

1-1-2015

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Available at: <https://journals.tubitak.gov.tr/chem/vol39/iss1/10>

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Synthesis and characterization of substituted benzimidazole Co(II), Fe(II), and Zn(II) complexes and structural characterization of dichlorobis{1-[2-(1-piperidinyl)ethyl]-1H-benzimidazole-*K*N³} zinc(II)[†]

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Received: 16.05.2014 • Accepted: 22.08.2014 • Published Online: 23.01.2015 • Printed: 20.02.2015

Abstract: The Co(II), Fe(II), and Zn(II) complexes of 1-(3-phenyl)propylbenzimidazole (PPBI), 5-nitro-1-(3-phenyl)propylbenzimidazole (PPNBI), 1-[2-(4-morpholinyl)ethyl]benzimidazole (MEBI), 1-[2-(1-piperidinyl)ethyl]benzimidazole (PEBI), and 5-nitro-1-[2-(1-piperidinyl)ethyl]benzimidazole (PENBI) were synthesized and characterized by ¹H NMR, ¹³C NMR, and elemental analyses. The magnitudes of the magnetic moments for paramagnetic complexes were between 4.07 and 5.11 B.M. Moreover, the crystal structure of dichlorobis{1-[2-(1-piperidinyl)ethyl]-1*H*-benzimidazole-*K*N³} zinc(II) was determined by single crystal X-ray diffraction.

Key words: Benzimidazole metal complexes, transition metal complexes, coordination compounds, crystal structure

1. Introduction

Designing molecules bearing suitable functionalities is one of the main targets in chemistry.¹ From this perspective, benzimidazole is an important heterocyclic ligand with nitrogen as the donor, common in biological important molecules.² The chemistry and pharmacology of benzimidazoles are of interest in medicinal chemistry because of their ability to interact with a range of different enzymes and receptors.^{3,4} Transition-metal complexes of benzimidazoles are progressively being used to model important bioinorganic systems.⁵ Metal complexes of biological important ligands are sometimes more effective than free ligands.^{6–12} Benzimidazole metal complexes have also been of great interest due to their versatile properties including catalytic activities^{13–17} and potential applications as functional materials in the areas of electronics, magnetism, and optics.¹⁸ In recent years, considerable attention has also been given to the benzimidazole metal complexes because of their properties in cancer therapy.^{19–22}

There are many reports of benzimidazole transition metal complexes. Some consist of 2-substituted benzimidazoles and the others consist of benzimidazole-based mixed ligands.^{23–25} We have reported on the structural and chemical properties of some transition metal phenyl or (trimethylsilyl)methyl substituted benzimidazole complexes,^{26–30} but there is no example containing morpholine, piperidine, or 3-phenylpropyl substituted ben-

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[†]In memory of Prof Dr Michael Franz Lappert

imidazole metal complexes in the literature. In order to fill the gap in the literature, we aimed to synthesize these types of benzimidazole metal complexes and investigate some of their properties.

We herein report the preparation and characterization of ten 3-phenylpropyl, (4-morpholinyl)ethyl, and (1-piperidinyl)ethyl substituted benzimidazole or 5-nitrobenzimidazole cobalt(II), iron(II), and zinc(II) complexes. The crystal structure of dichlorobis{1-[2-(1-piperidinyl)ethyl]-1*H*-benzimidazole-*K*N³} zinc(II) was determined by single-crystal X-ray diffraction.

2. Results and discussion

The cobalt(II), iron(II), and zinc(II) coordination compounds of PPBI, MEBI, PEPI, and PENBI were obtained through reflux in ethanol. The complexes were smoothly crystallized in DMF. The IR spectra of the Co(II), Zn(II), and Fe(II) complexes are closely related to those of their corresponding free ligands. IR spectra of the complexes show that the strong $\nu_{(C=N)}$ bands in free PPBI at 1493 cm⁻¹, in PPNBI at 1494 cm⁻¹, in MEBI at 1489 cm⁻¹, and in PENBI at 1494 cm⁻¹ shift to 1463–1453 cm⁻¹ for Co(II), 1464–1453 cm⁻¹ for Zn(II), and 1452–1453 cm⁻¹ for Fe(II) complexes. The red shift indicates the coordination of tertiary nitrogen to metal atoms. Similar red shifts are also reported in the literature.^{31–37} N–O asymmetric and symmetric stretching frequencies for the nitro group in free PPNBI were observed at 1512 and 1337 cm⁻¹, respectively. These stretching frequencies were observed for corresponding metal complexes **4**, **5**, and **6** at 1520 and 1340, 1524 and 1340, and 1525 and 1345, respectively. N–O asymmetric and symmetric stretching frequencies for the nitro group in free PENBI were observed at 1511 and 1328 cm⁻¹, respectively. These values were observed in complex **10** as 1519 and 1335, respectively. The nitro group frequencies shifted slightly higher after, perhaps from balancing the electron-withdrawing effect of nitro on free ligands after the formation of Fe(II), Co(II), and Zn(II) complexes. ¹H NMR signals for the proton attached at position 2 of the imidazole ring in free ligands PPBI, PPNBI, MEBI, PEPI, and PENBI were observed as 8.12, 8.73, 8.0, 7.9, and 8.6 ppm, respectively. The signals for the complexes **1**, **3**, **4**, **6**, **8**, **9**, and **10** were observed at 9.84, 8.71, 8.71, 8.84, 8.60, 8.57, and 8.78 ppm, respectively. As expected, the coordination to the Zn(II) and Fe(II) ions shifts the ¹H NMR signals of the complexes downfield from those of the free ligands ($\Delta\delta = 0.10$ ppm and 0.67 ppm, respectively) for the proton at position 2 of the imidazole ring. As mentioned in the Experimental section, the proton NMR of Co(II), and Fe(II) were recorded as broad peaks in diluted solvents with more scans. Even under these conditions, we could not observe any carbon signals for these paramagnetic complexes. Similar broad ¹H NMR peaks were also reported for paramagnetic complexes in the literature.^{26,27,38} The carbon peaks at position 2 of the imidazole ring of the ligands PPBI, PPNBI, MEBI, PEPI, and PENBI were observed at 143.7, 147.4, 141.1, 141.0, and 147.1 ppm, respectively. These values were also shifted downfield about 1.2–4.4 ppm after coordination to the Zn(II) and Fe(II) ions.

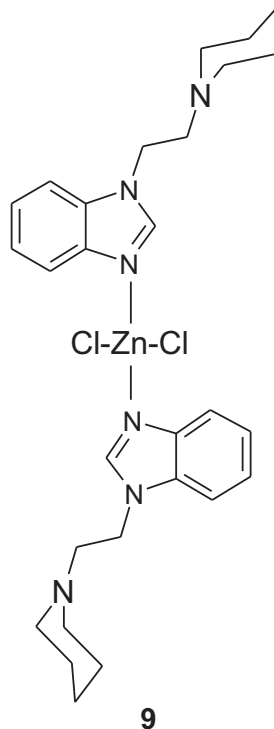
The UV-Vis spectra of PPBI, PPNBI, MEBI, PEPI, and PENBI and complexes (**1–10**) were determined in 190–800 nm regions in DMSO (Table 1). The free ligands PPBI, PPNBI, MEBI, PEPI, and PENBI have absorption maxima at 278, 225, and 205; 304, 249, 222, and 202; 283, 244, 236, and 193; 306, 244, and 210; and 282, 244, 233, 217, and 210 nm, attributed to $\pi - \pi^*$ and $n - \pi^*$ transitions, respectively. In complexes **1**, **2**, and **3**, these peaks are shifted to longer wavelengths by 10–62 nm and 15–72 nm according to those of the free ligand PPBI. In complexes **4**, **5**, and **6**, these peaks are shifted similarly to longer wavelengths by 95–105 nm and 3–19 nm according to those of the free ligand PPNBI. In complexes **7** and **8**, these peaks are also shifted to longer wavelengths by 28–26 nm and 37–38 nm according to those of the free ligand MEBI. In complex **9**,

$\pi - \pi^*$ and $n - \pi^*$ transitions were observed at 312 and 259 nm, whereas in PEBI these peaks were observed at 306 and 244 nm. In complex **10**, $\pi - \pi^*$ and $n - \pi^*$ transitions were observed at 289 and 253 nm, whereas in PENBI these peaks were observed at 282 and 244 nm. The d-d bands for the iron(II) complexes **1** and **4** were observed at 711 nm ($\varepsilon = 54 \text{ M}^{-1} \text{ cm}^{-1}$) and 712 nm ($37 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. The d-d bands for the cobalt(II) complexes **2**, **5**, and **7** were observed at 699 nm ($\varepsilon = 68 \text{ M}^{-1} \text{ cm}^{-1}$), 678 nm ($\varepsilon = 126 \text{ M}^{-1} \text{ cm}^{-1}$), and 669 nm ($\varepsilon = 76 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. All benzimidazole complexes studied in this work show tetrahedral geometry.

The Fe(II) (**1** and **4**) and Co(II) (**2**, **5**, and **7**) are paramagnetic and their magnetic susceptibilities are 5.11, 5.03, 4.42, 4.21, and 4.07 B.M., respectively.

2.1. Molecular structures of benzimidazole complexes of **9**

In the compound $[\text{ZnCl}_2(\text{PEBI})_2]$ (**9**), the environment around the Zn atom is distorted tetrahedral formed by 2 Cl atoms and 2 N atoms of the 1-[(2-piperidin-1-yl)ethyl]benzimidazole ligands (Figure 1).



The average Zn-Cl distance of 2.2315 (11) Å is comparable with the average corresponding distances reported for related metal complexes with distorted ZnN_2Cl_2 tetrahedral environments, cf. 2.261 (1) Å in bis(2-benzyl-1*H*-benzimidazole-*N*³) dichlorozinc(II),³⁹ 2.224 (1) Å in $\text{ZnCl}_2(5,7\text{-dimethyl-}1,2,4\text{-triazolo}[1,5\text{-}a]\text{pyrimidine})_2$,⁴⁰ 2.212 (4) Å in $\text{ZnCl}_2(2,9\text{-dimethyl-}1,10\text{-phenanthroline})$,⁴¹ 2.226 (2) Å in $\text{ZnCl}_2(\text{purine})_2$,⁴² and 2.209 (3) Å in $\text{ZnCl}_2(4\text{-vinylpyridine})_2$,⁴³ but comparable to the value of 2.255 (1) Å in $\text{ZnCl}_2[1\text{-}(5,6\text{-dimethylbenzimidazolyl})\text{-}3\text{-benzimidazolyl-}2\text{-thiapropane}]$.⁴⁴ The average Zn-N bond distance of 2.019 (2) Å is comparable to reported average values, e.g., 2.039 (3) Å in $\text{ZnCl}_2(5,7\text{-dimethyl-}1,2,4\text{-triazolo}[1,5\text{-}$

a]pyrimidine)₂,⁴⁰ 2.05 (1) Å in ZnCl₂(1-methyltetrazole)₂,⁴⁵ 2.059 (3) Å in ZnCl₂(1-methylcytosine)₂,⁴⁶ and 2.027 (3) Å in ZnCl₂[1-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-thiapropane].⁴⁴

Table 1. Electronic absorption spectral bands and magnetic moments of the ligands and their complexes **1–10**.

Compound	Electronic absorption bands*, λ_{max} (nm) Intraligand and charge transfer bands	Magnetic moment, μ_{eff} (B.M.) d-d Bands	
PPBI	278, 225, 205	—	—
PPNBI	304, 249, 222, 202	—	—
MEBI	283, 244, 236, 193	—	—
PEBI	306, 244, 210	—	—
PENBI	282, 244, 233, 217, 210	—	—
1	340, 297, 224, 209	711	5.11
2	288, 265, 209	669	4.42
3	289, 240, 204	—	Diamagnetic
4	387, 271, 226, 212	712	5.03
5	373, 336, 268, 250, 238	678	4.21
6	371, 251	—	Diamagnetic
7	311, 281, 248, 224, 202	669	4.07
8	309, 291, 258	—	Diamagnetic
9	312, 259, 244, 212	—	Diamagnetic
10	289, 253, 241	—	Diamagnetic

* DMSO used as a solvent.

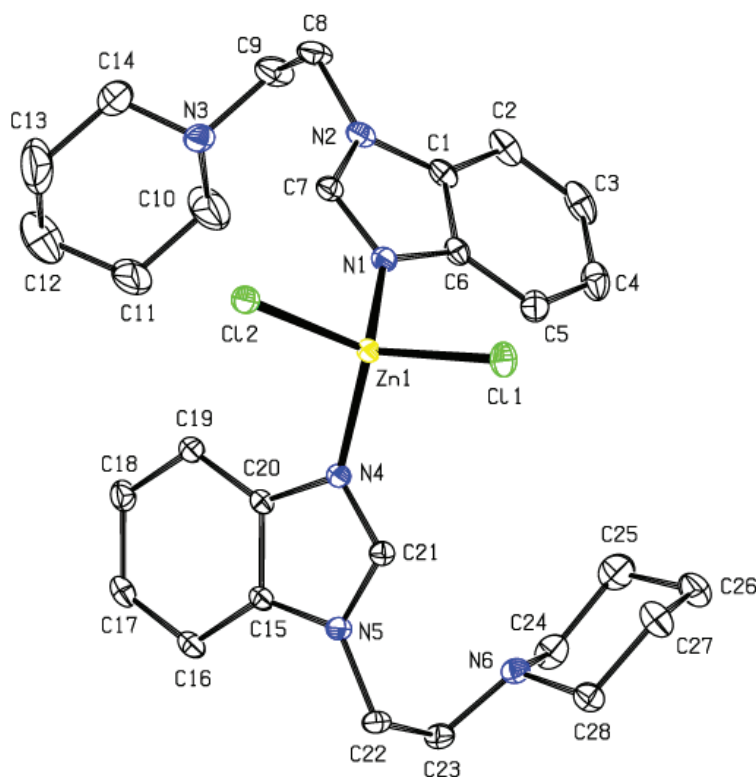


Figure 1. View of compound **9** with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level. H atoms are omitted for clarity.

The mean planes of the benzimidazole moieties (involving N1/N2 and N4/N5) form a dihedral angle of 75.04 (11)°, while the piperidine rings adopt a chair conformation.

The more important geometric parameters of the crystalline compound of **9** are summarized in Table 2.

Table 2. Geometric parameters (Å, °) for **9**.

Zn1—Cl1	2.2217 (11)	N3—C10	1.351 (9)
Zn1—Cl2	2.2413 (9)	N3—C14	1.357 (9)
Zn1—N1	2.037 (2)	N4—C20	1.389 (4)
Zn1—N4	2.000 (2)	N4—C21	1.320 (3)
N1—C6	1.392 (4)	N5—C15	1.383 (4)
N1—C7	1.315 (3)	N5—C21	1.346 (4)
N2—C1	1.389 (4)	N5—C22	1.458 (3)
N2—C7	1.338 (4)	N6—C23	1.450 (5)
N2—C8	1.460 (4)	N6—C24	1.458 (4)
N3—C9	1.453 (5)	N6—C28	1.441 (5)
Cl1—Zn1—Cl2	118.69 (4)	C23—N6—C24	112.4 (3)
Cl1—Zn1—N1	106.92 (7)	C23—N6—C28	113.5 (2)
Cl1—Zn1—N4	108.10 (7)	C24—N6—C28	110.4 (3)
Cl2—Zn1—N1	105.13 (6)	N2—C1—C2	132.2 (3)
Cl2—Zn1—N4	108.39 (7)	N2—C1—C6	106.1 (3)
N1—Zn1—N4	109.34 (9)	N1—C6—C1	108.7 (3)
Zn1—N1—C6	128.54 (18)	N1—C6—C5	130.2 (3)
Zn1—N1—C7	125.8 (2)	N1—C7—N2	113.4 (3)
C6—N1—C7	105.4 (2)	N2—C8—C9	112.2 (3)
C1—N2—C7	106.5 (2)	N3—C9—C8	112.9 (3)
C1—N2—C8	127.1 (3)	N3—C10—C11	114.6 (7)
C7—N2—C8	126.3 (3)	N3—C14—C13	112.9 (5)
C9—N3—C10	114.0 (5)	N5—C15—C16	132.8 (2)
C9—N3—C14	112.8 (4)	N5—C15—C20	105.4 (3)
C10—N3—C14	110.2 (6)	N4—C20—C15	108.8 (2)
Zn1—N4—C20	127.97 (16)	N4—C20—C19	131.1 (2)
Zn1—N4—C21	125.6 (2)	N4—C21—N5	112.6 (3)
C20—N4—C21	105.8 (2)	N5—C22—C23	110.5 (2)
C15—N5—C21	107.5 (2)	N6—C23—C22	111.1 (3)
C15—N5—C22	126.7 (3)	N6—C24—C25	108.2 (3)
C21—N5—C22	125.0 (3)	N6—C28—C27	110.6 (3)

The molecules are linked by C-H...Cl intermolecular hydrogen bonds into infinite chains in the [011] direction (Figure 2). Further, the crystal structure is stabilized by C-H... π interactions (Table 3).

Table 3. Hydrogen-bond parameters (Å, °) for **9**.

	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8—H8A...Cl2 ⁱ	0.97	2.76	3.719 (4)	169
C12—H12B...Cg5 ⁱⁱ	0.97	2.95	3.664 (8)	131
C25—H25B...Cg6 ⁱⁱⁱ	0.97	2.69	3.628 (5)	162

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1+x, y, z$; (iii) $1-x, 2-y, 1-z$.

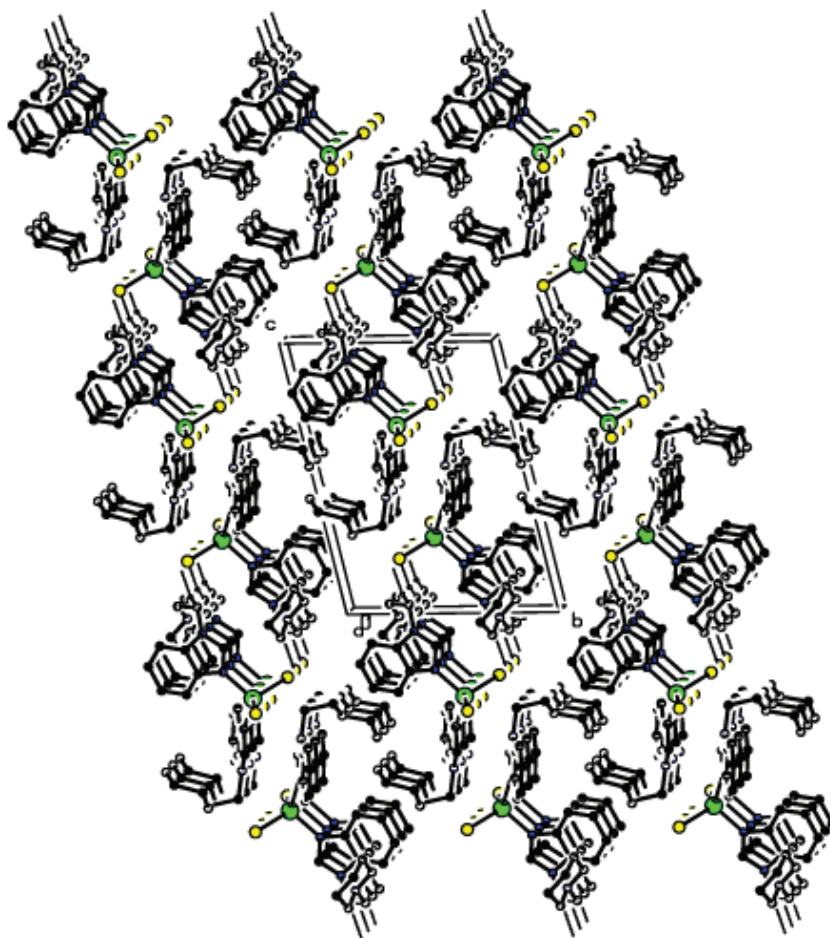
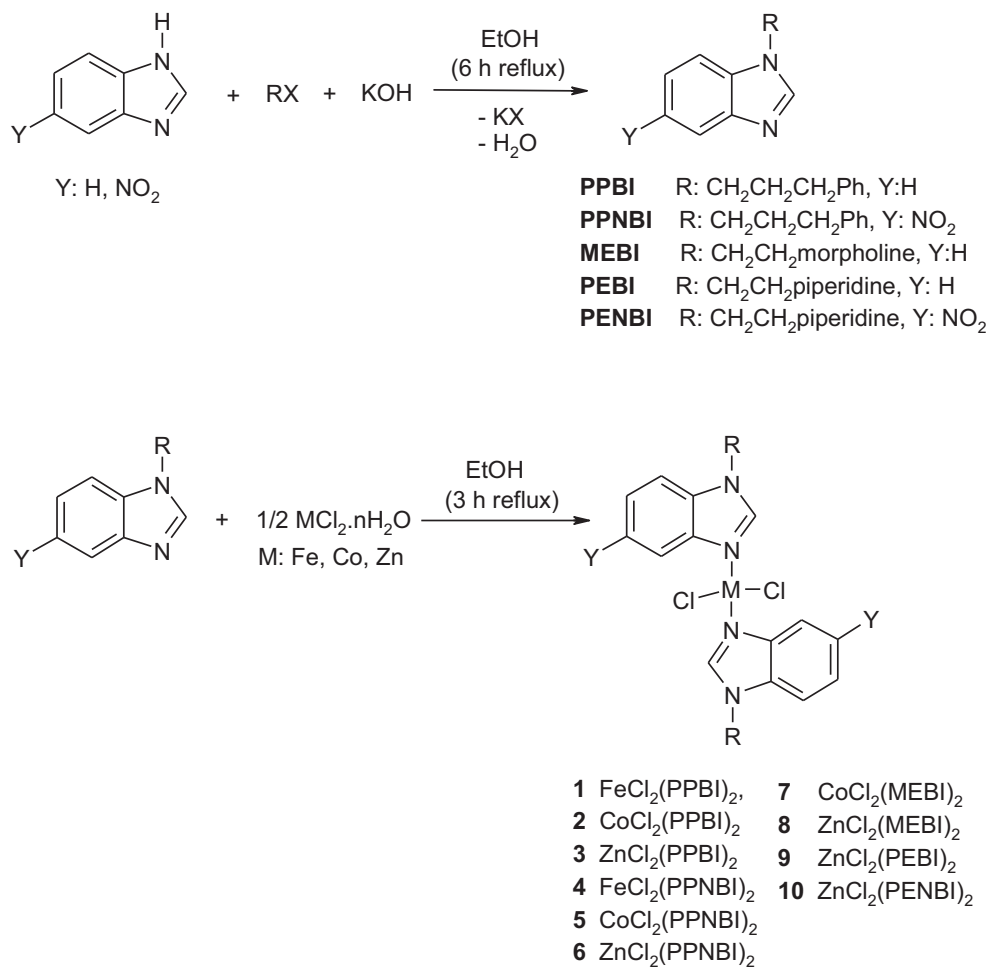


Figure 2. The packing of compound 9 viewed down the a-axis.

3. Experimental

All reactions were performed under an ambient atmosphere. All of the chemicals used were supplied commercially by Aldrich, Merck Chemical Co., Fluka, Carlo Erba, or Acros. Solvents were dried with standard methods and freshly distilled prior to use. Both ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were determined using a Bruker DPX-300 high performance digital FT NMR spectrometer. ^{13}C NMR spectra of the cobalt and iron complexes could not be recorded due to their paramagnetic properties. Because of the paramagnetic properties of the iron atom, ^1H NMR spectra of iron complexes were recorded as broad peaks through diluted sample solutions by increasing the scan number 2-fold. Even under these conditions, appropriate ^1H NMR spectra of paramagnetic cobalt complexes were not obtained. Infrared spectra were recorded as KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$ on a PerkinElmer FT-IR spectrophotometer. UV-Vis spectra were measured on a PerkinElmer Lambda 35 spectrophotometer. Elemental analyses were performed by LECO CHNS-932 elemental analyzer at the Scientific and Technological Research Center of İnönü University (Malatya, Turkey). The melting points were recorded using an Electrothermal-9200 melting point apparatus and they were uncorrected. Magnetic measurements were made on a Sherwood Scientific apparatus at room temperature by Gouy's method using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant and were corrected for dia-

magnetism by applying Pascal's constant. The compounds 1-(3-phenylpropyl)benzimidazole (PPBI),⁴⁷ 1-[2-(4-morpholinyl)ethyl]benzimidazole (MEBI),⁴⁸ 1-[2-(1-piperidinyl)ethyl]benzimidazole (PEBI),⁴⁹ and 5-nitro-1-[2-piperidin-1-yl]ethylbenzimidazole (PENBI)⁵⁰ were prepared according to the literature procedures. The benzimidazole ligand 5-nitro-1-(3-phenyl)propylbenzimidazole (PPNBI) was synthesized for the first time in this work similar to the literature method.³¹ All compounds synthesized in this work are given in the Scheme.



Scheme. Synthesis procedures of benzimidazole ligands and complexes.

3.1. Preparation of 5-nitro-1-(3-phenylpropyl)benzimidazole (PPNBI)

A mixture of 5(6)-nitrobenzimidazole (2.72 g, 16.7 mmol), KOH (0.95 g, 17.0 mmol), and 3-phenylpropyl bromide (2.6 mL, 17.2 mmol) was refluxed for 6 h in ethanol (30 mL). The mixture was then cooled, after which potassium bromide was filtered, washed with a little ethanol, and the solvent was removed from the filtrate in vacuo. The residue was extracted with chloroform (15 mL) and the extract was then evaporated in vacuo. The obtained crude product was crystallized from ethanol/diethyl ether (1:5) (20 mL). Yield: 4.03 g (86%); mp: 97–98 °C. Anal. Calc. for C₁₆H₁₅N₃O₂ (%): C, 68.31; H, 5.37; N, 14.94. Found (%): C, 68.05; H, 5.06; N, 14.58%. IR: $\nu_{(C=N)}$ = 1494 cm⁻¹. ¹H NMR (CDCl₃): δ = 8.70 (s, 1H, N=CH-N); 8.33–7.16 (m, 8H, Ar-H); 4.25 (t, 2H, CH₂CH₂CH₂C₆H₅, J = 7.2 Hz); 2.70 (t, 2H, CH₂CH₂CH₂C₆H₅, J = 7.2 Hz); 2.30 ppm

(quint, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3): $\delta = 147.4$ ($\text{N}=\text{CH}-\text{N}$), 143.8, 133.9, 128.8, 126.7, 120.6, 118.7, 118.0, 117.2, 109.7, 106.8 (C_6H_4 and C_6H_5), 44.7 ($\text{N}-\text{CH}_2-$), 32.6 ($-\text{CH}_2-\text{Ph}$), 30.9 ppm ($-\text{CH}_2-$).

3.2. Preparation of $[\text{FeCl}_2(\text{PPBI})_2]$, **1**

A mixture of PPBI (0.78 g, 3.3 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.33 g, 1.7 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The brown crude product was crystallized from DMF. Yield: 0.86 g (87%); mp: 229–230 °C. IR: $\nu_{(\text{C}=\text{N})}$: 1452 cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{32}\text{N}_4\text{Cl}_2\text{Fe}$: C, 64.12; H, 5.38; N, 9.35. Found: C, 63.95; H, 5.14; N, 9.17%. ^1H NMR ($\text{DMSO}-d_6$): $\delta = 9.84$ (br s, 2H, NCHN); 8.15–6.93 (br m, 18H, $\text{Ar}-\text{H}$); 4.55 (br s, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$); 2.59 (br s, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$); 2.19 ppm (br s, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$).

3.3. Preparation of $[\text{CoCl}_2(\text{PPBI})_2]$, **2**

A mixture of PPBI (0.75 g, 3.2 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.38 g, 1.6 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The obtained blue crude product was crystallized from DMF. Yield: 0.84 g (88%); mp: 177–178 °C. IR: $\nu_{(\text{C}=\text{N})}$: 1463 cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{32}\text{N}_4\text{Cl}_2\text{Co}$: C, 63.80; H, 5.35; N, 9.30. Found: C, 63.09; H, 5.25; N, 9.46%.

3.4. Preparation of $[\text{ZnCl}_2(\text{PPBI})_2]$, **3**

A mixture of PPBI (0.68 g, 2.9 mmol) and ZnCl_2 (0.2 g, 1.5 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The obtained cream color crude product was crystallized from DMF. Yield: 0.80 g (91%); mp: 176–177 °C. IR: $\nu_{(\text{C}=\text{N})}$: 1464 cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{32}\text{N}_4\text{Cl}_2\text{Zn}$: C, 63.12; H, 5.30; N, 9.20. Found: C, 62.62; H, 5.14; N, 8.59%. ^1H NMR ($\text{DMSO}-d_6$): $\delta = 8.71$ (s, 2H, NCHN); 7.93 (d, 4H, $\text{Ar}-\text{H}$, $J = 7.5$ Hz); 7.72 (d, 4H, $\text{Ar}-\text{H}$, $J = 7.5$ Hz); 7.39–7.10 (m, 10H, $\text{Ph}-\text{H}$); (4.41 (t, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, $J = 7.2$ Hz); 2.57 (t, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, $J = 7.9$ Hz); 2.12 (quint, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, $J = 7.5$ Hz). ^{13}C NMR ($\text{DMSO}-d_6$): $\delta = 144.8$ ($\text{N}=\text{CH}-\text{N}$), 140.7, 139.8, 132.9, 128.3, 125.9, 123.7, 123.2, 118.3, 113.6, 111.5 (C_6H_4 and C_6H_5), 44.7 ($\text{N}-\text{CH}_2-$), 32.0 ($-\text{CH}_2-\text{Ph}$), 30.7 ppm ($-\text{CH}_2-$).

3.5. Preparation of $[\text{FeCl}_2(\text{PPNBI})_2]$, **4**

A mixture of PPNBI (0.90 g, 3.2 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.32 g, 1.6 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The obtained brown crude product was crystallized from DMF. Yield: 0.72 g (80%); mp: 219–220 °C. IR: $\nu_{(\text{C}=\text{N})}$: 1453 cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2\text{Fe}$: C, 55.75; H, 4.39; N, 12.19. Found: C, 54.70; H, 4.35; N, 11.94%. ^1H NMR ($\text{DMSO}-d_6$): $\delta = 8.80$ (br s, 2H, NCHN); 7.95 (br s, 4H, $\text{Ar}-\text{H}$); 7.09 (br s, 12H, $\text{Ar}-\text{H} + \text{Ph}-\text{H}$); 4.39 (br s, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$); 2.52 (br s, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$); 2.08 ppm (br s, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$).

3.6. Preparation of $[\text{CoCl}_2(\text{PPNBI})_2]$, **5**

A mixture of PPNBI (0.65 g, 2.3 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.28 g, 1.2 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The obtained blue crude product was crystallized from DMF.

Yield: 0.58 g (84%); mp: 188–189 °C. IR: $\nu_{(C=N)}$: 1452 cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2\text{Co}$: C, 55.50; H, 4.37; N, 12.14. Found: C, 55.28; H, 4.38; N, 12.20%.

3.7. Preparation of $[\text{ZnCl}_2(\text{PPNBI})_2]$, **6**

A mixture of PPNBI (0.72 g, 2.6 mmol) and ZnCl_2 (0.17 g, 1.3 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The obtained cream color crude product was crystallized from DMF. Yield: 0.82 (92%); mp: 191–192 °C. IR: $\nu_{(C=N)}$: 1454 cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2\text{Zn}$: C, 54.99; H, 4.33; N, 12.02. Found: C, 54.45; H, 4.32; N, 12.11%. ^1H NMR (DMSO- d_6): δ = 8.84 (s, 2H, NCHN); 8.82 (s, 2H, Ar-H); 8.70 (d, 2H, Ar-H), J = 7.5 Hz; 8.20 (d, 2H, Ar-H, J = 7.5 Hz); 7.9–7.1 (m, 10H, Ph-H); 4.45 (t, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, J = 7.3 Hz); 2.56 (t, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, J = 7.8 Hz); 2.15 (quint, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, J = 7.4 Hz). ^{13}C NMR (DMSO- d_6): δ = 149.1 (N=CH-N), 143.7, 138.0, 133.2, 128.8, 128.6, 126.4, 119.1, 115.6, 112.4, 108.9 (C_6H_4 and C_6H_5), 45.4 (N- CH_2 -), 32.6 (- CH_2 -Ph), 31.3 ppm (- CH_2 -).

3.8. Preparation of $[\text{CoCl}_2(\text{MEBI})_2]$, **7**

A mixture of MEBI (0.78 g, 3.4 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.4 g, 1.7 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The obtained blue crude product was crystallized from DMF. Yield: 0.88 g (88%); mp: 164–165 °C. IR: $\nu_{(C=N)}$: 1463 cm^{-1} . Anal. Calc. for $\text{C}_{26}\text{H}_{34}\text{N}_6\text{O}_2\text{Cl}_2\text{Co}$: C, 52.71; H, 5.78; N, 14.19. Found: C, 52.16; H, 5.58; N, 14.20%.

3.9. Preparation of $[\text{ZnCl}_2(\text{MEBI})_2]$, **8**

A mixture of MEBI (0.78 g, 3.4 mmol) and ZnCl_2 (0.24 g, 1.7 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was filtered off while hot. The obtained cream color crude product was crystallized from DMF. Yield: 0.96 g (93%); mp: 168–169 °C. IR: $\nu_{(C=N)}$: 1464 cm^{-1} . Anal. Calc. for $\text{C}_{26}\text{H}_{34}\text{N}_6\text{O}_2\text{Cl}_2\text{Zn}$: C, 52.14; H, 5.72; N, 14.03. Found: C, 51.78; H, 5.57; N, 13.86%. ^1H NMR (DMSO- d_6): δ = 8.60 (s, 2H, NCHN); 7.81 (d, 2H, Ar-H, J = 7.81 Hz); 7.76 (d, 2H, Ar-H, J = 7.8 Hz); 7.39–7.12 (m, 4H, Ar-H); 4.47 (t, 4H, =N- CH_2 -, J = 6.0 Hz); 3.50 (t, 8H, ring CH_2 -O-, J = 4.5 Hz); 2.70 (t, 4H, -N- CH_2 -, J = 6.0 Hz); 2.42 (t, 8H, ring CH_2 -N-, J = 4.5 Hz). ^{13}C NMR (DMSO- d_6): δ = 145.7 (NCHN), 140.6, 133.6, 123.9, 123.3, 118.7, 111.9 (Ar-C), 66.6 (=N CH_2 -), 57.2 (- CH_2 -O), 53.5 (CH_2 -N-), 42.1 ppm (ring N- CH_2 -N).

3.10. Preparation of $[\text{ZnCl}_2(\text{PEBI})_2]$, **9**

A mixture of PEBI (1.00 g, 4.40 mmol) and ZnCl_2 (0.30 g, 2.20 mmol) in ethanol (20 mL) was heated under reflux for 3 h. All volatiles were removed in vacuo. The cream color crude product, **9**, was crystallized from DMF. Yield: 1.17 g (90%); mp: 179–180 °C. IR: $\nu_{(C=N)}$: 1465 cm^{-1} . Anal. Calc. for $\text{C}_{28}\text{H}_{38}\text{N}_6\text{Cl}_2\text{Zn}$: C, 56.53; H, 6.44; N, 14.13. Found: C, 55.32; H, 6.52; N, 13.34%. ^1H NMR (DMSO- d_6): δ = 8.57 (s, 2H, NCHN); 7.82 (d, 2H, Ar-H, J = 7.8 Hz); 7.75 (d, 2H, Ar-H, J = 8.1 Hz); (m, 4H, Ar-H); 4.45 (t, 4H, N- CH_2 -, J = 6.0 Hz); 2.64 (t, 4H, N- CH_2 -, J = 6.0 Hz); 2.37 (m, 8H, ring CH_2 -N); 1.40–1.37 (m, 12H, ring - CH_2 -). ^{13}C NMR (DMSO- d_6): δ = 145.4 (NCHN), 139.4, 133.0, 123.6, 123.1, 118.0, 111.5, 56.9, 53.7, 42.1, 25.4, 23.9 ppm.

3.11. Preparation of [ZnCl₂(PENBI)₂], **10**

A mixture of PENBI (0.98 g, 3.6 mmol) and ZnCl₂ (0.24 g, 1.8 mmol) in ethanol (20 mL) was refluxed 3 h. All volatiles were removed in vacuo. The cream color crude product, **10**, was crystallized from DMF. Yield: 1.04 g (85%); mp: 225–226 °C. IR: $\nu_{(C=N)}$: 1453 cm⁻¹. Anal. Calc. for C₂₈H₃₆N₈O₄Cl₂Zn: C, 49.10; H, 5.30; N, 16.36. Found: C, 49.00; H, 5.03; N, 16.02%. ¹H NMR (DMSO-*d*₆) δ 8.78 (s, 2H, NCHN); 8.62–7.86 (m, 6H, Ar-H); 4.52 (t, 4H, N-CH₂-, *J* = 6.0 Hz); 2.77 (t, 4H, N-CH₂-, *J* = 6.0 Hz); 2.44–2.40 (t, 8H, ring CH₂-N-, *J* = 6.5 Hz); 1.44–1.38 (m, 12H, ring -CH₂-). ¹³C NMR (DMSO-*d*₆) δ 148.3 (NCHN), 119.9, 118.5, 117.7, 115.9, 111.9, 109.0, 58.0, 54.3, 43.2, 25.8, 24.0 ppm.

3.12. X-ray structural determination of dichlorobis{1-[2-(1-piperidiny)ethyl]-1*H*-benzimidazole-*K*N³} zinc(II), **9**

The X-ray crystallographic data of **9** were collected on a STOE IPDS 2 diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) radiation at 293(2) K. The structures were solved by direct methods using the SIR-97 program and refined on *F*² by full matrix least-squares using the SHELXL-97 program. A summary of the crystal data, experimental details, and refinement results for **9** is given in Table 4. Hydrogen atoms were included at calculated positions and refined with a riding model.

Table 4. Crystallographic data for **9**.

Compounds	9
formula	C ₂₈ H ₃₈ Cl ₂ N ₆ Zn
<i>M</i> , g mol ⁻¹	594.93
space group	<i>P</i> -1
<i>a</i> , Å	10.2414 (6)
<i>b</i> , Å	11.3634 (7)
<i>c</i> , Å	14.3358 (9)
α , °	99.432 (5)
β , °	100.926 (5)
γ , °	110.801 (5)
Volume, Å ³	1481.97 (18)
<i>Z</i>	2
<i>d</i> calcd., g cm ⁻¹	1.333
μ , mm ⁻¹	1.04
total reflns	26085
indep reflns	5734
parameters	334
GOF	0.99
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	0.039
<i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.086
<i>R</i> 1 (all data)	0.064
<i>wR</i> 2 (all data)	0.093

3.13. Refinement

In **9**, all H atoms were placed in calculated positions and refined using a riding model with C—H in the range 0.93–0.97 Å and *U*_{iso}(H) = 1.2 or 1.5*U*_{eq}(C).

3.14. Computer programs

Data collection: X-AREA.⁵¹ Cell refinement: X-AREA. Data reduction: X-RED32.⁵¹ Program(s) used to solve structure: SIR-97.⁵² Program(s) used to refine structure: SHELXL97.⁵³ Molecular graphics: ORTEP-3 for Windows.⁵⁴ Software used to prepare material for publication: WINGX.⁵⁵

4. Conclusions

Ten novel Co(II), Fe(II), and Zn(II) complexes of substituted benzimidazole ligands and 1 new benzimidazole ligand, 5-nitro-1-(3-phenyl)propylbenzimidazole (PPNBI), were synthesized successfully and their full characterization was performed. Among the 10 complexes, dichlorobis{1-[2-(1-piperidinyl)ethyl]-1*H*-benzimidazole-*K*N³} zinc(II) was structurally analyzed by X-ray diffraction. X-ray diffraction analysis of dichlorobis{1-[2-(1-piperidinyl)ethyl]-1*H*-benzimidazole-*K*N³} zinc(II) showed that the zinc atom in the complex is coordinated tetrahedrally by 2 chlorine atoms and 2 nitrogen atoms from 2 benzimidazole rings.

Supplementary material

Crystallographic data for the structural analysis of **9** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No: 742389 for C₂₈H₃₈Cl₂N₆Zn.

Acknowledgments

We wish to thank İnönü University Research Fund (BAPB-2008/05) for its financial support of this study. The authors also acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe *IPDS* II diffractometer (purchased under grant F.279 of the University Research Fund).

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