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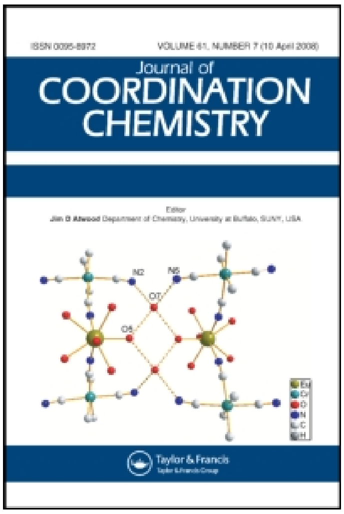

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Synthesis and complexation of two new phenylaminoglyoxime ligands

Pervİn Devecİ[a]; Emİne Özcan[a]; Bİlge Taner[a]; Ömer Arslan[a]
[a] Faculty of Arts and Sciences, Department of Chemistry, Selcuk University, Konya, Turkey

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Synthesis and complexation of two new phenylaminoglyoxime ligands

PERVİN DEVECİ*, EMİNE ÖZCAN,
BİLGE TANER and ÖMER ARSLAN

Faculty of Arts and Sciences, Department of Chemistry,
Selcuk University, 42031, Konya, Turkey

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Two new soluble phenylaminoglyoxime ligands, 4-isopropylanilinephenylglyoxime (L^1H_2), 4-benzylpiperidinephenylglyoxime (L^2H_2), were prepared by reacting 4-isopropylaniline and 4-benzylpiperidine with chlorophenylglyoxime. Mononuclear nickel(II), cobalt(II), copper(II), zinc(II), and cadmium(II) complexes with these ligands were synthesized. On the basis of the magnetic and spectral evidence a square-planar geometry for Ni(II) and Cu(II) complexes, a tedrahedral geometry for Cd(II) and Zn(II) complexes and octahedral geometry for Co(II) complexes are proposed. These compounds were elucidated by elemental analysis, IR, UV-Vis, and magnetic moments. The ligands were additionally characterized by ^1H NMR and ^{13}C NMR spectra.

Keywords: Phenylaminoglyoxime; 4-Isopropylaniline; 4-Benzylpiperidine; Transition metal complexes

1. Introduction

vic-Dioxime complexes are readily prepared and highly stable leading to applications in different areas such as organic, inorganic, bioinorganic, pigment, analytical, dyes and medical chemistry [1–6]. For example *vic*-dioximes play an important role in modeling such biological processes as electron transfer [7–9], vitamin B_{12} mimics [9–11], the biosynthesis of nitric oxide [12, 13] oxidation reagents [14], additive materials for the improvement of pigments, mechanic oils, epoxy resins and rubber [15]. A number of articles have appeared dealing with the synthesis, structure and magnetic properties of *vic*-dioxime complexes [16, 17]. The main reason for the current interest in phenylaminoglyoximes is the ability of these ligands to coordinate in different modalities to metals as well as the easy tunability of their substituents [18]. In the present study we report the synthesis and characterization of soluble phenylaminoglyoxime ligands and their mononuclear complexes with copper (II), nickel(II), zinc(II), cobalt(II) and cadmium(II).

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*Corresponding author. Email: pervindeveci@gmail.com

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2. Experimental

2.1. *Materials*

4-Isopropylaniline, 4-benzylpiperidine, all solvents and all metal salts purchased from E. Merck, were reagent grade and were used as received. Chlorophenylaminoglyoxime was synthesized as described [19–21].

2.2. *Physical measurements*

Elemental analyses (C, H, N) were determined using a LECO-932 CHNSO model analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR spectrometer (in DMSO-d_6). IR spectra were performed on a Perkin Elmer Model 1605 FT-IR spectrophotometer as KBr pellets. The UV-Vis spectra were recorded on a Shimadzu 160 A spectrofotometer. Magnetic moments of the complexes were measured using a Sherwood Scientific Model MX1 Gouy magnetic susceptibility balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants.

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2.3. *Synthesis of 4-isopropylanilinephenylglyoxime (L^1H_2) and 4-benzylpiperidinephenylglyoxime (L^2H_2)*

4-isopropylaniline (1.4 mL, 5 mmol) and 4-benzylpiperidine (0.9 mL, 5 mmol) were dissolved in absolute ethanol (15 cm^3). A solution containing chlorophenylglyoxime (0.1 g, 5 mmol), in ethanol (5 cm^3) was added slowly at room temperature with constant stirring. The reaction mixture was stirred continuously for 1 h at room temperature. The pH of the mixture was about 7.0–7.5. Its volume was then doubled by adding distilled water. The precipitated ligands were filtered off, washed with cold water, dried and crystallized from water-ethanol (1 : 2) (scheme 1).

L^1H_2 and L^2H_2 are soluble in common solvents such as $CHCl_3$, EtOH, THF, DMSO and acetonitrile. Characteristic ^{13}C NMR spectral data for L^1H_2 ($CDCl_3$, TMS, δ, ppm); C_1(23.20), C_2(32.40), C_3(134.80), C_4(128.65), C_5(120.08), C_6(142.28), C_7(143.28), C_8(170.47), C_9(133.20), C_{10}(126.40), C_{11}(126.80), C_{12}(129.65).

Characteristic ^{13}C NMR spectral data for L^2H_2 ($CDCl_3$, TMS, δ, ppm); C_1(125.32), C_2(126.12), C_3(128.24), C_4(141.72), C_5(41.48), C_6(33.87), C_7(31.22), C_8(45.16), C_9(145.28), C_{10}(170.38). C_{11}(133.20), C_{12}(125.40), C_{13}(126.80), C_{14}(128.72).

Table 1 gives analytical and physical data for ligands, IR, ^{1}H NMR and UV-Vis spectra data of the ligands are given tables 2–4, respectively.

2.4. *Synthesis of the Ni(II), Co(II), Cu(II) complexes of L^1H_2 and L^2H_2*

A solution of the metal salt $NiCl_2 \cdot 6H_2O$ (1.189 g, 5 mmol), $CoCl_2 \cdot 6H_2O$ (1.190 g, 5 mmol), $CuCl_2 \cdot 2H_2O$ (0.852 g, 5 mmol) dissolved in H_2O (15 cm^3) was added dropwise to a stirred solution of the ligand [L^1H_2 (2.97 g, 10 mmol) or L^2H_2 (3.37 g, 10 mmol)] dissolved in EtOH (20 cm^3). The pH of the reaction mixture 3.5–4.0 was then adjusted to 5.5–6.0 by addition of 1% NaOH in EtOH. The mixture was stirred on a water bath at 45–50°C for 1 h. The precipitates were filtered, washed with cold water and dried.

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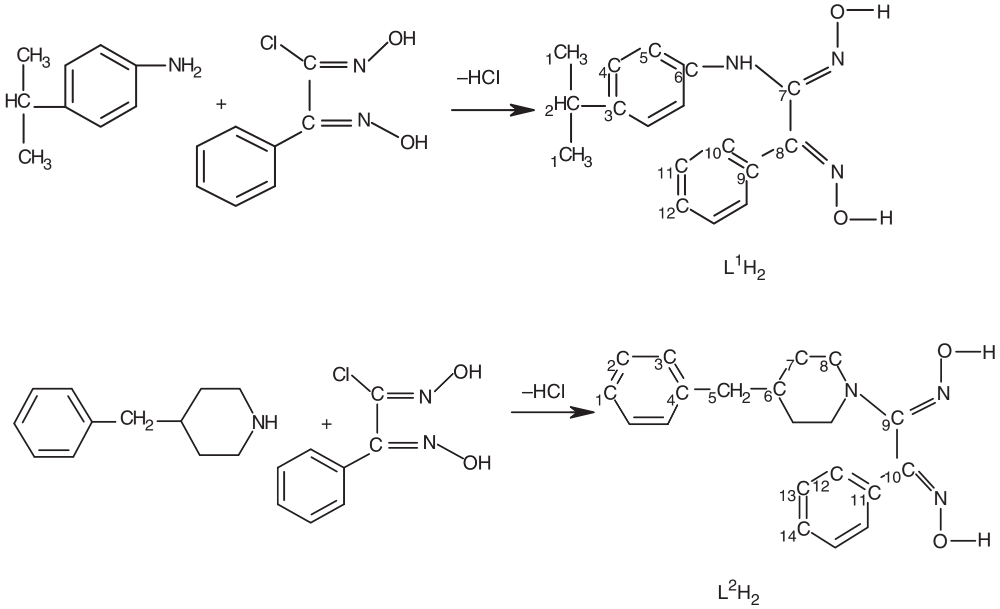

Scheme 1. The synthesis of *vic*-dioxime ligands.

Table 1. Analytical and physical data for ligands and their complexes.

Compound	Formula (F.W.) (g mol^{-1})	Color	M.p. (°C)	Yield (%)	Calcd (Found) (%) C	Calcd (Found) (%) H	Calcd (Found) (%) N
L^{1}H$_2$	$C_{17}H_{19}N_3O_2$ (297.25)	White	181	70	0.72 (69.67)	6.82 (6.74)	13.99 (14.03)
(L^{1}H)$_2$Ni	$C_{34}H_{36}O_4N_6Ni$ (651.19)	Dark red	306*	60	62.93 (62.75)	5.65 (5.83)	12.82 (12.89)
(L^{1}H)$_2$Cu	$C_{34}H_{36}O_4N_6Cu$ (656.04)	Green	310	45	61.18 (61.29)	5.78 (5.58)	12.46 (12.70)
(L^{1}H)$_2$Co · 2H$_2$O	$C_{34}H_{40}N_6O_6Co$ (686.46)	Brown	305	52	58.35 (58.44)	6.02 (5.83)	12.70 (12.54)
(L^{1}H)Cl(H$_2$O)Cd	$C_{17}H_{20}N_3O_3ClCd$ (464.08)	Yellow	192*	52	42.80 (42.89)	4.10 (4.30)	9.20 (9.04)
(L^{1}H)Cl(H$_2$O)Zn	$C_{17}H_{20}N_3O_3$ ClZn (415.12)	White	300	44	48.96 (48.74)	4.75 (4.82)	10.39 (10.12)
L^{2}H$_2$	$C_{20}H_{23}N_3O_2$ (337.31)	White	188	60	70.35 (70.21)	6.73 (6.82)	12.08 (12.45)
(L^{2}H)$_2$Ni	$C_{40}H_{44}N_6O_4Ni$ (731.31)	Red	277	55	64.05 (64.44)	6.26 (6.02)	11.51 (11.49)
(L^{2}H)$_2$Cu	$C_{40}H_{44}N_6O_4Cu$ (736.35)	Dark Green	300*	50	64.55 (64.18)	5.34 (5.68)	12.14 (12.41)
(L^{2}H)$_2$Co · 2H$_2$O	$C_{40}H_{48}N_6O_6Co$ (803.56)	Brown	351	65	64.63 (64.29)	6.54 (6.87)	10.65 (10.40)
(L^{2}H)Cl(H$_2$O)Cd	$C_{20}H_{24}N_3O_3ClCd$ (502.19)	Yellow	211*	50	47.13 (47.29)	4.73 (4.79)	9.28 (9.36)
(L^{2}H)Cl(H$_2$O)Zn	$C_{20}H_{24}N_3O_3ClZn$ (455.18)	White	250	52	53.35 (53.73)	5.31 (5.27)	10.08 (10.22)

*Decomposition point.

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The Ni(II) complexes of the ligands are soluble in DMSO, DMF, and $CHCl_3$. Characteristic ^{13}C NMR spectral data for the Ni(II) complexes of L^1H_2 ($CDCl_3$, TMS, δ, ppm); C1(24.20), C2(30.40), C3(132.80), C4(126.65), C5(121.02), C6(144.62), C7(141.01), C8(172.47), C9(130.22), C10(124.40), C11(121.80), C12(124.65), Characteristic ^{13}C NMR spectral data for the Ni(II) complexes of L^2H_2 ($CDCl_3$, TMS, δ, ppm); C_1(123.36), C_2(124.21), C_3(128.27), C_4(143.54), C_5(39.48), C_6(31.87), C_7(28.22), C_8(44.36), C_9(144.73), C_{10}(168.47). C_{11}(131.27), C_{12}(127.40), C_{13}(124.23), C_{14}(127.63).

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

Compounds	ν(O–H)	ν(N–H)	ν(O$\cdots$H–O)	ν(C=N)	ν(N–O)	Others
L^1H_2	3315	3405	–	1660	990	
$(L^1H)_2Ni$	–	3397	1772	1620	978	
$(L^1H)_2Cu$	–	3393	1764	1619	970	
$(L^1H)_2Co \cdot 2H_2O$	–	3392	1770	1622	976	3430 (H_2O)
$(L^1H)Cl(H_2O)Cd$	3307	3285	–	1634	952	
$(L^1H)Cl(H_2O)Zn$	3310	3162	–	1622	960	
L^2H_2	3240	3424	–	1663	970	
$(L^2H)_2Ni$	–	3418	1761	1624	960	
$(L^2H)_2Cu$	–	3412	1780	1622	955	
$(L^2H)_2Co \cdot 2H_2O$	–	3424	1800	1626	958	3450 (H_2O)
$(L^2H)Cl(H_2O)Cd$	3312	3340	–	1624	960	
$(L^2H)Cl(H_2O)Zn$	3312	3270	–	1634	950	

Table 3. ^1H NMR spectra of the ligands and their Ni(II) complexes in DMSO-d_6.

Compound	O–H[a]	O–H[a]	H_{Arom}	[a]HN–C=	O–H$\cdots$O
L^1H_2	9.80	9.82	6.40–7.20	9.82	–
$(L^1H)_2Ni$	–	–	6.20–7.15	9.80	15.25
L^2H_2	9.35	9.42	6.90–7.52	–	–
$(L^2H)_2Ni$	–	–	6.80–7.20	–	16.15

[a] Disappears on D_2O exchange.

Table 4. Magnetic moments and characteristic UV-Vis bands of the ligands and complexes.

Compounds	$\mu_{eff}/_{atom}$ (B.M.)	λ_{max} (nm)[a]
L^1H_2	–	240
$(L^1H)_2Ni$	dia	322, 434, 476, 693
$(L^1H)_2Cu$	1.69	302, 660, 671
$(L^1H)_2Co \cdot 2H_2O$	3.81	305, 630
$(L^1H)ClH_2O)Cd$	dia	302, 611
$(L^1H)ClH_2O)Zn$	dia	289, 310, 691
L^2H_2	–	231, 260
$(L^2H)_2Ni$	dia	252, 325, 440, 680
$(L^2H)_2Cu$	1.89	269, 338, 550, 670
$(L^2H)_2Co \cdot 2H_2O$	4.04	272, 350, 480
$(L^2H)ClH_2O)Cd$	dia	280, 572
$(L^2H)ClH_2O)Zn$	dia	270, 302, 420

[a] In DMF.

dia. diamagnetic.

2.5. *Synthesis of the Cd(II), Zn(II), complexes of L^1H_2 and L^2H_2*

A solution of the metal salt $CdCl_2 \cdot H_2O$ (1.005 g, 5 mmol), $ZnCl_2$ (0.670 g, 5 mmol) dissolved in H_2O (15 cm^3) was added dropwise to a stirred solution of the ligand [L^1H_2 (1.49 g, 5 mmol) or L^2H_2 (1.69 g, 5 mmol)]. The pH of the reaction mixture, 3.5–4.0, was then adjusted to 10.0–11.0 for Cd(II) and 7.0–7.5 for Zn(II) by addition of 1% NaOH in EtOH. The mixture was stirred on a water bath at 45–50°C for 1 h. The precipitates were filtered, washed with cold water and dried.

3. Results and discussion

The newly synthesized phenylglyoxime ligands and their complexes are stable at room temperature in the solid state. The ligands are soluble in common organic solvents such as EtOH, $CHCl_3$, acetonitrile or DMSO. Their Ni(II) complexes are generally soluble in DMF $CHCl_3$, and DMSO; solubility of complexes is very low. The structure of the ligands and their complexes were determined by a combination of elemental analyses, IR, UV-Vis, ^{1}H-NMR, ^{13}C-NMR spectral data, and magnetic moments.

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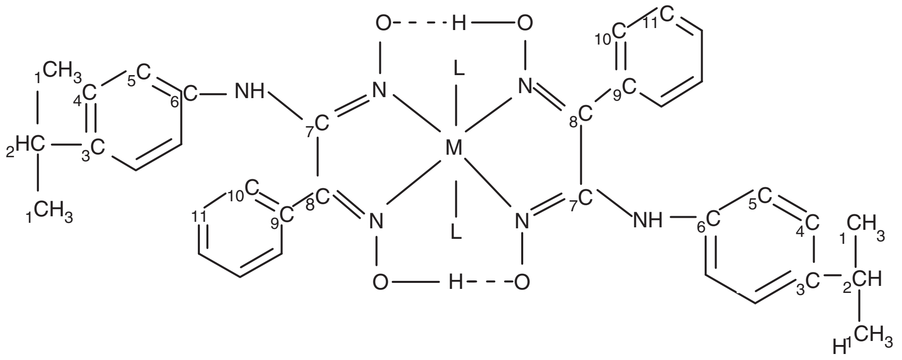
3.1. *Infrared spectra*

The most important infrared spectral bands of the ligands(L^1H_2–L^2H_2) and metal complexes are summarized in table 2. For the ligands, the bands in the 3315–3240 cm^{-1} range may be assigned to ν(O–H) stretching [22] and, the strong bands observed in the 1660–1663 cm^{-1} range are assigned to the azomethine group vibrations [23]. These bands are slightly shifted towards lower frequencies in the complexes; this change in frequencies shows that the imine nitrogen is coordinated to the metal [24]. The IR spectra of the cobalt complexes shows a strong broad band in the region 3430–3450 cm^{-1}, confirming the presence of water coordinated to the metal ion [25]. Since a distinct lowering in the pH of the solution was observed during complex formation, deprotonation of the ligand with subsequent N,N-chelation with the *vic*-dioxime probably occurs [26]. The usual hydrogen bridges (HO $\cdots$ H) associated with square-planar *vic*-dioxime complexes were characterized by weak deformation bands [4, 5, 7–20] at 1760–1800 cm^{-1} (figures 1 and 2, table 2). The reaction of L^1H_2 and L^2H_2 with nickel(II), cobalt(II), copper(II), gives products with 1 : 2, metal–ligand ratios (figures 1 and 2). L^1H_2 and L^2H_2 react with zinc(II) and cadmium(II) salts in a 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 and the O atom of the other group. Chloride and water are also coordinated to the metal in these complexes [27]. The physical data and IR spectra are consistent with the structure shown in figure 3. The analytical data and other spectral analyses are in good agreement with the proposed stoichiometry of the complexes in figures 1–3.

3.2. *^{1}H NMR and ^{13}C NMR spectra*

In the ^{1}H NMR spectra of the ligands L^1H_2 and L^2H_2 (table 3), two peaks are present for the –OH protons of the oxime groups which can be identified easily by deuterium



M	L
Ni	no L
Cu	no L
Co	H_2O

Figure 1. Suggested structure of Ni(II), Cu(II) and Co(II) complexes of the L^1H_2 ligand.

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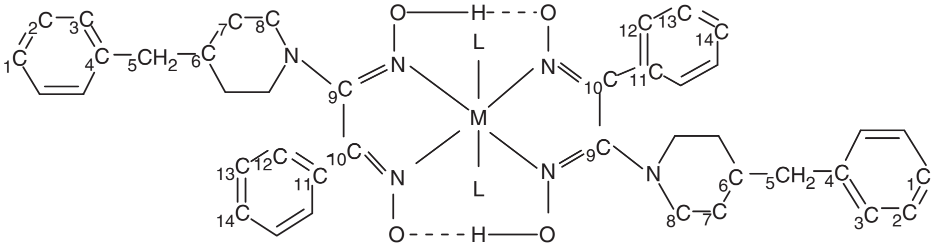

M	L
Ni	no L
Cu	no L
Co	H_2O

Figure 2. Suggested structure of Ni(II), Cu(II), Co(II) complexes of the L^2H_2 ligand.

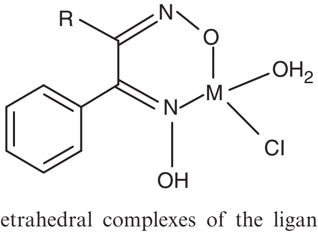

Figure 3. Suggested structure of tetrahedral complexes of the ligands (M = Cd(II), Zn(II) R = $C_9H_{12}N$ for L^1H_2, R = $C_{12}H_{16}N$ for L^2H_2).

exchangeable characteristics of these protons. The two deuterium exchangeable singlets correspond to two non-equivalent OH protons indicating anti-configuration of the OH groups relative to each other [28]. In the spectrum of L^1H_2 and L^2H_2, the phenyl multiplet was observed between 6.40–7.20 ppm and 6.90–7.52 respectively. The ^1H NMR spectrum of Ni(II) complexes show approximately the same peaks as observed for the free ligands. In the ^1H NMR spectra of Ni(II) complexes, there is no OH peak, as expected, but ^1HNMR spectral data proved the hydrogen-bridged structure for the (*E*,*E*)-Ni(II) complex with a chemical shift at lower field (15.25 ppm ($(L^1H)_2Ni$) and 16.15 ppm ($(L^2H)_2Ni$) for the deuterium exchangable $O–H\cdots O$ protons [29]. The deuterium-exchangeable NH protons, neighboring the oxime groups were observed at 9.82 ppm for L^1H_2 and 9.80 ppm for $(L^1H)_2Ni$. These values are in good agreement with those of *vic*-dioximes [30–32]. Due to the low solubilities of the Cu(II), Co(II), Zn(II) and Cd(II) complexes in organic solvents, ^1HNMR spectra could not be obtained. A ^{13}C NMR spectrum is one of the most convenient way to prove the true structure of *vic*-dioximes. In the ^{13}C NMR spectrum of the ligands (L^1H_2–L^2H_2) the carbon resonances of oxime groups are observed at 143.28 ppm and 170.47 ppm for L^1H_2 and 145.28 ppm and 170.38 ppm for L^2H_2. Observation of dioxime carbons in ^{13}C NMR spectra at two different frequencies indicates that the *vic*-dioxime ligands have the anti-structure [33].

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3.3. *Electronic spectra and magnetic properties*

Electronic spectra of *vic*-dioxime ligands (L^1H_2–L^2H_2), and complexes were taken in DMF (table 4). The UV-Vis spectra of the ligands and complexes showed absorption bands between 231–693 nm. In the complexes the low intensity bands in the 550–693 range nm are consistent with $d \rightarrow d$ transitions of the metal ions. The 250–380 nm bands seem to be due to both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of C=N and charge–transfer transition arising from π electron interactions between the metal and ligand [34, 35]. The UV-Vis peaks corresponding to the $\pi \rightarrow \pi$ transitions in the *vic*-dioxime ligands were observed at about 240 nm; these transitions shift to longer wavelength as a consequence of coordination, confirming the formation of *vic*-dioxime metal complexes [36]. The common features of the *vic*-dioxime complexes are their insolubility which hinders solution spectral investigations. However, magnetic susceptibility measurements provide suffcient information to identfy the structures. The room-temperature solid-state magnetic moment data of the complexes are reported in table 4. The mononuclear Ni(II) complexes are diamagnetic, as expected for a square-planar d^8 complex while the d^9 Cu(II) complexes and Co(II) complexes are paramagnetic [27]. The Zn(II) and Cd(II) complexes are also diamagnetic. The measured values for the Cu(II) and Co(II) complexes are 1.69–1.89 B.M. and 3.81–4.04 B.M. which correspond to a single electron. On the basis of the magnetic and spectral evidence, a square-planar geometry for Ni(II) and Cu(II) complexes and a tedrahedral geometry for Cd(II) and Zn(II) complexes and octahedral geometry for the Co(II) complex are proposed [36]. The suggested structures of the complexes are shown in figures 1–3.

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