Formation of Novel Amino *Vic*-dioxime Complexes of Cu(II), Ni(II), Co(II) and Cd(II) of 1,3-Dioxalane Groups Containing the Oxime Moiety: Thermal, Magnetic and Spectral Studies

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Summary: A novel substituted *vic*-dioxime ligand containing the amino group, N,N′-[2,2′-{ethane-1,2-di-yl-bis(oxy)bis(2,1-phenylene)}bis(N′-hydroxy)-2-(hydroxyimino)acetimidamide] (L^1) has been prepared from 1,2-bis(o-aminophenoxy)ethane, *anti*-chloroglyoxime. The new complexes derived from L^1 with Cu(II), Ni(II), Co(II) and Cd(II) complexes of 6,7-O-Cyclopentlydine-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 new Cu(II), Ni(II), Co(II) and Cd(II) complexes of these ligands are proposed to be octahedral. These new complexes have been characterized by elemental analyses, molar conductivity, magnetic susceptibility, IR, ^{1}H-NMR, UV-Vis spectra and TGA techniques.

Keywords: *Vic*-dioxime, Transition metal complexes, amine.

Introduction

Vic-dioximes and their complexes constitute an important class of compounds having versatile reactivities [1]. Oxime metal chelates are biologically active and are reported to posses semiconducting properties [2,3]. The substitution of the *vic*-dioxime moiety affects the structure and stability of the complex [4]. Compounds containing the 1,3-dioxalane groups are used as solvents, additive compounds, and corrosion retardants, while polymers containing 1,3-dioxalane groups exhibit semiconducting behavior [5,6].

In the present study, new amino *vic*-dioxime complexes derived from N,N′-[2,2′-{ethane-1,2-di-yl-bis(oxy)bis(2,1-phenylene)}bis(N′-hydroxy)-2-(hydroxyimino)acetimidamide] (L^1) with Cu(II), Ni(II), Co(II) and Cd(II) complexes of 6,7-O-cyclopentilydine-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 in addition to elemental and thermo gravimetrical analyses. The data revealed same geometries around the metal ions, depending on both the ligand and metal ions.

Results and Discussion

The ligand used for this work, L^1 contains amino and *vic*-dioximes groups. Its synthesis was accomplished in 82.77% yield by the reaction of 1,2-bis(o-aminophenoxy)ethane and *anti*-chloroglyoxime in ethanol. The impurities were checked by L^1 gives dinuclear complexes $[L^1Cu_2L^2_2(OH)_4]\cdot 3H_2O$, $[L^1Ni_2L^2_2(OH)_4]\cdot 3H_2O$, $[L^1Co_2L^2_2(OH)_4]\cdot 3H_2O$ and $[L^1Cd_2L^2_2(OH)_4]\cdot 5H_2O$ with Cu(II), Ni(II), Co(II) and Cd(II) complexes of L^2, respectively. The analytical data of these complexes indicate 1:2:2 ligand[1]:metal:ligand[2] stoichiometry. Additional analyticcal data are given in Table-1, 2. Attempt to crystallize the ligand complexes from different solvents were failure. The structure of the L^1 and L^2 ligands were confirmed by a combination of elemental analyses, ^{1}H-NMR, IR and UV-Vis spectral data.

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.

Conductance Measurements

These new 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 at 7.78, 13.45, 15.57 and 11.13 $\Omega^{-1}cm^2mol^{-1}$ [7,8], respectively (Table 1).

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 assignment are listed in Table 2. Generally, oximes are characterized by three IR absorption bands at 3423-3445 cm^{-1} ($O\text{-}H_{str.}$), 1615-1574 cm^{-1} ($C{=}N_{str}$) and 1064-1053 cm^{-1} ($N\text{-}O_{str.}$) [9]. 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 3361-3292 cm^{-1}, which are assigned to ν(N-H) and ν(-NH_2) and 1111 cm^{-1} that is assigned to the ν(C-O-C) group [6,10]. These values are in harmony with previously reported diamino-glyoxime derivatives [15].

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Table-1: Analytical and Physical Data of the Ligands and Their Complexes

Compounds	Formula (F.W.) g/mole	Color	Yield(%)	μ_{eff}/atom(B.M.)	Λ_M	Elemental analyses Calc. (found), %		
						C	H	N
L^1	$C_{18}H_{20}N_6O_6$ (416.39)	Dark yellow	82.77	—	—	51.92 (51.81)	4.84 (5.18)	20.18 (19.84)
L^2	$C_{11}H_{22}N_2O_2$ (214.0)	Colorless	46.73	—	—	61.68 (61.38)	10.28 (10.42)	13.08 (13.23)
$[L^1Cu_2L^2_2(OH)_4]\cdot 3H_2O$	$Cu_2C_{40}H_{74}N_{10}O_{17}$ (1094.16)	Brown	62.53	1.57	7.78	43.91 (43.96)	6.82 (6.72)	12.80 (13.11)
$[L^1Ni_2L^2_2(OH)_4]\cdot 3H_2O$	$Ni_2C_{40}H_{74}N_{10}O_{17}$ (1084.46)	Dark brick red	78.42	2.90	13.45	44.30 (44.24)	6.88 (6.61)	12.92 (12.69)
$[L^1Co_2L^2_2(OH)_4]\cdot 3H_2O$	$Co_2C_{40}H_{74}N_{10}O_{17}$ (1084.94)	bordeaux	74.57	4.25	15.57	44.28 (44.62)	6.87 (6.61)	12.91 (13.20)
$[L^1Cd_2L^2_2(OH)_4]\cdot 5H_2O$	$Co_2C_{40}H_{78}N_{10}O_{19}$ (1227.92)	Light yellow	56.95	Dia	11.13	39.13 (39.24)	6.40 (6.72)	11.41 (11.07)

Λ_M =($\Omega^{-1}cm^2mol^{-1}$)

In the new complexes of amine and *vic*-dioxime, the oxime C=N stretching vibrations are shifted to 1598-1574 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 at *ca.* 1662-1681 cm^{-1} [4,11]. 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 3340 cm^{-1}. Aromatic C-H stretching vibrations in the L^1 are 3219-3060 cm^{-1}, whereas, aliphatic C-H stretching vibrations in the L^1 and L^2 are 2923-2857 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^1H_4. 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 [12]. In the spectra of the Cu(II), Ni(II), Co(II) and Cd(II) complexes a few new bands occur at lower regions 455, 463, 459 and 458 cm^{-1}, and 518, 516, 520 and 524 cm^{-1} which are attributed to the ν(M-O) and ν(M-N) vibrations, respectively [13,14].

^{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 7.21-6.67 ppm as multiplet. In the spectrum of L^1, the N-H protons in the neighbored of oxime groups as multiplet at 6.44-6.19 ppm were exhibited. The singlets at 12.08, 11.36, 10.82 and 10.14 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 [15,16]. The spectrum also shows singlets at 4.72-1.12 ppm $–CH_2$ protons. In the ^{1}H-NMR spectrum of the ligand, the resonance observed at 8.54 and 8.13 ppm as two singlets were assigned to the azomethine protons of the oxime groups(HC=N-).

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 [17] 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.

Magnetic Data and Electronic Spectra

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 1.57 B.M. for $[L^1Cu_2L^2_2(OH)_4]\cdot 3H_2O$, 2.90 B.M. for $[L^1Ni_2L^2_2(OH)_4]\cdot 3H_2O$ and 4.25 B.M. for $[L^1Co_2L^2_2(OH)_4]\cdot 3H_2O$. 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, $[L^1Cd_2L^2_2(OH)_4]\cdot 5H_2O$ 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	N-O	O-H···O	$C_{aliph.}$-O-C	$C_{arom.}$-O-C	M-O	M-N
L^1	3423	3247	3087	2923-2857	1615	1053	—	—	1248	—	—
L^2	—	3361	—	2934-2873	—	—	—	1111	—	—	—
$[L^1Cu_2L^2_2(OH)_4]\cdot 3H_2O$	3456	3348	3060	2926-2873	1599	1062	1681	1116	1282	455	518
$[L^1Ni_2L^2_2(OH)_4]\cdot 3H_2O$	3445	3347	3065	2926-2873	1596	1062	1675	1100	1281	463	516
$[L^1Co_2L^2_2(OH)_4]\cdot 3H_2O$	3421	3342	3060	2936-2873	1574	1045	1668	1103	1260	459	520
$[L^1Cd_2L^2_2(OH)_4]\cdot 5H_2O$	3410	3365	3065	2934-2868	1598	1064	1662	1111	1256	458	524

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 at 270-320 and 350-400 nm for free L^1 [18] and 216-290 and 320-400 nm for free L^2 ligand [19] are reasonably accounted for $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions.

The electronic spectrum of the $[L^1Cu_2L^2_2(OH)_4]\cdot 3H_2O$ complex shows a shoulder at 650-725 nm, assignable to $^2B_{1g}\rightarrow{}^2E_g$ transition of the metal ion, suggesting a octahedral geometry [20].

The electronic spectrum of the $[L^1Ni_2L^2_2(OH)_4]\cdot 3H_2O$ complex has absorption bands at 425 and 730-765 nm assigned to the $^3A_{2g}\rightarrow{}^3T_{2g}(P)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ transition, indicating a high-spin octahedral configuration [12,21].

The electronic spectrum of the $[L^1Co_2L^2_2(OH)_4]\cdot 3H_2O$ complex has absorption bands at 520 and 745-780 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 [22].

A presumably octahedral structure is suggested for the diamagnetic $[L^1Cd_2L^2_2(OH)_4]\cdot 5H_2O$ complexes [18]. The electronic spectra of this complex shows absorption bands at 390 and 415 nm, which are attributed to the charge transfer transitions from the ligand to metal ions and from the metal ions to ligand [23]. The suggested general structure of all the complexes is shown in Fig. 3.

Thermal Studies

The decomposition temperature and the weight losses of the complexes and the ligands were taken from the TGA data. The TGA curves showed that the thermal decomposition of the complexes takes place in three steps. Thermogravimetric studies of all the complexes showed weight loss up to 32.56 ºC, indicating existence of water molecules in the complexes. The inflation of the TGA curves of all the complexes at a temperature below 625 ºC, indicates the decomposition of the fully organic part of the chelate, leaving metallic oxide at the final temperature [24].

Experimental

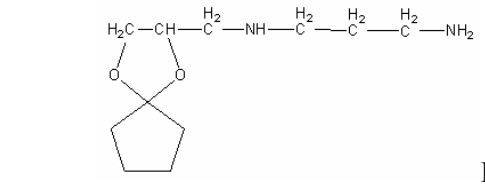
A new amino *vic*-dioxime ligand, (L^1), derived from reaction of 1,2-bis(oamino-phenoxy)ethane [11,25] and *anti*-chloroglyoxime [11,25] were synthesized and characterized as described in the literature [26]. All the reagents used were purchased from Merck, Across or Labkim Company and chemically pure.

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 (in 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 [7]. Molar conductances were measured on a CMD 750WPA conductometer [10]. Melting points were determined on a Gallenkamp melting points apparatus. TGA curve was recorded on a Shimadzu DTG-60AH thermobalance.

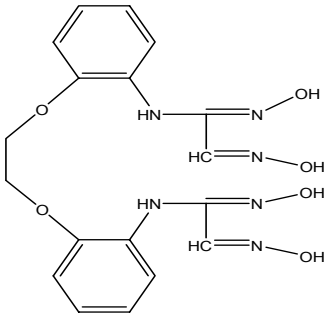
Synthesis of L^1 and L^2

A solution 1,2-bis(o-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 ºC 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 ^{1}H-NMR peaks (DMSO-d_6; δ, ppm; 300 MHz): 4.72-4.24 (m, 4H, O-CH_2), 8.54, 8.13 (s, 2H, H-C=N), 12.08, 11.36, 10.82, 10.14 (s, 4H, N-OH), 6.44, 6.19 (s, 2H, N-H), 7.21-6.67 (m, 8H, C-$H_{(Ar.)}$) [4].

L^2 was synthesized and characterized as described in the literature [6,27-31].



L^1



L^2

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

Synthesis of the Cu(II), Ni(II), Co(II) and Cd(II) complexes of L^2

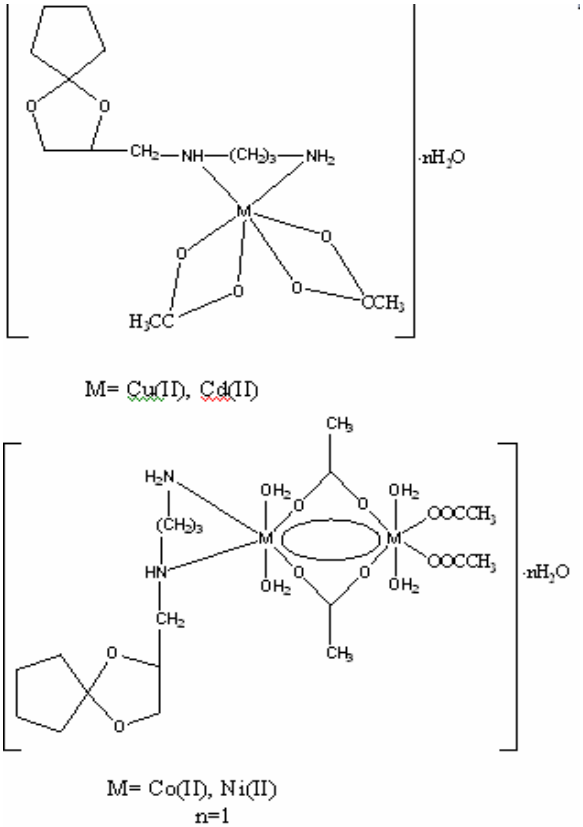


Fig. 2**:** Structures of the distorted octahedral Cu(II), Ni(II), Co(II) and Cd(II) complex of the 6,7-O-cyclopentlydine-1-amino-4-azaheptane (L^2).

Cu(II), Ni(II), Co(II) and Cd(II) complexes of L^2 was synthesized and characterized as described in the literature [6,27].

Synthesis of $[L^1M_2L^2{}_2(OH)_4]\cdot nH_2O$ complexes (M: Cu(II), Ni(II), Co(II) and Cd(II) and n: 3,3,3,5)

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 L^1, (0.21 g, 0.5 mmol) in EtOH (50 cm^3) at 60-65 °C 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 color powder. These compounds are little soluble in DMF and DMSO, and insoluble water and ethanol.

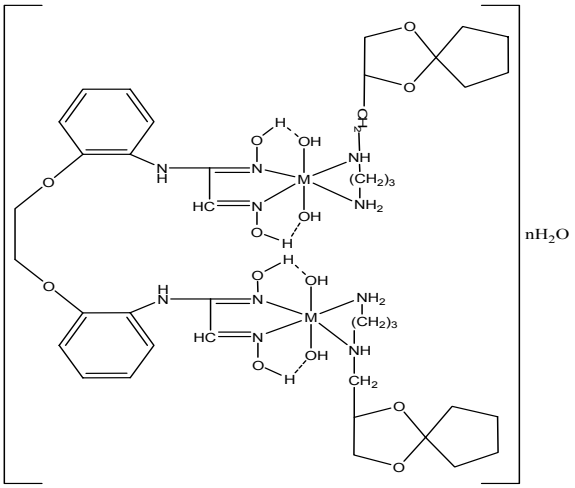


Fig. 3: Proposed suggested structure of the octahedral $[L^1M_2L^2{}_2(OH)_4]\cdot nH_2O$ (M: Cu(II), Ni(II), Co(II) and Cd(II)).

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