TGA curves of the Mn(II), Ru(III), Co(II), Ni(II) and Cd(II) complexes are shown in Figure 2. The samples of the complexes were heated from room temperature up to 800 °C. Thermal analysis results exhibited the valuable information about the water coordination state of the complexes. Thermal degradation of complexes occurred in three stages. At the first stage, uncoordinated lattice water was lost through evaporation from 50 to 100 °C (Table 2, first column). At the second stage, the coordinated water molecules are removed from all the complexes except Pd(II) complex at temperatures between 100 and 150 °C (Table 2, second column) [34, 35]. In all complexes, weight losses observed above 250 °C can be explained in terms of cleavage of the Br and nitro groups and also as decomposition of the anions. Above 350 °C, all other organic parts of complexes are oxidized to carbon dioxide, nitrogen oxides and water (third stage). The decomposition reactions result in the formation of metal oxides.

Table 2. TGA data of the complexes (thermal decomposition).

Temperature (°C) →	100	150	200	250	300	350	400	450	500	550	600	650	700
Complex	Weight loss (%)												
$[\text{Mn}(\mathbf{L})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$	3.2	4.8	5.9	9.0	12.0	21.2	25.4	48.0	58.7	67.1	80.4	90.6	91.8
Fe(III) complex ^a	4.2	4.5	7.6	8.1	8.8	9.7	74.6	88.5	90.4	90.4	90.4	90.4	90.4
Ru(III) complex ^b	6.5	7.6	8.9	9.3	16.1	22.4	31.3	64.7	81.0	82.4	83.4	84.5	84.5
Co(II) complex ^c	6.5	9.5	11.1	14.5	17.2	20.6	26.6	56.6	64.0	73.5	84.3	84.9	84.9
Ni(II) complex ^d	4.9	7.1	13.2	16.6	20.3	25.0	27.0	37.1	47.2	63.4	67.8	79.3	83.3
$[\text{Pd}(\mathbf{HL})_2\text{Cl}_2]$	1.1	3.6	10.0	16.4	20.8	24.0	35.4	45.6	50.0	58.9	69.0	76.1	84.5
$[\text{Cu}(\mathbf{L})_2(\text{EtOH})_2]\cdot\text{H}_2\text{O}$	2.9	8.5	9.6	10.9	14.6	15.3	57.2	80.7	82.1	86.1	89.1	91.2	91.2
$[\text{Ag}(\mathbf{HL})(\mathbf{L})]\cdot\text{H}_2\text{O}^e$	2.2	2.9	4.5	9.9	16.0	19.4	22.1	26.5	31.5	37.9	44.0	53.4	61.5
$[\text{Cd}(\mathbf{HL})(\mathbf{L})\text{Cl}]\cdot\text{H}_2\text{O}^f$	1.9	2.7	3.6	5.75	9.3	11.9	15.0	19.4	27.3	33.2	45.7	69.9	93.7
$[\text{Hg}(\mathbf{HL})\text{Cl}_2]\cdot 2\text{H}_2\text{O}$	5.3	7.1	12.7	35.8	38.8	44.8	48.2	52.7	56.8	65.3	74.3	88.9	100

^a $[\text{Fe}(\mathbf{L})_2(\text{OH})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$; ^b $[\text{Ru}(\mathbf{L})_2(\text{DMSO})_2\text{Cl}]\cdot 4\text{H}_2\text{O}$; ^c $[\text{Co}(\mathbf{HL})\text{Cl}_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$; ^d $[\text{Ni}(\mathbf{HL})\text{Cl}_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$; ^e 750 °C: 64.5; 800 °C: 69.3; 850 °C: 84.5; ^f 750 °C: 98.5; 800 °C: 100.

TGA data are compatible with the suggested structures of the complexes. Molecular weight ratio of the amount of metal oxide show very good agreement for the proposed structures according to the TGA data. The weight loss is 100% in the Hg(II) and Cd(II) complexes around 700 and 800 °C, respectively (Figure 3). This anomaly is due to the volatility in the second phase of decomposition [36, 37] (HgO and CdO decompose around 500 °C and metallic mercury vapors at 357 °C, and metallic Cd vapors at 767 °C).

Vibrational spectroscopy

The FT-IR (mid-IR and far-IR) and FT-Raman spectral data of the compounds are given in Table 3. In addition, far-IR spectra of the **HL**, Ru(III) and Cu(II) complexes in Figure 3 and FT-Raman spectra of **HL** and Cd(II) complex are given in Figure 4.

Interpretation of the Raman, mid-IR and far-IR spectra is based on changes in the spectra of the complexes relative to that of free ligand. The characteristic $\nu(\text{O-H})$ and $\nu(\text{N-H})$ vibration frequencies of the ligand exhibit only a medium broad band at 3327 cm^{-1} in the IR spectra, caused by double intramolecular hydrogen bonding between the phenoxyl hydrogen atom and one of the imine nitrogen atom [4, 22, 38, 39]. This band is changed significantly upon metal complexation indicating deprotonation and subsequent involvement of the phenoxyl group in metal coordination in the Mn(II), Fe(III), Ru(III), Cu(II) and Cd(II) complexes [40]. The phenolic oxygen atom coordination could also be supported by the appearance of medium bands at a lower frequency region ca. 535 cm^{-1} , assignable to $\nu(\text{M-OC})$ vibration frequencies. The medium broad bands between 3300 and 3400 cm^{-1} in the complexes strongly support the presence of the coordinated and uncoordinated water molecules.

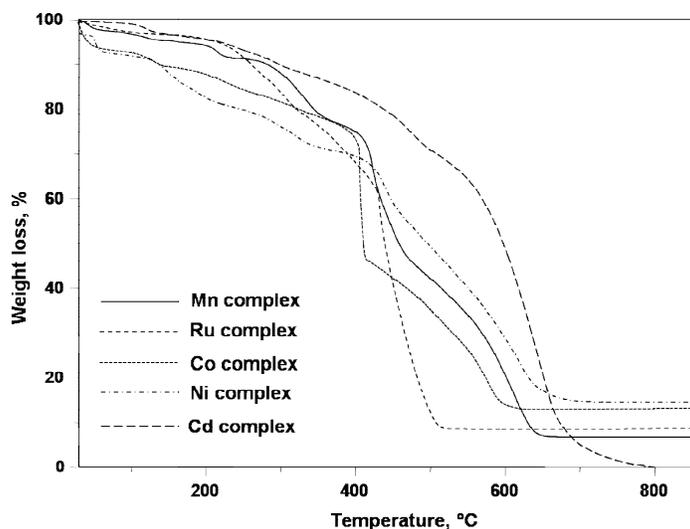


Figure 2. TGA curves of the Mn(II), Ru(III), Co(II), Ni(II) and Cd(II) complexes.

The characteristic $\nu(\text{C-H})$ and $\delta(\text{C-H})$ modes of ring residues in the ligand and the complexes are observed in the wave region between $3132\text{--}3076\text{ cm}^{-1}$ and $822\text{--}723\text{ cm}^{-1}$ (Table 3), respectively, particularly in the Raman spectra of the compounds. The C=C and C=N stretching frequencies are expected to appear at between 1631 and 1594 cm^{-1} with their own characteristics for the ligand and the complexes. Specific differences between spectra of the free ligand and the complexes in this region support the formation of new complexes. The coordination of imine nitrogen atom could also be confirmed by appearance of two new bands around 400 and 200 cm^{-1} may be assignable to $\nu(\text{M-N})$ and $\delta(\text{M-N})$ vibration modes [8, 41, 42]. Similar vibrational changes are detected in the Raman spectra (Table 3). In the IR spectra of the ligand and the complexes, the strong or medium bands at the ranges $1514\text{--}1524$ and $1308\text{--}1341\text{ cm}^{-1}$ are assigned to the symmetric and asymmetric $\nu(\text{NO}_2)$, respectively. The C-Br stretching vibration is seen at the range $525\text{--}554\text{ cm}^{-1}$ as medium bands [43].

NMR spectroscopy

$^1\text{H-NMR}$ spectral data of the ligand and the diamagnetic complexes and their assignments are present in Table 4. $^1\text{H-NMR}$ spectra of the ligand were reported in our previous study [20]. In the $^1\text{H-NMR}$ spectra, two broad singlets are observed for the NH and OH protons at 13.41 and 12.37

ppm, respectively. The OH proton appears at higher ppm values than the expected because of the hydrogen bonding between C=N nitrogen and OH hydrogen atoms [10, 22]. The OH and NH protons show considerable changes in NMR spectra on complexation. This should be connected with the coordination of the phenolic OH oxygen atom and removing the hydrogen bonding mentioned above.

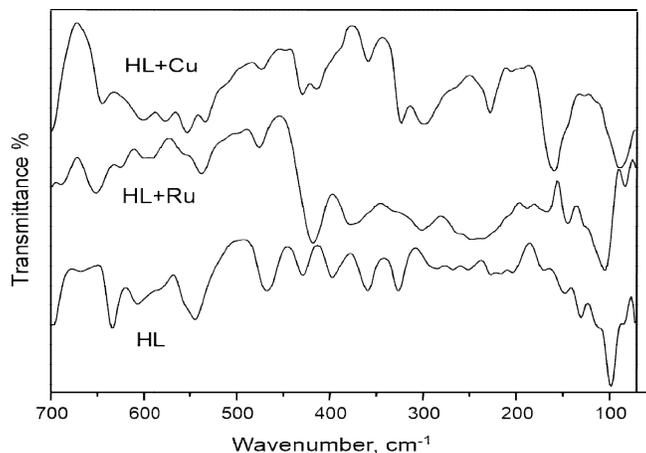


Figure 3. Far-IR spectra of the ligand and Ru(III) and Cu(II) complexes.

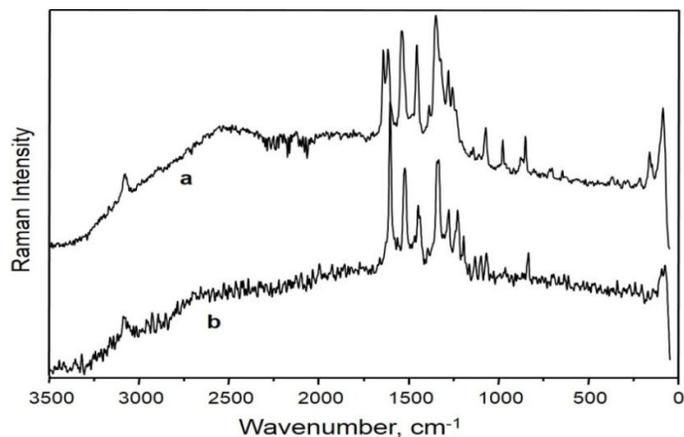


Figure 4. FT-Raman spectra of **HL** (a) and its Cd(II) complex (b).

Table 3. The FT-IR (mid- and far-IR) and Raman spectral data of the ligand and the complexes (frequencies, cm^{-1}).

Compound	FT-IR	FT-Raman
HL	3327 m,br, 3085 m, 1630 m, 1597 m, 1583 m, 1518 s, 1483 s, 1339 s, 1322 s, 1249 s, 1065 m, 970 m, 817 m, 737 m, 633 m, 554 m, 468 w, 394 m, 356 m, 323 m, 224 w, 144 w, 127 w, 96 m	3074 m, 2978 w, 2887 w, 1630 m, 1605 m, 1526 m, 1442 m, 1375 w, 1337 s, 1312 sh, 1269 m, 1244 m, 1130 w, 1060 m, 965 m, 867 w, 840 m, 793 w,

		690 w, 633 w, 357 w, 270 w, 202 w, 145 m, 72 s
[Mn(L) ₂ (H ₂ O)]·H ₂ O	3346 m, 3080 m, 2907 w,br, 1631 m, 1603 m, 1522 m, 1478 m, 1438 m, 1329 s, 1256 m, 1095 m, 1068 m, 822 m, 737 m, 693 m, 633 m, 544 m, 460 m, 382 w, 354 m, 265 w, 207 m, 135 m, 107 m, 87 m	Could not be obtained
[Fe(L) ₂ (OH)(H ₂ O)]·2H ₂ O	(A very broad band at 3500-2500 cm ⁻¹ range) 3084 m,br, 3067 m,br, 2927 m,br, 2855 m,br, 1631 m, 1603 m, 1522 m, 1470 m, 1417 m, 1341 s, 1249 m, 1176 m, 878 m, 822 s, 733 m, 652 m, 624 m, 540 m, 427 m, 375 m, 325 m, 281 m, 225 m, 153 m, 78 m	1592 m, 1533 m, 1478 m, 1364 w, 1303 s, 1245 m, 878 m, 835 w, 713 m, 656 s, 478 w, 421 m, 370 m, 284 m, 190 w, 129 m
[Ru(L) ₂ (DMSO) ₂ Cl] ₂ ·4H ₂ O	3390 m,br, 3092 m,br, 3011 m,br, 2923 w, 1627 m, 1594 m, 1518 m, 1469 m, 1417 m, 1337 s, 1293 m, 1240 m, 1071 m, 1015 m, 990 m, 878 m, 822 s, 736 m, 692 m, 652 m, 535 m, 414 m, 375 m, 299 m, 246 m, 166 m, 143 m, 106 s, 82 w.	Could not be obtained
[Co(HL)Cl ₂ (H ₂ O)]·2H ₂ O	3382 m,br, 3180 m,br, 3129 m,br, 2927 w,br, 1627 m, 1599 m, 1518 m, 1474 m, 1417 m, 1337 s, 1249 m, 1071 m, 982 m, 878 m, 818 s, 737 m, 692 m, 632 m, 544 m, 467 w, 451 m, 393 m, 321 m, 276 m, 208 m, 185 m, 149 s, 116 m	Could not be obtained
[Ni(HL)Cl ₂ (H ₂ O)]·4H ₂ O	3491 m, 3382 m, 3350 m,br, 3080 m,br, 2923 m,br, 1627 sh, 1603 m, 1519 m, 1478 m, 1337 m, 1285 m, 1245 m, 1139 m, 1064 m, 882 m, 818 s, 729 m, 693 m, 564 m, 544 m, 471 m, 427 w, 393 m, 278 m, 221 m, 158 m, 116 m, 91 m	3074 w, 2811 w, 1602 s, 1556 m, 1520 m, 1448 m, 1330 m, 1290 m, 1253 m, 1063m, 965 w, 839 m, 764 w, 700 w, 629 w, 75 m
[Pd(HL) ₂ Cl ₂]	3411 m, 3113 m, 2937 w,br, 1626 m, 1604 m, 1515 m, 1470 s, 1381 m, 1314 m, 1252 m, 1146 m, 1068 m, 816 s, 738 m, 693 m, 568 m, 525 m, 428m, 333 m, 268 w, 192 m, 159 m, 114 sh, 100 m	Could not be obtained
[Cu(L) ₂ (EtOH) ₂] ₂ ·H ₂ O	3366 m,br, 3328 m,br, 3132 m, 1629 m, 1604 m, 1537 m, 1515 m, 1473 m, 1311 m, 1252 m, 1149 m, 1057 m, 817 s, 736 m, 644 m, 599 m, 551 m, 426 m, 412 m, 357 m, 321 m, 296 m, 225 m, 156 m, 87 m.	Could not be obtained
[Ag(HL)(L)]·H ₂ O	3332 m,br, 3094 m,br, 2930 w,br, 1607 m, 1523 m, 1450 m, 1418 m, 1336 s, 1283 s, 1176 m, 1115 m, 1091 m, 877 m, 815 s, 732 m, 692 w, 623 m, 573 w, 541 m, 433 m, 377 m, 298 m, 239 m, 183 m, 159 m, 142 s, 125 m, 74 m	Could not be obtained
[Cd(HL)(L)Cl]·H ₂ O	3350 m, 3084 w, 2866 w, 1626 m, 1601 m, 1524 s, 1477 m, 1436 m, 1331 s, 1285 m, 1258 m, 1229 m, 1143 m, 1093 m, 1066 m, 883 m, 818 m, 732 m, 693 m, 657 m, 632 m, 541 m, 474 m, 459 m, 394 m, 355 m, 326 m, 293 w, 266 m, 207 m, 173 m, 98 m.	3083 m, 2823 w, 1600 s, 1521 m, 1443 m, 1342 m, 1329 m, 1275 m, 1228 m, 1193 m, 1127 m, 1095 m, 1063 m, 958 w, 829 m, 692 w, 629 w, 335 w, 238 w, 198 w, 89 m, 69 m
[HgCl ₂ (HL)]·2H ₂ O	3382 m, 3350 m, 3076 m, 2903 w,br, 1631 m, 1598 m, 1514 s, 1478 m, 1445 m, 1308 s, 1252 s, 1059 m, 967 m, 906 m, 817 s, 757 m, 736 m, 692 m, 632 m, 539 m, 467 m, 427 m, 359 m, 323 m, 289 m, 266 m, 239 m, 211 m, 188 m, 147 m, 113 m, 83 s.	1632 m, 1532 m, 1445 m, 1378 w, 1326 m, 1310 m, 1269 m, 1245 m, 1060 m, 965 m, 867 w, 840 w, 707 w, 634 w, 474 w, 354 w, 145 w, 96 m

Table 4. ¹H-NMR spectral data of the ligand and the diamagnetic complexes (the chemical shift values, δ_{H} , ppm, with coupling constants, J , Hz, in DMSO- d_6).

Compound	The benzimidazole protons				The phenolic protons			
	H4	H6	H7	NH	H3'	H5'	H6'	OH
HL	8.51 s,br	8.14 dd J=8.9, 1.5	7.78 d J=8.8	13.41 s,br	8.29 d J=2.2	7.55 dd J=8.8, 2.4	7.04 d J=8.9	12.37 s,br
[Pd(HL) ₂ Cl ₂]	8.60 s,br	8.18 d,br	7.96 s,br	12.46 s,br	8.43 d J=2.0	7.58 dd J=8.8, 2.4	7.12 d J=8.8	---
[Ag(HL)(L)]·H ₂ O	8.69 s	8.24 d J=8.3	7.55 d J=8.3	10.98 s,br	7.53 s	6.98 d J=8.8	6.71 d J=8.8	10.20 s,br
[Cd(HL)(L)Cl]·H ₂ O	8.46 s	8.10 dd J=8.8, 2.0	7.76 d J=8.8	13.24 s,br	8.23 d J=2.4	7.52 dd J=8.8, 2.4	7.01 d J=8.8	12.93 s,br
[HgCl ₂ (HL)]·2H ₂ O	8.48 d J=1.5	8.13 dd J=8.8, 2.0	7.78 d J=8.8	--	8.25 d J=2.4	7.54 dd J=8.8, 2.4	7.02 d J=8.8	--

The proton H4, neighboring to the nitro group, is observed at 8.51 ppm and it appears at the 8.46–8.69 ppm range at the complexes (Table 4). The OH proton of Ag(I) complex shows a different behavior by appearing at higher field according to the other complexes. This may be relevant with a different coordination of the Ag(I) complex, namely non-chelate structure.

Fluorescence spectroscopy

Excitation and emission spectra of the compounds were obtained in ethanol at room temperature (excitation wavelength: 354 nm; concentration: $\sim 10^{-4}$ M). The emission spectral data are presented in Table 5. The fluorescence spectra of HL and its Hg(II), Cd(II), Ag(I), Fe(III) and Mn(II) complexes are shown in Figure 5.

It was reported that 2-(2'-hydroxyphenyl)benzimidazole (HPBI) and its derivatives can undergo an excited-state intramolecular proton transfer (ESIPT) from the acidic (hydroxyl proton) to the basic site (aromatic nitrogen) when photoexcitation changes their charge density distribution [44–46]. In the ground state, the most stable form of HPBI is usually the enol form. However, in the first excited singlet state, in which the hydroxyl group is much more acidic and the nitrogen much more basic than in the ground state, the most stable structure is usually the keto tautomer. As a result, excitation of the enol form of HPBI tends to be followed by transformation to the keto form in the excited state via ESIPT reaction [46].

The ligand (HL) shows only a strong emission at 460 nm. All the complexes have fluorescence characteristic and considerable changes are observed in the fluorescence spectra of the complexes according to the ligand. The Cd(II) complex exhibited triple fluorescence and Ni(II), Cu(II), Ru(III), Pd(II) and Hg(II) complexes showed dual fluorescence while the uncomplexed ligand gave only single fluorescence at 460 nm. A blue shift is observed at Cu(II) and Ru(III) complexes whereas the other complexes red-shifted with respect to HL. Intensity of fluorescence generally decreases in the complexes, however in Co(II) and Fe(III) complexes it is almost same with the ligand, and increasing is observed at Mn(II) and Hg(II) complexes. The keto structure turned into the enol form as a consequence of complexation. And this change will affect the fluorescence characteristics of the complexes with respect to HL significantly. It is observed that all of the compounds have been emitting fluorescence in the visible region. Especially, dual fluorescence of Ru(III), Ni(II), Pd(II), Cu(II), Cd(II) and Hg(II) complexes is interesting. Thus, these compounds have potential applications as a luminescent material in light-emitting devices.

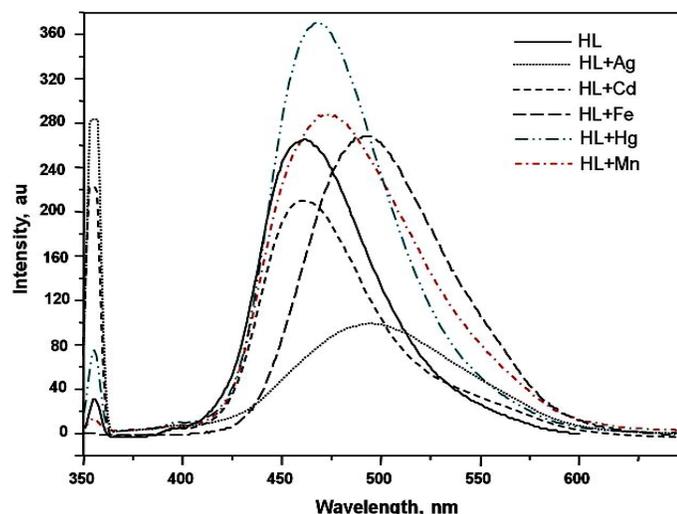


Figure 5. The fluorescence spectra of **HL** and Hg(II), Cd(II), Ag(I), Fe(III) and Mn(II) complexes in ethanol.

Table 5. UV-Visible and emission maximum wavelengths (nm) of the compounds (in ethanol, $\sim 10^{-4}$ M).

Compound	UV-visible data*	Emission maximum*
HL	230 m, 268 m, 342 sh, 349 m	460 s
[Mn(L) ₂ (H ₂ O)]·H ₂ O	232 m, 267 m, 350 m,br	469 s
[Fe(L) ₂ (OH)(H ₂ O)]·2H ₂ O	232 m, 284 m, 342 m,br, 549 m,vbr	493 s
[Ru(L) ₂ (DMSO) ₂ Cl]·4H ₂ O	247 m, 291 sh, 347 m,br, 510 sh, 581 m,br	394 w, 457 m
[Co(HL)Cl ₂ (H ₂ O) ₂]·2H ₂ O	227 m, 336 sh, 264 m, 347 m,br, 600 w,br, 661 w,br	469 s
[Ni(HL)Cl ₂ (H ₂ O) ₂]·4H ₂ O	232 m, 261 sh, 266 m, 338 sh, 353 m	394 w, 460 m
[Pd(HL) ₂ Cl ₂]	249 m, 320 m,br, 415 w,br	394 w, 474 w,br
[Cu(L) ₂ (EtOH) ₂]·H ₂ O	237 m, 263 m, 352 sh, 399 m,br,	394 w, 452 w,br
[Ag(HL)(L)]·H ₂ O	230 m, 266 m, 349 m	492 m,vbr
[Cd(HL)(L)Cl]·H ₂ O	228 m, 270 m, 351 m	397 w, 459 m,vbr, 547 w,vbr
[HgCl ₂ (HL)]·2H ₂ O	229, 267 m, 347 m,br	397, 465 s

* vbr: very broad, sh: shoulder, s: strong, m: medium, w: weak, br: broad.

UV-visible spectroscopy

The UV-visible absorption spectra of the compounds were obtained in methanol at room temperature. The UV-visible spectral data are given in Table 5. The UV-visible spectra of the compounds are shown in Figure 6. The electronic spectra of the compounds exhibit intense bands in the 200–400 nm region, which can be assigned to the $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The bands below 250 nm are due to the $n \rightarrow \sigma^*$ transitions. The compounds exhibit intense intra-ligand absorption bands in the 250–350 nm region. The $\pi \rightarrow \pi^*$ transitions of the aromatic rings are observed in the 250–300 nm region whereas the $\pi \rightarrow \pi^*$ transitions of the C=N bond are in between 300 and 350 nm [47]. The electronic spectra of the complexes are of little help in the present case at the visible region, since the d→d transitions are masked by the strong charge-transfer transition bands. The very broad bands at 581, 415 and 549 nm for Ru(III), Pd(II) and Fe(III) complexes, respectively, can be attributed to LMCT (ligand to metal charge transfer) transitions. The cobalt complex, [Co(HL)Cl₂(H₂O)₂]·2H₂O, exhibited two weak bands at 600 nm (16667 cm^{-1}), 661 nm (15129 cm^{-1}) which may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1)

and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively, and these are suggestive of octahedral geometry around the cobalt(II) ions [48, 49].

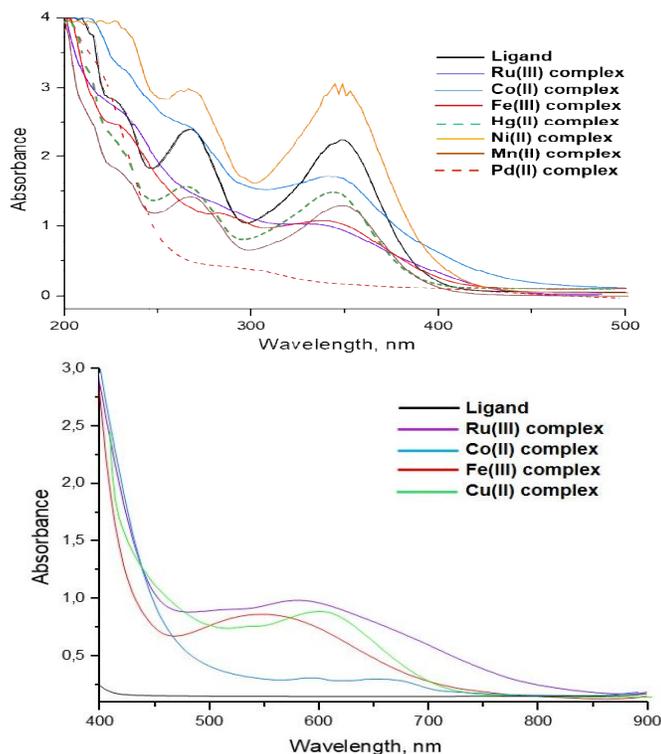


Figure 6. The UV-visible spectra of the ligand and complexes in ethanol.

Antimicrobial activity

The results concerning *in vitro* antimicrobial activity of the complexes together with the MIC values are presented in Table 6. Antimicrobial activity of **HL** and its $Fe(NO_3)_3$, $Cu(NO_3)_2$ and $Zn(NO_3)_2$ complexes were reported in previous studies [20, 21]. **HL** showed considerable activity on *S. aureus* and *S. epidermidis* as 2.4 and 19.5 $\mu g/mL$, respectively. In addition, antibacterial activity of hydrochloride form of **HL** (**HL** $\cdot HCl$) toward *S. epidermidis* was 2.4 $\mu g/mL$, a remarkable value. It was also reported that the Zn(II), Fe(III) and Cu(II) complexes was also effective on these two bacteria although weaker compared to the **HL** ligand [20, 21]. Actually six bacteria and one fungus each with multiple, fresh clinical isolates, have been studied in the antimicrobial activity tests. It is considerable (and expected) result that Ag(I) and Hg(II) complexes show strong antimicrobial activity against to all the microorganisms. In addition, the Ag(I) complex shows prominent activity on *P. mirabilis* and *C. albicans* (MIC values are 39 and 19.5 $\mu g/mL$, respectively) whereas $AgNO_3$ and the ligand itself do not show any activity towards to these two microorganisms. This can be considered one of the most important results of this study.

It is also observed that the Pd(II) and Cd(II) complexes are strongly and selectively effective on *S. aureus* and *C. albicans* (Table 6). The other complexes – except the Co(II) and Ru(III) complexes – generally exhibited activity towards *S. aureus* and *S. epidermidis* that they are

Gram positive bacteria. The Ni(II) complex is more effective on *S. epidermidis* (MIC: 9.75 µg/mL) than the ligand (MIC: 19.5 µg/mL). The results of our study indicate that the ligand and most of the complexes have the potential to generate novel metabolites, by displaying high affinities towards some of the receptors. The superior antimicrobial activities of the complexes mentioned above against *S. aureus*, *S. epidermidis* and *C. albicans* are considered to be valuable contribution to the researches on metal-based drugs field and encourage working further investigation on these compounds.

Table 6. *In vitro* antimicrobial activity of the compounds (MIC, µg/mL).

Compound	Microorganisms						
	<i>Sa</i> ^a	<i>Se</i> ^a	<i>Ec</i> ^b	<i>Kp</i> ^b	<i>Pa</i> ^b	<i>Pm</i> ^b	<i>Ca</i>
HL*	2.4	19.5	— ^c	—	—	—	—
HL·HCl*	2.4	2.4	—	—	—	—	—
[Zn(L) ₂]·2H ₂ O*	19.5	156	—	—	—	—	—
[Fe(L) ₂ (H ₂ O) ₂](NO ₃)·3H ₂ O*	9.8	39	—	—	—	—	—
[Cu(L) ₂]·2H ₂ O*	19.5	39	—	—	—	—	—
[Mn(L) ₂ (H ₂ O)]·H ₂ O	4.9	—	—	—	—	—	—
[Fe(L) ₂ (OH)(H ₂ O)]·2H ₂ O	4.9	—	—	—	—	—	—
[Ru(L) ₂ (DMSO) ₂ Cl]·4H ₂ O	—	—	—	—	—	—	—
[Co(HL)Cl ₂ (H ₂ O) ₂]·2H ₂ O	—	—	—	—	—	—	—
[Ni(HL)Cl ₂ (H ₂ O) ₂]·4H ₂ O	19.5	—	—	—	—	—	—
[Pd(HL) ₂ Cl ₂]	4.9	—	—	—	—	—	78
[Cu(L) ₂ (EtOH) ₂]·H ₂ O	4.9	—	—	—	—	—	—
[Ag(HL)(L)]·H ₂ O	4.9	39	39	156	39	39	19.5
[Cd(HL)(L)Cl]·H ₂ O	4.9	—	—	—	—	—	39
[HgCl ₂ (HL)]·2H ₂ O	4.9	4.9	4.9	4.9	4.9	4.9	39
MnCl ₂ ·6H ₂ O	—	—	—	—	—	—	—
FeCl ₃ ·6H ₂ O	—	—	—	—	—	—	—
CoCl ₂ ·6H ₂ O	—	—	—	—	—	—	—
NiCl ₂ ·6H ₂ O	—	—	—	—	—	—	—
CuCl ₂ ·2H ₂ O	—	—	—	—	—	—	—
Ru(DMSO) ₄ Cl ₂	—	—	—	—	—	—	—
PdCl ₂	—	—	—	—	—	—	—
AgNO ₃	9.8	4.9	4.9	4.9	4.9	—	—
CdCl ₂ ·H ₂ O	—	—	—	—	—	—	—
HgCl ₂ ·H ₂ O	0.65	0.65	1.3	0.49	10.4	1.30	2.6
Ciprofloxacin	0.25	0.0625	0.0156	0.0078	1.0	0.0156	—
Fluconazole	—	—	—	—	—	—	1.0

*Taken from literatures 20 and 21. *Sa* *Staphylococcus aureus* ATCC 6538; *Se* *Staphylococcus epidermidis* ATCC 12228; *Ec* *Escherichia coli* ATCC 8739; *Kp* *Klebsiella pneumoniae* ATCC 4352; *Pa* *Pseudomonas aeruginosa* ATCC 1539; *Pm* *Proteus mirabilis* ATCC 14153; *Ca* *Candida albicans* ATCC 10231. ^aGram positive; ^bGram negative; ^c—: No antimicrobial effect at 5000 µg/mL and lower dilutions.

CONCLUSION

In the present study, MnCl₂, FeCl₃, CoCl₂, NiCl₂, CuCl₂, Ru(DMSO)₄Cl₂, PdCl₂, AgNO₃, CdCl₂ and HgCl₂ complexes of **HL** were synthesized and characterized by using analytical and spectroscopic techniques such as molar conductivity, magnetic moment, TGA, UV-Vis, FT-IR, FT-Raman, NMR and fluorescence spectroscopy. Their antibacterial and antifungal activities were evaluated by the disk diffusion method against six bacteria and *C. albicans* as yeast. It was observed that most of the complexes exhibited considerable activity on *S. aureus* especially. The Hg(II) and Ag(I) complexes were found to have superior activity toward all of the microorganisms whereas the Pd(II) and Cd(II) complexes showed considerably antimicrobial effect on *S. aureus* and *C. albicans* selectively.

ACKNOWLEDGMENTS

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