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The Synthesis and Spectral Characterization of *N,N*-Bis(2-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino}ethyl)*N′,N′*-dihydroxyethanediimidamide and Its Complexes

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N,N-Bis(2-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino}ethyl)*N′,N′*-dihydroxyethanediimidamide (LH_2) has been synthesized and its mononuclear complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} ions have been obtained. The mononuclear complexes indicated that the metal ions are ligand coordinated through the two N atoms, as do most of the *vic*-dioximes. The authenticity of the ligands and their complexes have been established by IR, ^1H- and ^{13}C-NMR spectra, UV-Visible spectroscopy, elemental analyses and magnetic susceptibility measurements.

Key words: dioximes, complexes, transition metals, synthesis of *vic*-dioxime complexes

Metal complexes of *vic*-dioximes represent an important and interesting class of coordination compounds. Studies of the complexes of these compounds were begun first by Tschugaeff in 1907 and have increased up to now [1–6]. The coordination chemistry of *vic*-dioximates is an area of intensive study, and numerous transition metal complexes of *vic*-dioximes have found application as analytical reagents, models for biological systems such as vitamin B_{12} [7–9]. The model studies, though primarily aimed at elucidating the mechanism of biological reactions mediated by coenzyme B_{12}, exceeded this objective and have become a general contribution to coordination chemistry [10–12]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make *vic*-dioximes amphoteric ligands which form corrin-type square-planar, square pyramidal and octahedral complexes with transition metal ions such as Ni(II), Cu(II), Co(II) and Co(III) as central atoms [13]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding [14]. We have long had an interest in the chemical behavior of complexes containing a planar MN_4 core structure and additional donor sites [13–15].

In our previous studies we have investigated the synthesis and characterization of various transition metal complexes of novel *vic*-dioxime [16–23]. Since this ligand has not been reported in the literature our paper deals with in preparation (Scheme 1) and characterization, as well as their complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}.

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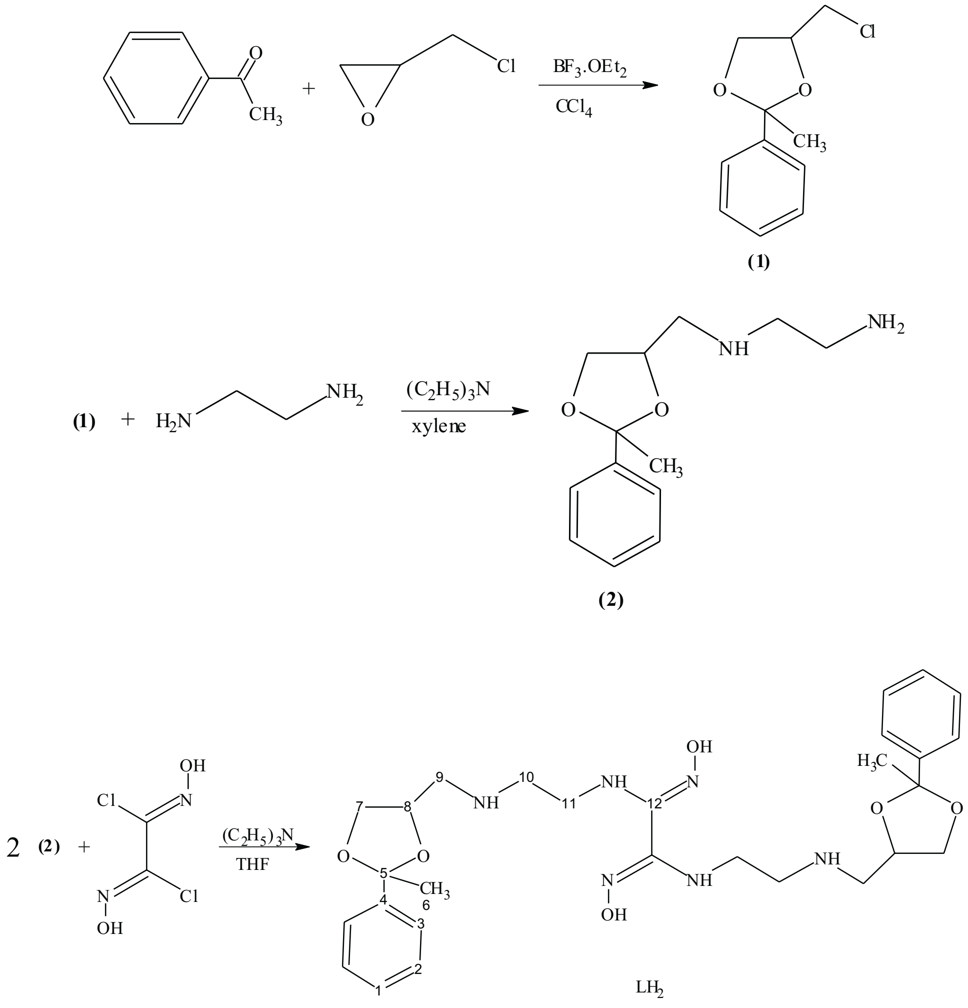
Scheme 1



EXPERIMENTAL

The preparation of *(E,E)*-dichloroglyoxime has been described previously [24]. All the reagents used, purchased from Merck, Fluka or Sigma Company were chemically pure.

Physical measurements: Elemental analyses (C, H, N) were performed on a LECO–932 CHNSO elemental analyses 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 Spectrometers. Electronic spectra were obtained on a Shimadzu 1240 UV Spectrophotometer. 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.

Preparation of the ligand (LH_2): A solution of triethylamine (2.53 g, 25.00 mmole) was added to a solution of *N*-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]ethane-1,2-diamine **(2)** (4.72 g, 20.00 mmole) in THF (30 cm^3), then a solution of *(E,E)*-dichloroglyoxime (1.57 g, 10.00 mmole) in THF (50 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.

LH_2: ^{1}H-NMR (DMSO–d_6, δ ppm, 400 MHz): 1.61 (s, 6H, CH_3), 2.70–3.35 (m, 12H, N–CH_2), 3.74–3.85 (m, 4H, CH_2–O), 3.96–4.42 (m, 2H, CH–O), 5.60–6.30 (m, 4H, N–$H_{exchangeable}$), 7.40–7.71 (m, 10H, Ar–H), 11.57 (s, 2H, N–$OH_{exchangeable}$); ^{13}C-NMR (DMSO–d_6, δ ppm, 400 MHz): 25.13 (C_6), 39.06 (C_{11}), 48.18 (C_{10}), 52.74 (C_9), 75.31 (C_7), 78.22 (C_8), 111.03 (C_5), 128.00 (C_2), 129.30 (C_1), 130.10 (C_3), 142.50 (C_4), 156.64 (C_{12}).

Preparation of the Co^{2+}, Ni^{2+} and Cu^{2+} complexes: A sample of the ligand, LH_2 (0.56 g, 1.00 mmole) was dissolved in absolute ethanol (10 cm^3). Solution (0.50 mmole) 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 (5 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 for 4 h at 50°C, filtered and the precipitate was washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C.

$Ni(LH)_2$: ^{1}H-NMR (DMSO–d_6, δ ppm, 400 MHz): 1.60 (s, 12H, CH_3), 2.74–3.40 (m, 24H, N–CH_2), 3.75–3.88 (m, 8H, CH_2–O), 3.95–4.40 (m, 4H, CH–O), 5.65–6.42 (m, 8H, N–$H_{exchangeable}$), 7.50–7.75 (m, 20H, Ar–H), 14.92 (s, 2H, O···H—$O_{exchangeable}$); ^{13}C-NMR (DMSO–d_6, δ ppm, 400 MHz): 25.14 (C_6), 39.07 (C_{11}), 48.21 (C_{10}), 52.76 (C_9), 75.29 (C_7), 78.24 (C_8), 111.04 (C_5), 128.00 (C_2), 129.29 (C_1), 130.08 (C_3), 142.49 (C_4), 158.94 (C_{12}).

Synthesis of the Zn^{2+} and Cd^{2+} complexes: A solution of $ZnCl_2$ (0.14 g, 1.00 mmole) or $CdCl_2 \cdot H_2O$ (0.20 g, 1.00 mmole) in absolute methanol (5 cm^3) was mixed with the ligand, LH_2 (0.56 g, 1.00 mmole), dissolved in absolute methanol (10 cm^3) and mixture was refluxed on a water bath at 50°C for 2 h in order to complete precipitation. The color of the solution immediately turned yellow. The solid complexes were filtered, washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C.

$Zn(LH_2)(Cl)_2$: ^{1}H-NMR (DMSO–d_6, δ ppm, 400 MHz): 1.58 (s, 6H, CH_3), 2.80–3.38 (m, 12H, N–CH_2), 3.72–3.90 (m, 4H, CH_2–O), 3.97–4.37 (m, 2H, CH–O), 5.69–6.37 (m, 4H, N–$H_{exchangeable}$), 7.50–7.83 (m, 10H, Ar–H), 11.64 (s, 2H, N–$OH_{exchangeable}$); ^{13}C-NMR (DMSO–d_6, δ ppm, 400 MHz): 25.15 (C_6), 39.07 (C_{11}), 48.19 (C_{10}), 52.75 (C_9), 75.31 (C_7), 78.22 (C_8), 111.04 (C_5), 128.01 (C_2), 129.30 (C_1), 130.11 (C_3), 142.53 (C_4), 159.52 (C_{12}).

$Cd(LH_2)(Cl)_2$: ^{1}H-NMR (DMSO–d_6, δ ppm, 400 MHz): 1.57 (s, 6H, CH_3), 2.82–3.40 (m, 12H, N–CH_2), 3.73–3.91 (m, 4H, CH_2–O), 3.98–4.39 (m, 2H, CH–O), 5.70–6.39 (m, 4H, N–$H_{exchangeable}$), 7.51–7.84 (m, 10H, Ar–H), 11.60 (s, 2H, N–$OH_{exchangeable}$); ^{13}C-NMR (DMSO–d_6, δ ppm, 400 MHz): 25.14 (C_6), 39.06 (C_{11}), 48.18 (C_{10}), 52.73 (C_9), 75.30 (C_7), 78.21 (C_8), 111.03 (C_5), 127.99 (C_2), 129.28 (C_1), 130.10 (C_3), 142.48 (C_4), 160.11 (C_{12}).

RESULTS AND DISCUSSION

Synthetic pathways for the preparation of the ligands are 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, CH_2Cl_2 and EtOH and in nonpolar organic solvents, such as *n*-hexane, diethyl ether. Unfortunately, we could not obtain any single crystals for ligand and its complexes were suitable for crystallographic studies. In general, reactions of the ligand LH_2, with metal salt were quick and gave good yield of mononuclear complexes corresponding to the general formula ML_2 or ML; they are stable at room temperature. Analyses confirmed the composition given.

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

Compounds	Formula (F.W) g/mol	Color	M.p. (°C)	Yield (%)
LH_2	$C_{28}H_{40}N_6O_6$ (556.74)	white	139	54
$Co(LH)_2(H_2O)_2$	$CoC_{56}H_{82}N_{12}O_{14}$ (1206.43)	dark brown	187	50
$Ni(LH)_2$	$NiC_{56}H_{78}N_{12}O_{12}$ (1170.65)	red	219	57
$Cu(LH)_2$	$CuC_{56}H_{78}N_{12}O_{12}$ (1175.00)	green	200	55
$Zn(LH_2)(Cl)_2$	$ZnC_{28}H_{40}N_6O_6Cl_2$ (693.03)	yellow	181	61
$Cd(LH_2)(Cl)_2$	$CdC_{28}H_{40}N_6O_6Cl_2$ (740.05)	yellow	213	63

The structure 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 and electronic spectral data.

The IR spectral data of the ligand and their metal complexes are listed in Table 2. In the IR spectrum of ligand, the O–H stretching vibrations were observed at 3310–3390 cm^{-1}. The stretching vibrations belonging to N–H, C=N, C–O–C and N–O groups occur at 3360, 1640, 1100 and 985 cm^{-1} respectively. These values are in harmony with the previously reported aminoglyoxime derivatives [25]. In the ^{1}H-NMR spectrum of ligand, a broad signal concerned with primary amine groups, disappeared and new chemical shifts at 5.60–6.30 and 11.57 ppm were observed which could be assigned to NH and N–OH protons [26]. The chemical shifts of the =N–OH protons were retained according to the ^{1}H-NMR spectral data [27]. The deuterium exchange properties of these protons also appeared during the formation of these desired compounds.

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

Compounds	$\upsilon(H_2O/O–H)$	υ(N–H)	$\upsilon(C–H)_{alip.}$	$\upsilon(C–H)_{arom.}$	υ(N–O)	υ(C=N)	υ(O···H—O)
LH_2	3310–3390	3360	2870–2990	3050–3100	985	1640	–
$Co(LH)_2(H_2O)_2$	3400–3450	3350	2870–2990	3050–3100	985	1632	1715
$Ni(LH)_2$	–	3350	2870–2990	3050–3100	990	1630	1725
$Cu(LH)_2$	–	3350	2870–2990	3050–3100	985	1625	1720
$Zn(LH_2)(Cl)_2$	3250	3345	2870–2990	3050–3100	990	1620	–
$Cd(LH_2)(Cl)_2$	3240	3345	2870–2990	3050–3100	987	1620	–

On the other hand, the equivalent proton signals of the hydroxyimino groups confirms the (*E,E*)-form of *vic*-dioxime [28]. More detailed information about the structure of ligand was provided by ^{13}C-NMR spectral data. After the condensation, two resonances belonging to azomethine carbon atoms were found at 156.64 ppm [29]. These equivalent carbon atoms, especially the adjacent hydroxyimino groups, also confirm the (*E,E*)-structure of ligand [30].

The mononuclear Co^{2+}, Ni^{2+} and Cu^{2+} complexes of the ligand were prepared in *ca.* 50–57% yields by treating $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ in an absolute ethanol mixture with the ligand in the presence of a base such as NaOH. Co^{2+}, Ni^{2+} and Cu^{2+} complexes have a metal:ligand ratio of 1:2 (see Fig. 1) according to the elemental analysis results. In the IR spectrum of mononuclear Co^{2+}, Ni^{2+} and Cu^{2+} complexes, the weak deformation band associated with intramolecular hydrogen bonding was observed around 1715–1725 cm^{-1} [31]. The infrared band observed near 1640 cm^{-1}, assigned to the C=N frequency in the free ligand is shifted to lower frequencies (1625–1632 cm^{-1}) after complexation due to N,N-metal coordination [32]. At the same time, the band, observed at 985 cm^{-1} in the free ligand assigned to the N–O, is shifted to higher frequencies (985–990 cm^{-1}) after complexation (Table 2). The absorptions indicate that the oxime group takes part in complexation of Co^{2+} complex with two coordinated water molecules. In the case of Co^{2+} complex the coordinated H_2O groups are identified by a broad OH absorption around 3400–3450 cm^{-1} that keeps its intensity even after heating at 110°C for 24 h. The Zn^{2+} and Cd^{2+} complexes were prepared in *ca.* 61–63% yields by treating $ZnCl_2$ and $CdCl_2 \cdot H_2O$ in an absolute methanol mixture. Ligand reacts with zinc(II) and cadmium(II) chloride

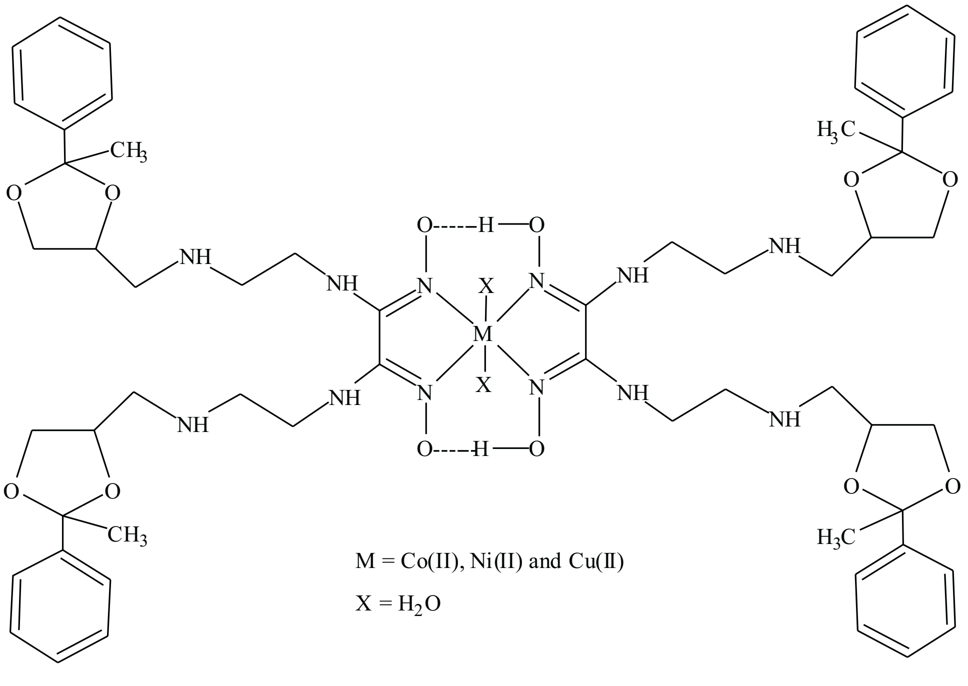


Figure 1. Suggested structure of the octahedral Co^{2+} and square-planar Ni^{2+} and Cu^{2+} complexes of the ligand.

salts in 1:1 metal:ligand ratio to give complexes with two of the four metal coordination sites occupied by the N atom of each oxime group. The stretching vibrations of azomethine group appearing at 1640 cm^{-1} in the free ligand is shifted at 1620 cm^{-1} in the Zn^{2+} and Cd^{2+} complexes. The stretching band of N–O appearing at 985 cm^{-1} in ligand is shifted in (987–990 cm^{-1}) Zn^{2+} and Cd^{2+} complexes. There is no O···H—O peak as expected for complexes formula [33].

The chemical shifts belonging to the OH protons in dioxime disappeared from the ^1H-NMR spectrum of Ni^{2+} complex after complexation and the presence of a new resonance at lower field at 14.92 ppm was assigned by formation of the hydrogen bridge which could easily be identified by deuterium exchange [32]. In the ^{13}C-NMR spectrum of Ni^{2+} complex carbon resonance of dioxime groups were observed at 158.94 ppm. In the ^1H-NMR spectrum of Zn^{2+} and Cd^{2+} complexes, there are no O···H—O peaks as expected for complexes formula in (Fig. 2), but there are a resonance around 11.60–11.64 ppm, which is assigned to OH [34]. In the ^{13}C-NMR spectrum of Zn^{2+} and Cd^{2+} complexes azomethine carbon atoms are observed around 159.52–160.11 ppm.

The electronic spectrum of ligand and its complexes were taken in DMSO (Table 3). The electronic spectrum of the Co^{2+}, Ni^{2+} and Cu^{2+} complexes shows absorption bands at 579, 675 and 641 nm respectively, which may be assigned to $^4T_{1g}\rightarrow{}^4A_{2g}(F)$ for Co^{2+}, $^1A_{1g}\rightarrow{}^1B_{1g}$ for Ni^{2+} and $^2T_{2g}\rightarrow{}^2E_g(G)$ for Cu^{2+} transition, which is compatible with these complexes having a square planar structure [35–37].

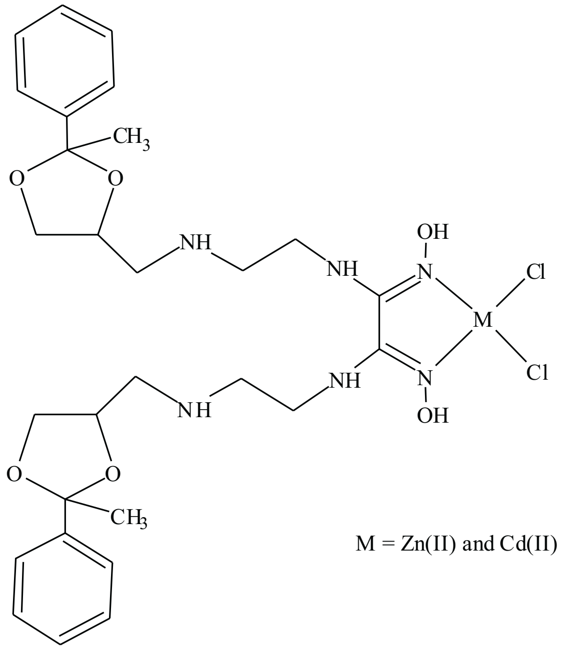


Figure 2. Suggested structure of the tetrahedral Zn^{2+} and Cd^{2+} complexes of the ligand.

There exist absorptions at 345 nm, which are ascribed to metal–to–ligand charge transfer transitions in the octahedral Co^{2+} complex [38]. The electronic spectrum of the Zn^{2+} and Cd^{2+} complexes shows an absorption band at *ca*. 400 nm which is attributed to the L→M (charge transfer) transition, which is compatible with the complexes with a tetrahedral structure [39]. The UV-visible peaks corresponding to the $\pi \rightarrow \pi^*$ transitions in the ligand was observed at 290 nm. The peaks belonging to the $\pi \rightarrow \pi^*$ transitions are shifted to a longer wavelength as a consequence of coordination when binding with the metal, confirming the formation of dioxime metal complexes.

Table 3. Magnetic moment and electronic spectral data of the ligand and the complexes.

Compound	μ_{eff}/atom (B.M)	λ_{max} (nm)[a]
LH_2	–	330, 290
$[Co(LH)_2(H_2O)_2]$	3.88	579, 420, 345, 279
$[Ni(LH)_2]$	dia	675, 460, 350, 300
$[Cu(LH)_2]$	1.77	641, 464, 359, 299
$[Zn(LH_2)(Cl)_2]$	dia	400, 354, 289
$[Cd(LH_2)(Cl)_2]$	dia	405, 352, 291

[a]in DMSO

As is known, magnetic susceptibility measurements provide information regarding the structure of the complexes. The magnetic moments of the complexes were measured at room temperature and are listed in Table 1. Co^{2+} and Cu^{2+} complexes of the ligand are paramagnetic, while its Ni^{2+}, Zn^{2+} and Cd^{2+} complexes are diamagnetic. The magnetic moments of the Co^{2+} and Cu^{2+} complexes of the ligand at room temperature fall in the range 3.88 B.M. for Co^{2+} and 1.77 B.M. for Cu^{2+} which is characteristic for mononuclear, octahedral Co^{2+} and square planar Cu^{2+} complexes. The magnetic moment values of the Ni^{2+}, Zn^{2+} and Cd^{2+} complexes of the ligand is also consistent with a square planar geometry for Ni^{2+} and tetrahedral geometry for Zn^{2+} and Cd^{2+}complexes [40–43].

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