



## Synthesis and spectral characterization of 1,2-bis(5-methyl/chloro-1*H*-benzimidazol-2-yl)ethanols and their Co(II), Pd(II) and Zn(II) complexes

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**Abstract:** 1,2-Bis(5-methyl/chloro-1*H*-benzimidazol-2-yl)ethanols (**1** and **2**), asymmetric bis-benzimidazoles, and their complexes with CoCl<sub>2</sub>, PdCl<sub>2</sub> and ZnCl<sub>2</sub> were synthesized and characterized by elemental analysis, molar conductivity, magnetic moment, TGA, FT-IR (mid- and far-IR), FT-Raman, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, ESI-MS and fluorescence spectroscopy. The spectral data suggest that the chiral chelating ligands acted as tridentate through both the C=N nitrogen and OH oxygen atoms. According to the molar conductance, the Zn(II) complexes are non-electrolyte whereas the Co(II) complexes are 1:2 and the Pd(II) complexes are 1:1 electrolytes. The ligands and most of the complexes show triple fluorescence in ethanol. In addition, the Zn(II) complex of **1** (**1e**) shows significant fluorescence characteristics compared to the other complexes.

**Keywords:** bis-benzimidazole; asymmetric; ethanol; cobalt(II); palladium(II); zinc(II); complex; fluorescence.

### INTRODUCTION

It was interpreted that some asymmetric bis-benzimidazole derivatives could be relevant for biomimicry and metal ion transport.<sup>1</sup> In biomimicry mode enzymes such as cyclodextrins<sup>2</sup> with two imidazole parts, poly(benzimidazoles),<sup>3</sup> *etc.* are considered as favourite targets to simulate the imidazoles in catalytic enzymes.<sup>1</sup> However, there is a very limited number of studies about asymmetric bis-benzimidazoles and their complexes although many bis- and poly(symmetric benzimidazoles) were synthesized and investigated.<sup>1,4–12</sup>

Tanious *et al.* investigated DNA sequence-dependent monomer–dimer binding modulation of the bis-benzimidazole derivatives DB183, DB210, DB185 and

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Hoechst 33258. They concluded from a number of their studies that some DNA sequences have significantly different physical and interaction properties.<sup>13</sup>

Matthews *et al.* synthesized and characterized a series of asymmetric bis-benzimidazoles and their Cu(II) complexes. Mono-*N*-alkylated bis-benzimidazoles having two halves of different basicity were also synthesized.<sup>1</sup> In addition, coordination of Zn(II), Cd(II), Hg(II), and Ag(I) with the above asymmetric bis-benzimidazole derivatives were investigated.<sup>14</sup>

Van Albada *et al.* reported a number of Ni(II), Cu(II) and Zn(II) complexes with the tridentate chiral chelating ligand 1,2-bis(benzimidazol-2-yl)ethanol (HEBBz).<sup>15</sup> HEBBz formed mononuclear complexes of the general formula  $M(\text{HEBBz})_2(\text{anion})_2$  for all metal ions and a variety of anions. Crystal structures of the monomeric Ni(II), dimeric and tetrameric Cu(II) complexes with HEBBz were also reported.<sup>15</sup> On the other hand, van Albada *et al.* reported the crystal structure of the  $\text{Cu}_2(\text{EBBz})(\mu\text{-Cl})(\text{Cl})_2(\text{CH}_3\text{OH})$  complex in which deprotonation of HEBBz was observed.<sup>16</sup> In addition, 1,3-bis(1*H*-benzimidazol-2-yl)propan-1-one as an asymmetric bis-benzimidazole derivative and its various Zn(II) complexes were reported.<sup>17</sup>

Besides, the introduction of an element of chirality is an attractive prospect as it could enhance the pharmacological uptake of the drug entity by adopting specific conformation and stereoselective binding with molecular target DNA.<sup>18,19</sup> It was reported that 1,2-bis(1*H*-benzimidazol-2-yl)-1,2-ethanediol, ( $\text{H}_2\text{BBz}$ ), and its methylated derivative ( $\text{H}_2\text{MBBz}$ ) acted as chiral, facially coordinating tridentate ligands, forming complexes of composition  $\text{ML}_2$  with octahedral transition metals ( $M = \text{Cu}^{2+}$  or  $\text{Ni}^{2+}$ ).  $\text{H}_2\text{BBz}$  gave octahedral complexes with metals through the coordination of one deprotonated alcohol group and C=N nitrogen atoms.<sup>20</sup> Isele *et al.* reported dinuclear and tetranuclear complexes with  $\text{H}_2\text{BBz}$  and  $\text{H}_2\text{MBBz}$  with  $\text{Cu}(\text{ClO}_4)_2$  through coordination of the alcohol groups of mono- and/or di-deprotonated ligands.<sup>21</sup> In addition, some transition metal complexes were reported of  $\text{H}_2\text{BBz}$  and 1,4-bis(2-benzimidazolyl)-1,2,3,4-butane-1,4-diol having chiral centre, in which the ligands acted as bidentate and tetradentate, respectively.<sup>22</sup>

In this study, the aim was to synthesize and characterize two new asymmetric chiral ligands, 1,2-bis(5-Me/Cl-1*H*-benzimidazol-2-yl)ethanols (methyl- and chloro-derivatives of HEBBz; **1** and **2**; Fig. 1) and their Co(II), Pd(II) and Zn(II) complexes. The effect of the electropositive (methyl) and electronegative (chloro) groups on the ligands and the complexes was investigated.

## EXPERIMENTAL

### Chemicals

All chemicals and solvents were of reagent grade and used without further purification.

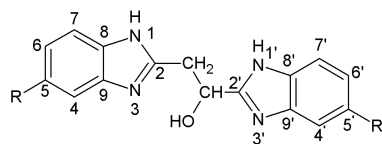


Fig. 1. Chemical structure of the ligands (R=CH<sub>3</sub>, **1**; R=Cl, **2**).

### Apparatus

Elemental analysis data were obtained with a Thermo Finnigan Flash EA 1112 analyzer. Molar conductivity of the complexes was measured on a WTW Cond315i conductivity meter in DMF at 25 °C. Magnetic moment measurements for the Co(II) complexes were performed on a Sherwood Scientific apparatus (MK1) at room temperature by the Gouy method using Hg[Co(SCN)<sub>4</sub>] as calibrant. FT-IR spectra (mid-IR and far-IR) were recorded on a Bruker Optics Vertex 70 spectrometer using ATR (Attenuated Total Reflection) techniques. The FT-Raman spectra were recorded using the same instrument with a R100/R RAMII Raman module equipped with an Nd:YAG laser source operating at the 1064 nm line with 200-mW power and a spectral resolution of  $\pm 2$  cm<sup>-1</sup>. The electron spray ionization-mass spectrometry (ESI-MS) analysis was realized in the positive ion modes using a ThermoFinnigan LCQ Advantage MAX LC/MS/MS. Samples were dissolved in MeOH of HPLC grade purity. The thermogravimetric (TG) study was made on a TG-60WS Shimadzu instrument, at a heating rate of 10 °C min<sup>-1</sup> under dynamic air at a flow rate of 50 mL min<sup>-1</sup>. The fluorescence spectra were recorded on a Shimadzu RF-5301 PC spectrofluorophotometer. The <sup>1</sup>H- and <sup>13</sup>C-NMR (APT) spectra were recorded in DMSO-*d*<sub>6</sub> solvent on a Varian Unity Inova 500 NMR spectrometer (at 500 and 125 MHz, respectively) using TMS as the internal standard. The chemical shift values are expressed in ppm ( $\delta$  / ppm) values and the coupling constants in Hz (*J* / Hz).

### Synthesis of the ligands

*1,2-Bis(5-methyl-1H-benzimidazol-2-yl)ethanol (1)*. Ligand **1** was synthesized from a 1:2 mole ratio of 2-hydroxybutanedioic acid (1.34 g, 0.010 mol) and 4-methylbenzene-1,2-diamine (2.44 g, 0.020 mol) in 5.5 M HCl (20 mL) according to the literature.<sup>1,15,16,23</sup>

*1,2-Bis(5-chloro-1H-benzimidazol-2-yl)ethanol (2)*. Ligand **2** was synthesized from a 1:2 mole ratio of 2-hydroxybutanedioic acid (1.34 g, 0.010 mol) and 4-chlorobenzene-1,2-diamine (2.85 g, 0.020 mol) in 5.5 M HCl (20 mL) according to the literature.<sup>1,15,16,23</sup>

### Synthesis of the complexes

*[Co(1)<sub>2</sub>(H<sub>2</sub>O)]Cl<sub>2</sub>·2H<sub>2</sub>O (1a)*. Ligand **1** (0.153 g, 0.00050 mol) was dissolved in ethanol (10 mL), to which a CoCl<sub>2</sub>·6H<sub>2</sub>O (0.060 g, ~0.00025 mol) solution in ethanol (5 mL) was added. The mixture was refluxed for 2 h and filtered after cooling to room temperature. The filtrate was kept at room temperature for two days during which a blue polycrystalline precipitate formed. The precipitate was washed with water, filtered and dried at room temperature (the same product was obtained when the metal salt and the ligand were used in a 1:1 ratio).

*[Pd(1)Cl]<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (1b)*. PdCl<sub>2</sub> (0.0885 g, 0.00050 mol) and KCl (0.0746 g, 0.0010 mol) were dissolved in ethanol (5 mL) and this solution was added to a ligand solution (0.153 g, 0.00050 mol) in ethanol (5 mL). The mixture was refluxed for 2 h and filtered after cooling to room temperature. The filtrate was kept at room temperature for two days during which a slightly khaki coloured polycrystalline precipitate was formed. The precipitate was filtered and dried at room temperature.

$[Zn(1)Cl_2] \cdot 2H_2O$  (**1c**). The ligand (0.153 g, 0.00050 mol) was dissolved in ethanol (10 mL) and  $ZnCl_2 \cdot 6H_2O$  (0.123 mg,  $\approx 0.00050$  mol) solution in ethanol (5 mL) was added to the ligand solution. The mixture was refluxed for 2 h and filtered. The filtrate volume was diminished to approx. 1 mL by heating and then 9 mL ethyl acetate were added. The solution was kept at room temperature for two days whereby colourless crystals were formed. The crystals were filtered and dried at room temperature.

$[Co(2)_2]Cl_2 \cdot 2H_2O$  (**2a**). This complex was obtained in a similar manner to **1a**. Thus, **2** (0.174 g, 0.00050 mol) was used for the complex preparation (The same product was obtained when the metal salt and the ligand were used in a 1:1 ratio).

$[Pd(2)Cl]_2Cl_2 \cdot 2H_2O$  (**2b**). This complex was obtained in a similar manner to **1b**. Thus,  $PdCl_2$  (0.0885 g, 0.00050 mol), KCl (0.0746 g, 0.0010 mol) and **2** (0.174 g, 0.00050 mol) were used.

$[Zn(2)Cl_2]$  (**2c**). The ligand (0.174 g, 0.00050 mol) was dissolved in ethyl acetate (15 mL).  $ZnCl_2 \cdot 6H_2O$  (0.123 g, 0.00050 mol) in ethyl acetate (5 mL) was added to the ligand solution. The mixture was refluxed for 2 h and filtered. The filtrate was kept at room temperature for 2 days. A slightly yellow precipitate was formed, which was filtered and dried at room temperature (the same product was obtained when the metal salt and the ligand were used in a 1:2 ratio).

The physical and spectral data for the ligands and complexes are given in the Supplementary material to this paper.

## RESULTS AND DISCUSSIONS

### General

The ligands, 1,2-bis(5-Me/Cl-1H-benzimidazol-2-yl)ethanol (**1** and **2**), are soluble in polar solvents such as ethanol, DMF, acetone *etc.* The Co(II) and Zn(II) complexes have moderate solubility whereas the Pd(II) complex has low solubility in polar solvents.

Decomposition points of **1** and **2** are 190 and 212 °C, respectively. It could be seen that the methyl and chloro substituents decrease the decomposition points of **1** and **2** with respect to 1,2-bis(benzimidazol-2-yl)ethanol (261 °C).<sup>15</sup> In addition, the methyl group decreases the decomposition point (190 °C) more than the chloro substituent (212 °C), as presented in the literature.<sup>24,25</sup> On the other hand, the decomposition point of the Pd(II) complexes is higher than the others (above 350 °C). The decomposition point order of the complexes is: Pd(II) > Zn(II) > Co(II). From this, it can be concluded that the Pd(II) complexes have high thermal stability.

It was reported that 1,2-bis(benzimidazol-2-yl)ethanol (HEBBz) is a tridentate ligand towards  $CuCl_2$ ,  $Cu(NO_3)_2$ ,  $Cu(ClO_4)_2$ ,  $Zn(ClO_4)_2$ ,  $Zn(BF_4)_2$ ,  $NiCl_2$ ,  $NiBr_2$ ,  $Ni(NO_3)_2$ ,  $Ni(BF_4)_2$ ,  $Ni(ClO_4)_2$  and  $Ni(CF_3SO_3)_2$  ( $CF_3SO_3$ : triflate, OTf).<sup>15,16</sup> Similarly, there are some findings showing that **1** and **2** (the methyl- and chloro-derivatives of HEBBz, respectively) also acted as tridentate towards Pd(II), Co(II) and Zn(II) ions in this study.

The Zn(II) complexes are non-electrolyte according to the molar conductivity data in DMF, whereas the Co(II) complexes are 1:1 electrolyte with the molar conductance value in the range of 86–105 S m<sup>2</sup> mol<sup>-1</sup>.<sup>26,27</sup>

Geary reported that molar conductivity values for 1:1 and 1:2 electrolyte in DMF generally falls between 65–90 and 130–170 S m<sup>2</sup> mol<sup>-1</sup>, respectively.<sup>27</sup> However, in this study the Pd(II) complexes show molar conductivity in the 112–123 S m<sup>2</sup> mol<sup>-1</sup> range. This range is lower than the range for 1:2 electrolyte but higher than the 1:1 electrolyte range. Nevertheless, it could be suggested that these complexes are 1:2 electrolytes because the molar conductance values of the Pd(II) complexes are closer to the 1:2 electrolyte range. This miss-match with expectation could be explained in two ways, *i.e.*, the two chloride ions are outside of the coordination sphere in the chlorine bridged complexes ([Pd(L)Cl]<sub>2</sub>Cl<sub>2</sub>) or the structures of the complexes may be changed in DMSO during the molar conductivity measurements.

Chlorides in the complexes were determined by means of AgCl precipitation from AgNO<sub>3</sub> solutions. With the Co(II) and Pd(II) complexes, the immediate precipitation of AgCl may show that the chlorides are outside the coordination sphere of these complexes. With the Zn(II) complexes (**1c** and **2c**), there was no instant precipitation or turbidity, but after a very short period a precipitation formed. This means that the chloride ions are coordinated to the metal ions in the Zn(II) complexes.

The room temperature magnetic moment value of **1a** ([Co(**1**)<sub>2</sub>(H<sub>2</sub>O)]Cl<sub>2</sub>·H<sub>2</sub>O),  $\mu_{\text{eff}} = 4.47 \mu_{\text{B}}$ , is typical for cobalt(II) complexes with a d<sup>7</sup> high spin electron configuration. This value lies in the range corresponding to three unpaired electrons for pentagonal bipyramidal geometry ( $S = 3/2$ ) around cobalt(II), d<sup>7</sup> complexes.<sup>28–30</sup> The calculated value for an octahedral d<sup>7</sup> high spin electronic distribution is 3.87  $\mu_{\text{B}}$ . The experimental value obtained for the magnetic moment of Co(II) in the cobalt(II) complex of **2** (**2a**) is 4.05  $\mu_{\text{B}}$ , from which it was concluded that Co(II) in **2a** is in an octahedral geometry with a high spin configuration.<sup>31,32</sup>

Distorted square pyramid structures could be suggested for the Pd(II) and Zn(II) complexes with coordination numbers of five.

#### *Infrared and Raman spectroscopy*

The FT-IR (mid-IR and far-IR) and FT-Raman spectral data of the compounds are given in the Supplementary material. Comparison of the FT-Raman spectra and FT-IR spectra of **2** and [Zn(**2**)Cl<sub>2</sub>] may be seen in Fig. 2; the far IR spectra of **2** and its Zn(II) complex are given in Fig. S-1 of the Supplementary material.

The broad bands above 3100 cm<sup>-1</sup> in the ligand spectrum may be attributed to stretching vibration of NH, and it shifts to near 3200 cm<sup>-1</sup> in the complexes.

The broad bands above  $3100\text{ cm}^{-1}$  in the complexes belong to stretching vibrations of the coordinated (only **1a**) and uncoordinated water molecules. The weak or medium bands between  $3000$  and  $2850\text{ cm}^{-1}$  are due to vibrations of the aliphatic  $\text{CH}_2$  groups.

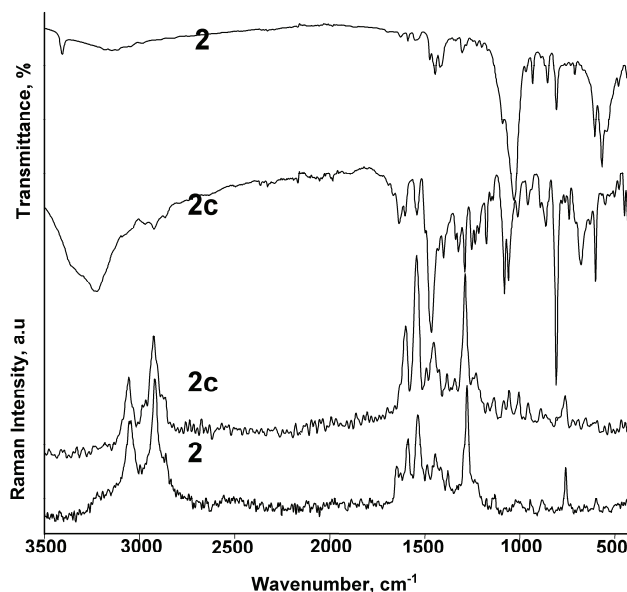


Fig. 2. Comparison of the FT-IR spectra of **2** and  $[\text{Zn}(\mathbf{2})\text{Cl}_2]$  (**2c**) together with the FT-Raman spectra of **2** and **2c** in the  $400\text{--}500\text{ cm}^{-1}$  range.

The  $\nu(\text{C}=\text{C})$  frequencies of the ring systems are expected to appear at around  $1625\text{ cm}^{-1}$  in the IR spectra. Similarly, the  $(\text{C}=\text{N})$  asymmetric stretching frequencies are expected to appear at *ca.*  $1600\text{ cm}^{-1}$ .<sup>33,34</sup> On complexation, especially the  $\text{C}=\text{N}$  bands show considerable changes, such as shifting to higher wavenumber or changing in the intensity from weak to medium. For example, the weak band at  $1594\text{ cm}^{-1}$  in the IR spectra of **1**, assignable to  $\nu(\text{C}=\text{N})$ , appears at  $1597$ ,  $1600$  and  $1597\text{ cm}^{-1}$  as medium strength bands in the spectra of the  $\text{Co}(\text{II})$ ,  $\text{Pd}(\text{II})$  and  $\text{Zn}(\text{II})$  complexes, respectively. Similarly, the weak band at  $1588\text{ cm}^{-1}$  in **2** is seen in the  $1590\text{--}1594\text{ cm}^{-1}$  range as medium strength bands in the  $\text{Co}(\text{II})$ ,  $\text{Pd}(\text{II})$  and  $\text{Zn}(\text{II})$  complexes. This indicates a fast tautomeric equilibrium of the ligands and the  $\text{NH}$  bond exhibits a weak vibration in the IR spectra. Upon complexation, the fluxional behaviour of the  $\text{NH}$  proton is inhibited and a stable permanent double bond between one nitrogen and the carbon atom,  $-\text{NH}-\text{C}=\text{N}-$ , is formed (Fig. 3).<sup>22</sup> This may be taken as strong evidence that the amino proton tautomerization is inhibited as a result of the coordination of the nitrogen to the metal ion.

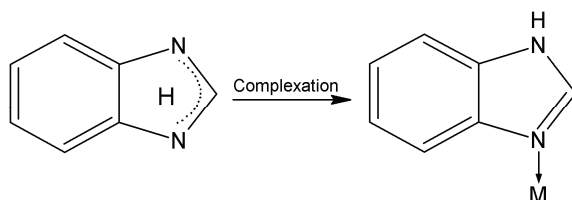


Fig. 3. Removal of the tautomeric structure from the ligands upon coordination.

The medium bands at around  $1020\text{ cm}^{-1}$  in the IR spectra of the ligands assigned to  $\nu(\text{C}-\text{O})$  shift to the range  $1045\text{--}1056\text{ cm}^{-1}$  on complexation.<sup>35</sup> This may be considered as evidence for coordination of the OH oxygen atom.

In all of the compounds, the characteristic  $\nu(\text{C}-\text{H})$  and  $\delta(\text{C}-\text{H})$  modes of ring residues are observed between  $3033$  and  $3087\text{ cm}^{-1}$  (medium or weak) and in the  $794\text{--}805\text{ cm}^{-1}$  region (strong or very strong), respectively.<sup>36,37</sup>

Differing from the spectra of the ligands, new broad medium bands at around  $670$  and  $710\text{ cm}^{-1}$  in the IR spectra of complexes **1** and **2**, respectively, could be attributed to  $\nu(\text{M}-\text{N})$  coordination bands.<sup>38</sup>

In the FT-Raman spectra of all the compounds, the aliphatic and aromatic  $\nu(\text{C}-\text{H})$  groups are seen clearly in the  $2900\text{--}3085\text{ cm}^{-1}$  range because the NH and OH bands are absent (Fig. 2).

#### NMR spectroscopy

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR (APT) spectral data of the ligands and Zn(II) and Pd(II) complexes are given in the Supplementary material. The NMR spectra of the compounds were measured in  $\text{DMSO-}d_6$  before and after  $\text{D}_2\text{O}$  exchange (Fig. 4). In addition, the  $^1\text{H}$ -NMR spectra of **2** and its Zn(II) complex (**2c**) are presented in Fig. 4. The signals of the NH and OH protons disappeared after  $\text{D}_2\text{O}$  exchange, as expected.

The ligands have a chiral carbon atom:  $-\text{CH}_2-\text{CHOH}-\text{C}_{\text{imidazole}}$ . In general organic chemistry, it is known that the signals of both hydrogen atoms in a methylene group linked to a chiral carbon atom split due to the effect of the chiral carbon (they give two different signals resulting an AB system). Therefore, it was observed that both hydrogen atoms of the  $\text{CH}_2$  next to the chiral carbon (in the chiral axis) split into two different peaks in **1** after  $\text{D}_2\text{O}$  exchange, **1c**, **2**, **2b** and **2c** between  $3.28$  and  $4.77$  ppm (Fig. 4).

In the literature, it was reported that the OH (alcohol) hydrogen atom of 1,2-bis(benzimidazol-2-yl)ethanol (HEBBz), 1,2-bis(1*H*-benzimidazol-2-yl)-1,2-ethanediol ( $\text{H}_2\text{BBz}$ ) and its *N*-methylated analogue ( $\text{H}_2\text{MBBz}$ ) was deprotonated upon complexation with various Cu(II) salts, such as  $\text{CuCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cu}(\text{ClO}_4)_2$ .<sup>15,16,20</sup> However, in this study, deprotonation was not observed, whereas spectral data showed the OH oxygen atom was coordinated toward the Co(II), Pd(II) and Zn(II) ions.

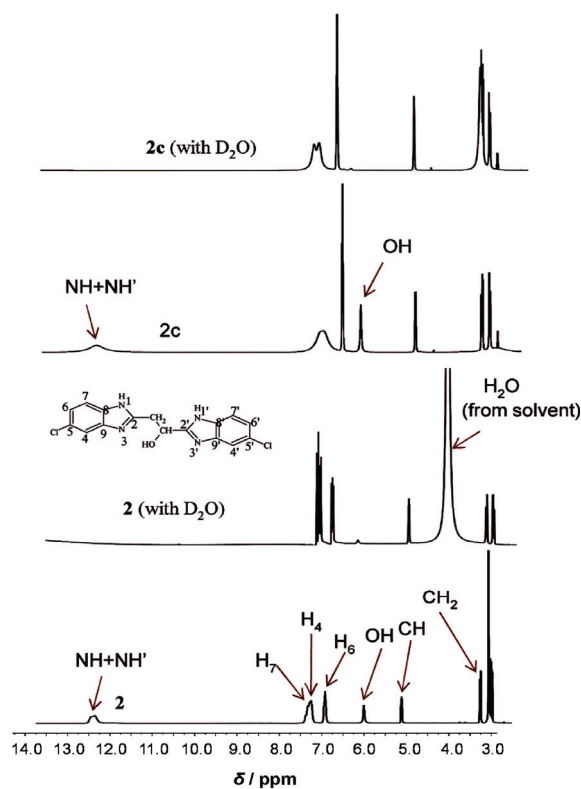


Fig. 4.  $^1\text{H-NMR}$  spectra of **2** and **2c** ( $\text{ZnCl}_2$  complex of **2**) in DMSO and  $\text{D}_2\text{O}$ .

In the  $\text{Zn(II)}$  and  $\text{Pd(II)}$  complexes, considerable shifts to higher frequencies for the OH protons were observed compared to the ligands. For example, the OH proton shifts from 6.13 ppm (ligand **1**) to 6.93 ppm in the  $\text{Zn(II)}$  complex of **1** (**1c**). In the  $\text{Pd(II)}$  complex of **1** (**1b**), the OH proton exhibits a considerable shift of 1.09 ppm (from 6.13 to 7.22 ppm). This observation gives clear-cut evidence that the OH oxygen atom coordinates to the metal ions without deprotonation. The shift values of the OH proton in the  $\text{Zn(II)}$  and  $\text{Pd(II)}$  complex of **2** are 0.69 and 0.92 ppm, respectively. On the other hand, the change in the character of OH hydrogen peak, *i.e.*, from a broad singlet (**1**) to a singlet (**1c**), is a prominent observation in the  $^1\text{H-NMR}$  spectra of the complexes compared to the ligands.<sup>14</sup> In addition, there are considerable downfield shifts of the H7 signal (*i.e.*, from 7.56 ppm in the spectrum of **1** to 8.08 ppm in that of **1c**) on complexation, as expected.

The  $^1\text{H-NMR}$  spectra of **1** and its  $\text{Zn(II)}$  complex were also obtained at  $0\text{ }^\circ\text{C}$ . No substantial differences between the room temperature and the  $0\text{ }^\circ\text{C}$   $^1\text{H-NMR}$  spectra were observed. At  $0\text{ }^\circ\text{C}$ , the aromatic proton signals are broader and the NH peak is absent.

All of the signals appear as broad singlet in the  $^1\text{H-NMR}$  spectra of **1** and the CH and  $\text{CH}_2$  protons become a doublet in the case of the  $\text{Zn(II)}$  complex of **1**.



It is interesting that both NH protons (NH' and NH) of **1** and its complexes (**1b** and **1c**) appear as a broad singlet at 12.17, 13.47 and 13.43 ppm, respectively. However, in the **2** spectra, they are seen as two separate signals that are very close to each other (12.57 and 12.50 ppm, Fig. 4). This can be considered as a result of the substituent (chloro) effect. In case of the Zn(II) complex of **2** (**2c**), these two signals become a broad signal as a result of complexation. The broadening of this band (NH+NH') makes it difficult to distinguish the signals for NH and NH'. The NH and NH' protons give two broad signals at 13.71 and 13.77 ppm, respectively, for the Pd(II) complex of **2** (**2b**).

Bigger shifts were observed for the Pd(II) complexes compared to those for the Zn(II) complexes, however, the splits in the peaks are not clear. The peaks of the Pd(II) complexes appear as broad singlet (*brs*), broad doublet (*brd*) and multiplets. For example, the aliphatic CH signal ( $-\text{CH}_2-\text{CHOH}-\text{C}_{\text{imidazole}}$ ) appears at 5.32 (*brs*) and 5.37 (*dd*) ppm for **1** and **2**, respectively, and at 6.77 (*brs*) and 6.65 (*s*) ppm in the Pd(II) complexes, **1b** and **2b**, respectively.

$^{13}\text{C}$ -NMR spectra (APT) of the ligands and the diamagnetic Zn(II) and Pd(II) complexes are informative, especially for the bridging aliphatic carbons. The carbon atom bonded to the OH (C–OH) shows considerable chemical shift values between 2.5 and 2.2 ppm in the complexes compared to those of the ligands: It appears at 67.2 ppm in the spectrum of **1** and shifts to 64.7 and 64.8 ppm for **1b** and **1c**, respectively (it is seen at 67.0, 64.6 and 64.8 ppm for **2**, **2b** and **2c**, respectively). The other bridging carbon atom ( $-\text{CH}_2-$ ) gives an upfield shift between 1.2 and 1.7 ppm for the Zn(II) and Pd(II) complexes compared to those for the ligands. These data strongly support the coordination of the OH oxygen atom to the metal ions. In light of the NMR data, it could be suggested that the ligands acted as tridentate through the OH oxygen and both the C=N nitrogen atoms.

#### Mass spectrometry

The ESI-MS spectral data of the complexes are given in the Supplementary material. Some  $m/z$  values assigned to the major fragmentations are also given.

A series of isotopic patterns were identified in the ESI-MS spectrum of **2** (chloro derivative) between  $m/z$  347 and 352 due to the various isotopes of the chlorine atom. Similarly, there are many peaks in the mass spectra of the Pd(II) and Zn(II) complexes due to palladium and zinc having various isotopes.

The mole peaks of all the complexes were observed, although in low relative percentage abundances, except for that of **2a** (Co(II) complex of **2**). It is interesting that the Pd(II) complexes give major peaks with 100 % abundance corresponding to half of the molecular ion, for example at  $m/z = 481.0$  for **1b** ( $\text{M}/2-\text{H}_2\text{O}-3$ ) and at  $m/z = 520.9$  for **2b** ( $\text{M}/2-\text{H}_2\text{O}-4$ ). These data show that the Pd(II) complexes undergo homolytic (symmetric) cleavage through two Pd( $\mu$ -

-Cl) bonds under MS conditions. Similar observations have been reported in the literature.<sup>39–42</sup>

The peaks of the ligand could be determined in the mass spectra of all the complexes.

#### Thermal analysis

The major features of the thermal analysis of the complexes are summarized in Table S-I of the Supplementary material. Thermogravimetric (TG) curves of the complexes are given in Fig. 5.

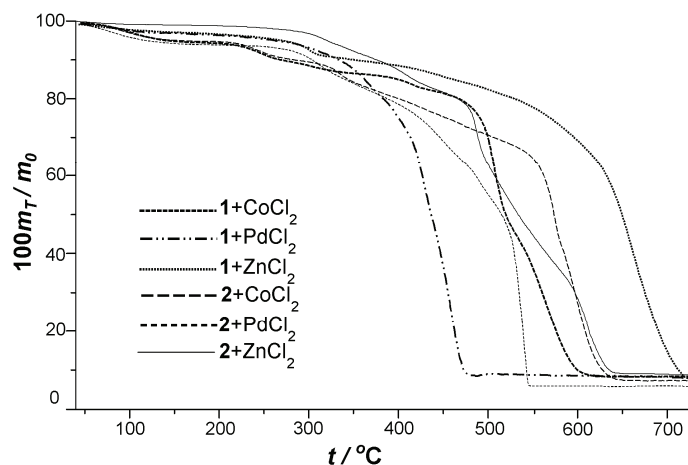


Fig. 5. TG curves of the complexes.

The samples of the complexes were heated from room temperature to 800 °C. There are uncoordinated water molecules in all the complexes according to the TG curves and elemental analysis data. The uncoordinated lattice water molecules were lost through evaporation in the 50 to 100 °C range for all the complexes (dehydration). Simultaneously, a small amount of residual solvent may be removed in this range. Contrary to the others, **1a** has one coordinated water molecule that is removed at temperatures near 150 °C.

The thermal degradation of the complexes occurred in three stages for most of the complexes. First, uncoordinated lattice water was released in the 50–100 °C range, as mentioned above. In the second stage, the small mass losses observed above 200, 250 and 300 °C for the Co(II), Zn(II) and Pd(II) complexes, respectively, could be explained in terms of cleavage of the hydroxyl group. Above 450 °C, all other organic parts of the complexes are oxidized to carbon dioxide and water. Complete decomposition of the complexes continues up to 650 °C probably with the formation of MO.

TGA data are compatible with the suggested structures of the complexes. Molecular weight ratio of the amount of metal oxide show very good agreement for the proposed structures, according to the TG data.

#### Fluorescence spectra

Excitation and emission spectra of the compounds were obtained in ethanol solution at room temperature (excitation wavelength: 354 nm; concentration:  $\approx 10^{-4}$  M). The emission spectral data of the compounds are presented as Supplementary material. The fluorescence spectra of the ligands and their Zn(II) complexes are shown in Fig. 6.

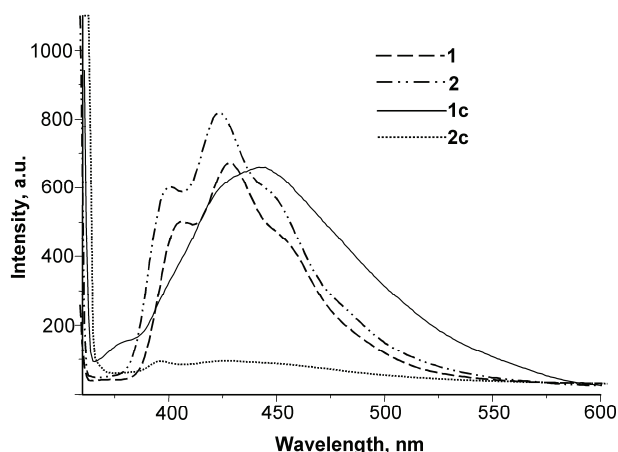


Fig. 6. Fluorescence spectra of the ligands (**1** and **2**) and their Zn(II) complexes (**1c** and **2c**).

All the compounds exhibited three emission bands in their fluorescence spectra, except **1b**. The fluorescence spectra of the ligands are very similar. Compound **2** (chloro derivative) fluoresces slightly more intensively than **1** (methyl derivative). Moreover, the emission bands of **2** complexed with ZnCl<sub>2</sub> (**2c**) are weaker compared to those of the other Zn(II) complex, **1c** (Fig. 6). The fluorescence intensity of complex **1c** is nearly the same as that of the uncomplexed ligand, but its characteristic was changed by coordination of Zn(II): It becomes a very broad band centred at 442 nm. However, there is considerable quenching of fluorescence of **2c** compared to both the ligand **2** and complex **1c**. This could be explained as the synergistic effect of zinc and chlorine atoms decreasing the fluorescence intensity of **2c**.<sup>43</sup>

The fluorescence characteristics of the cobalt complexes are moderate (weaker than the ligand but stronger than the Pd(II) complexes). The fluorescence characteristics of the Pd(II) complexes are very weak compared to the uncomplexed ligands and the other complexes. The quenching effect in the Pd(II) complexes is higher than those in the Co(II) and Zn(II) complexes.

Three bands were observed in the fluorescence spectrum of **1**, at 406 nm (*m, br*), 428 nm (*m*) and 456 nm (*sh*). These bands probably result from the following factors: 1 – the normal Stokes shift originating from a locally excited  $\pi^*$  electronic state, 2 – intramolecular charge transfer and 3 – monocation protonated at the benzimidazole nitrogen atom N3 as a result of an interaction, such as hydrogen bonding, with the solvent (ethanol).<sup>44,45</sup> Similar comments are feasible for the other compounds, except **1b**, which gives only two weak bands.

#### CONCLUSIONS

Asymmetric bis-benzimidazoles could be important for biomimicry and metal ion transport. However, there are very limited number of studies about the asymmetric bis-benzimidazoles and their complexes in literature. In this study, two new asymmetric bis-benzimidazole derivatives, 1,2-bis(5-methyl/chloro-1*H*-benzimidazol-2-yl)ethanols (**1** and **2**), and their complexes with CoCl<sub>2</sub>, PdCl<sub>2</sub> and ZnCl<sub>2</sub> were synthesized and characterized by elemental analysis, molar conductivity, magnetic moment, TGA, ESI-MS and FT-IR (mid- and far-IR), FT-Raman, <sup>1</sup>H- and <sup>13</sup>C-NMR and fluorescence spectroscopy. According to the spectral data, it could be concluded that the chiral chelating ligands acted as tridentate through both the C=N nitrogen and OH oxygen atoms. In the <sup>1</sup>H-NMR spectra, considerable shifts of the OH hydrogen atom and changes in their characters could be explained by the complexation effect between metal ions [(Zn(II) and Pd(II)] and the ligands.

The Zn(II) complexes are non-electrolyte, whereas the Co(II) complexes are 1:2 and the Pd(II) complexes are 1:1 electrolytes. The ligands and the complexes (except **1b**, Pd(II) complex of **1**) show triple fluorescence bands in ethanol. In addition, the Zn(II) complex of **1** (**1c**) exhibits significant fluorescence characteristics compared to the other complexes. According to the experimental data, it could be concluded that the Pd(II) complexes have 1:1 M:L ratio with bridging chlorides (binuclear), whereas the Co(II) complexes have a 1:2 M:L ratio. The M:L ratio is 1:1 in the Zn(II) complexes.

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#### SUPPLEMENTARY MATERIAL

Analytical, physicochemical and spectral data of the title compound are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД  
СИНТЕЗА И СПЕКТРОСКОПСКА КАРАКТЕРИЗАЦИЈА РАЗЛИЧИТИХ  
1,2-БИС(5-МЕТИЛ/ХЛОП-1Н-БЕНЗИМИДАЗОЛ-2-ИЛ)ЕТАНОЛА И  
ОДГОВАРАЈУЋИХ Co(II), Pd(II) И Zn(II) КОМПЛЕКСА

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Описана је синтеза различитих 1,2-бис(5-метил/хлор-1Н-бензимидазол-2-ил)етанола (**1** и **2**) и асиметричних бис-бензимидазола, као и њихових комплекса са CoCl<sub>2</sub>, PdCl<sub>2</sub> и ZnCl<sub>2</sub>. Наведени лиганди и одговарајући комплекси су окарактерисани на основу резултата елементалне микроанализе, мерења моларне проводљивости, магнетних момената, TGA, FT-IR, FT-Раманске, <sup>1</sup>H- и <sup>13</sup>C-NMR, ESI-MS и флуоресцентне спектроскопије. На основу спектроскопских података потврђено је да су наведени хирални лиганди тридентатно координовани за наведене јоне метала преко два C=N атома азота и атома кисеоника хидроксилне групе. На основу вредности за моларну проводљивост нађено је да су комплекси Zn(II) неелектролити, док су комплекси Co(II) и Pd(II) електролити, са молским односом лиганда и метала у овим комплексима 1:2 за Co(II) и 1:1 за Pd(II). Испитивани лиганди и највећи број комплекса показују три пута већу флуоресценцију у етанолу. Поред тога, комплекс Zn(II) (комплекс лиганда **1** (**1c**)) показује значајно већу флуоресценцију у односу на друге испитиване комплексе.

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REFERENCES

1. C. J. Matthews, T. A. Leese, W. Clegg, M. R. J. Elsegood, L. Horsburgh, J. C. Lockhart, *Inorg. Chem.* **35** (1996) 7563
2. J. M. Desprey, R. Breslow, *J. Am. Chem. Soc.* **116** (1994) 12081
3. J. H. Satcher, Jr., M. W. Droege, T. J. R. Weakley, R. T. Taylor, *Inorg. Chem.* **34** (1995) 3317
4. C. J. Matthews, W. Clegg, M. R. J. Elsegood, T. A. Leese, D. Thorp, P. Thornton, J. C. Lockhart, *J. Chem. Soc., Dalton Trans.* **1996** (1996) 1531
5. C. J. Matthews, T. A. Leese, D. Thorp, J. C. Lockhart, *J. Chem. Soc., Dalton Trans.* **1998** (1998) 79
6. J. J. Paul, S. R. Kircus, T. N. Sorrell, P. A. Ropp, H. H. Thorp, *Inorg. Chem.* **45** (2006) 5126
7. G. A. van Albada, I. Mutikainen, I. Riggio, U. Turpeinen, J. Reedijk, *Polyhedron* **21** (2002) 141
8. J. S. Kim, B. Gatto, C. Yu, A. Liu, L. F. Liu, E. J. LaVoie, *J. Med. Chem.* **39** (1996) 992
9. C. Liu, S. Yu, D. Li, Z. Liao, X. Sun, H. Xu, *Inorg. Chem.* **41** (2002) 913
10. L. Mishra, R. Sinha, *Monatsh. Chem.* **133** (2002) 59
11. N. Singh, D. O. Jang, *Org. Lett.* **9** (2007) 1991
12. N. Chandrashekhar, V. Gayathri, N. M. N. Gowda, *Magn. Reson. Chem.* **47** (2009) 666
13. F. A. Tanius, D. Hamelberg, C. Bailly, A. Czarny, D. W. Boykin, W. D. Wilson, *J. Am. Chem. Soc.* **126** (2004) 143
14. C. J. Matthews, W. Clegg, S. L. Heath, N. C. Martin, M. N. S. Hill, J. C. Lockhart, *Inorg. Chem.* **37** (1998) 199
15. G. A. van Albada, J. Reedijk, R. Hamalainen, U. Turpeinen, A. L. Spek, *Inorg. Chim. Acta* **163** (1989) 213
16. G. A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Polyhedron* **25** (2006) 81

17. A. Tavman, *Main Group Met. Chem.* **35** (2012) 81
18. a) S. C. Stinson, *Chem. Eng. News* **79** (2001) 45; b) X. Qu, J. O. Trent, I. Fokt, W. Priebe, J. B. Chaires, *Proc. Natl. Acad. Sci.* **97** (2000) 12032
19. F. Arjmand, F. Sayeed, S. Parveen, *J. Organomet. Chem.* **696** (2011) 3836
20. K. Isele, V. Broughton, C. J. Matthews, A. F. Williams, G. Bernardinelli, P. Franz, S. Decurtins, *J. Chem. Soc., Dalton Trans.* **2002** (2002) 3899
21. K. Isele, P. Franz, C. Ambrus, G. Bernardinelli, S. Decurtins, A. F. Williams, *Inorg. Chem.* **44** (2005) 3896
22. A. Tavman, B. Ulküseven, N. M. Agh-Atabay, *Transition Met. Chem.* **25** (2000) 324
23. R. L. Shrinier, R. W. Upson, *J. Am. Chem. Soc.* **63** (1941) 2277
24. A. Tavman, S. Ikiz, A. F. Bağcigil, N. Y. Özgür, S. Ak, *J. Serb. Chem. Soc.* **74** (2009) 537
25. A. Tavman, S. Ikiz, A. F. Bağcigil, N. Y. Özgür, S. Ak, *Turk. J. Chem.* **33** (2009) 321
26. D. Kong, Y. Xie, *Inorg. Chim. Acta* **338** (2002) 142
27. W. J. Geary, *Coord. Chem. Rev.* **7** (1971) 81
28. J. Matsumoto, T. Suzuki, Y. Kajita, H. Masuda, *Dalton Trans.* **41** (2012) 4107
29. U. K. Das, J. Bobak, C. Fowler, S. E. Hann, C. F. Petten, L. N. Dawe, A. Decke, M. Kerton, C. M. Kozak, *Dalton Trans.* **39** (2010) 5462
30. C. Gökçe, N. Dilek, R. Güp, *Inorg. Chim. Acta* **432** (2015) 213
31. A. C. Massabni, P. P. Corbi, P. Melnikov, M. A. Zachariasc, H. R. Rechenberg, *J. Braz. Chem. Soc.* **16** (2005) 718
32. D. F. Shriver, P. W. Atkins, C. H. Langford, *Inorganic Chemistry*, 2<sup>nd</sup> ed., Oxford University Press, Wallingford, 1994
33. I. Yılmaz, A. Çukurovalı, *Transition Met. Chem.* **28** (2003) 399
34. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5<sup>th</sup> ed., Wiley-Interscience, New York, 1988
35. A. Tavman, *J. Serb. Chem. Soc.* **71** (2006) 521
36. A. Tavman, N. M. Agh-Atabay, A. Neshat, F. Gücin, B. Dülger, D. Hacıu, *Transition Met. Chem.* **31** (2006) 194
37. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5<sup>th</sup> ed., John Wiley, New York, 1997
38. V. T. Yılmaz, S. Hamamci, Ö. Andac, K. Z. Güven, *Z. Anorg. Allg. Chem.* **629** (2003) 172
39. M. Y. Wong, G. Xie, C. Tourbillon, M. Sandroni, D. B. Cordes, A. M. Z. Slawin, I. D. W. Samuel, E. Zysman-Colman, *Dalton Trans.* **44** (2015) 8419
40. S. Bettington, A. L. Thompson, A. Beeby, A. E. Goeta, *Acta Crystallogr., E: Struct. Rep. Online* **60** (2004) m827
41. K. Qiao, R. D. Fischer, G. Paolucci, P. Traldi, E. Celon, *Organometallics* **9** (1990) 1361
42. A. L. Balch, B. C. Noll, S. M. Reid, E. P. Zovinka, *Inorg. Chem.* **32** (1993) 2610
43. Z. Xu, Y. Xiao, X. Qian, J. Cui, D. Cui, *Org. Lett.* **7** (2005) 889
44. M. Mosquera, M. C. R. Rodriguez, F. Rodriguez-Prieto, *J. Phys. Chem. A* **101** (1997) 2766
45. F. Rodriguez-Prieto, J. C. Penedo, M. Mosquera, *J. Chem. Soc., Faraday Trans.* **94** (1998) 2775.