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COORDINATION COMPOUNDS

Zn(II) and Cu(II) Complexes of 2-(2-Hydroxy-5-methylphenyl)-1*H*-benzimidazole and Crystal Structure of 2-(2-Hydroxy-5-methylphenyl)-1*H*-benzimidazolium Chloride[1]

Aydin Tavman
Istanbul University, Faculty of Engineering, Chemistry Department, Avcilar, 34320, Istanbul, Turkey
e-mail: atavman@istanbl. edu. tr

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Abstract—2-(2-Hydroxy-5-methylphenyl)-1*H*-benzimidazole ligand (HL) and its complexes with $Cu(NO_3)_2$, $Zn(NO_3)_2$ 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. Cu(II) complex has 1 : 2 metal : ligand ratio, while Zn(II) complex is 1 : 1. Crystal structure of 2-(2-hydroxy-5-methylphenyl)-1*H*-benzimidazolium chloride (HL · HC1) was determined by single-crystal X-ray diffraction. It crystallizes in the orthorombic, space group $P2_12_12_1$and $Z = 4$.

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2-Substituted benzimidazoles have varied pharmacological activities, such as antitumor, antiverminous, antiviral, hypotensive, spasmolytic etc. [1].

2-Hydroxyphenyl-1*H*-benzimidazole and its derivatives are known to be strong chelating agents. Various transition metal complexes of hydroxyphenyl-1*H*-benzimidazole type ligands are reported [2, 3]. These ligands are potential N, O donors and they react easily with the metal ions to give stable chelate complexes.

There are a lot of crystal structure of benzimidazole derivatives and their salts in the literature. For example, crystal structure of 2-(3-methoxy-2-hydroxyphenyl)benzimidazole [4], 1,3-bis(4-methylbenzyl)benzimidazolium chloride monohydrate [5], 2,2'-(propane-1,3-diyl)bis(benzimidazolium) dichloride dihydrate [6], 2,2'-(iminodimethylene)bis(1*H*-benzimidazolium)(1+) chloride [7] and 2,2'-(butane-1,4-diyl)dibenzimidazolium dichloride dihydrate [8] were reported. However, studies on crystal structures of 2-hydroxyphenyl benzimidazole derivatives and their hydrochloride salts are very limited. In this study, 2-(2-hydroxy-5-methylphenyl)-1*H*-benzimidazole ligand (HL) and its complexes with $Cu(NO_3)_2$, $Zn(NO_3)_2$ have been synthesized and characterized. Crystal structure of 2-(2-hydroxy-5-methylphenyl)-1*H*-benzimidazolium chloride (HL · HC1) was determined by single-crystal X-ray diffraction.

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 analyzer. Atomic absorption data were obtained with a Perkin Elmer Analyst 200 flame spectrometer for Cu and Zn analysis. Molar conductivity of the complexes was measured on a WPA CMD750 conductivity meter in dimethylsulfoxide (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. UV-Visible spectra were performed on a Perkin Elmer Lambda 25 UV/Visible Spectrometer. 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.

Synthesis of HL. The ligand was prepared according to literature procedures [9, 10], by reacting 2-hydroxy-5-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

$[Cu(L)_2] \cdot 3H_2O$. 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.

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[1] The article is published in the original.

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

Compound	Elemental analysis Found (Calcd), %				Yield, %*	M.P., °C	Colour
	C	H	N	M			
HL $C_{14}H_{12}N_2O$	75.3 (75.0)	5.7 (5.4)	12.2 (12.5)	–	70	257	colorless
$[Cu(\mathbf{L})_2] \cdot 3H_2O$ [1, 2] $C_{28}H_{28}CuN_4O_5$	58.8 (59.6)	4.6 (5.0)	9.6 (9.9)	10.8 (11.3)	75	>350	dark green
$[Zn(\mathbf{L})(H_2O)_2]NO_3$ [1] $C_{14}H_{15}N_3O_6Zn$	42.9 (43.5)	3.6 (3.9)	10.8 (10.9)	16.0 (16.9)	65	>350	dark yellow

[1] Molar conductivity of the Cu(II) and Zn(II) complexes are 9.5 and 47 Ω^{-1} cm^2 mol^{-1} (25°C), respectively.
[2] μ_{eff} value for $[Cu(\mathbf{L})_2] \cdot 3H_2O$ is 1.61 BM. * approximately values.

Table 2. IR and UV-Vis. spectral data of the ligand and the complexes

Compound	Frequency (cm^{-1}), KBr pellets	Wavelength, nm (in methanol)
HL	3330 s, 3284 s, 3057 w, 2918 w, 1640 m, 1613 m, 1590 m, 1569 s, 1455 m, 1397 m, 1286 s, 1262 s, 1235 m, 808 s, 731 m, 643 m	242, 289, 297, 324, 335
$[Cu(\mathbf{L})_2] \cdot 3H_2O$	3431 m, br, 3038 m, 2915 m, 1631 m, 1623 m, 1554 m, 1492 s, 1383 m, 1308 m, 1262 s, 1138 m, 1046 m, 831 m, 808 m, 600 m	251, 294, 304, 344, 417, 641
$[Zn(\mathbf{L})(H_2O)_2]NO_3$	3430 m, br, 3322 m, br, 3064 w, 2922 w, 1632 m, br, 1513 s, 1470 m, 1386 s, 1355 m, 1259 m, 1035 m, 827 m, 747 m, 623 m	264, 270 sh, 284, 365, 409 br

$[Zn(L)(H_2O)_2]NO_3$. 112 mg ligand (0.5 mmol) suspended in ethylacetate (5 mL), 164 mg $Zn(NO_3)_2 \cdot 6H_2O$ (0.55 mmol) in 10 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.

Preparation of HL · HCl. HL was synthesized according to above method. It was crystallized from ethanol : HCl (10%) mixture (v : v, 95 : 5). The colorless crystals (mp 286–313°C), suitable for X-ray analysis, were obtained at room temperature by slow evaporation.

X-ray crystallography. Diffraction measurements were carried out at 20±1°C on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated MoK_α) radiation ($\lambda = 0.71070$ Å), at the 127.40 mm distance between the crystal and the detector (Istanbul University Advanced Analyses Laboratory).

For the structure solution, 4790 reflections were collected, 2395 were unique ($R_w = 0.034$); equivalent reflections were merged. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.74 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR92) and expanded using Fourier techniques [11]. The non-hydrogen atoms were refined anisotropically. H atoms were treated as riding, with C–H = 0.95(6) Å and $U_{iso}(H) = 1.2U_{eq}(C)$ and were constrained refinement. All calculations were performed using the CrystalStructure [12] crystallographic software package.

RESULTS AND DISCUSSIONS

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

The molar conductivity value of Zn(II) complex, 47 Ω^{-1} cm^2 mol^{-1}, is indicative for 1 : 1 electrolyte complexes. Cu(II) complex has non-ionic character according to the molar conductivity. Magnetic moment value of $[Cu(\mathbf{L})_2] \cdot 2H_2O$ complex is 1.61 BM,

Table 3. ^{1}H NMR spectral data (the chemical shift values, δ_H, ppm, with coupling constants, *J*, Hz, in DMSO-d_6)

Compound	The benzimidazole protons					The phenolic protons				
	H4	H5	H6	H7	NH	H3’	H5’	H6’	OH	CH_3
HL	7.70 m	7.27 s, br	7.27 s, br	7.60 s, br	13.12 s	7.88 d *J* = 1.5	7.19 d-d *J* = 8.3, 2.4	6.93 d *J* = 8.3	12.86 s	2.33 s
$[Zn(\mathbf{L})(H_2O)_2]NO_3$	7.95 s, br	7.26 s, br	7.26 s, br	7.63 d, br *J* = 1.8	13.25 s, br	7.95 s, br	7.57 d, br *J* = 7.3	7.30 d, br *J* = 7.3	–	2.30 s

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

Compound	Quaternary carbons	H-bonded carbons
HL	156.59, 152.47, 128.39, 112.92	133.14, 126.89, 117.71, 20.92
$[Zn(\mathbf{L})(H_2O)_2](NO_3)$	161.87, 152.33, 143.74, 140.58, 132.92, 120.57, 117.09	133.44, 128.37, 124.47, 123.31, 112.08, 20.28

which is in the expected range for a typical d^9 Cu(II) complex. The high melting points of the complexes (>350°C) show their high thermal stabilities.

IR Spectra. FT-IR spectral data of the ligand and the complexes are given in Table 2. In the IR spectra of HL the bands at 3330 and 3284 cm^{-1} are due to OH and NH stretching vibration frequencies, respectively. These bands appear closer to each other due to intramolecular hydrogen bonding between the phenoxyl hydrogen atom and one of the imine nitrogen atoms [3, 13, 14]. These bands change significantly upon metal complexation indicating deprotonation and subsequent involvement of the phenoxyl group in metal coordination.

The 3431 cm^{-1} medium broad band at the Cu(II) complex spectra is assigned to the imine proton remains attached at the N-1 position (NH) and uncoordinated water molecules stretching vibrations, while at Zn(II) complex 3430 cm^{-1} band is assigned to ν(NH) only. The 3322 band at Zn(II) complex is assigned to the coordinated water molecules stretching vibrations.

The characteristic ν(C–H) modes of ring residues are observed in the wave region between 3038 and 3064 cm^{-1}. The sharp or medium bands at the 830–730 cm^{-1}

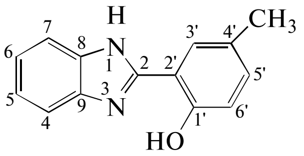
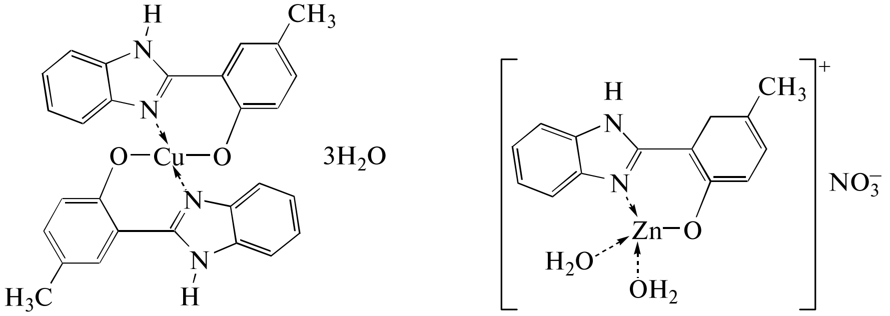


Fig. 1. Structure of the ligand.



$[Cu(\mathbf{L})_2] \cdot 3H_2O$ $[Zn(\mathbf{L})(H_2O)_2]NO_3$

Fig. 2. The proposal structures for the Cu(II) and Zn(II) complexes in the present study.

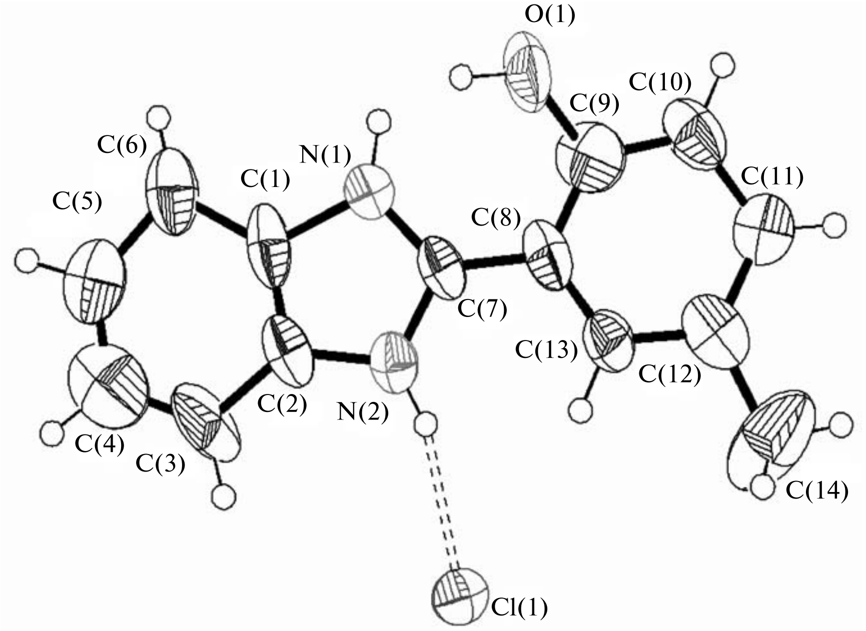


Fig. 3. The molecular structure of HL · HCl showing the atom-labelling scheme and 50% probability displacement ellipsoids. Broken line shows hydrogen bond.

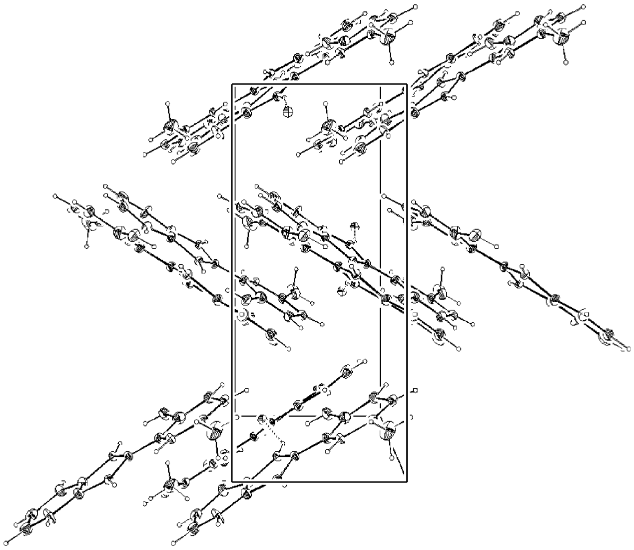


Fig. 4. Packing diagram of HL · HCl along the a axis (the broken lines show hydrogen bonds).

range are due to the out-of-plane deformation bands for the aromatic C–H.

The ν(C=C) frequencies for the ring residues are expected to appear at *ca.* 1640 cm^{-1} with their own characteristics for the ligand 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.* 1590 cm^{-1}.

$[Zn(\mathbf{L})(H_2O)_2]NO_3$ complex shows a strong band at 1386 cm^{-1} in IR spectra, supporting the presence of uncoordinated nitrate ion, which was also confirmed by conductivity data [15–17].

Electronic spectra. The lower wavelength bands (240–300 nm) in the electronic spectra of the ligand and the complexes correspond to $\pi \longrightarrow \pi^*$ transition of the aromatic rings. The other bands at the UV region are due to $n \longrightarrow \pi^*$ transitions. The bands at the

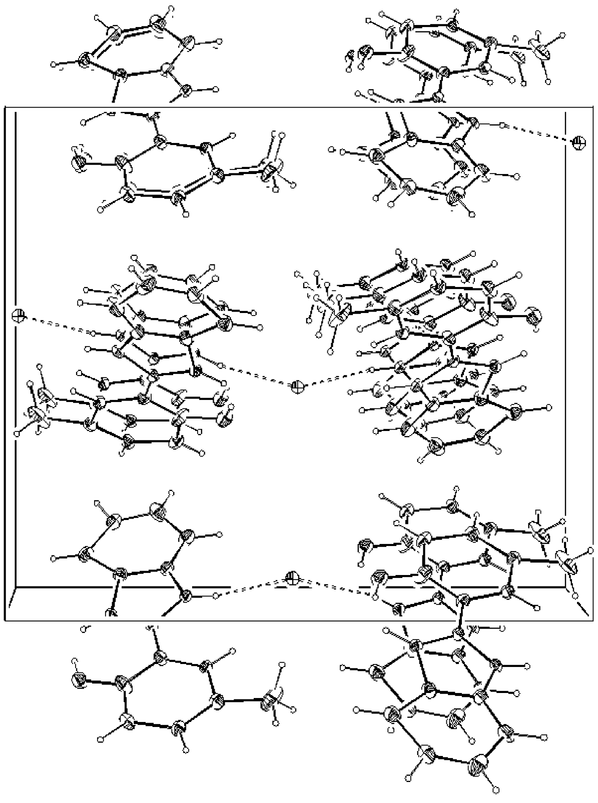


Fig. 5. Packing diagram of HL · HCl along the b axis (the broken lines show hydrogen bonds).

visible region (>350 nm) in the Zn(H) complex are due to L $\longrightarrow$ Zn (oxygen $\longrightarrow$ zinc) charge transfer (reason of the dark yellow color of the complex).

The electronic spectra of the Cu(II) complex showed three bands at 641, 417 and 344 nm. The 344 nm band is assigned to a ligand-to-metal charge transfer. The other two bands are assigned to $^2B_{1g} \longrightarrow {}^2A_{1g}$ and $^2B_{1g} \longrightarrow {}^2E_g$ transitions, respectively. These assignments are typically characteristic for square-planar geometry for Cu(II) complex (Fig. 2) [18, 19].

NMR Spectra. ^{1}H NMR spectral data of HL and its Zn(II) complex, and the assignments of the peaks are presented in Table 3. The ligand gives two singlets at 13.12 and 12.86 ppm for NH and OH protons, respectively. These signals are very closer to each other because of intramolecular hydrogen bonding between the OH hydrogen and the C=N nitrogen atoms.

The characteristic of the phenolic and benzimidazole protons of the Zn(II) complex have changed according to the ligand. For instance, in the Zn(II) complex, multiplet and doublets 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 ^{1}H 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. 2).

^{13}C NMR (APT) spectral data of HL and its Zn(II) complex are given in Table 4. In the APT spectra of HL spectra only eight carbons were determined; in the Zn(II) complex spectra all of the carbon atoms were observed. 156.59 and 159.87 ppm signals are attributed to Cl' carbon atom (OH bonded carbon) in HL and its Zn(II) complex, respectively. 152.47 and 152.33 ppm signals are assigned C2 carbon atom (C=N). C8 and C9 carbons were seen at 142.25 ppm in the ligand spectra, however they appear separately at 143.74 and 140.58 ppm values at the APT spectra of $[Zn(\mathbf{L})(H_2O)_2](NO_3)$, respectively. The low ppm signals of the ligand and its Zn(II) complex, 20.92 and 20.28 ppm, are due to methyl carbon atoms, respectively. The other assignments are given in Table 4.

The proposal structures of the Cu(II) and Zn(II) complexes in Fig. 2, are in best accord with the experimental data obtained from the analytical data, molar conductivity, magnetic moments, UV-visible, FT-IR and NMR spectroscopic measurements.

X-ray crystallography. The crystal structure of HL · HCl is shown in Fig. 3. The packing diagrams along a and b axes are given in Figs. 4 and 5. Because of the deposits of the complexes are in the small disperse

Table 5. Crystallographic characteristics and experimental and refinement details for the structure of HL · HCl

Formula: $C_{14}H_{13}N_2OCl$

Formula weight = 260.72

Crystal system: orthorombic

Space group: $P2_12_12_1$ $Z = 4$

$a = 16.2919(5)$ Å $V = 1408.93(8)$ Å^3

$b = 6.3302(2)$ Å $D_x = 1.229$ g/cm^3

$c = 13.6616(4)$ Å

Crystal size = 0.50 × 0.30 × 0.20 mm

$F(000) = 544$

No. of observations ($I > 3.00\ \sigma(I)$) = 2298

No. of parameters = 176

Refinement on F: Full-matrix least-squares on F

Data collection: *CRYSTALCLEAR*

Structure solution: Direct Methods (SIR92)

Goodness-of-fit: 1.088

Least squares weights: Chebychev polynomial with 3 parameters, 27.2025, 31.9192, 17.9013

R ($I > 3.00\ \sigma(I)$) = 0.297

R_w ($I > 3.00\ \sigma(I)$) = 0.308

CCDC 692344 contains the supplementary crystallographic data for this paper.

Table 6. Hydrogen-bond geometry (Å, °) in the present study and in some literatures

D–H···A	D–H	H···A	D···A	D–H···A
N2–H12···Cl$^{\mathrm{i}}$	0.88	2.225	3.079	163.5
[6]	0.86	2.308	3.135	160
[7]	0.86	2.31	3.146	164
[8]	0.88	2.280	3.117	159

Symmetry code: (i) $+x$, $+y$, $+z$.

Table 7. Atomic coordinates and temperature factors (Å^2) for HL · HCl

Atom	x	y	z	B_{eq}
Cl(1)	0.49172(13)	0.1806(4)	1.0712(2)	4.55(4)
O(1)	0.1269(9)	–0.079(1)	0.8902(8)	6.7(2)
N(1)	0.1775(4)	0.2314(12)	0.9954(6)	4.08(12)
N(2)	0.3069(5)	0.2366(11)	1.0320(5)	3.88(11)
C(7)	0.2496(6)	0.1295(13)	0.9815(5)	4.04(13)
C(13)	0.3411(6)	–0.134(2)	0.9196(6)	4.4(1)
C(8)	0.2639(8)	–0.063(1)	0.9321(7)	4.8(2)
C(1)	0.1929(10)	0.4132(13)	1.0632(6)	5.2(2)
C(12)	0.3584(9)	–0.322(2)	0.8690(7)	5.5(2)
C(2)	0.2749(9)	0.420(2)	1.0752(7)	5.1(2)
C(10)	0.2089(11)	–0.356(2)	0.8338(11)	6.1(3)
C(5)	0.1794(12)	0.727(2)	1.1524(10)	6.4(3)
C(11)	0.2937(8)	–0.450(2)	0.8283(8)	5.2(2)
C(9)	0.2017(12)	–0.172(2)	0.889(2)	7.7(4)
C(3)	0.3094(11)	0.589(3)	1.1270(9)	7.8(3)
C(4)	0.259(2)	0.737(3)	1.171(2)	8.5(5)
C(6)	0.1309(13)	0.561(2)	1.0959(8)	6.3(3)
C(14)	0.449(2)	–0.398(4)	0.880(3)	11.9(8)

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$.

powders forms; the crystal structure of the complexes was not obtained. It was not accomplished to grow up crystals of complexes from methanol or other any other organic solvent.

Crystallographic characteristics and experimental and refinement details are given in Table 5; hydrogen bonding geometry is in Table 6 and the bond lengths, bond angles and torsion angles are given in Tables 7–9.

The N1–C7 and N2–C7 distances of HL · HCl, 1.35(1) and 1.34(1) Å, are in the between the C–N and C=N bond lengths because of the hydrochloride bonded to the N2 atom. These lengths were reported 1.371 and 1.325 Å, respectively, for 2-(3-methoxy-2-hydroxyphenyl)benzimidazole [4]; 1.3346 and 1.3337 Å for 2,2'-(butane-1,4-diyl)dibenzimidazolium dichloride dihydrate [8]; 1.342 and 1.322 Å for 2,2'-(propane-1,3-diyl)bis((benzimidazolium) dichloride dihydrate [6], 1.334 and 1.315 Å for 2,2'-(iminodimethylene)bis(1*H*-benzimidazolium)(1+) chloride [7],

Table 8. Bond lengths (Å) bond angles (deg) for HL · HCl

O(1)–C(9)	1.35(2)	N(1)–C(7)	1.35(1)
N(1)–C(1)	1.50(1)	N(2)–C(7)	1.34(1)
N(2)–C(2)	1.40(1)	C(7)–C(8)	1.41(1)
C(13)–C(8)	1.35(2)	C(13)–C(12)	1.40(1)
C(8)–C(9)	1.36(2)	C(1)–C(2)	1.35(2)
C(1)–C(6)	1.45(2)	C(12)–C(11)	1.44(2)
C(12)–C(14)	1.56(3)	C(2)–C(3)	1.40(2)
C(10)–C(11)	1.50(2)	C(10)–C(9)	1.40(2)
C(5)–C(4)	1.32(3)	C(5)–C(6)	1.52(2)
C(3)–C(4)	1.38(3)		
C(7)N(1)C(1)	107.9(8)	C(7)N(2)C(2)	112.0(9)
C(8)C(7)N(1)	128.4(9)	C(8)C(7)N(2)	124.5(9)
N(1)C(7)N(2)	106.9(7)	C(8)C(13)C(12)	122(1)
C(9)C(8)C(7)	121(1)	C(9)C(8)C(13)	118(1)
C(7)C(8)C(13)	120(1)	C(2)C(1)C(6)	129(1)
C(2)C(1)N(1)	105.4(9)	C(6)C(1)N(1)	124(1)
C(11)C(12)C(14)	123(1)	C(11)C(12)C(13)	121(1)
C(14)C(12)C(13)	113(1)	C(3)C(2)N(2)	134(1)
C(3)C(2)C(1)	118(1)	N(2)C(2)C(1)	107.0(9)
C(11)C(10)C(9)	115(1)	C(4)C(5)C(6)	129(1)
C(12)C(11)C(10)	115(1)	O(1)C(9)C(8)	116(1)
O(1)C(9)C(10)	116(1)	C(8)C(9)C(10)	126(1)
C(4)C(3)C(2)	119(1)	C(5)C(4)C(3)	117(1)
C(1)C(6)C(5)	103(1)		

Table 9. Selected torsion angles (deg) for HL · HCl

C(1)N(1)C(7)N(2)	−1.8(9)
C(8)C(9)O(1)(H13)	−2(2)
N(1)C(7)C(8)C(9)	1(1)
C(1)N(1)C(7)C(8)	172.6(8)
C(10)C(9)O(1)H(13)	−174(1)

and were to be found 1.357 and 1.311 Å for 1,4-bis(benzimidazol-2-yl)butane [20].

N1–C1 and N2–C2 distances are to be found 1.50(1) and 1.40(1) Å, respectively, as expected because of two nitrogen atoms have different chemical environments.

Dihedral angle between phenol and imidazol rings (torsion angle of N(1)C(7)C(8)C(9)) is 1(1) Å shows that the molecule is almost planar.

There is a strong intramolecular hydrogen bonding in the molecule between Cl and H12 atoms, H···Cl bond length is 2.225(8) Å and D···A (N2···Cl) distance is 3.079 Å. These values are compared with the literature values and it is seen that they are in the line with the literatures (Table 6). In addition, a weak intermolecular interaction is observed between Cl and Cl3 atoms (D···A distance: 3.81 Å). The crystal structure of HL · HCl is stabilized by N-H···Cl (intramolecular) and C-H···Cl (intermolecular) hydrogen-bonding interactions as mentioned above. Consequently, melting point of HL · HCl is higher than that of HL (286–313 > 257°C) as a result of hydrogen bondings.

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