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Preparation and spectral characterization of 1,3-bis(1*H*-benzimidazol-2-yl)-propan-1-one and its various Zn(II) complexes

Abstract: A new asymmetric bis-benzimidazole ligand, 1,3-bis(1*H*-benzimidazol-2-yl)-propan-1-one (L), was synthesized by known methods. ZnX_2 (X=Cl, Br, I, ClO_4, NO_3, OAc) complexes of the ligand were synthesized and characterized by elemental analysis, molar conductivity, TGA, ESI-MS, FT-IR, NMR and fluorescence spectroscopy. According to the spectral data, the ligand exhibits a keto-enol equilibrium in polar solvents. The ligand gave complexes with eight-membered chelate ring coordinating through both of the C=N nitrogen atoms, whereas the C=O oxygen atom does not bind to the Zn(II) ion. Fluorescence properties of the ligand and the complexes were investigated. Considerable red shift is observed in $ZnBr_2$, ZnI_2 and $Zn(OAc)_2$ complexes according to the ligand. By contrast, the $Zn(OAc)_2$ complex differs from the other Zn(II) complexes by thermal composition, molar conductivity and fluorescence characteristics, probably due to the coordination of the acetate oxygen atom.

Keywords: bis-benzimidazole; fluorescence; keto-enol tautomerism; propan-1-one; Zn(II) complexes.

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Introduction

Asymmetric bis-benzimidazoles could be important for biomimicry and metal ion transport. Matthews et al. (1996) synthesized and characterized a series of asymmetric bis-benzimidazoles such as 1-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-oxapropane (**1**), 1-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-thiapropane (**2**), 1-(*N*-methylbenzimidazolyl)-3-benzimidazolyl-2-oxapropane (**3**), 1-(*N*-methylbenzimidazolyl)-3-benzimidazole-2-thiapropane (**4**), 1-(5-nitrobenzimidazolyl)-3-benzimidazolyl-2-oxapropane (**5**), 1-[(5-trifluoromethyl)benzimidazolyl]-3-benzimidazolyl-2-oxapropane (**6**) and their Cu(II) complexes. They also synthesized mono-N-alkylated bis(benzimidazoles) (R=alkyl, R′=H), again having the two halves of different basicity but lacking the prototropy on one subunit (Matthews et al., 1996).

Also, coordination of Zn(II), Cd(II), Hg(II), and Ag(I) with the above asymmetric bis-benzimidazol derivatives, **1**, **2**, **3**, and 1,7-bis(benzimidazol-2-yl)-2,6-dithiaheptane ligands, were investigated (Matthews et al., 1998).

1,2-Bis-(1*H*-benzimidazol-2-yl)-1,2-ethanediol (H_2BBz), and its methylated derivative (H_2MBBz) acted as chiral, facially coordinating tridentate ligands, forming complexes of composition ML_2 with octahedral transition metals (M=Cu^{2+}, Ni^{2+}). H_2BBz gave octahedral complexes with metals through the alcohol group and C=N nitrogen atoms monodeprotonation of the coordinated alcohol group (Isele et al., 2002). Also, Isele et al. reported dinuclear and tetranuclear complexes with H_2BBz and H_2MBBz with $Cu(ClO_4)_2$ through the alcohol group mono- and di-deprotonation of the ligands (Isele et al., 2005).

A number of nickel(II), copper(II), and zinc(II) complexes with the tridentate chiral chelating ligand 1,2-bis(benzimidazol-2-yl)-l-hydroxyethane (HEBBz) was described (van Albada et al., 1989). The ligand formed mononuclear complexes of general formula $M(HEBBz)_2(anion)_2$ for all metal ions and a variety of anions. By contrast, crystal structures for the monomeric Ni(II), dimeric and tetrameric Cu(II) complexes with HEBBz were reported (van Albada et al., 2006).

There are very limited studies reported in the literature about bis-benzimidazoles containing a keto group. For example, crystal structure and spectral properties of bis-benzimidazolyl-methanone (da Silva et al., 2009) and 1,1′-(4-oxoheptane-1,7-diyl)-bis-(2-methyl-1*H*-benzimidazole) pentahydrate (Zhang et al., 2008) were reported. In addition, studies on synthesis, characterization, and metal complexes of asymmetric bis-benzimidazoles are rather scarce in the open literature. In this study, it is aimed to synthesize and characterize a new asymmetric bis-benzimidazole derivative, 1,3-bis(1*H*-benzimidazol-2-yl)-propan-1-one (ligand, **L**), (Figure 1) and its ZnX_2 (X=Cl, Br, I, ClO_4, NO_3, OAc) complexes. The effect of Zn(II) ion and the anions on the fluorescence characteristics of the

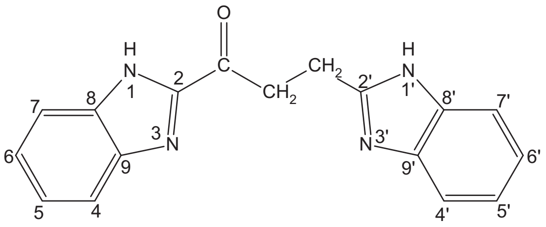


Figure 1 Schematic drawing of the ligand.

ligand was studied. In addition, anion effect on the complexation was also investigated.

Results and discussion

General properties

The analytical data and physical properties of the compounds are summarized in Table 1. All of the complexes are electrolyte according to the molar conductivity data except $[Zn(\mathbf{L})(OAc)_2]$.

Except for $Zn(OAc)_2$, the melting points of the complexes are lower than that of the ligand. The thermal stability of the complexes decreases probably due to the formation of eight-membered chelate rings. It is known that chelate rings of more than six members decreases the stability of the complexes. The complex $[Zn(\mathbf{L})(OAc)_2]$ differs from the other complexes as structurally and it has high thermal stability (mp>350°C). Chloride, bromide, and iodide ions were determined by reaction with $AgNO_3$ to give the corresponding silver salts. There was no precipitation of silver halide in the three complexes, indicating that the halide anions are inside the coordination sphere of the complexes. It can be deduced that Zn(II) halide complexes have hexa-coordination with octahedral geometry by two halogen and four C=N nitrogen atoms.

FT-IR spectra

FT-IR spectral data of the compounds are given in Table 2. The broad band at 3408 cm^{-1} in the ligand spectrum may be attributed to stretching vibration of NH, and probably it shifts near 3200 cm^{-1} in the complexes. The weak or medium bands between 2900 and 2970 cm^{-1} are due to vibrations of the aliphatic CHs.

The ν(C=O) band was not observed in the ligand spectrum. This means that the enol form is dominant rather than the keto form in the solid state of the ligand (Figure 2). The strong band at 1661 cm^{-1} in the ligand is likely to originate from intra- and/or intermolecular hydrogen bonds (with the NH), and it does not change significantly at the spectra of the complexes.

The absorption band at 1624 cm^{-1}, which it appears as a shoulder because of strong 1661 cm^{-1} band, can be assigned to ν(C=C) and ν(C=N) combination. This band exhibited a considerable change in the complexes by splitting into two bands: a band near 1620 cm^{-1} and a new band around 1580 cm^{-1}. They are possibly due to ν(C=C) and ν(C=N), respectively (Nakamoto, 1997; Tavman et al., 2006). This change may support the argument that coordination occurs via the imine nitrogen atom.

Appearance of the strong or medium broad bands above 3400 cm^{-1} in the complexes strongly supports the presence of coordinated and uncoordinated water molecules. These bands may contain the OH stretching vibrations of enol tautomer and mask the NH bands expected at the same region. The characteristic ν(C–H) and δ(C–H) modes of ring residues are observed near 3060 cm^{-1} and at the 746–758 cm^{-1} region, respectively.

The antisymmetric and symmetric stretching vibrations of the carboxylate groups of acetate anion of $[Zn(\mathbf{L})(OAc)_2]$ complex are seen at 1566 and 1430 cm^{-1} as strong bands, respectively (Nakamoto, 1997; Seguel et al., 2005). $[Zn(\mathbf{L})(H_2O)_2](NO_3)_2$ complex shows a strong

Compound	Elemental analysis found (Calcd) %			Y %	Mp °C	Λ	Color
	C	H	N				
L $C_{17}H_{14}N_4O$	70.19 (70.33)	4.64 (4.86)	19.02 (19.30)	73	308	–	Slightly yellow
$[Zn(\mathbf{L})(OAc)_2]$ $C_{21}H_{20}N_4O_5Zn$	52.91 (53.23)	4.69 (4.25)	11.74 (11.82)	87	>350	4.4	Bright yellow
$[Zn(\mathbf{L})_2](NO_3)_2\cdot 2H_2O$ $C_{34}H_{32}N_{10}O_{10}Zn$	50.89 (50.66)	4.24 (4.00)	17.05 (17.38)	69	240	109	Orange
$[Zn(\mathbf{L})(H_2O)_2](ClO_4)_2C_{17}H_{18}Cl_2N_4O_{11}Zn$	34.96 (34.57)	3.31 (3.07)	9.80 (9.49)	67	208	91	Orange
$[Zn(\mathbf{L})_2Cl_2]\cdot H_2O$ $C_{34}H_{30}Cl_2N_8O_3Zn$	55.20 (55.56)	4.18 (4.11)	14.92 (15.25)	61	285	82	Light yellow
$[Zn(\mathbf{L})_2Br_2]\cdot 2H_2O$ $C_{34}H_{32}Br_2N_8O_4Zn$	48.82 (48.51)	4.08 (3.83)	13.54 (13.31)	70	288	118	Yellow
$[Zn(\mathbf{L})_2I_2]\cdot 4H_2O$ $C_{34}H_{36}I_2N_8O_6Zn$	41.77 (42.02)	3.42 (3.73)	11.12 (11.53)	65	271	105	Dark orange

Table 1 Analytical data and some physical properties of the ligand and the complexes.
Y, Yield; Λ, Molar conductivity, $\Omega^{-1} cm^2 mol^{-1}$ (25±1°C).

Compound	Frequency (cm^{-1})
L	3408 m,br, 3054 m, 2923 m, 2854 m, 1661 s, 1624 sh, 1438 s, 1277 s, 1222 m, 1152 m, 1032 m, 753 s, 590 m, 478 m
$[\mathrm{Zn}(\mathbf{L})(\mathrm{OAc})_2]$	3428 w, 3108 m, 3018 m, 2932 m, 1668 s, 1620 s, 1593 s, 1548 s, 1464 m, 1414 s, 1283 m, 1053 m, 865 w, 746 m, 692 m, 611 w, 475 w
$[\mathrm{Zn}(\mathbf{L})_2](\mathrm{NO}_3)_2\cdot 2\mathrm{H}_2\mathrm{O}$	3452 s,br, 3423 s,br, 3227 m,br, 3177 m,br, 3054 w, 2972 w, 1668 s, 1623 s, 1569 m, 1462 m, 1388 s, 1340 m, 1319 m, 1282 m, 1221 m, 1151 m, 1048 w, 754 m, 594 m, 471 w
$[\mathrm{Zn}(\mathbf{L})(\mathrm{H}_2\mathrm{O})_2](\mathrm{ClO}_4)_2$	3530 m,br, 3203 m,br, 3063 m,br, 2960 m,br, 1661 s, 1619 m, 1570 m, 1464 m, 1423 m, 1340 m, 1279 m, 1152 m, 1115 s, 1090 s, 758 m, 630 m, 594 m, 475 w
$[\mathrm{Zn}(\mathbf{L})_2\mathrm{Cl}_2]\cdot\mathrm{H}_2\mathrm{O}$	3458 m,br, 3202 m, 3138 m,br, 3055 m,br, 2907 w, 1671 s, 1621 sh, 1572 m, 1460 m, 1421 m, 1280 m, 1115 w, 1055 w, 854 w, 752 m, 686 w, 593 w, 478 w
$[\mathrm{Zn}(\mathbf{L})_2\mathrm{Br}_2]\cdot 2\mathrm{H}_2\mathrm{O}$	3455 s,br, 3198 m, 3055 m, 2968 m, 1668 s, 1647 sh, 1614 m, 1569 m, 1461 m, 1421 m, 1279 m, 1163 m, 1053 m, 754 m, 663 w, 594 m, 475 m
$[\mathrm{Zn}(\mathbf{L})_2\mathrm{I}_2]\cdot 4\mathrm{H}_2\mathrm{O}$	3433 s,br, 3392 m, 3177 m, 3066 m, 2921 m, 1662 s, 1617 sh, 1563 m, 1453 m, 1423 m, 1339 m, 1279 m, 1227 m, 1154 m, 754 m, 598 m, 478 w

Table 2 IR spectral data of the ligand and the complexes (in KBr pellet).

band at 1388 cm^{-1} assigned to ν(NO_3^-); it also supports the presence of the uncoordinated nitrate ion (Nakamoto, 1997; Kong and Xie, 2000; Tavman, 2006). $[\mathrm{Zn}(\mathbf{L})_2](\mathrm{ClO}_4)_2\cdot 2\mathrm{H}_2\mathrm{O}$ complex has a strong band at 1115 cm^{-1} can be assigned to the stretching vibrations of the uncoordinated perchlorate anion, ν(Cl=O). Also the medium band at 630 cm^{-1} is due to ν_4 mode of perchlorate anion (Nakamoto, 1997; Gu and Coates, 2006; Tavman et al., 2010).

NMR spectra

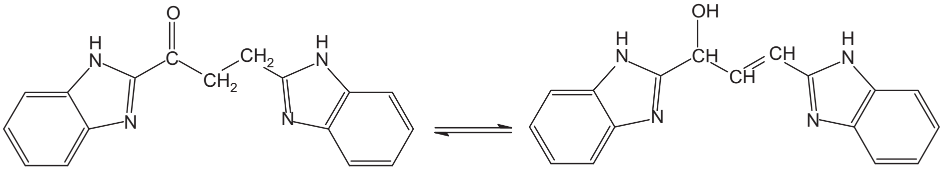
The ^{1}H- and ^{13}C-NMR (APT) spectral data of the ligand and the complexes are given in Tables 3 and 4, respectively.

The ^{1}H-NMR spectra of the ligand in DMSO and at three different temperatures in methanol are shown in Figures 3 and 4, respectively. ^{13}C-NMR (APT) spectrum of the ligand is shown in Figure 5. Two different NH signals are observed in the spectrum of the ligand as expected. The sharp singlet at 12.32 ppm must belong to the NH proton that is closer to C=O (NH1). The other NH proton (NH1′) gives a very broad singlet due to its fast tautomeric character. Considering this observation, it can be concluded that tautomerism on the imidazole ring near the C=O group is much slower than that of the other imidazole ring, it may be that there is not tautomerism.

The doublet of doublet at 7.69 ppm, which corresponds to one proton, may be due to H4 at the ring closer to the C=O group in the ligand spectrum.

It is expected that the following protons are identical: H4 and H7, H4′ and H7′, H5 and H6, and H5′ and H6′. However, H4 and H7 (at the ring closest to the carbonyl group) are not identical probably because of the electronegativity effect of the carbonyl oxygen atom. Also, the identities of the protons mentioned above were degenerated in the complexes as a result of C=N nitrogen atom coordination to the Zn(II) ion.

^{1}H-NMR spectra of the ligand were obtained at 0°C, 25°C and 50°C in methanol. Considering the ^{1}H-NMR spectra of the ligand in methanol at three different temperatures, it can be said that there are keto-enol forms depending on temperature and solvent. The broad singlet at 4.72 ppm, obtained at 0°C, changes to very broad singlet and weakens at higher temperatures. In addition, it shifts to 4.48 and 4.23 ppm at 25°C and 50°C, respectively (Figure 4). This signal can be assigned to the –CH=CH– (methylene) protons of the enol form. The multiplet at 3.21 ppm should belong to $-CH_2-CH_2-$ protons of the keto form (The 3.34 ppm signal is due to the residual solvent). The signal intensity of $-CH_2-CH_2-$ protons increases while that of –CH=CH– protons weakens at the higher temperatures. Namely, the keto form becomes more dominant with increasing



1,3-bis-(1*H*-benzimidazol-2-yl)-propan-1-one (2*E*)-1,3-bis-(1*H*-benzimidazol-2-yl)-prop-2-en-1-ol

Figure 2 Keto-enol forms of the ligand.

Compound	NH	NH′	H4	H7	H5	H6	H4′	H7′	H5′	H6′	a[a]	b[b]
L	12.32 s	12.25 s,br	7.69 d-d J=8.3;1.5	7.46 m	7.27 m	7.27 m	7.46 m	7.46 m	7.09 m	7.09 m	3.28 d J=6.8	3.32 d J=6.8
$[Zn(\mathbf{L})(OAc)_2]$[c]	12.34 s,br	12.34 s,br	7.66 d,br	7.66 d,br	7.29 d J=7.3	7.23 s,br	7.45 s,br	7.45 s,br	7.13 s,br	7.13 s,br	3.32 s,br	3.32 s,br
$[Zn(\mathbf{L})_2](NO_3)_2{\cdot}2H_2O$	12.33 s	12.33 s	7.56 m,br	7.56 m,br	7.28 d J=8.3	7.21 s,br	7.56 m,br	7.45 t J=7.3;7.3	7.21 s,br	7.21 s,br	3.32 s,br	3.43 d J=7.3
$[Zn(\mathbf{L})(H_2O)_2](ClO_4)_2$	12.35 s	12.35 s	7.63 d J=7.8	7.56 m,br	7.46 d-t J=1.5; 8.3;7.3	7.23 m	7.56 m,br	7.28 d-d J=8.3; 1.0	7.23 m	7.23 m	3.37 d J=5.9	3.40 d J=5.9
$[Zn(\mathbf{L})_2Cl_2]{\cdot}H_2O$	12.33 s	12.33 s	7.65 d J=8.3	7.46 d-t J=8.3; 7.3;1.0	7.28 d J=8.3	7.24 d-t[d] J=8.3; 7.3	7.62 s,br	7.62 s,br	7.18 m	7.18 m	3.31 d J=7.8	3.45 d J=7.8
$[Zn(\mathbf{L})_2Br_2]{\cdot}2H_2O$	12.33 s	12.33 s	7.70 s,br	7.28 d J=8.3	7.24 d J=7.3	7.20 m	7.65 d J=7.8	7.46 t J=8.3; 6.8	7.20 m	7.20 m	3.32 t J=7.3	3.51 t J=7.3
$[Zn(\mathbf{L})_2I_2]{\cdot}4H_2O$	12.56 s	12.32 s	8.04 m	7.52 t J=7.8;7.3	7.26 d J=8.3	7.32 d J=8.3	8.04 m	7.20 d J=7.8	7.17 s,br	7.17 s,br	3.29 s,br	3.41 s,br

Table 3 ^{1}H-NMR spectral data of the ligand and the complexes (δ_H, ppm; *J*, Hz; in DMSO-d_6).

[a] $-(C{=}O)-CH_2-\underline{C}H_2-$.

[b] $-(C{=}O)-CH_2-$.

[c] 1.77 ppm (s, 6H, CH_3COO).

[d] Unsplit triplet.

temperature. On the other hand, the signals of the ring protons in methanol are similar to those of the spectra in DMSO.

It is expected that C8 and C9 carbons at the imidazole ring near the carbonyl group give NMR signals separately in the ligand, as well. However, it seems that both gave only one signal in the APT spectrum because of the fast tautomeric equilibrium of the proton atom in the imidazole ring between the two nitrogen atoms (Tavman et al., 2000). The other imidazole rings C8 and C9 carbons show only one signal because of their identities. In the complexes, the equalities of the C8 and C9 carbons are degenerated because of coordinating Zn(II) ion via the C=N nitrogen atoms. As a result of Zn(II) coordination, the tautomerism is removed and, consequently, NMR signals of the C8 and C9 appear separately.

It is expected that ^{13}C-NMR signal of C=O carbon of the ligand would appear near 180 ppm. However, it appears at 161.1 ppm in the ligand spectra (at around 160 ppm at the complexes). This data may be evidence for a keto-enol equilibrium in the ligand (Figure 2) and the complexes rather than the exact keto form.

Only four signals were obtained from ^{13}C-NMR spectra of $[Zn(\mathbf{L})(OAc)_2]$ because of its very low solubility in DMSO and the other polar solvents (Table 4).

Mass spectra

The ESI-MS data of the ligand and the complexes are given in Table 5 as molecular ions with relative abundance.

There are ion peaks in the zinc(II) halogenide complexes corresponding to [2L+Zn+X] fragment. This situation may be attributed to the existence of the keto-enol form in the ligand and consequently a HX leaves from complex during ionization. Some of the ion peaks, especially belonging to the ligand, appear as sodiated peaks such as in the ESI mass spectra of the ligand, $[Zn(\mathbf{L})_2Cl_2]{\cdot}H_2O$, $[Zn(\mathbf{L})_2Br_2]{\cdot}2H_2O$ and $[Zn(\mathbf{L})(H_2O)_2](ClO_4)_2$ (Table 5). In addition, in all of the complexes a peak at $m/z = 603$ is observed that may be due to the [2L+23] fragment. A lot of isotopic patterns are observed at the spectra of the complexes due to the fact that zinc has five stable isotopes.

In addition, the peaks of the ligand are easily determined in the mass spectra of the complexes (the ligand was shown as L in Table 5).

Thermogravimetric studies

The major features of thermogravimetric analysis (TGA) of the complexes are summarized in Table 6. The thermal

Compound	C2	C2′	C8+C9	C8′+C9′	C4+C7	C4′+C7′	C5+C6	C5′+C6′	C=O	a[a]	b[b]
L	155.3	155.2	132.5	132.3	130.2	128.8	123.7 121.8	115.9	161.1	25.7	31.4
$[Zn(\mathbf{L})(OAc)_2]$	–	–	–	–	129.6	–	124.5	–	–	23.9	26.8
$[Zn(\mathbf{L})_2](NO_3)_2 \cdot 2H_2O$	156.2	155.2	143.2 136.8	132.4 132.1	130.3 128.7	123.7	123.4	116.0 115.0	160.2	25.0	31.0
$[Zn(\mathbf{L})(H_2O)_2](ClO_4)_2$	156.4	155.3	136.4 132.5	132.1	130.3 128.7	123.8	123.5	116.0 114.8	160.4	24.8	30.8
$[Zn(\mathbf{L})_2Cl_2] \cdot H_2O$	156.6	155.2	132.5	132.2	130.3 128.8	123.7	122.9	115.9	160.4	25.2	31.4
$[Zn(\mathbf{L})_2Br_2] \cdot 2H_2O$	156.8	155.4	133.0 132.7	132.5 132.2	130.3 128.8	124.4 123.8	123.3	116.1 115.9	160.2	25.1	31.4
$[Zn(\mathbf{L})_2I_2] \cdot 4H_2O$	156.4	155.4	133.0 131.7	132.6 132.4	131.3 130.3	124.4 129.0	123.7 123.4	116.1 115.9	160.1	25.1	31.1

Table 4 ^{13}C-NMR (APT) spectral data of the ligand and the complexes (δ_C, ppm; in DMSO-d$_6$).

[a] -(C=O)-CH$_2$-$\underline{C}$H$_2$-.

[b] -(C=O)-$\underline{C}$H$_2$-.

analysis curves of ZnI_2, $Zn(NO_3)_2$ and $Zn(OAc)_2$ complexes are shown in Figure 6. The samples of the complexes were heated from room temperature up to 800°C. Thermal degradation of complexes occurred at three stages in the most of the complexes. At the first stage, uncoordinated lattice water was lost through evaporation from 50°C to 100°C. At the second stage, small weight losses observed above 350°C can be explained in terms of leaving the carbonyl group. Different from the others, the coordinated water molecules are removed from the $Zn(ClO_4)_2$ complex at temperatures near 150°C (Yusuff and Sreekala, 1991; Soliman and Linert, 1999). Above 450°C, all other organic parts of the complexes are oxidized to carbon dioxide and water. Complete decomposition of the complexes that contains halogen atom continues up to 700°C probably due to the formation of ZnO through ZnX_2.

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 TGA data.

According to the experimental data, the structures in Figure 7 can be proposed for the complexes as a conclusion.

Fluorescence spectra

Excitation and emission spectra of the compounds were obtained in ethanol solution at room temperature (excitation wavelength: 354 nm; concentration: ~10^{-4} M). The emission spectral data of the compounds are presented in Table 7. The fluorescence spectra of the ligand and its $Zn(ClO_4)_2$ and ZnI_2 complexes are shown in Figure 8.

Three emission bands were observed in the fluorescence spectrum of the ligand: 560 nm (shoulder), 412 (broad medium), and 394 nm (shoulder). Based on the excited-state proton transfer (ESPT) theory, the fluorescence band (shoulder) with a peak at 560 nm is attrib-

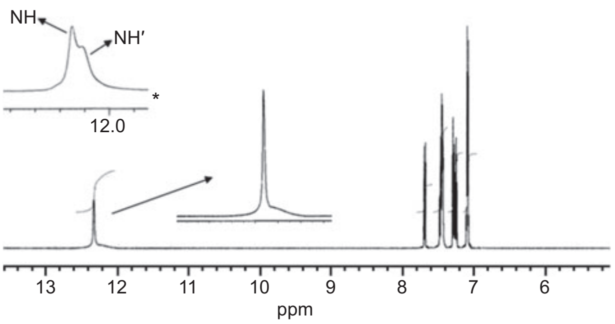


Figure 3 ^{1}H-NMR spectra of the ligand (*recorded on a Bruker Ac-200 NMR spectrometer).

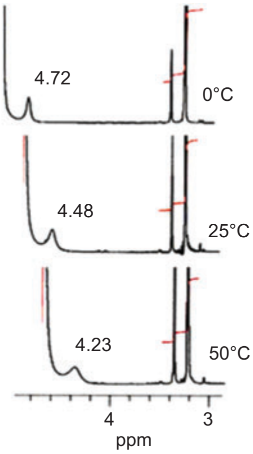


Figure 4 ^{1}H-NMR spectra of the ligand between 3 and 5 ppm in methanol at three different temperatures.

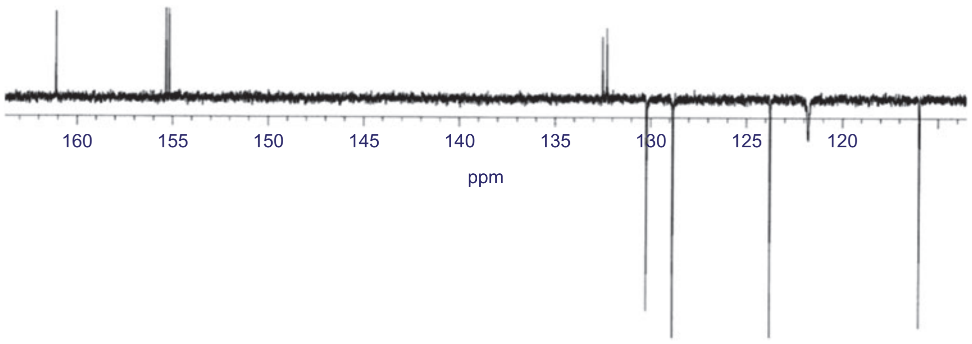


Figure 5 ^{13}C-NMR (APT) spectrum of the ligand at the 115–165 ppm range.

uted to the emission from a weak enol form of the ligand, whereas the band with a peak at 412 nm is attributed to the emission from the tautomer form (i.e., keto form) via the ESPT process. The shoulder at 394 nm may result from the dissociated form. Two and three emission bands at the complexes show that keto-enol tautomerism does not remove on complexation. This observation may be considered as evidence for no coordination of C=O oxygen atom to the Zn(II) ion.

The considerable red shifts in $Zn(OAc)_2$, $ZnBr_2$ and ZnI_2 complexes are observed as compared to the ligand. In addition, the fluorescence spectrum of $Zn(OAc)_2$ complex is very different from the others. Two medium bands at 461 and 491 nm, a broad medium band at 409 nm, and a shoulder 528 nm are observed (Figure 9). The new bands in this complex are probably due to the charge transfer transition from acetate oxygen atoms to the Zn(II) ion as a result of coordination of the acetate oxygen atoms.

Compound and molecular mass (g/mol)	Molecular ions (m/z) with relative abundance (%)
L; $C_{17}H_{14}N_4O$ 290.3	291.5 (100, $[M+1]^+$), 292.6 (14.4, $[M+2]^+$), 293.7 (5.6, $[M+3]^+$), 313.0 (47.0, $[L+23^a]$), 602.8 (16.0, $[2L+23^a]$)
$[Zn(\mathbf{L})(OAc)_2]$ 473.82	953.0 (15.9, $[2M+5]^+$), 603.0 (14.1, $[2L+23^a]$), 585.5 (12.1, [2L+5]), 496.1 (12.1, $[M-1+23^a]$), 291.8 (100, [L+2]), 292.9 (11.8, [L+3])
$[Zn(\mathbf{L})_2](NO_3)_2\cdot 2H_2O$ 806.1	806.4 (11.3, $[M]^+$), 805.4 (16.9, $[M-1]^+$), 807.3 (13.6, $[M+1]^+$), 809.3 (11.1, $[M+3]^+$), 603.1 (11.5, $[2L+23^a]$), 643.7 (30.2, [2L+Zn]), 581.4 (16.1, [2L]), 354.2 (13.9, [L+Zn-1]), 371.6 (18.7, [L+Zn-2]), 291.8 (100, [L+2]), 294.1 (63.4, [L+4])
$[Zn(\mathbf{L})(H_2O)_2](ClO_4)_2$590.7	580.7 (11.2, $[M-2H_2O+23^a]$), 603.0 (14.6, $[2L+23^a]$), 313.0 (29.1, $[L+23^a]$), 291.4 (100, [L+1]) Mol. peak could not be determined
$[Zn(\mathbf{L})_2Cl_2]\cdot H_2O$ 735.0	738.8 (17.3, $[M+4]^+$), 736.8 (13.9, $[M+2]^+$), 740.8 (12.1, $[M+6]^+$), 680.1 (59.8, [2L+Zn+Cl]), 643.3 (26.3, [2L+Zn-1]), 603.1 (41.1, $[2L+23^a]$), 580.8 (22.1, [2L]), 313.1 (26.2, $[L+23^a]$), 291.3 (100, L+1)
$[Zn(\mathbf{L})_2Br_2]\cdot 2H_2O$ 841.9	844.1 (7.4, $[M+2]^+$), 805.3 (12.1, $[M-2H_2O]$), 827.3 (11.3, $[M-H_2O+2]$), 868.1 (9.4, $[M+23^a +3]$), 725.6 (75.2, [2L+Zn+Br]), 644.4 (13.6, [2L+Zn]), 435.4 (15.6, [L+Zn+Br]), 291.9 (90.3, [L+1]), 294.2 (100, [L+3])
$[Zn(\mathbf{L})_2I_2]\cdot 4H_2O$ 971.9	970.9 (15.2, [M-1]+), 920.5 (11.2, $[M-3H_2O]$), 900.1 (9.6, $[M-4H_2O]$), 771.2 (53.6, [2L+Zn+I]), 643.5 (18.4, $[L+ZnI_2+2H_2O]$), 603.1 (16.1, $[2L+23^a]$), 482.1 (19.6, [L+Zn+I]), 291.7 (100, [L])

Table 5 The ESI-MS data of the compounds.

$^a M_{Na}$: 23.

Temperature (°C)→	100	150	200	250	300	350	400	450	500	550	600	650	700
Complex													**Weight loss (%)**
$[Zn(\mathbf{L})(OAc)_2]$	0.7	0.7	1.5	9.0	23.5	26.0	31.8	54.6	83.0	84.4	84.8	84.7	84.7
$[Zn(\mathbf{L})_2](NO_3)_2\cdot 2H_2O$	4.8	7.1	13.3	18.4	25.2	30.1	33.5	39.4	81.1	90.4	90.4	90.3	90.3
$[Zn(\mathbf{L})(H_2O)_2](ClO_4)_2$	2.6	6.7	7.6	12.1	20.1	33.7	37.6	34.6	39.2	45.6	78.0	88.4	88.2
$[Zn(\mathbf{L})_2Cl_2]\cdot H_2O$	3.1	3.2	4.7	6.5	7.2	18.8	24.2	25.9	28.6	30.9	53.3	88.7	91.1
$[Zn(\mathbf{L})_2Br_2]\cdot 2H_2O$	3.6	4.5	5.1	6.9	7.7	15.8	18.9	21.6	24.3	26.6	42.4	85.7	91.6
$[Zn(\mathbf{L})_2I_2]\cdot 4H_2O$	6.6	7.1	8.6	9.6	10.4	11.6	13.4	15.8	18.4	31.2	84.3	90.9	90.9

Table 6 TGA data of the complexes (thermal decomposition).

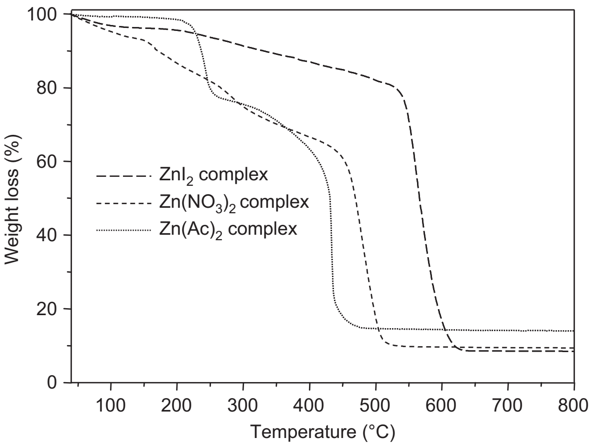


Figure 6 TGA curves of ZnI_2, $Zn(NO_3)_2$ and $Zn(OAc)_2$ complexes.

The fluorescent emission for all of the compounds is observed in the visible region. Thus, these compounds have potential applications as a luminescent material in light-emitting devices.

Conclusions

A new asymmetric bis-benzimidazole ligand, 1,3-bis(1*H*-benzimidazol-2-yl)-propan-1-one (**L**), was synthesized by reacting 2-ketoglutaric acid and *o*-phenylenediamine in 1:2 molar ratio. The complexes of **L** with ZnX_2 (X = Cl, Br, I, ClO_4, NO_3, OAc) were synthesized and characterized by elemental analysis, molar conductivity, FT-IR, NMR, TGA, ESI-MS, and fluorescence spectroscopy. Spectral data show that the ligand has keto-enol equilibrium in polar solvents such as methanol. In methanol, the keto form is more dominant at room temperature and at higher temperatures. The ligand gave chelate complexes coordinating through both C=N group nitrogen atoms. According to IR spectral data, C=O oxygen atom does not coordinate to the Zn(II) ion at the complexes. In the fluorescence spectra, considerable red shift is observed in $ZnBr_2$, ZnI_2 and $Zn(OAc)_2$ complexes according to the ligand. By contrast, the $Zn(OAc)_2$ complex is different from the other Zn(II) complexes as thermal composition, molar conductivity, and fluorescence characteristics are probably due to acetate group coordination.

Experimental

All chemicals and solvents (Merck and Fluka) are of reagent grade and were used without further purification. Elemental analysis data were obtained with a Thermo Finnigan Flash EA 1112 analyzer (Thermo Fisher Scientific, USA). Decomposition points were determined using an electrothermal melting point apparatus (UK). Molar conductivity of the complexes was measured on a WTW Cond315i conductivity meter in DMSO at 25°C (Nova Analytics, USA). ^1H- and ^{13}C-NMR spectra were run on a Varian Unity Inova 500 NMR spectrometer

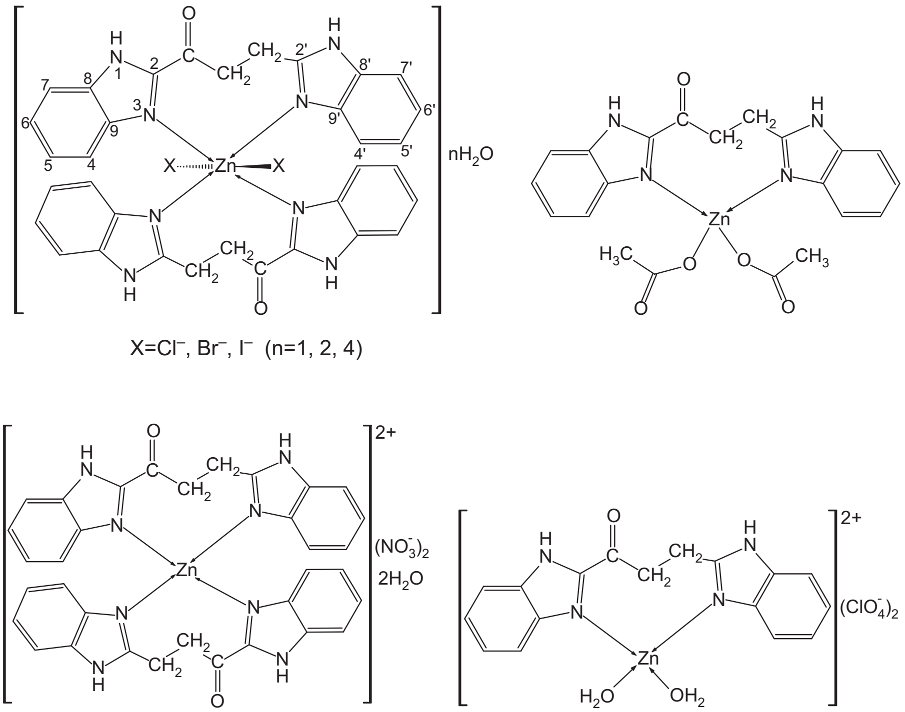


Figure 7 The proposed structures for the complexes in the study.

Compound	Emission maximum wavelength (nm)
L	560 sh, 412 m,br, 394 sh
[Zn(**L**)(OAc)$_2$]	409 m,br, 461 s, 491 s, 528 sh
[Zn(**L**)$_2$](NO$_3$)$_2$·2H$_2$O	417 m,br, 392 sh
[Zn(**L**)(H$_2$O)$_2$](ClO$_4$)$_2$	565 sh, 417 m,br, 396 sh
[Zn(**L**)$_2$Cl$_2$]·H$_2$O	415 m,br, 394 sh
[Zn(**L**)$_2$Br$_2$]·2H$_2$O	481 m,br, 448 sh
[Zn(**L**)$_2$I$_2$]·4H$_2$O	482 m,br, 453 sh, 394 w

Table 7 Emission maximum wavelengths of the compounds.

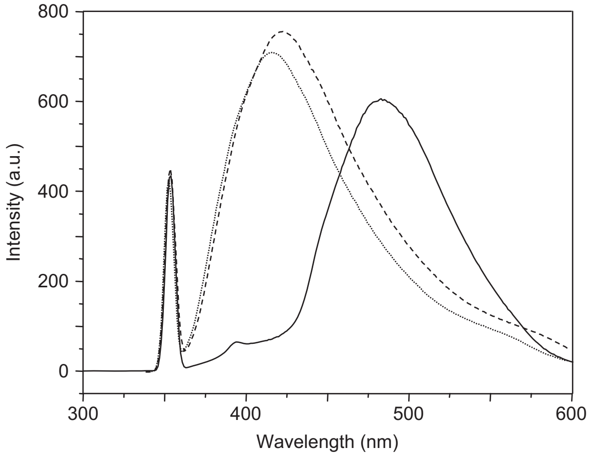


Figure 8 Fluorescence spectra of the ligand (······) and its Zn(ClO$_4$)$_2$ (– – –), ZnI$_2$ (——) complexes in ethanol.

(USA). The residual DMSO-d$_6$ signal was also used as an internal reference. FT-IR spectra were recorded in KBr disks on a Nicolet 380 FT-IR spectrometer (Thermo Fisher Scientific, USA). Electrospray ionization-mass spectrometry (ESI-MS) analyses were carried out in positive ion modes using a Thermo Finnigan LCQ Advantage MAX LC/MS/MS (Thermo Fisher Scientific, USA). Thermogravimetric (TG) studies were made on a TG-60WS Shimadzu, with a heating rate of 10°C/min under flowing air at the rate of 50 ml/min (Japan). Fluorescence spectra were performed on a Shimadzu RF-5301 PC spectrofluorophotometer (Japan).

Synthesis of the ligand

2-Ketoglutaric acid (or 2-oxopentanedioic acid; 1.46 g, 10 mmol) and *o*-phenylenediamine (2.16 g, 0.20 mmol) were refluxed in 20 ml 5.5 N HCl and the ligand was synthesized according to literature methods (Shriner and Upson, 1941; Matthews et al., 1996).

Synthesis of the complexes

[Zn(**L**)$_2$](NO$_3$)$_2$·2H$_2$O: The ligand (145 mg, 0.5 mmol) was dissolved in ethanol (15 ml). A solution of Zn(NO$_3$)$_2$·6H$_2$O (150 mg, 0.5 mmol) in ethanol (10 ml) was added. After the reaction mixture had been heated at reflux for 2 h, the solution was kept at room temperature overnight during which an orange precipitate was formed. This precipitate was filtered and dried at room temperature.

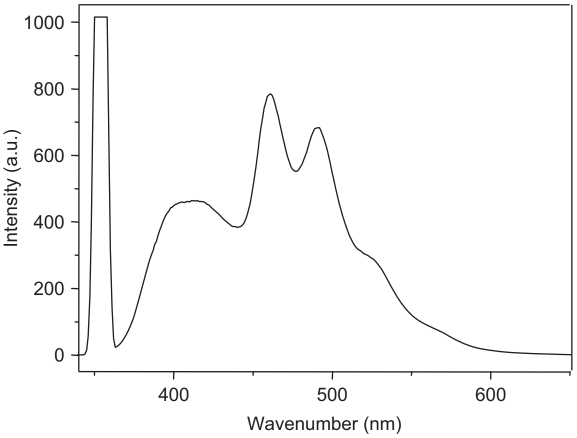


Figure 9 Fluorescence spectrum of the Zn(OAc)$_2$ complex in ethanol.

[Zn(**L**)$_2$Cl$_2$]·H$_2$O: The ligand (145 mg, 0.5 mmol) was dissolved in ethanol (15 ml). A solution of ZnCl$_2$·6H$_2$O (123 mg, 0.5 mmol) in ethanol (10 ml) was added. After the reaction mixture had been heated at reflux for 2 h, the reaction mixture was kept at room temperature for a few days. The precipitate that formed after this time was filtered and dried at room temperature.

[Zn(**L**)(OAc)$_2$]: The ligand (145 mg, 0.5 mmol) was dissolved in ethanol (15 ml). A solution of Zn(CH$_3$COO)$_2$·2H$_2$O (110 mg, 0.5 mmol) in ethanol (10 ml) was added. As soon as the solutions were mixed together, a precipitation was formed immediately. After 3 h reflux, the mixture was cooled to room temperature, filtered, and dried at room temperature.

[Zn(**L**)$_2$Br$_2$]·2H$_2$O: The ligand (145 mg, 0.5 mmol) was dissolved in ethanol (15 ml). A solution of ZnBr$_2$·2H$_2$O (131 mg, 0.5 mmol) in ethanol (10 ml) was added. After the reaction mixture had been heated at reflux for 2 h, the reaction mixture was kept at room temperature. The crystals formed after approximately 1 week were filtered and dried at room temperature.

[Zn(**L**)$_2$I$_2$]·4H$_2$O: The ligand (145 mg, 0.5 mmol) was dissolved in ethanol (15 ml). A solution of ZnI$_2$·4H$_2$O (196 mg, 0.5 mmol) in ethanol (10 ml) was added. After 2 h reflux a slight turbidity was formed. The mixture was filtered and the filtrate was kept at room temperature. The red crystals formed after approximately 1 week were filtered and dried at room temperature.

[Zn(**L**)(H$_2$O)$_2$](ClO$_4$)$_2$: The ligand (145 mg, 0.5 mmol) was dissolved in ethanol (15 ml). A solution of Zn(ClO$_4$)$_2$·6H$_2$O (187 mg, 0.5 mmol) in ethanol (10 ml) was added. After the reaction mixture had been heated at reflux for 2 h, the reaction mixture was kept at room temperature. The amorphous crystals formed after a few days were filtered and dried at room temperature.

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