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COORDINATION COMPOUNDS

Spectral Characterization and Antibacterial Effect of 2-Methyl-6-(5-H/Me/Cl/NO_2-1*H*-Benzimidazol-2-yl)-Phenols and Some Transition Metal Complexes[1]

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Abstract—2-Methyl-6-(5-H/methyl/chloro/nitro-1*H*-benzimidazol-2-yl)-phenols ($HL_x : x = 1–4$) ligands and HL_1 complexes with $Fe(NO_3)_3$, $Cu(NO_3)_2$, $AgNO_3$, $Zn(NO_3)_2$ have been synthesized and characterized. The structures of the compounds were confirmed on the basis of elemental analysis, molar conductivity, magnetic moment, FT-IR, ^1H- and ^{13}C-NMR. Antibacterial activity of the free ligands, their hydrochloride salts and the complexes were evaluated using the disk diffusion method in dimethyl sulfoxide as well as the minimum inhibitory concentration dilution method, against nine bacteria. While HL_1 ligand has not any activity, it's Ag(I) complex show antibacterial effect toward almost to all the bacteria. Zn(II) complex has antibacterial effect on especially *K. pneumoniae*, *S. epidermidis* and *S. aureus* bacteria.

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Investigation of biological activity of complex compounds is a field that has developed over the years. In the literature, antimicrobial activity of many metal complexes is investigated. For example, Ag(I) complexes of quinoxaline, dimethylpyrazine, aminopyridine and nicotinate-type ligands have considerable antimicrobial activity [1, 2].

Likewise, in the literature some metal complexes showed a change in the antimicrobial [3] and antifungal effect of the ligands [4].

Cytotoxicity of some trimethylsilylpropyl substituted benzimidazolinium salts and their metal complexes with $CuCl_2$, $ZnCl_2$, $CoCl_2$, $PdCl_2$, and $AgNO_3$ was tested and it was determined that the cytotoxicity of the complexes depended on the metal [5].

Fe(III), Ag(I), and Hg(II) complexes of some 5-substituted 2-(2'-hydroxyphenyl)-1*H*-benzimidazoles [6] and Cu(II), Zn(II), Ag(I) complexes of some 2- and 3-pyridinyl-1*H*-benzimidazoles have an antibacterial and antifungal effect [7].

Iron, copper and zinc are essential elements and Fe(III), Cu(II) and Zn(II) ions play important roles in biochemical systems. Silver compounds are known have high antimicrobial effect. In our previous work, 2-methoxy-6-(5-H/methyl/chloro/nitro-1*H*-benzimidazol-2-yl)-phenols and some transition metal complexes were synthesized and characterized. Some ligands and Cu(II) and Zn(II) complexes showed antibacterial activity against Gram positive bacteria [8]. In this work, 2-methyl-6-(1*H*-benzimidazol-2-yl)-phenol (HL_1), it's methyl, chloro, nitro derivatives [2-methyl-6-(5-methyl/chloro/nitro-1*H*-benzimidazol-2-yl)-phenols (HL_x): $x = 2–4$] and Fe(III), Cu(II), Ag(I) and Zn(II) nitrate complexes are reported. Antibacterial activities of the compounds are evaluated by the disk diffusion method against nine bacteria. Herein, we discuss the differences of 5-substituents and metal ion complexes with the free HL_1 ligand in their structural-biological activity relationship.

EXPERIMENTAL

Chemistry

All chemicals and solvents were reagent grade and were used as purchased without further purification. Melting points were determined using an Electrothermal melting-point apparatus. Analytical data were obtained with a Thermo Finnigan Flash EA 1112 analyser. Atomic absorption data were obtained with a Perkin Elmer Analyst 200 flame spectrometer. Molar conductivity of the complexes was measured on a WPA CMD750 conductivity meter in DMSO at 25°C. ^1H and ^{13}C-NMR spectra were run on a Varian Unity Inova 500 NMR spectrometer. The residual DMSO-d_6 signal was also used as an internal reference. FT-IR spectra were recorded in KBr disks on a Mattson 1000 FT-IR spectrometer. Magnetic measurements were carried out on a Sherwood Scientific apparatus at room temperature by Gouy's method.

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Synthesis of the Ligands: General Procedure

2-Methyl-6-(1*H*-benzimidazol-2-yl)-phenol (HL_1). The ligands were prepared according to literature procedures [9, 10], by reacting 2-hydroxy-3-methylbenzaldehyde (1.36 g, 10 mmol) and an equivalent amount of $NaHSO_3$ (1.04 g, 10 mmol) at room temperature in EtOH (25 mL) for several h. The mixture was treated with *o*-phenylenediamine (1.08 g, 10 mmol) in dimethylformamide (15 mL) and gently refluxed for 2 h. The reaction mixture was then poured into iced H_2O (500 mL), filtered and crystallized from EtOH.

Synthesis of the Complexes

$[Fe(L_1)(OH)(H_2O)_3](NO_3)$. A hot solution of the ligand HL_1 (112 mg, 0.5 mmol) in *i*-PrOH (10 mL) was treated with $Fe(NO_3)_3 \cdot 9H_2O$ (222 mg, 0.55 mmol) in *i*-PrOH (5 mL) at ~60°C for several h. The solution mixture was allowed to stand at ~4°C for several days to precipitate black solid products, which were collected by filtration and dried at 80–90°C.

$[Cu(L_1)_2] \cdot 2H_2O$. 112 mg ligand (0.5 mmol) and 133 mg $Cu(NO_3)_2 \cdot 3H_2O$ (0.55 mmol) were reacted in 10 mL methanol. After 4 h reflux the precipitate was filtered and dried at 80–90°C.

$[Ag(HL_1)](NO_3)$. 112 mg ligand (0.5 mmol) and 94 mg $AgNO_3$ (0.55 mmol) was treated 10 mL ethanol at room temperature for 6 h with stirring. The precipitate was filtered and dried at 80–90°C.

$[Zn(L_1)(H_2O)_2](NO_3)$. 112 mg ligand (0.5 mmol) suspended in ethyl acetate, 164 mg $Zn(NO_3)_2 \cdot 6H_2O$ (0.55 mmol) 15 mL ethylacetate was added to the ligand solution. The mixture was refluxed for 2 h. The dark yellow precipitate was filtered and dried at 80–90°C.

Microorganisms

The antimicrobial activities are evaluated against Gram positive (*Staphylococcus aureus* ATCC 29213, *Bacillus cereus* ATCC 11778, *Bacillus subtilis* ATCC 6633, *Staphylococcus epidermidis* ATCC 12228) and Gram negative (*Escherichia coli* ATCC 25922, *Klebsiella pneumoniae* ATCC 4352, *Pseudomonas aeruginosa* ATCC 27853, *Salmonella enteritidis* KUEN 349, *Proteus mirabilis* CCM 1944) bacteria using disk diffusion method as well as the minimum inhibitory concentration (MIC) dilution method. The strains were provided from the Centre for Research and Application of Culture Collections of Microorganisms, Istanbul University (KUKENS) were used for the detection of antibacterial effect of the strains.

Test Media. Mueller-Hinton Agar (Fluka 70191) were used for the detection of the antibacterial effect qualitatively and to maintain the strains. For the detection of the quantitative antibacterial effect by MIC, Mueller-Hinton broth (Fluka 70192) (CAMBH) with Mg^{2+} (10 mg Mg^{2+}/mL) and Ca^{2+} (20 mg Ca^{2+}/L) was used as the medium.

Detection of the Antibacterial Activity

Qualitative antibacterial evaluation. Disc diffusion method was used for the detection of the antibacterial effect of the chemical agents, qualitatively [11]. For this purpose, filter papers (Whatman No. 1) with 6 mm diameter were autoclaved and dried at 37°C for overnight. Each chemical agent (21.27 mg) was dissolved in dimethyl sulfoxide and 23.5 μl of this solution (containing 500 μg chemical agent) were soaked on to the sterile discs. Bacterial suspension with $1–2 \times 10^8$ cfu/mL (McFarland 0.5) were prepared from each bacterial strain and streaked onto the agar, chemical agents impregnated discs were placed onto the agar surface and incubated at 37°C for 24 h. Chemical agents with growth inhibition zones were used for the further examinations.

Quantitative antibacterial evaluation. For the detection of the antibacterial effect of the chemical agents, quantitatively, macro dilution broth method according to clinical and laboratory standards institute (formerly NCCLS) were performed [12]. Serial dilutions of the chemical agents between 532–0.26 μg/mL with CAMBH were prepared within sterile tubes. Bacterial suspension with 10^7 cfu/mL final concentration was inoculated. Positive (without tested chemical agent) and negative (without bacterial suspension) tubes were used at the end of the each organism tested. Tubes were incubated at 37°C for 24 h. The MIC value was defined as the lowest concentration of the chemical agent giving complete inhibition of visible growth.

RESULTS AND DISCUSSIONS

Physical Properties

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

The molar conductivity values of the complexes are 46, 51 and 37 Ω^{-1} cm^2 mol^{-1} for Fe(III), Ag(I) and Zn(II) complexes, respectively. These results are indicative for 1 : 1 electrolyte complexes. Cu(II) complex has non-ionic character according to the molar conductivity.

The room temperature effective magnetic moment value of $[Fe(L_1)(OH)(H_2O)_3](NO_3)$ is 3.90 BM, indicating stabilization of the species having intermediate ferric spin (S = 3/2) state. The occurrence of such an intermediate spin state is typical for the six and five coordinate ferric complexes (Fig. 4) [13–15]. Magnetic moment value of $[Cu(L_1)_2] \cdot 2H_2O$ complex is 1.67 BM, which is in the expected range for a typical d^9 Cu(II) complex.

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

Compound	Found (calcd.) %				Yield % *	M.p.dec.	Color	Λ
	C	H	N	M				
HL_1	75.3	5.6	12.1	–	60	281	dirty	–
$C_{14}H_{12}N_2O$	(75.0)	(5.4)	(12.5)				white	
HL_2	75.5	5.8	11.0	–	55	232	dirty	–
$C_{15}H_{14}N_2O$	(75.6)	(5.9)	(11.8)				white	
HL_3	65.1	4.1	10.6	–	60	273	grey	–
$C_{14}H_{11}ClN_2O$	(65.0)	(4.3)	(10.8)					
HL_4	61.9	4.6	15.6	–	60	226	yellow	–
$C_{14}H_{11}N_3O_3$	(62.4)	(4.1)	(15.6)					
$[Fe(\mathbf{L_1})(OH)(H_2O)_3](NO_3)$	40.0	3.9	9.8	14.8	65	>350	black	46
$C_{14}H_{18}FeN_3O_8$	(40.8)	(4.4)	(10.2)	(13.6)				
$[Cu(\mathbf{L_1})_2] \cdot 2H_2O$	61.1	4.4	10.8	11.2	70	210	dark	16
$C_{28}H_{26}CuN_4O_4$	(61.6)	(4.8)	(10.3)	(11.6)			green	
$[Ag(\mathbf{HL_1})](NO_3)$	42.2	2.8	10.4	24.6	65	169	light	51
$C_{14}H_{12}AgN_3O_4$	(42.7)	(3.1)	(10.7)	(27.4)			brown	
$[Zn(\mathbf{L_1})(H_2O)_2](NO_3)$	44.2	3.4	11.5	16.0	70	>350	dark	37
$C_{14}H_{15}N_3O_6Zn$	(43.5)	(3.9)	(10.9)	(16.9)			yellow	

μ_{eff} values for $[Fe(\mathbf{L_1})(OH)(H_2O)_3]NO_3$ and $[Cu(\mathbf{L_1})_2] \cdot 2H_2O$ are 3.90 and 1.67 BM, respectively.
* approximately values; dec., decomposed; Λ, molar conductivity, Ω^{-1} cm^2 mol^{-1} (25°C).

FT-IR Spectra

FT-IR spectral data of the ligands and the complexes are given in Table 2. The characteristic ν(O–H) and ν(N–H) vibration frequencies of the HL_1, HL_2 and HL_3 ligands exhibit only a single strong band at *ca.* 3340 cm^{-1} in the IR spectra, probably caused by doubly intramolecular hydrogen bonding between the phenoxyl hydrogen atom and one of the imine nitrogen atom (Table 2, Fig. 2) [16–18]. The 3338 cm^{-1} band in the HL_1 changes significantly upon metal complexation indicating deprotonation and subsequent involvement of the phenoxyl group in metal coordination [19]. In HL_4 spectra ν(O–H) and ν(N–H) vibration frequencies appear separately because of weak intramolecular hydrogen bonding.

Appearance of a strong broad band at *ca.* 3400 cm^{-1} in the Fe(III), Cu(II) and Zn(II) complexes strongly supports the presence of coordinated water molecules. The characteristic ν(C–H) modes of ring residues and methyl groups are observed in the wave region between 3107–2903 cm^{-1}. The sharp or medium bands at the 900–740 cm^{-1} range are due to the out-of-plane deformation bands for the aromatic C–H.

The ν(C=C) frequencies for the ring residue are expected to appear at *ca.* 1625 cm^{-1} with their own characteristics for the ligands in the IR spectra. These frequencies are expected to shift at lower frequency upon complex formation. Similarly the (C=N) asymmetric stretching frequencies are expected to appear at *ca.* 1600 cm^{-1}.

Fe(III), Ag(I) and Zn(II) complexes show strong bands at 1386 cm^{-1} in their IR spectra, supporting the presence of uncoordinated nitrate ion, which was also confirmed by conductivity data [20–22].

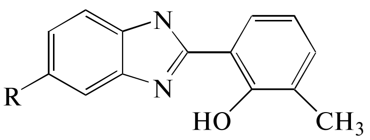

Fig. 1. Structure of the ligands R = H, HL_1; R = CH_3, HL_2; R = Cl, HL_3; R = NO_2, HL_4.

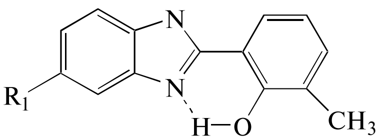

Fig. 2. The intramolecular hydrogen bonding in the ligands.

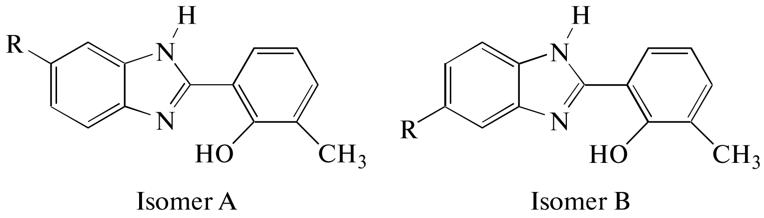

Fig. 3. Isomeric structures of HL_2 ($R = CH_3$) and HL_4 ($R = NO_2$).

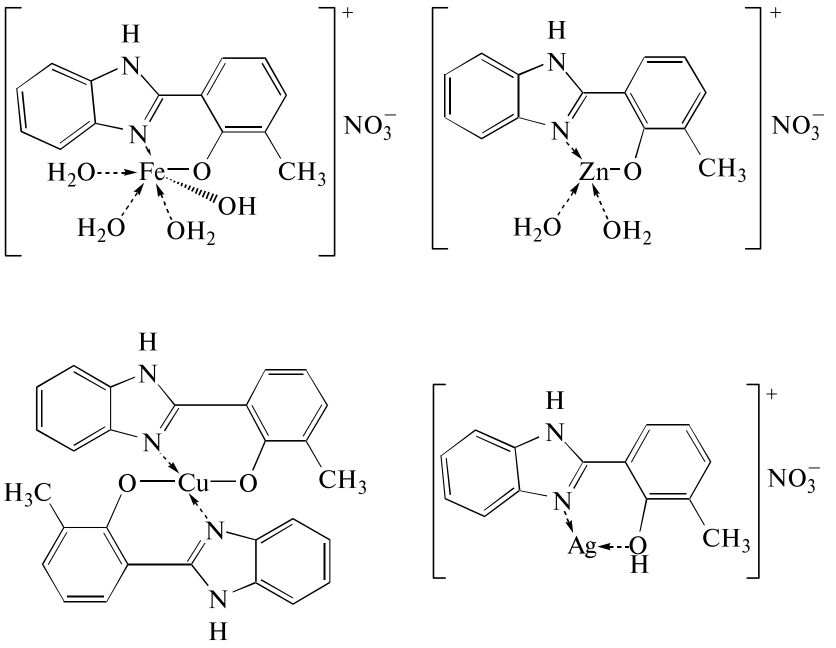

Fig. 4. The proposal structures for the complexes under study.

NMR Spectra

^1H- and ^{13}C-NMR spectral data and assignments are given in Tables 3 and 4. According to the ^1H-NMR spectra HL_2 and HL_4 have two isomeric forms (Fig. 3, Table 3). The isomer structures are observed for the benzimidazole protons only.

The ligands give two singlets over 13 ppm belonging to NH (broad singlet) and OH (sharp singlet) protons (except HL_4). These signals are closer each other because of intra-molecular hydrogen bonding between the OH hydrogen and the C=N nitrogen atoms.

The phenolic and benzimidazole protons of the Ag(I) and Zn(II) complexes change their characteristics according to the ligand. In the Zn(II) complex, all of the multiplet, doublet or triplet peaks change to broad singlets or broad doublets because of the metal ion's strong perturbing effect. It can be said that, on complexation, acidic character of the benzimidazole and the phenol moiety protons is increased.

The OH proton signal in the ^1H-NMR spectra of the Zn(II) complex is removed as expected. This observation is an evidence for the OH hydrogen's eliminating and the phenolic oxygen's coordinating to the Zn(II) ion (Fig. 4). In the Ag(I) complex, the singlet at 13.25 ppm shows that the phenolic OH hydrogen is not eliminated; however changes in the chemical shift and the coupling constant values show that a complex is formed.

All of the carbon atoms were observed in the ^{13}C-NMR (APT) spectra of the HL_1 and its Ag(I), Zn(II) complexes. In the ^{13}C-NMR spectra of the HL_1 and its Ag(I) and Zn(II) complexes the signal around 152.87, 152.60 and 153.71 ppm belongs to imidazole C=N (C-2) carbon atom, respectively. The highest ppm values of these compounds, 157.18, 156.87 and 164.02, are due to C1' carbon atom (phenolic oxygen bonded C atoms), respectively. The low ppm signals, 16.53, 16.63 and 18.20 ppm, are assigned to the 2'-substituted methyl carbon atoms. C8 and C9 carbon atoms appear in 130–141 ppm range (Table 4). In HL_1 ^{13}C-NMR spectra, it is expected C4 + C7, C5 + C6 and C8 + C9 are to be identical, however they are

Table 2. IR spectral data of the ligands and the complexes

Compound	Frequency (cm^{-1})
$\mathbf{HL_1}$	3338 s, 3056 w, 2903 w, 1628 m, 1601 m, 1532 m, 1454 m, 1474 s, 1428 s, 1389 m, 1320 m, 1259 m, 1228 m, 1089 m, 820 m, 743 m, 642 m
$[\mathrm{Fe}(\mathbf{L_1})(\mathrm{OH})(\mathrm{H_2O})_3](\mathrm{NO_3})$	3407 s,br, 3238 m,br, 3107 m,br, 1624 m, 1605 w, 1559 m, 1463 m, 1386 s, 1262 m, 1031 w, 750 m, 666 w
$[\mathrm{Cu}(\mathbf{L_1})_2] \cdot 2\mathrm{H_2O}$	3408 m,br, 3215 m,br, 3062 m,br, 2969 w, 1623 m, 1608 m, 1562 m, 1462 m, 1354 m, 1315 m, 1215 m, 1108 m, 1046 m, 831 m, 746 s
$[\mathrm{Ag}(\mathbf{HL_1})](\mathrm{NO_3})$	3344 m, 3301 m, 3057 m, 2918 w, 1624 m, 1598 m, 1528 m, 1478 s, 1455 s, 1431 m, 1386 s, 1320 m, 1272 m, 1216 m, 1035 m, 819 m, 743 s, 572m
$[\mathrm{Zn}(\mathbf{L_1})(\mathrm{H_2O})_2](\mathrm{NO_3})$	3434 m,br, 3288 s, 3057 w, 2918 w, 1628 w, 1601 m, 1540 m, 1493 m, 1474 s, 1455 m, 1386 s, 1305 s, 1232 m, 1170 m, 1112 m, 1043 m, 904 m, 789 m, 747 m, 716 m
$\mathbf{HL_2}$	3342 s, 3080 w, 2964 w, 2918 w, 1632 m, 1605 m, 1474 s, 1428 m, 1386 m, 1320 m, 1278 m, 1259 m, 1228 m, 1089 m, 804 m, 750 m
$\mathbf{HL_3}$	3331 s, 3075 w, 2917 w, 1615 m, 1602 m, 1531 m, 1477 s, 1423 m, 1387 s, 1307 m, 1254 s, 1225 m, 1064 m, 931 m, 810 m, 790 s, 645 m
$\mathbf{HL_4}$	3420 br, 3328 s, 3078 m, 2927 m, 1624 m, 1597 m, 1523 s, 1497 m, 1455 m, 1352 s, 1212 m, 1089 m, 1035 m, 820 m, 742 m, 550 m

Table 3. ^{1}H-NMR spectral data of the ligands and the complexes (in DMSO-d_6)

Compound	Chemical shifts, δ_H, ppm and coupling constants (J, Hz)									
	Benzimidazole protons					Phenolic protons				
	H4	H5	H6	H7	NH	H3'	H4'	H5'	OH	CH_3
HL_1	7.71 d J = 7.8	7.31 m	7.31 m	7.59 d J = 7.8	13.50 s	7.27 d-d J = 7.3, 1.0	6.92 t J = 7.8, 7.3	7.88 d-d J = 7.8, 1.0	13.19 s	2.26 s
A	7.78 d J=7.8	7.28 t 8.8, 6.3	7.28 t 8.8, 6.3	7.68 d J = 7.8	13.28 s	7.30 d J = 7.3	6.97 t J = 7.8, 7.3	7.88 d,br J = 7.7	13.25 s	2.26 s
B	8.95 s,br	8.04 s,br	7.31 d,br	7.60 s,br	13.57 s,br	7.25 s,br	7.25 s,br	7.87 s,br	–	2.07 s
HL_2, IsomerA (55%)	7.58 d J = 8.3	7.11 d J = 8.3	2.46 s*	7.50 s	13.50 s,br	7.25 d J = 7.3	6.90 t J = 7.8, 7.3	7.85 d J = 7.8	13.02 s	2.26 s
HL_2, IsomerB (45%)	7.37 s	2.44 s*	7.09 d J = 8.3	7.46 d J = 8.3	13.50 s,br	7.25 d J = 7.3	6.90 t J = 7.8, 7.3	7.85 d J = 7.8	13.02 s	2.26 s
HL_3	7.72 s,br	–	7.28 d,br J = 7.3	7.61 s,br	13.36 s,br	7.32 s,br	6.94 t J = 7.8, 7.8	7.87 d,br J = 8.0	13.21 s,br	2.26 s
HL_4, IsomerA (50%)	8.97 s	–	7.56 d J = 7.1	7.35 d,br J = 7.3	12.57 s,br	6.62 s,br	6.93 t J = 7.6, 7.3	6.62 s,br	–	2.25 s
HL_4, IsomerB (50%)	6.83 d J = 8.9	7.96 d-d J = 8.8, 2.4	–	8.01 d J = 2.4	12.57 s,br	6.62 s,br	6.93 t J = 7.6, 7.3	6.62 s,br	–	2.25 s

* 3H (CH_3); A: $[\mathrm{Ag}(\mathbf{HL_1})]\mathrm{NO_3}$; B: $[\mathrm{Zn}(\mathbf{L_1})(\mathrm{H_2O})_2](\mathrm{NO_3})$.

Table 4. ^{13}C-NMR (APT) spectral data of the HL_1 and its Ag(I) and Zn(II) complexes (δ_C, ppm; in DMSO-d_6)

Compound	The benzimidazole carbons				The phenolic carbons						
	C2	C4+C7	C5+C6	C8+C9	C1'	C2'	C3'	C4'	C5'	C6'	CH_3
$\mathbf{HL_1}$	152.87	112.15	124.33	141.46	157.18	126.40	133.27	119.26	123.11	112.32	16.53
		118.58	124.00	133.84							
A	152.60	112.71	124.76	141.27	156.87	126.49	133.47	119.47	123.08	112.16	16.63
		118.55	123.70	133.86							
B	153.71	112.16	24.61	140.74	164.02	126.91	133.29	119.16	123.14	111.72	18.20
		132.34	124.46	133.85							

A: $[Ag(\mathbf{HL_1})]NO_3$, B: $[Zn(\mathbf{L_1})(H_2O)_2](NO_3)$

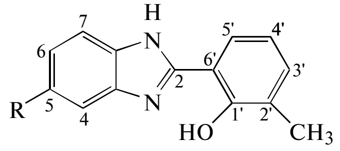

Table 5. In vitro antimicrobial activity of the compounds (inhibition zone, mm)

Compound	Microorganisms								
	1	2	3	4	5	6	7	8	9
HL_1	–	–	–	–	–	–	–	–	–
$HL_1 \cdot HCl$	–	–	–	–	–	–	–	–	–
HL_2	–	–	–	–	–	–	–	–	–
$HL_2 \cdot HCl$	–	–	–	–	–	–	–	–	–
HL_3	–	–	–	–	–	–	–	–	–
$HL_3 \cdot HCl$	–	–	–	–	–	–	–	–	–
HL_4	–	–	–	–	–	–	–	–	–
$HL_4 \cdot HCl$	–	–	–	–	–	–	8	–	<5
$[Fe(\mathbf{L_1})(OH)(H_2O)_3](NO_3)$	–	–	8	–	7	–	8	–	–
$[Cu(\mathbf{L_1})_2] \cdot 2H_2O$	–	–	–	–	–	8	–	–	–
$[Ag(\mathbf{HL_1})](NO_3)$	10	8	10	–	10	14	10	8	7
$[Zn(\mathbf{L_1})(H_2O)_2](NO_3)$	–	–	–	–	8	12	8	–	–

– : zone did not form.

appear as separately because of the strong intramolecular hydrogen bonding with phenolic oxygen and C=N nitrogen atoms in the solvent (Fig. 2). It is likely that the hydrogen bonding changed the identity of the benzimidazole ring carbon atoms as in the metal complexes.

The other signals belong to the benzimidazole benzen and phenol rings carbon atoms (Table 5).

Antibacterial Effect

The results concerning in vitro antibacterial activity of the ligand, their hydrochloride salts and the complexes together with the inhibition zone (mm) and MIC values are presented in Tables 5 and 6.

It is observed that Ag(I) complex is effective toward almost to all the bacteria. Besides of this, Zn(II) com-

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

Compound	Microorganisms								
	1	2	3	4	5	6	7	8	9
HL_1	–	–	–	–	–	–	–	–	–
$HL_1 \cdot HCl$	–	–	–	–	–	–	–	–	–
HL_2	–	–	–	–	–	–	–	–	–
$HL_2 \cdot HCl$	–	–	–	–	–	–	–	–	–
HL_3	–	–	–	–	–	–	–	–	–
$HL_3 \cdot HCl$	–	–	–	–	–	–	–	–	–
HL_4	–	–	–	–	–	–	–	–	–
$HL_4 \cdot HCl$	–	–	–	–	–	–	266	–	266
$[Fe(\mathbf{L_1})(OH)(H_2O)_3](NO_3)$	–	–	–	–	–	–	–	–	–
$[Cu(\mathbf{L_1})_2] \cdot 2H_2O$	–	–	–	–	–	133	–	–	–
$[Ag(H\mathbf{L_1})](NO_3)$	8.3	16.6	8.3	–	8.3	2.1	16.6	16.6	33.2
$[Zn(\mathbf{L_1})(H_2O)_2](NO_3)$	–	–	–	–	*	*	66.5	–	–

1. *P. aeruginosa ATCC 27853*, 2. *S. enteriditis KUEN 349*, 3. *E. coli ATCC 25922*,

4. *P. mirabilis CCM 1944*, 5. *K. pneumoniae ATCC 4352*, 6. *S. epidermidis ATCC 12228*,

7. *S. aureus ATCC 29213*, 8. *B. cereus ATCC 11778,* 9. *B.subtilis ATCC 6633.*

– : No antibacterial activity qualitatively.

* : MIC value was not detected in the test concentrations (<532 μg/mL).

plex has antibacterial effect on especially *K. pneumoniae*, *S. epidermidis* and *S. aureus* bacteria, while the ligand has not any activity. Also, Cu(II) complex is effective selectively on *S. epidermidis*. It is observed that Fe(III) complex has antibacterial effect toward *E. coli*, *K. pneumoniae* and *S. aureus* considering the zone values. These observation shows that a metal ion coordinates to the organic compound increases the antimicrobial activity probably due to synergic effect.

On the other hand, HL_4 is only ligand exhibits microbial effect among the ligands (on *S. aureus*). This may be resulted from the nitro group existence as reported in the literature [23].

As a result, it can be said that the antibacterial activities of these compounds against tested organisms suggested further investigation on these compounds.

In conclusion, the optimized structures for the complexes in Fig. 3, are in best accord with the analytical data, molar conductivity, magnetic moments, FT-IR and NMR spectroscopic measurements.

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