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Transition Metal Complexes Derived From 1,3-Dioxalane Groups and *vic*-Dioxime Ligands: Thermal, Magnetic and Spectral Studies

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A novel substituted *vic*-dioxime ligand containing the amino group, N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] (L^1) has been prepared from 1,2-*bis*(*p*-aminophenoxy)ethane, *anti*-chloroglyoxime. This *vic*-dioxime ligand with Cu(II), Ni(II), Co(II) and Cd(II) complexes of 6,7-O-cyclopentylidine-1-amino-4-azaheptane (L^2) have been reacted at 60-65 ºC temperature. The ligand^1:metal:ligand^2 ratio of these complexes have been found to be 1:2:2. The Cu(II), Ni(II), Co(II) and Cd(II) complexes of these ligands are proposed to be octahedral. The *vic*-dioxime (L^1) with some transition metal complexes of amine (L^2) have been characterized by elemental analyses, molar conductivity, magnetic susceptibility, IR, ^{1}H NMR, UV-Vis spectra and TGA techniques.

Key Words: *vic*-Dioxime, *anti*-Chloroglyoxime, Transition metal complexes.

INTRODUCTION

Oximes and their metal complexes are of current interest due to their rich physicochemical properties, reactivity patterns and potential applications in many important chemical processes in the areas of medicine, bioorganic system and catalysis, electrochemical and electrooptical sensors[1-4]. The presences of mildly acidic hydroxyl groups and slightly basic nitrogen atoms makes *vic*-glyoximes amphoteric ligands which from corrin-type square planar, square-pyramidal and octahedral complexes with metal ions such as nickel(II), copper(II), cobalt(II) and cobalt(III) as central atoms[5,6]. The high stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for purposes including model compounds for vitamin B_{12} or trace metal analysis[7,8].

vic-Dioximes and their complexes constitute an important class of compounds having versatile reactivities[9]. Oxime metal chelates are biologically active and are reported to posses semiconducting properties[10,11]. The substitution of the *vic*-dioxime moiety affects the structure and stability of the complex[12]. Compounds containing

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the 1,3-dioxalane groups are used as solvents, additive compounds and corrosion retardants, while polymers containing 1,3-dioxalane groups exhibit semiconducting behaviour[13,14].

We already investigated the synthesis and characterization of various transition metal complexes of novel bidentate compounds[15,16]. In the present study, new amino *vic*-dioxime complexes derived from N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] (L^1) with Cu(II), Ni(II), Co(II) and Cd(II) complexes of 6,7-O-cyclopentylidine-1-amino-4-azaheptane (L^2) used as metal salts have been prepared and characterized by electronic, infrared, molar conductivity, magnetic and ^{1}H NMR spectral measurements, elemental and thermogravimetrical analyses. The data revealed same geometries around the metal ions, depending on both the ligand and metal ions. The structure of the ligands showed as in Fig. 1.

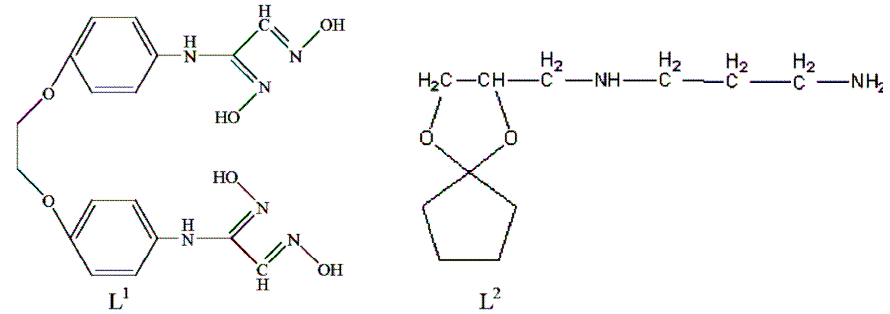

Fig. 1. Structures of the (L^1) and (L^2) ligands

EXPERIMENTAL

A new amino *vic*-dioxime ligand, N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] (L^1), derived from reaction of 1,2-*bis*(*o*-aminophenoxy)ethane[17,18] and *anti*-chloroglyoxime[19] were synthesized and characterized as described in the literature. All the reagents used were purchased from Merck, Across or Labkim company and chemically pure.

Elemental analyses (C, H, N) were performed on a LECO-932 CHNS-O elemental analyses apparatus. IR spectra were recorded on a Perkin-Elmer precisely spectrum one spectrometer as KBR pellets. ^{1}H NMR spectra were recorded on a Bruker GmbH DPX-300 MHz high performance digital FT-NMR spectrometers (DMSO-d_6). Electronic spectra were obtained on a Shimadzu UV-1700 spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrate; diamagnetic corrections were calculated from Pascal's constants[20]. Molar conductances were measured on a CMD 750WPA conductometer[21]. Melting points were determined on a Gallenkamp melting points apparatus. TGA curve was recorded on a Shimadzu DTG-60AH thermo balance.

Synthesis of N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] (L^1): A solution 1,2-*bis*(*p*-aminophenoxy)ethane (2.44 g, 0.01 mol) was added to a solution of anti chloroglyoxime (2.46 g, 0.02 mol) in ethanol (50 mL). Then a solution of Na_2CO_3 (2.65 g, 0.03 mol) in ethanol (50 mL) was added dropwise to this mixture at 60 °C over 12 h, the mixture filtred and ethanol was removed by evaporation. The solid product was filtred off, washed with H_2O several times, dried in vacuum and crystallized from aqueous diethyl ether (1:3). Characteristic ^1H NMR peaks (DMSO-d_6; δ ppm; 300 MHz): 4.62-4.08 (m, 4H, OCH_2), 8.75, 8.31 (s, 2H, H-C=N), 10.75, 10.50, 10.38, 10.25 (s, 4H, N-OH), 5.75, 5.44 (s, 2H, N-H), 7.12-6.50 (m, 8H, C-$H_{(Ar.)}$)[21].

Preparation of 6,7-O-cyclopentylidine-1-amino-4-azaheptane (L^2): 16.74 mL (0.20 mol) of 1,3-diaminopropane, 8.0 mL (0.06 mol) of triethylamine and 60 mL absolute xylene were mixed in a reaction vessel and stirred at room temperature. To this solution, a solution of 8.83 g (0.05 mol) of 1-chloro-2,3-O-cyclopentylidine-propane in 20 mL absolute xylene was added dropwise. The mixture was refluxed for 28 h with continuous strirring. After cooling to room temperature, the mixture was filtered. The filtrate was distilled at 111 °C at 1 mm-Hg. The product is soluble in common solvents such as chloroform, benzene, water, xylene or ethanol. Characteristic ^1H NMR signals ($CDCl_3$; δ ppm; 90 MHz): 4.03 (1H, p, -O-CH-), 3.67 (2H, t, -O-CH_2-), 2.68 (6H, m, -CH_2-N), 1.69 and 1.29 (13H, m, -C-CH_2)[14,22,23].

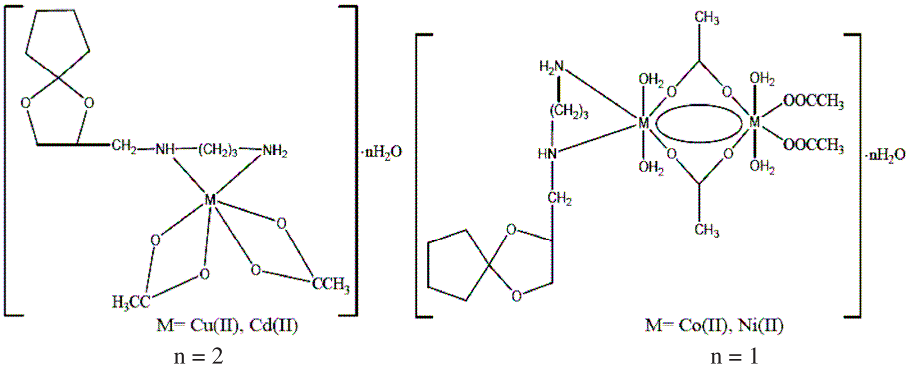

Fig. 2. Structures of the distorted octahedral Cu(II), Ni(II), Co(II) and Cd(II) complex of the 6,7-O-cyclopentlydine-1-amino-4-azaheptane (L^2)

Synthesis of the Cu(II), Ni(II), Co(II) and Cd(II) complexes of 6,7-O-cyclopentlydine-1-amino-4-azaheptane (L^2): The ligand (L^2) (0.214 g, 1 mmol) was dissolved in 10 mL absolute ethanol in a 50 mL round-bottom flask. A solution of 2 mmol of metal salts [$Co(OAc)_2·4H_2O$] (0.498 g), $Ni(OAc)_2·4H_2O$ (0.496 g)] in 5 mL of absolute ethanol was added dropwise in a 15 min period with continuous stirring at room temperature. The ligand (L) (0.428 g, 2.0 mmol) was dissolved in 10 mL absolute ethanol in a 50 mL round-bottom flask. A solution of 2.0 mmol of the metal salt $Cu(OAc)_2{\cdot}H_2O$ (0.398 g) and $Cd(OAc)_2$ (0.462 g) in 5 mL of absolute ethanol was added dropwise in a 0.5 h period with continuous stirring at room temperature. The reaction mixtures were then further stirred for 8 h at 150 ºC temperature. The resulting precipitates were filtered off and washed with absolute ether. The products were dissolved in chloroform and precipitated by addition of *n*-hexane (1/5). The resulting crystals were filtered off and were dried at room temperature. Yields of complexes were found to be 0.51 g (63.20%) for Cu(II), 0.78 g (59.55 %) for Ni(II), 0.72 g (56.26 %) for Co(II) and 0.55 g (57.43 %) for Cd(II)[14,22,23].

Synthesis of final product $[L^1M_2L_2^2(OH)_4]{\cdot}nH_2O$ [M = Cu(II) Ni(II), Co(II) and Cd(II)]: The solution of $[ML^2(AcO)_2]{\cdot}nH_2O$ where M is Cu(II) and Cd(II), n is 0 and 2, respectively, (0.40 g for Cu(II), 0.48 g for Cd(II), 1.0 mmol) and the solution of $[M_2L^2(AcO)_4{\cdot}4H_2O]{\cdot}nH_2O$ where M is Ni(II) and Co(II), n is 1 and 0, respectively, (0.66 g for Ni(II), 0.64 g Co(II), 1.0 mmol) in hot EtOH (15 cm^3) were slowly added with stirring to a solution of N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*-(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] (L^1), (0.21 g, 0.5 mmol) in EtOH (50 cm^3) at 60-65 ºC temperature. The pH of the mixtures was *ca.* 4-5. NaOH was added to the mixture to adjust the pH of the mixture and to complete the precipitation after the mixture had been heated on a water-bath 5 h. Finally, the mixtures were centrifuged several times with water and ethanol and the product dried in vacuum to yields a different colour powder. These compounds are soluble in DMF and DMSO and insoluble in water and ethanol.

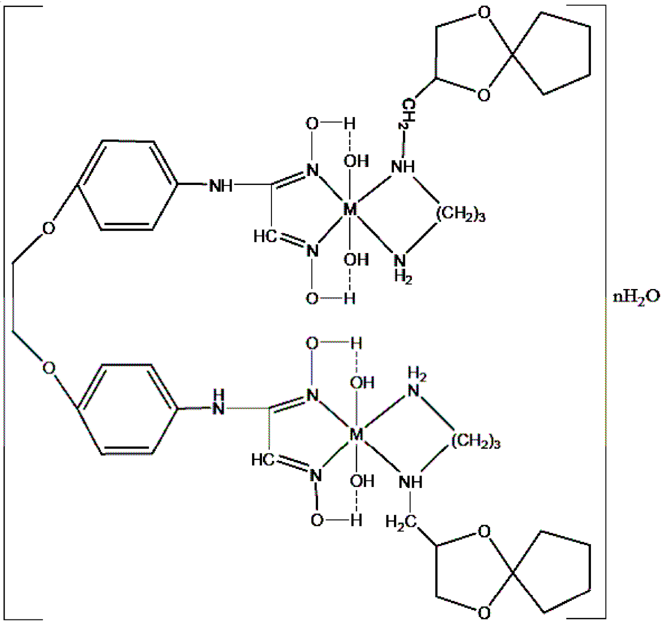

Fig. 3. Proposed suggested structure of the octahedral $[L^1M_2L^2_2(OH)_4]{\cdot}nH_2O$ (M: Cu(II), Ni(II), Co(II) and Cd(II))

RESULTS AND DISCUSSION

The ligand used for this work, N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] (L^1), contains amino and *vic*-dioximes groups. Its synthesis was accomplished in 59.80 % yield by the reaction of 1,2-*bis*(*p*-aminophenoxy)ethane and *anti*-chloroglyoxime in ethanol. The impurities were checked by N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] (L^1), gives dinuclear complexes $[L^1Cu_2L^2_2(OH)_4]\cdot 2H_2O$, $[L^1Ni_2L^2_2(OH)_4]\cdot 4H_2O$, $[L^1Co_2L^2_2(OH)_4]\cdot H_2O$ and $[L^1Cd_2L^2_2(OH)_4]\cdot 3H_2O$ with Cu(II), Ni(II), Co(II) and Cd(II) complexes of 6,7-O-cyclopentlydine-1-amino-4-azaheptane (L^2), respectively. The analytical data of these complexes indicate 1:2:2 ligand^1:metal:ligand^2 stoichiometry. Additional analytical data are given in Tables 1-3. Attempt to crystallize the ligand complexes from different solvents were failure. The structure of the L^1 and L^2 ligands were confirmed by of elemental analyses, ^{1}H NMR, IR and UV-Vis spectral data.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE LIGANDS AND THEIR COMPLEXES

Compounds (colour)	m.f. (m.w.)	Yield (%)	μ_{eff} (BM)	Λ_M	Elemental analysis (%): Calcd. (Found)		
					C	H	N
L^1	$C_{18}H_{20}N_6O_6$	59.80	–	–	51.92	4.84	20.18
(Brown)	(416.39)				(52.09)	(5.02)	(20.29)
L^2	$C_{11}H_{22}N_2O_2$	46.73	–	–	61.68	10.28	13.08
(Colourless)	(214.0)				(61.58)	(10.42)	(13.23)
$[L^1Cu_2L^2_2(OH)_4]\cdot 2H_2O$	$Cu_2C_{40}H_{72}N_{10}O_{16}$	61.37	1.67	10.07	44.64	6.74	13.02
(Light brown)	(1076.15)				(44.76)	(6.62)	(13.15)
$[L^1Ni_2L^2_2(OH)_4]\cdot 4H_2O$	$Ni_2C_{40}H_{76}N_{10}O_{18}$	65.32	2.85	13.34	43.58	6.95	12.70
(Tile red)	(1102.47)				(43.46)	(6.75)	(12.59)
$[L^1Co_2L^2_2(OH)_4]\cdot H_2O$	$Co_2C_{40}H_{70}N_{10}O_{15}$	69.75	3.97	14.13	45.80	6.73	13.35
(Wine red)	(1048.91)				(45.62)	(6.87)	(13.20)
$[L^1Cd_2L^2_2(OH)_4]\cdot 3H_2O$	$Cd_2C_{40}H_{74}N_{10}O_{17}$	53.29	Diamag.	12.27	40.31	6.26	11.75
(Dark yellow)	(1191.89)				(40.24)	(6.32)	(11.92)

$\Lambda_M = (\Omega^{-1}\ cm^2\ mol^{-1})$

All of the newly synthesized complexes are stable in air. The results of elemental analyses of the ligands and complexes are in agreement with the chemical formulas.

Magnetic susceptibility measurements provided sufficient data to characterize the structures. The copper(II), nickel(II) and cobalt(II) complexes are paramagnetic. Their magnetic susceptibilities are 1.67 BM for $[L^1Cu_2L^2_2(OH)_4]\cdot 2H_2O$, 2.85 BM for $[L^1Ni_2L^2_2(OH)_4]\cdot 4H_2O$ and 3.97 BM for $[L^1Co_2L^2_2(OH)_4]\cdot H_2O$. The alternative chemical environments will give four (O–H···O) bridge protons between hydroxyl ions with –OH groups in the *anti*-form of L^1. The complex of Cd(II) ion, $[L^1Cd_2L^2_2(OH)_4]\cdot 3H_2O$ is diamagnetic. All of the complexes are proposed to be octahedral.

TABLE-2
CHARACTERISTIC IR BANDS (cm^{-1}) OF THE LIGANDS AND THEIR COMPLEXES IN KBr PELLETS

Compounds	H_2O/OH	N–H	C–H$_{arom.}$	CH$_{aliph.}$	C=N
L^1	3400	3208	3070	2923-2873	1670
L^2	–	3361	–	2934-2873	–
$[L^1Cu_2L^2_2(OH)_4]\cdot 2H_2O$	3436	3314	3061	2928-2862	1656
$[L^1Ni_2L^2_2(OH)_4]\cdot 4H_2O$	3442	3303	3049	2923-2868	1643
$[L^1Co_2L^2_2(OH)_4]\cdot H_2O$	3433	3347	3060	2930-2862	1671
$[L^1Cd_2L^2_2(OH)_4]\cdot 3H_2O$	3428	3326	3054	2927-2868	1654

Compounds	N–O	O–H···O	C$_{aliph.}$-O-C	C$_{arom.}$-O-C	M–O	M–N
L^1	1067	–	–	1237	–	–
L^2	–	–	1111	–	–	–
$[L^1Cu_2L^2_2(OH)_4]\cdot 2H_2O$	1064	1730	1106	1269	450	516
$[L^1Ni_2L^2_2(OH)_4]\cdot 4H_2O$	1065	1735	1114	1284	460	519
$[L^1Co_2L^2_2(OH)_4]\cdot H_2O$	1060	1712	1116	1240	457	523
$[L^1Cd_2L^2_2(OH)_4]\cdot 3H_2O$	1056	1708	1100	1267	463	529

TABLE-3
TGA DATA OF the metal COMPLEXES

Complexes	Step 1	Step 2	Step 3	Weight loss (%)	Residue (%): Calcd. (Found)
$[L^1Cu_2L^2_2(OH)_4]\cdot 2H_2O$	45.0-117.5	117.5-275.3	275.3-800.0	87.19 (87.44)	CuO 12.81 (12.56)
$[L^1Ni_2L^2_2(OH)_4]\cdot 4H_2O$	37.5-110.0	110.0-297.6	297.6-752.7	85.20 (84.70)	NiO 14.80 (15.30)
$[L^1Co_2L^2_2(OH)_4]\cdot H_2O$	52.3-92.3	92.3-286.9	286.9-796.7	87.14 (88.48)	CoO 12.86 (11.52)
$[L^1Cd_2L^2_2(OH)_4]\cdot 3H_2O$	32.5-105.0	105.0-241.1	241.1-796.9	92.34 (91.75)	CdO 7.66 (8.25)

Based on the elemental analyses, spectroscopic characterization and magnetic studies, these binuclear complexes are presumed to have the coordination environment shown in Fig. 3.

IR spectra: The infrared spectra of the *vic*-dioxime ligand (L^1), 1,3-dioxolane containing amine ligand (L^2) and their metal complexes have been studied in order to characterize their structures. The relevant IR bands and their assignments are listed in Table-2. Generally, oximes are characterized by three IR absorption bands at 3442-3400 cm^{-1} (O-H *str.*), 1671-1643 cm^{-1} (C=N *str.*) and 1067-1056 cm^{-1} (N-O *str.*)[17,18]. In order to study the bridging of the dioxime ligand to the metal in the complexes, the IR spectrum of the free oxime ligand was compared with the spectra of the metal complexes. In the IR spectrum of L^2, the characteristic peaks are at 3347-3208 cm^{-1}, which are assigned to ν(N-H) and ν(-NH_2) and 1111 cm^{-1} is assigned to the ν(C-O-C) group[14,21]. These values are in harmony with previously reported diaminoglyoxime derivatives[24].

In the new complexes of amine and *vic*-dioxime, the oxime C=N stretching vibrations are shifted to 1671-1643 cm^{-1}. These observations indicate the involvement of the nitrogen atom of the azomethine C=N group. In the IR spectra of the binuclear complexes weak O–H···O deformation vibrations are observed[12,17] at *ca.* 1735-1708

cm^{-1}. The disappearance of the OH stretching band and the shift of the C=N band to lower frequency in the IR spectra of binuclear complexes may be attributed to N,N-chelation. N-H stretching vibrations are positioned at near 3330 cm^{-1}. Aromatic C-H stretching vibrations in the L^1 are 3223-3070 cm^{-1}, whereas, aliphatic C-H stretching vibrations in the L^1 and L^2 are 2923-2873 and 2934-2873 cm^{-1}, respectively. At the same time, the infrared bands observed near 3361 and 3247 cm^{-1}, which are assigned to the –NH– and $–NH_2$ frequency is shifted to lower frequency after complexation with respect to the free L^2, whereas, the –NH– and $–NH_2$ frequency is shifted to higher frequency after complexation with respect to the free L^1. The strong absorption at 3356-3337 cm^{-1} in the complexes can be assigned to $\nu(-NH_2)$ of the intramolecular hydrogen bonded 1,3-diaminopropane moiety[25]. In the spectra of the Cu(II), Ni(II), Co(II) and Cd(II) complexes a few new bands occur at lower regions 450, 460, 457 and 463 cm^{-1} and 516, 519, 523 and 529 cm^{-1} which are attributed to the ν(M-O) and ν(M-N) vibrations, respectively[26,27].

^{1}H NMR spectra: In order to identify structures of the amino and *vic*-dioxime ligands in solution, the ^{1}H NMR spectra was recorded in DMSO-d_6 or $CDCl_3$. The ^{1}H NMR assignments are also given in experimental.

The ^{1}H NMR spectrum of *vic*-dioxime ligand (L^1) in DMSO-d_6 resulted in peak corresponding to the aromatic protons at 7.12-6.50 ppm as multiplet. In the spectrum of L^1, the N-H protons in the neighbourhood of oxime groups as multiplet at 5.75-5.44 ppm were exhibited. The singlets at 10.75, 10.56, 10.38 and 10.25 ppm are assigned to the hydroxyl protons of *vic*-dioxime, which disappeared upon addition of D_2O. The singlets for the oxime groups showed that the L^1 was *anti*-configuration[24]. The spectrum also show singlets at 4.62-1.12 ppm $–CH_2$ protons. In the proton NMR spectrum of the ligand, the resonance observed at 8.75 and 8.31 ppm as two singlets were assigned to the azomethine protons of the oxime groups (HC=N–)[28].

In the ^{1}H NMR spectrum of L^2, there are two characteristic peaks, 1.75 and 2.40-3.20 ppm, which are attributable to the –NH- and $–NH_2$ groups, which were also identified by D_2O exchange[29] and $–CH_2$ groups, respectively. There is another $-O-CH_2-$ peaks at 4.03 ppm as multiplet. These are in good agreement with literature.

^{1}H NMR spectra of the Cu(II), Ni(II) and Co(II) complexes could not be taken because of their paramagnetic character. At this time, since Cd(II) complex could not be soluble from DMSO and DMF, ^{1}H NMR spectra of the Cd(II) complex could not be taken clearly.

Electronic spectra, magnetic and molar measurements: The UV-Vis spectra of the ligands and their complexes were recorded in DMSO-DMF mixture solution in the wavelength range from 200 to 1100 nm. The spectra showed a sharp and intense two bands observed[30] at 270-300 and 370-420 nm for free L^1 and 216-290 and 320-400 nm for free L^2 ligand[21,31] are reasonably accounted for $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions.

The electronic spectrum of the $[L^1Cu_2L^2_2(OH)_4]\cdot 2H_2O$ complex shows a shoulder at 620-750 nm, assignable to $^2B_{1g}\rightarrow{}^2E_g$ transition of the metal ion, suggesting a octahedral geometry[21,32].

The electronic spectrum of the $[L^1Ni_2L^2_2(OH)_4]\cdot 4H_2O$ complex has absorption bands at 415 and 715-775 nm assigned to the $^3A_{2g}\rightarrow{}^3T_{2g}(P)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ transition, indicating a high-spin octahedral configuration[21,25,33].

The electronic spectrum of the $[L^1Co_2L^2_2(OH)_4]\cdot H_2O$ complex has absorption bands at 530 and 755-800 nm attributable to the $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ and $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ transitions, suggesting a high-spin octahedral geometry around the Co(II) ions[21,34].

A presumably octahedral structure is suggested for the diamagnetic $[L^1Cd_2L^2_2(OH)_4]\cdot 5H_2O$ complexes[37]. This electronic spectra of this complex shows absorption bands at 370 and 435 nm, which are attributed to the charge transfer transitions from the ligand to metal ions and from the metal ions to ligand[35]. The suggested general structure of all the complexes is shown in Fig. 3.

The complexes are non-electrolytes as shown by their molar conductivity (Λ_M) measurements in DMSO, which are in the range for Cu(II), Ni(II), Co(II) and Cd(II) complexes[36] at 10.07, 13.34, 14.13 and 12.27 Ω^{-1} cm^2 mol^{-1}, respectively (Table-1).

Thermal studies: The thermal behaviour of the complexes was studied at a heating rate of 10 K/min in a nitrogen atmosphere over a temperature range of 20-1000 ºC. The TGA and DTA curves all of the complexes are thermally unstable up to room temperature.

The decomposition temperature and weight losses of the complexes were calculated from the TGA data (Table-3). It may be seen from the TGA data that all the complexes decompose in three steps at different temperature ranges. In the TGA curves of Cu(II), Ni(II), Co(II) and Cd(II) complexes, 3.25, 6.37, 1.67 and 4.32 % weight losses were observed at 117.5, 110.0, 92.30 and 105.0 ºC, respectively. This shows that these complexes have 2, 4, 1 and 3 mole of crystal water per molecule, respectively. The IR spectra of the complexes are characterized by the appearance of a broad band in the region of 3428-3442 cm^{-1} due to the ν(OH) of water of crystallization[37]. This water content was also identified by the elemental analyses. The weight losses have been found to approximate the percentages estimated stoichiometrically from their chemical formulas given in Table-1. When the complexes are heated to higher temperatures, they decompose to give oxides MO type[38].

Conclusion

A novel, *vic*-dioxime ligand, N,N′-[4,4′-{ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene)}*bis*(N′-hydroxy)-2-(hydroxyimino)acetamidamide] L^1, derived from 1,2-*bis*(*p*-aminophenoxy)ethane with *anti*-chloroglyoxime. Then, some transition metal complexes of 6,7-O-cyclopentylidine-1-amino-4-azaheptane L^2, have been prepared. These metal complexes of L^2 used as metal salts with *vic*-dioxime ligand (L^1) have been reacted and new metal complexes of *vic*-dioxime-amine mixture have been obtained. The analytical data and spectroscopic studies suggest that the complexes were of the general formula $[L^1M_2L^2_2(OH)_4]\cdot nH_2O$ where M is Cu(II), Ni(II), Co(II) and Cd(II), n is 2, 4, 1, 3, respectively. According to the ^{1}H NMR and IR data of the *vic*-dioxime ligand, L^1 and amine ligand, L^2 are coordinated with the metal ions through the hydroxyimino nitrogens and amino nitrogens.

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