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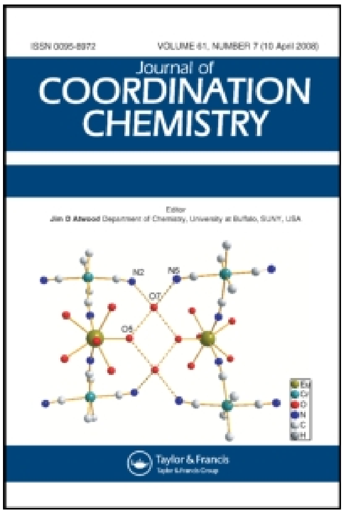

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The synthesis, characterization and spectral studies of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with *N,N*-bis(2-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl) methyl]amino}butyl) *N′,N′*-dihydroxyethanediimidamide

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The synthesis, characterization and spectral studies of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with *N*,*N*-bis(2-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl) methyl]amino}butyl) *N*′,*N*′-dihydroxyethanediimidamide

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Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} complexes of *N*,*N*-bis(2-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino}butyl)*N*′,*N*′-dihydroxyethanediimidamide (LH_2) were synthesized and characterized by elemental analyses, IR, ^{1}H- and ^{13}C-NMR spectra, electronic spectra, magnetic susceptibility measurements, conductivity measurements and thermogravimetric analyses (TGA). The Co^{II}, Ni^{II} and Cu^{II} complexes of LH_2 were synthesized with 1 : 2 metal ligand stoichiometry. Zn^{II} and Cd^{II} complexes with LH_2 have a metal ligand ratio of 1 : 1. The reaction of LH_2 with Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} chloride give complexes $Ni(LH)_2$, $Cu(LH)_2$, $Zn(LH_2)(Cl)_2$, $Cd(LH_2)(Cl)_2$, respectively.

Keywords: Synthesis of dioxime complexes; Cobalt(II); Nickel(II); Copper(II); Zinc(II) and Cadmium(II)

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1. Introduction

Oxime/oximate metal complexes have been investigated actively since the early 1900s [1]. In general, oxime and dioxime derivatives are very important compounds in chemical industry and in medicine. Technetium(V) and copper(II) containing *vic*-dioximes currently are used as cerebral and myocardial perfusion imaging agents [2]. Some oximes and their alkyl, oxyalkyl and amino derivatives have physiological and biological activity [3]. Some oximes are widely used for various purposes in organic, analytical, inorganic, pigment, and industrial chemistry [4]. Numerous transition metal complexes of vicinal dioximes [5] have received attention as model compounds which mimic biofunctions such as the reduction of vitamin B_{12} [6]. The chemistry of oxime/oximato metal complexes has been investigated since the synthesis, nickel(II) dimethylglyoximate, and recognition of the chelate five-membered character of this complex

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by Chugaev [1]. Coordinated oxime ligands and oxime complexes display an impressive variety of reactivity modes which lead to unusual types of chemical compounds [7]. Some recently reviewed data show that oximes, although being classical ligands [8], display a variety of reactivity modes unusual even for modern coordination chemistry [9,10].

In this work substituted dioximes and their metal complexes have been synthesized, extending our previous work [11–19], to add new complexes to the literature of coordination chemistry.

2. Experimental

2.1. *Materials*

The preparation of (*E*,*E*)-dichloroglyoxime has been described previously [20,21]. All reagents used were purchased from Merck or Fluka or Sigma Company and are chemically pure.

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2.2. *Measurements*

Elemental analyses (C, H, N) were performed on a LECO-932 CHNSO elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV Spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. The melting points were determined on a Gallenkamp melting point apparatus. Molar conductances of the *vic*-dioxime ligand and its transition metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. TGA curves were recorded on a Shimadzu TG-50 thermo balance.

2.3. *Preparation of the ligand, LH_2*

A solution of triethylamine (2.53 g, 25.00 mmol) was added to a solution of *N*-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]ethane-1,4-diamine (**2**) (5.28 g, 20.00 mmol) in THF (40 cm^{3}), then a solution of (*E*,*E*)-dichloroglyoxime (1.57 g, 10.00 mmol) in THF (40 cm^{3}) was added dropwise over 4 h to the mixture at −10°C. The mixture was filtered and THF was removed by evaporation. The oily product was dissolved in ethanol (10 cm^{3}) and precipitated by diethyl ether (100 cm^{3}). Obtained product was filtered off, washed with diethyl ether several times and dried in vacuum for 10 h.

2.4. *Preparation of the Co^{II}, Ni^{II} and Cu^{II} complexes*

A sample of the ligand, LH_2 (0.61 g, 1.00 mmol) was dissolved in absolute ethanol (15 cm^{3}). Solution (0.50 mmol) of metal salts [$CoCl_2 \cdot 6H_2O$ (0.12 g), $NiCl_2 \cdot 6H_2O$ (0.12 g) and $CuCl_2 \cdot 2H_2O$ (0.09 g)] in (10 cm^{3}) of absolute ethanol was added dropwise with continuous stirring at 50°C. The pH dropped to around 3–4 and was raised to around 5–6 by addition of 1 M NaOH in ethanol. Every mixture was stirred 4 h more at 50°C, filtered and the precipitate was washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C.

2.5. *Preparation of the Zn^{II} and Cd^{II} complexes*

A solution of $ZnCl_2$ (0.14 g, 1.00 mmol) or $CdCl_2 \cdot H_2O$ (0.20 g, 1.00 mmol) in absolute methanol (20 cm^3) was mixed with the ligand, LH_2 (0.61 g, 1.00 mmol), dissolved in absolute methanol (15 cm^3) and mixture was refluxed on a water bath at 50°C for 2 h in order to complete precipitation. The solid complexes were filtered, washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C.

3. Results and discussion

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The new ligand used for this study, *N*,*N*-bis(2-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino}butyl)*N*′,*N*′-dihydroxyethanediimidamide (LH_2), contains two amine donors and a dioxime group. Its synthesis was accomplished in 56% yield by reaction of (*E*,*E*)-dichloroglyoxime and *N*-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]ethane-1,4-diamine (**2**) as shown in scheme 1. Table 1 lists the analytical and physical data for the ligand and its complexes. The ligand and its complexes are very soluble in polar organic solvents, such as $CHCl_3$ and MeOH and in nonpolar organic solvents such as *n*-hexane, diethyl ether. Unfortunately, we could not obtain single crystals for the ligand or its complexes suitable for crystallographic studies. In general, reactions of the ligand LH_2, with metal salt were rapid and gave good yield of mononuclear complexes corresponding to the general formula ML_2 or ML, stable at room temperature. The structures of the ligand and its complexes were determined by a combination of elemental analysis, ^{1}H- and ^{13}C-NMR spectroscopy, IR techniques, magnetic susceptibility, electronic spectral data, conductivity measurements and thermogravimetric analyses (TGA).

The IR spectral data of the ligand and complexes are listed in table 2. In the IR spectrum of ligand, the O–H stretching vibrations were observed at 3300–3380 cm^{-1}. The stretching vibrations belonging to N–H, C=N, C–O–C and N–O groups occur at 3360, 1630, 1110 and 995 cm^{-1}, respectively, in agreement with previously reported aminoglyoxime derivatives [12,22]. The mononuclear Co^{II}, Ni^{II} and Cu^{II} complexes of the ligand were prepared in *ca*. 53–61% yields by treating $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ in absolute ethanol with the ligand in the presence of a base such as NaOH. Co^{II}, Ni^{II} and Cu^{II} complexes have a metal : ligand ratio of 1 : 2 according to the elemental analysis. In the IR spectrum of Co^{II}, Ni^{II} and Cu^{II} complexes, the weak deformation band associated with intramolecular hydrogen bonding was observed around 1711–1723 cm^{-1} [16,23]. The infrared band observed near 1630 cm^{-1}, assigned to the C=N frequency in the free ligand, is shifted to lower frequencies (1620–1625 cm^{-1}) after complexation due to N,N-metal coordination [17,24]. The band observed at 995 cm^{-1} in the free ligand, assigned to the N–O, is shifted to higher frequencies (1000–1005 cm^{-1}) after complexation (table 2). The absorptions indicate that the oxime group takes part in complexation of Co^{II} with two coordinated water molecules. The coordinated H_2O groups are identified by a broad OH absorption

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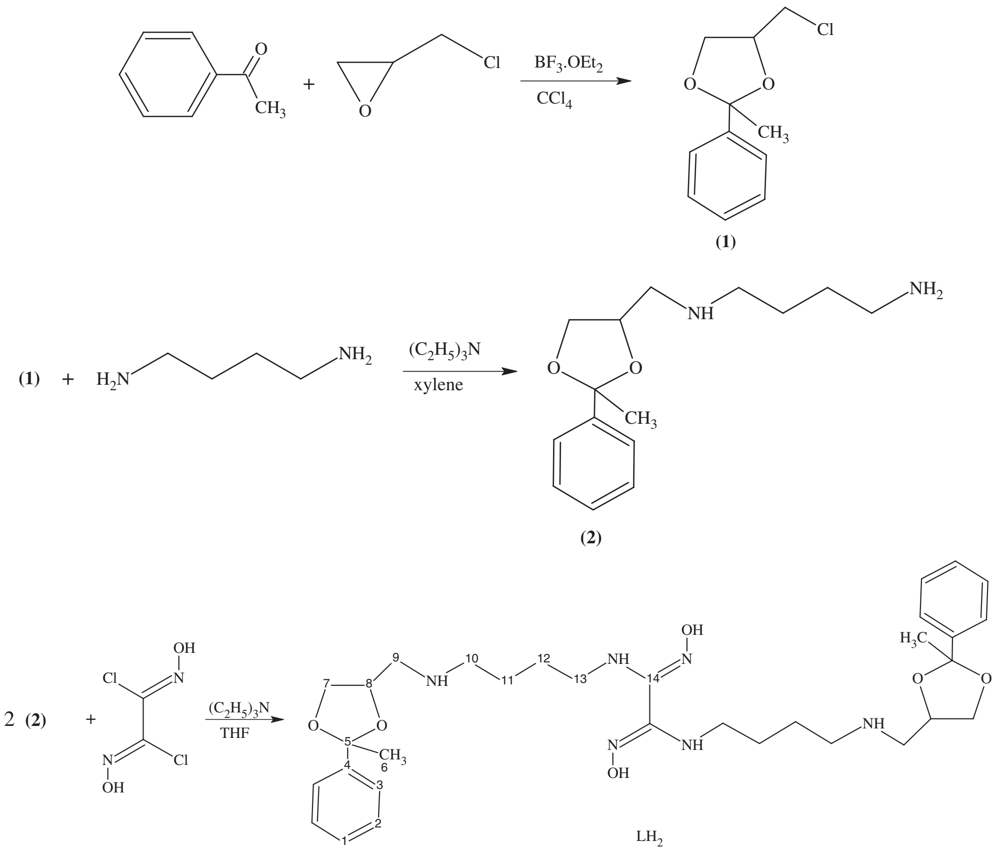


Scheme 1.

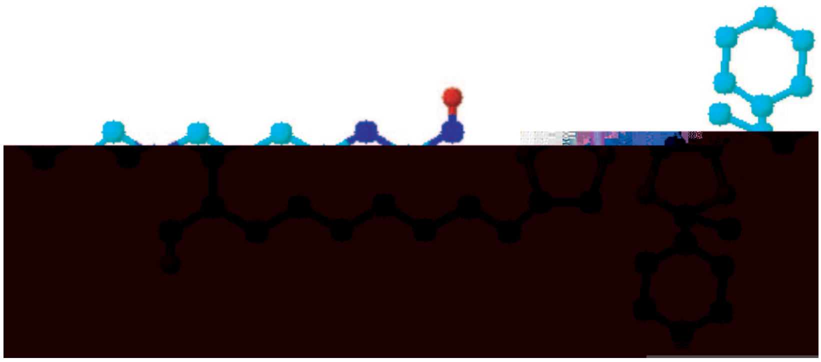


Figure 1. Conformation of the ligand LH_2.

around 3400–3500 cm^{-1} that keeps its intensity even after heating at 110°C for 24 h. The Zn^{II} and Cd^{II} complexes were prepared *ca*. 64–66% yields by treating $ZnCl_2$ and $CdCl_2 \cdot H_2O$ an absolute methanol. Ligand reacts with zinc(II) and cadmium(II) chloride salts in 1 : 1 metal : ligand ratio to give complexes with two of the four metal

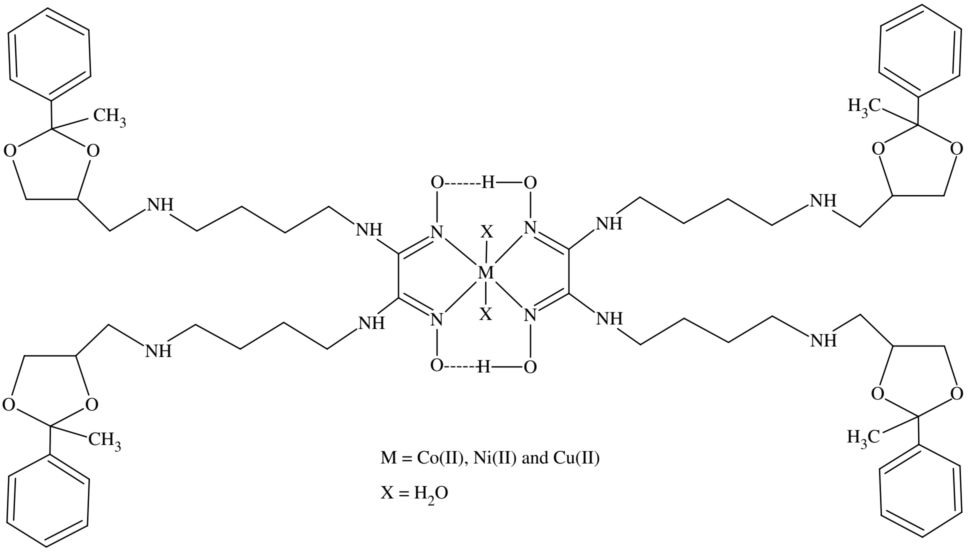
Table 1. Analytical and physical data of the ligand and the complexes.

							Calculated (Found) %		
Compounds	Formula (F.W) g mol^{-1}	Color	μ_{eff}/atom (B.M.)	$^a\Lambda_M$	m.p. (°C)	Yield (%)	C	H	N
LH_2	$C_{32}H_{48}N_6O_6$ (612.86)	dirty white	–	2.3	151	56	62.71 (63.04)	7.91 (8.25)	13.72 (14.07)
$Co(LH)_2(H_2O)_2$	$CoC_{64}H_{98}N_{12}O_{14}$ (1318.67)	brown	3.74	9.7	196	53	58.29 (57.93)	7.51 (7.87)	12.75 (13.03)
$Ni(LH)_2$	$NiC_{64}H_{94}N_{12}O_{12}$ (1282.39)	red	Dia	4.9	200	61	59.94 (60.27)	7.4 (7.13)	13.11 (12.88)
$Cu(LH)_2$	$CuC_{64}H_{94}N_{12}O_{12}$ (1287.24)	dark green	1.75	5.8	183	59	59.71 (60.02)	7.38 (7.22)	13.06 (12.87)
$Zn(LH_2)(Cl)_2$	$ZnC_{32}H_{48}N_6O_6Cl_2$ (749.15)	dark yellow	Dia	20.5	172	64	51.3 (51.12)	6.47 (6.71)	11.22 (11.00)
$Cd(LH_2)(Cl)_2$	$CdC_{32}H_{48}N_6O_6Cl_2$ (796.17)	dark yellow	Dia	21.6	215	66	48.27 (48.04)	6.09 (5.77)	10.56 (10.85)

$^a\Omega^1\,cm^2\,mol^{-1}$.

Table 2. Characteristic IR bands of the ligand and the complexes as KBr pellets (in cm^{-1}).

Compounds	$\nu(H_2O/O–H)$	$\nu(N–H)$	$\nu(N–O)$	$\nu(C{=}N)$	$\nu(O\cdots H–O)$
LH_2	3300–3380	3360	995	1630	–
$Co(LH)_2(H_2O)_2$	3400–3500	3350	1000	1625	1711
$Ni(LH)_2$	–	3345	1000	1620	1723
$Cu(LH)_2$	–	3350	1005	1620	1719
$Zn(LH_2)(Cl)_2$	3245	3355	1010	1615	–
$Cd(LH_2)(Cl)_2$	3235	3355	1005	1618	–



M = Co(II), Ni(II) and Cu(II)

X = H_2O

Figure 2. Suggested structure of the octahedral and square-planar complexes of the ligand LH_2.

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coordination sites occupied by the N atoms of each oxime group. The azomethine stretching vibration at 1630 cm^{-1} in the free ligand, is shifted to 1615–1618 cm^{-1} in the Zn^{II} and Cd^{II} complexes. The N–O stretching band at 995 cm^{-1} in ligand, is shifted to (1005–1010 cm^{-1}) for the Zn^{II} and Cd^{II} complexes. There is no O···H–O peak as expected from the formula [18,25].

Since the –OH protons of these oximes are equivalent in the (*E*,*E*)-form, two peaks are present in the ^1H-NMR spectrum for the protons in LH_2, chemical shifts for (=N–OH) protons were observed at 11.70 ppm as singlet and NH protons were observed at 5.90 ppm. These bands are easily identified by deuterium exchange [13,14,26,27]. More detailed information about the structure of the ligand was provided by ^{13}C-NMR spectral data. The two azomethine carbons are magnetically equivalent and appear as one singlet at 155.09 ppm. These equivalent carbon atoms, especially the adjacent hydroxyimino groups, also confirm the (*E*,*E*)-structure [15,28]. The chemical shifts belonging to the OH protons in dioxime disappeared from the ^1H-NMR spectrum of Ni^{II} complex. After complexation a new resonance at 15.03 ppm was assigned by formation of the hydrogen bridge which could easily be identified by deuterium exchange [19,29]. In the ^{13}C-NMR spectrum of the Ni^{II} complex carbon resonance of dioxime groups were observed at 153.74 ppm. In the ^1H-NMR spectrum of Zn^{II} and Cd^{II} complexes, there are no O···H–O peaks as expected (figure 3), but there is a resonance around 12.07–12.11 ppm, which is assigned to OH [13,30]. In the ^{13}C-NMR spectrum of Zn^{II} and Cd^{II} complexes azomethine carbon atoms are observed around 152.51–153.44 ppm.

The electronic spectra of ligand and complexes were taken in DMSO. The bands at 290–333 and 215–280 nm were assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. The electronic spectra of the Ni^{II} complex exhibit two bands at 560 nm ($\varepsilon = 235\ L\,mol^{-1}\,cm^{-1}$) and 487 nm ($\varepsilon = 836\ L\,mol^{-1}\,cm^{-1}$) assignable to $^1A_{1g} \rightarrow {}^1A_{2g}$

Table 3. ^1H- and ^{13}C-NMR spectral data of the selected compounds in DMSO-d_6, 400 MHz, δ (ppm).

Compounds	^1H-NMR	^{13}C-NMR
LH_2	1.72 (s, 6H, CH_3), 1.89 (m, 8H, –CH_2), 3.15 (m, 12H, N–CH_2), 3.80 (d, 4H, CH_2–O), 4.22 (m, 2H, CH–O), 5.90 (m, 4H, N–$H_{exchangeable}$), 7.61–7.79 (m, 10H, Ar–H), 11.70 (s, 2H, N–$OH_{exchangeable}$)	25.83 (C_6), 26.92 (C_{11}), 28.90 (C_{12}), 39.06 (C_{13}), 47.87 (C_{10}), 53.11 (C_9), 75.69 (C_7), 79.02 (C_8), 110.56 (C_5), 127.90 (C_2), 129.10 (C_1), 129.79 (C_3), 140.01 (C_4), 155.09 (C_{14})
$Ni(LH)_2$	1.70 (s, 12H, CH_3), 1.86 (m, 16H, –CH_2), 3.17 (m, 24H, N–CH_2), 3.77 (d, 8H, CH_2–O), 4.19 (m, 4H, CH–O), 5.93 (m, 8H, N–$H_{exchangeable}$), 7.55–7.80 (m, 20H, Ar–H), 14.95 (s, 2H, O···H–O^a)	25.86 (C_6), 26.97 (C_{11}), 28.94 (C_{12}), 38.91 (C_{13}), 47.90 (C_{10}), 53.15 (C_9), 75.70 (C_7), 79.00 (C_8), 110.57 (C_5), 127.92 (C_2), 129.09 (C_1), 129.80 (C_3), 140.00 (C_4), 153.74 (C_{14})
$Zn(LH_2)(Cl)_2$	1.71 (s, 6H, CH_3), 1.87 (m, 8H, –CH_2), 3.14 (m, 12H, N–CH_2), 3.82 (d, 4H, CH_2–O), 4.20 (m, 2H, CH–O), 5.89 (m, 4H, N–$H_{exchangeable}$), 7.58–7.81 (m, 10H, Ar–H), 11.81 (s, 2H, N–$OH_{exchangeable}$)	25.85 (C_6), 26.88 (C_{11}), 28.94 (C_{12}), 38.85 (C_{13}), 47.83 (C_{10}), 53.12 (C_9), 75.65 (C_7), 78.98 (C_8), 110.55 (C_5), 127.88 (C_2), 129.07 (C_1), 129.76 (C_3), 139.99 (C_4), 153.44 (C_{14})
$Cd(LH_2)(Cl)_2$	1.69 (s, 6H, CH_3), 1.90 (m, 8H, –CH_2), 3.16 (m, 12H, N–CH_2), 3.79 (d, 4H, CH_2–O), 4.21 (m, 2H, CH–O), 5.92 (m, 4H, N–$H_{exchangeable}$), 7.60–7.78 (m, 10H, Ar–H), 11.77 (s, 2H, N–$OH_{exchangeable}$)	25.84 (C_6), 26.93 (C_{11}), 28.96 (C_{12}), 38.82 (C_{13}), 47.85 (C_{10}), 53.16 (C_9), 75.67 (C_7), 78.98 (C_8), 110.53 (C_5), 127.91 (C_2), 129.08 (C_1), 129.77 (C_3), 139.98 (C_4), 152.51 (C_{14}).

s: singlet, d: doublet, m: multiplet.

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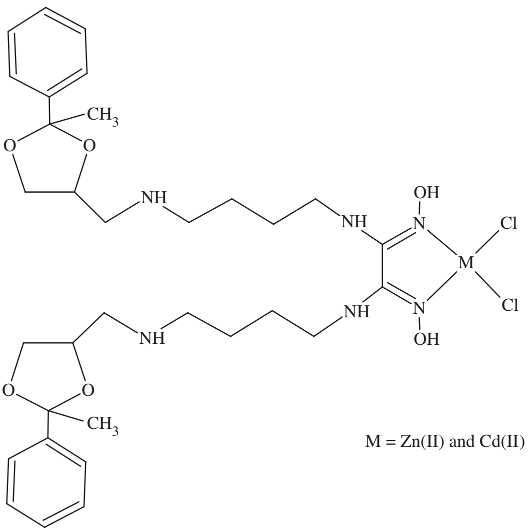

Figure 3. Suggested structure of the tetrahedral complex of the ligand LH$_2$.

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and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively, supporting a square planar geometry [31]. In the electronic spectra of the complex there is an intense charge transfer band at 370 nm ($\varepsilon = 2410\,\mathrm{L\,mol^{-1}\,cm^{-1}}$). The Cu$^{\mathrm{II}}$ complex shows a broad band at 625 nm ($\varepsilon = 800\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), which can be assigned to a $^2B_{1g} \rightarrow {}^2A_{1g}$ transition. This together with the measured μ_{eff} values suggests square planar geometry [32]. No weak d–d transition is observed in the Co$^{\mathrm{II}}$ complex. Intense charge transfer bands at 450 nm ($\varepsilon = 2775\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) for Cu$^{\mathrm{II}}$ and at 360 nm ($\varepsilon = 5810\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) for Co$^{\mathrm{II}}$, respectively, are observed. The electronic spectra of the Zn$^{\mathrm{II}}$ and Cd$^{\mathrm{II}}$ complexes show a charge transfer absorption band around 385–400 nm, compatible with a tetrahedral structure [33,34].

Magnetic susceptibility measurements provide information regarding the structure of complexes. The magnetic moments of the complexes were measured at room temperature and are listed in table 1. Co$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ complexes are paramagnetic, while Ni$^{\mathrm{II}}$, Zn$^{\mathrm{II}}$ and Cd$^{\mathrm{II}}$ complexes are diamagnetic. The magnetic moments of the Co$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ complexes at room temperature fall in the range 3.74 B.M. for Co$^{\mathrm{II}}$ and 1.75 B.M. for Cu$^{\mathrm{II}}$, characteristic for mononuclear, octahedral Co$^{\mathrm{II}}$ and square-planar Cu$^{\mathrm{II}}$ complexes [35]. The magnetic moment values Ni$^{\mathrm{II}}$, Zn$^{\mathrm{II}}$ and Cd$^{\mathrm{II}}$ complexes are also consistent with a square planar geometry for Ni$^{\mathrm{II}}$ and tetrahedral geometry for Zn$^{\mathrm{II}}$ and Cd$^{\mathrm{II}}$ complexes [36].

The molar conductance values, measured in DMSO solutions (*ca.* 1×10^{-3} M) for the mononuclear complexes are in the 4.9–21.6 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$ range, showing that the complexes are not electrolytes [37].

The decomposition temperature and the weight losses of the complexes and the ligand were taken from the TGA data. The decomposition of ligand starts at 168°C and ends at 784°C. The complexes are stable up at 132–183°C and the decompositions are completed at 697–795°C. In the TGA curve of the Co$^{\mathrm{II}}$ complex (calculated: 2.73%, found 2.85%) weight loss was observed at 132°C, showing that the complex contains two moles of water. The thermal stability of all complexes increases in the order: Ni < Cu < Co < Zn < Cd. When the complexes are heated to higher temperatures, they decompose to give oxides of the MO type [38,39].

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