

μ -Acetato / μ -Aqua Bridged Binuclear *Vic*-Dioxime Complexes Thermal, Magnetic and Spectral Studies

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Summary: A new amino *vic*-dioxime ligand, N,N'-[3,3'-{ethane-1,2-di-yl-bis(oxy)bis(3,1-phenylene)}bis(N'-hydroxy-)-2-(hydroxyimino)-acetimidamide] (LH₄) was synthesized by reaction of 1,2-bis(m-aminophenoxy)ethane and *anti*-chloroglyoxime. Then, its Cu(II), Ni(II), Co(III) and Cd(II) complexes were synthesized by the ligand and Cu(AcO)₂·H₂O, Ni(AcO)₂·4H₂O, Co(AcO)₂·4H₂O and Cd(AcO)₂ metal salts, respectively. The ligand and its metal complexes were characterized by elemental analysis, FT-IR, ¹H-NMR, UV-vis spectra, magnetic measurements and thermal analysis (TGA-DTA) techniques. All complexes were diamagnetic and binuclear. The Co(II) complex was oxidized to Co(III). While suggested structures of Cu(II) and Ni(II) complexes were found as square-planar, Co(III) and Cd(II) complexes were found as octahedral geometries.

Keywords: Amino *vic*-dioxime ligand, *anti*-chloroglyoxime, Thermal analysis.

Introduction

A significant interest in coordination chemistry has been devoted to the interaction of a central atom with surrounding atoms, ions or molecules. Coordination compounds containing *vic*-dioxime ligands have been known since the beginning of the last century; the chemistry of transition metal complexes with *vic*-dioxime ligands has been studied in detail and has been the subject of several reviews [1, 2]

Vic-dioximes have a high tendency to form isomers. When the molecule is formally symmetrical, three forms are possible; *syn*-, *anti*- and *amphi*-. The *amphi*-isomers are known to react with Ni(II), but their complexes have not been well characterized until recently, metal-ligand ratio 2:2 has been reported [2, 3] The dioxime *anti*-isomers are responsible for the formation of brightly colored chelate derivatives with nickel and the other transition metal ions [4]. Especially, the *anti*-isomer gives blood-red complexes with nickel ions. The substitution pattern of the *vic*-dioxime moiety affects the structure and the stability of the complexes, *e.g.*, Co(II) complexes of dialkyl- or diaryl-glyoximes can be obtained by reducing Co(III) compounds [2-5] but the complexes decompose in the case of diaminoglyoxime derivatives [6].

In this paper, we now report that the synthesis and characterization of this N,O-type substituted amino *vic*-dioxime and its μ -acetato / μ -aqua bridged binuclear complexes with Cu(II), Ni(II), Co(III) and Cd(II).

Experimental

Material and Methods

The preparation of 1,2-bis(m-aminophenoxy)ethane [7] and *anti*-chloroglyoxime [8] had been previously described. All the reagents 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. FT-IR spectra were recorded on a Perkin Elmer Precisely Spectrum One Spectrometer as KBr pellets. ¹H-NMR spectra were recorded on a Bruker GmbH DPX-300 MHz High Performance Digital FT-NMR spectrometers (in DMSO-d₆). 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 [9]. Melting points were determined on a Gallenkamp melting points apparatus. TGA and DTA curves were recorded on a Shimadzu DTG-60AH and DSC-60A thermo balance, respectively.

Synthesis of N,N'-[3,3'-{ethane-1,2-di-yl-bis(oxy)bis(3,1-phenylene)}bis(N'-hydroxy-)-2-(hydroxyimino) acetimidamide] (LH₄)

A solution 1,2-bis(m-aminophenoxy)ethane (2.44 g, 0.01 mol) was added to a solution of *anti*-

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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 drop wise to this mixture at 60°C over 12 h., the mixture filtered, and ethanol was removed by evaporation. The solid product was filtered off, washed with H_2O several times, dried in vacuum, and crystallized from diethyl ether. The compound was found to be soluble in DMF and DMSO and insoluble in chloroform, acetone, ethyl acetate, diethyl ether, and water [2, 10, 11].

Spectral Characterization of Ligand, LH_4

Characteristic IR bands (KBr , cm^{-1}): 3370 $\nu(\text{OH})$, 3203 $\nu(\text{N-H})$, 3065 $\nu(\text{C-H})_{\text{arom}}$, 2930-2857 $\nu(\text{C-H})_{\text{aliph}}$, 1593 $\nu(\text{C=N})$, 1494 $\nu(\text{C=C})_{\text{arom}}$, 1375 $\nu(\text{C-N})$, 1259 $\nu(\text{C}_{\text{arom}}-\text{O}-\text{C})$, 1078 $\nu(\text{N-O})$, 690 $\nu(\text{m-subst.})$. Characteristic UV-Vis spectra (λ_{max} , nm, ϵ): 260 (17868), 400 (5444). Characteristic $^1\text{H-NMR}$ peaks (DMSO-d_6 ; δ , ppm; 300 MHz): 4.27-4.15 (m, 4H, O-CH_2), 8.27, 7.96 (s, 2H, H-C=N), 11.92, 11.45, 10.89, 10.07 (s, 4H, N-OH), 6.49, 6.11 (s, 2H, N-H), 7.32-6.76 (m, 8H, $\text{C-H}_{(\text{Ar.})}$).

Synthesis of the $[\text{Cu}_2(\text{LH}_2)_2]\cdot 2\text{H}_2\text{O}$, $[\text{Ni}_2(\text{LH}_2)_2]\cdot \text{H}_2\text{O}$, $[\text{Co}_2(\text{LH}_2)_2(\text{AcO})_2]$ and $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ Complexes

The ligand LH_4 (0.35 g, 0.40 mmol) was dissolved in absolute ethanol (5ml). Solutions of metal salts $\text{Cu}(\text{AcO})_2\cdot \text{H}_2\text{O}$ (0.08 g, 0.40 mmol), $\text{Ni}(\text{AcO})_2\cdot 4\text{H}_2\text{O}$ (0.09 g, 0.40 mmol), $\text{Co}(\text{AcO})_2\cdot 4\text{H}_2\text{O}$ (0.09 g, 0.40 mmol), $\text{Cd}(\text{AcO})_2$ (0.09 g, 0.40 mmol) in absolute ethanol (5 mL) were added drop wise to the ligand solution with continuous stirring at 50°C . The color of the solutions immediately changed. The reaction mixtures were stirred at this temperature for 2 h and filtered, on the precipitate was washed with water, ethanol and diethyl ether and dried in vacuum at 60°C [10].

Spectral Characterization of Complexes

Characteristic IR bands for $\text{Cu}(\text{II})$ complex (KBr , cm^{-1}): 3346 $\nu(\text{H}_2\text{O}/\text{OH})$, 3211 $\nu(\text{N-H})$, 1664 $\nu(\text{O-H}\cdots\text{O})$, 1596 $\nu(\text{C=N})$, 1061 $\nu(\text{N-O})$, 466 $\nu(\text{M-O})$. Characteristic $^1\text{H-NMR}$ peaks (DMSO-d_6 ; δ , ppm; 300 MHz) for $[\text{Cu}_2(\text{LH}_2)_2]\cdot 2\text{H}_2\text{O}$: 4.42-4.15 (m, 8H, O-CH_2), 8.62, 8.31, 8.12, 7.97 (s, 4H, H-C=N), 6.51, 6.23 (d, $J = 84$, 4H, N-H), 7.73-6.77 (m, 16H, $\text{C-H}_{(\text{Ar.})}$), 15.03 (s, 2H, $\text{O-H}\cdots\text{O}$). Characteristic UV-Vis spectra (λ_{max} , nm, ϵ) for $\text{Cu}(\text{II})$ complex: 800 (1575), 318 (18200), 262 (20000). Characteristic IR bands for $\text{Ni}(\text{II})$ complex (KBr , cm^{-1}): 3368 $\nu(\text{H}_2\text{O}/\text{OH})$, 3207 $\nu(\text{N-H})$, 1676 $\nu(\text{O-H}\cdots\text{O})$, 1599

$\nu(\text{C=N})$, 1062 $\nu(\text{N-O})$, 452 $\nu(\text{M-O})$. Characteristic UV-Vis spectra (λ_{max} , nm, ϵ) for $\text{Ni}(\text{II})$ complex: 420 (5717), 304 (12750), 267 (18350). Characteristic $^1\text{H-NMR}$ peaks (DMSO-d_6 ; δ , ppm; 300 MHz) for $[\text{Ni}_2(\text{LH}_2)_2]\cdot 1.5\text{H}_2\text{O}$: 4.58-4.17 (m, 8H, O-CH_2), 8.87, 8.25, 8.13 7.92 (s, 4H, H-C=N), 6.50, 6.17 (d, $J = 99$, 4H, N-H), 7.58-6.67 (m, 16H, $\text{C-H}_{(\text{Ar.})}$), 14.92 (s, 2H, $\text{O-H}\cdots\text{O}$). Characteristic IR bands for $\text{Co}(\text{III})$ complex (KBr , cm^{-1}): 3362 $\nu(\text{H}_2\text{O}/\text{OH})$, 3208 $\nu(\text{N-H})$, 1679 $\nu(\text{O-H}\cdots\text{O})$, 1596 $\nu(\text{C=N})$, 1062 $\nu(\text{N-O})$, 1530 $\nu_{\text{uns}}(\text{COO}^-)$, 1344 $\nu_{\text{s}}(\text{COO}^-)$, 450 $\nu(\text{M-O})$. Characteristic UV-Vis spectra (λ_{max} , nm, ϵ) for $\text{Co}(\text{III})$ complex: 494 (1765), 424 (1665), 314 (150000) 268 (10333). Characteristic IR bands for $\text{Cd}(\text{II})$ complex (KBr , cm^{-1}): 3367 $\nu(\text{H}_2\text{O}/\text{OH})$, 3208 $\nu(\text{N-H})$, 1646 $\nu(\text{O-H}\cdots\text{O})$, 1599 $\nu(\text{C=N})$, 1061 $\nu(\text{N-O})$, 455 $\nu(\text{M-O})$. Characteristic UV-Vis spectra (λ_{max} , nm, ϵ) for $\text{Cd}(\text{II})$ complex: 426 (4415), 369 (46880), 319 (19000), 259 (19667). Characteristic $^1\text{H-NMR}$ peaks (DMSO-d_6 ; δ , ppm; 300 MHz) for $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$: 4.42-4.02 (m, 8H, O-CH_2), 8.25, 8.06, 7.92, 7.54 (s, 4H, H-C=N), 6.37, 6.08 (d, $J = 87$, 4H, N-H), 7.30-6.50 (m, 16H, $\text{C-H}_{(\text{Ar.})}$), 14.75 (s, 2H, $\text{O-H}\cdots\text{O}$).

Results and Discussion

The data on the ligand and complexes are summarized in Tables 1-3. Attempts to crystallize the ligand complexes from different solvents were failure. The novel ligand, $\text{N,N}'\text{-}[3,3'\text{-}\{\text{ethane-1,2-di-yl-bis(oxy)bis(3,1-phenylene)}\}\text{bis}(\text{N}'\text{-hydroxy)-2-(hydroxyimino)-acetimidamide}]$ (LH_4) was synthesized by the condensation of 1,2-bis(m-aminophenoxy)ethane and *anti*-chloroglyoxime (Fig. 1).

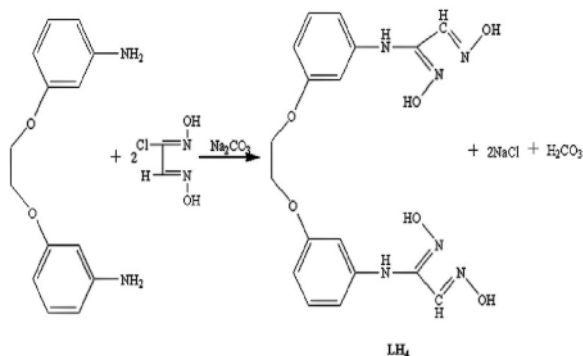


Fig. 1: The synthesis of ligand: $\text{N,N}'\text{-}[3,3'\text{-}\{\text{ethane-1,2-di-yl-bis(oxy)bis(3,1-phenylene)}\}\text{bis}(\text{N}'\text{-hydroxy)-2-(hydroxyimino)-acetimidamide}]$ (LH_4).

Table-1: Analytical and physical data on the LH₄ and its complexes.

Compounds	Empirical Formula	F.W., g/mol	Color	M.p., °C	Yield, %	Contents (Cal./found), %		
						C	H	N
LH ₄	C ₁₈ H ₂₀ N ₆ O ₆	416.39	Dark yellow	110 ^d	82.77	51.92/51.54	4.84/5.08	20.18/19.87
[Cu ₂ (LH ₂) ₂]-2H ₂ O	Cu ₂ C ₃₆ H ₃₈ N ₁₂ O ₁₄	987.94	Black	125 ^d	62.01	43.68/43.29	3.87/4.11	16.98/16.69
[Ni ₂ (LH ₂) ₂]-H ₂ O	Ni ₂ C ₃₆ H ₃₆ N ₁₂ O ₁₃	961.38	Tile red	140 ^d	98.36	44.93/44.59	3.74/4.12	17.47/17.53
[Co ₂ (LH ₂) ₂ (AcO) ₂]	Co ₂ C ₄₀ H ₄₀ N ₁₂ O ₁₆	1062.68	Dark blue	340 ^d	78.61	45.21/45.50	3.79/4.16	15.82/15.95
[Cd ₂ (LH ₂) ₂ (H ₂ O) ₂]-2H ₂ O	Cd ₂ C ₃₆ H ₄₂ N ₁₂ O ₁₆	1123.61	Light yellow	240 ^d	63.47	38.48/38.17	3.77/3.65	14.96/14.62

d: decomposition

Table-2: TGA data of Cu(II), Ni(II), Co(III) and Cd(II) complexes of LH₄.

Complexes	Step 1	Step 2	Step 3	Weight	Residue, %
[Cu ₂ (LH ₂) ₂]-2H ₂ O	43.75-168.75	168.75-581.25	—	52.53 (51.85)	47.47/48.15
[Ni ₂ (LH ₂) ₂]-H ₂ O	25.00-137.50	137.50-818.75	—	52.57 (51.84)	47.43/48.16
[Co ₂ (LH ₂) ₂ (AcO) ₂]	—	118.75-362.50	362.50-912.50	48.33 (48.88)	51.67/51.12
[Cd ₂ (LH ₂) ₂ (H ₂ O) ₂]-2H ₂ O	43.70-150.00	150.00-368.75	368.75-743.75	49.46 (50.36)	50.54/49.64

Table-3: DTA data of Cu(II), Ni(II), Co(III) and Cd(II) complexes of LH₄.

Complexes	Endo peaks (°C)	Exo peaks (°C)
[Cu ₂ (LH ₂) ₂]-2H ₂ O	168.75, 218.75	225.00, 415.63
[Ni ₂ (LH ₂) ₂]-H ₂ O	81.25, 193.75	137.50, 268.75, 331.25, 387.50, 737.50
[Co ₂ (LH ₂) ₂ (AcO) ₂]	806.25	200.00, 393.75
[Cd ₂ (LH ₂) ₂ (H ₂ O) ₂]-2H ₂ O	321.88, 725.00	212.50, 325.00

The ligand and its complexes were characterized by elemental analysis, FT-IR, ¹H-NMR, UV-vis spectroscopy, thermogravimetric analyses (TGA), differential analyses (DTA) and magnetic susceptibility.

The elemental analysis of LH₄ and its Cu(II), Ni(II), Co(III) and Cd(II) complexes are in agreement with theoretical expectations (Table-1). The analytical and physical data show a metal to ligand ratio of 2:2 for all complexes. The reaction of the ligand with Cu(II), Ni(II), Co(III) and Cd(II) acetate salts yield complexes corresponding to the formulas: [Cu₂(LH₂)₂]-2H₂O, [Ni₂(LH₂)₂]-H₂O, [Co₂(LH₂)₂(AcO)₂] and [Cd₂(LH₂)₂(H₂O)₂]-2H₂O.

IR Spectra

The characteristic IR data of the N,O-type substituted amino *vic*-dioxime (LH₄) and its metal complexes are listed in Experimental Section. IR spectra of free N,O-type substituted amino *vic*-dioxime ligand and its μ -acetato / μ -aqua bridged binuclear complexes are exhibited various bands in the 400-4000 cm⁻¹ region. In the IR spectrum of the ligand (Fig. 3), the most characteristic peaks are appeared around 1078 cm⁻¹ ν (N-O), 1593 cm⁻¹ ν (C=N), 3203 cm⁻¹ ν (N-H), and 3370 cm⁻¹ ν (O-H) (N-H bands are covered by O-H bands) and exhibited stretching frequencies as substituted amino *vic*-dioximes [10-12].

The FT-IR spectrums of complexes (Fig. 4) show four characteristic absorption bands in the ranges of 1062-1061, 1599-1596, 3211-3207, 3368-3346 cm⁻¹ assigned as ν (N-O), ν (C=N), ν (N-H) (broad peak) and ν (H₂O/O-H) (broad peak),

respectively. All complexes were showed very less change for ν (C=N) stretching due to free ligand. At the same time, the N-O band at 1078 cm⁻¹ in the free ligand is shifted to lower frequency by around 16-17 cm after complexation. These results suggest that the ligand is coordinated to metal ions through nitrogen and oxygen donor [13]. Moreover, another new absorption band as different from ligand peaks at the region of 1679-1646 cm⁻¹ is attributed to ν (O-H...O). Two acetate ions are coordinated to Co(III) metal ions while two water molecules are coordinated to Cd(II) metal ions. Additionally, the spectrum, shown in Fig. 4c, also reveals the peak at 1530 cm⁻¹ is associated with the C-O unsymmetrical mode and the peak at 1344 cm⁻¹ represents the C-O symmetrical mode of the coordinating acetate carbons chain to Co(III) complex. The $\Delta\nu = 186$ cm⁻¹ can be thought as evidence for the existence of a bridging bidentate acetate groups in this complex **Error! Bookmark not defined.**[14]. In addition, a broad band centered at 2232 cm⁻¹ is observed in the FT-IR spectra of Cd(II) complex (Fig. 4d) and attributed to the asymmetric O-H stretching of the bridging water [15]. At the same time, the absorption peak at 850 cm⁻¹, shown in Fig. 4d, represents ν (M-H₂O) of the coordinating water molecules to the Cd(II) metal ions. In addition to, another new band is observed in the spectrum of the all complexes in the regions 450-466 cm⁻¹, which is assigned to ν (M-O) stretching vibrations. The absorption bands at 518-524 cm⁻¹ have been indicated to presence of ν (M-N) mode [16]. So, the geometric structures were suggested that as distorted square-planar for [Cu₂(LH₂)₂]-2H₂O, square-planar for [Ni₂(LH₂)₂]-1.5H₂O, octahedral for [Co₂(LH₂)₂(OAc)₂] and [Cd₂(LH₂)₂(H₂O)₂]-2H₂O (Fig. 2).

¹H-NMR Spectra

¹H-NMR spectral data of the [Cu₂(LH₂)₂].2H₂O, [Ni₂(LH₂)₂].H₂O and [Cd₂(LH₂)₂(H₂O)₂].2H₂O complexes and free N,O-type substituted amino *vic*-dioxime ligand (LH₄) are set in the Experimental Section and the representative spectra are shown in Fig. 5a. The ¹H-NMR spectrum is taken from DMSO-d₆. In the ¹H-NMR spectrum of the LH₄, the calculated 4 protons for O-CH₂ of LH₄ appear in the range δ 4.27-4.15 ppm as partially overlapping signals due to similar chemical shifts of many protons. The two singlets corresponding to the N=C-H proton is observed near δ 8.27 and 7.96 ppm. The other proton signals of LH₄ appear at δ 11.92,

11.45, 10.89 and 10.07 (N-OH, singlet), δ 6.49 and 6.11 (N-H, singlet) and δ 7.32-6.76 ppm (C-H_(Ar.), multiplet), respectively. The coordinated O-H...O protons of [Cu₂(LH₂)₂].2H₂O, [Ni₂(LH₂)₂].H₂O and [Cd₂(LH₂)₂(H₂O)₂].2H₂O are seen at δ 15.03, 14.92 and 14.75 ppm as singlet, respectively. Four singlets (H-C=N) at δ 8.62, 8.31, 8.12, 7.97 for [Cu₂(LH₂)₂].2H₂O, δ 8.87, 8.25, 8.13, 7.92 for [Ni₂(LH₂)₂].1.5H₂O and δ 8.25, 8.06, 7.92, 7.54 ppm for [Cd₂(LH₂)₂(H₂O)₂].2H₂O show as Fig. 2 proposed structures in presence of the amino *vic*-dioxime moiety in the complexes (Fig. 5b-d). At this time, since Co(III) complex could not be soluble in DMSO-d₆, ¹H-NMR spectra of the Co(III) complex could not be taken clearly.

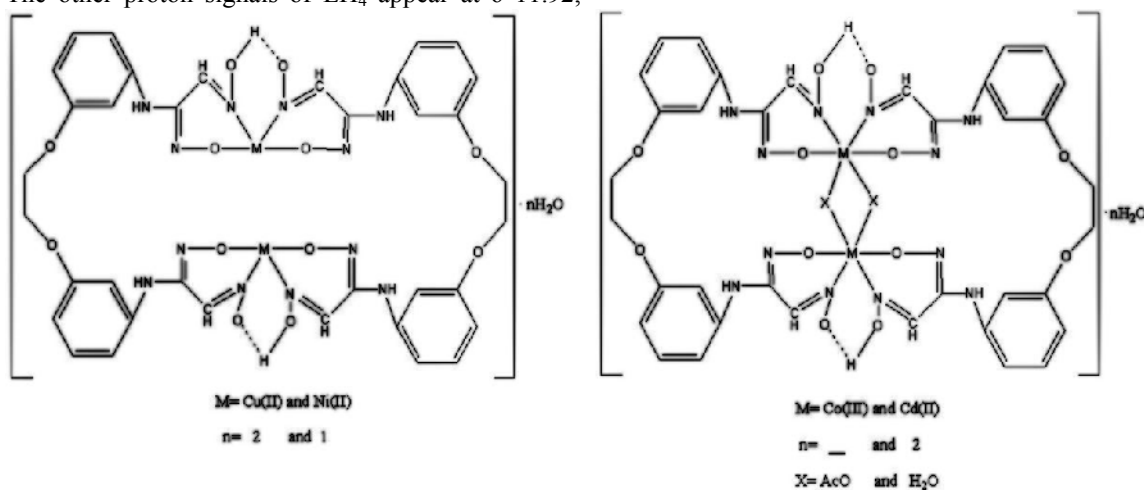


Fig. 2: Suggested structure of the square-planar Cu(II) and Ni(II), and octahedral Co(III) and Cd(II) complexes of LH₄.

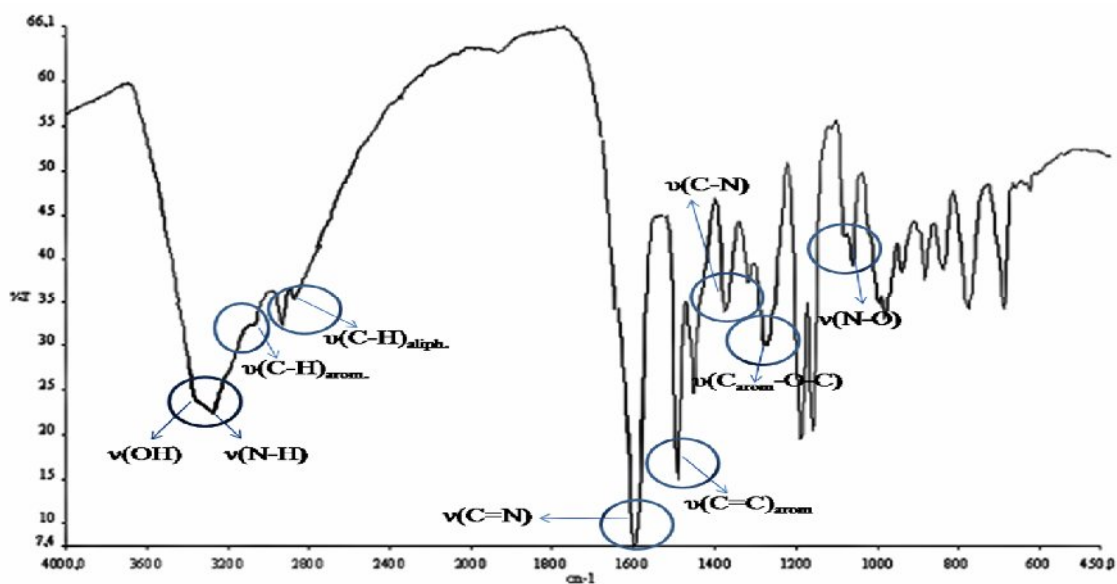


Fig. 3: FT-IR spectra of LH₄.

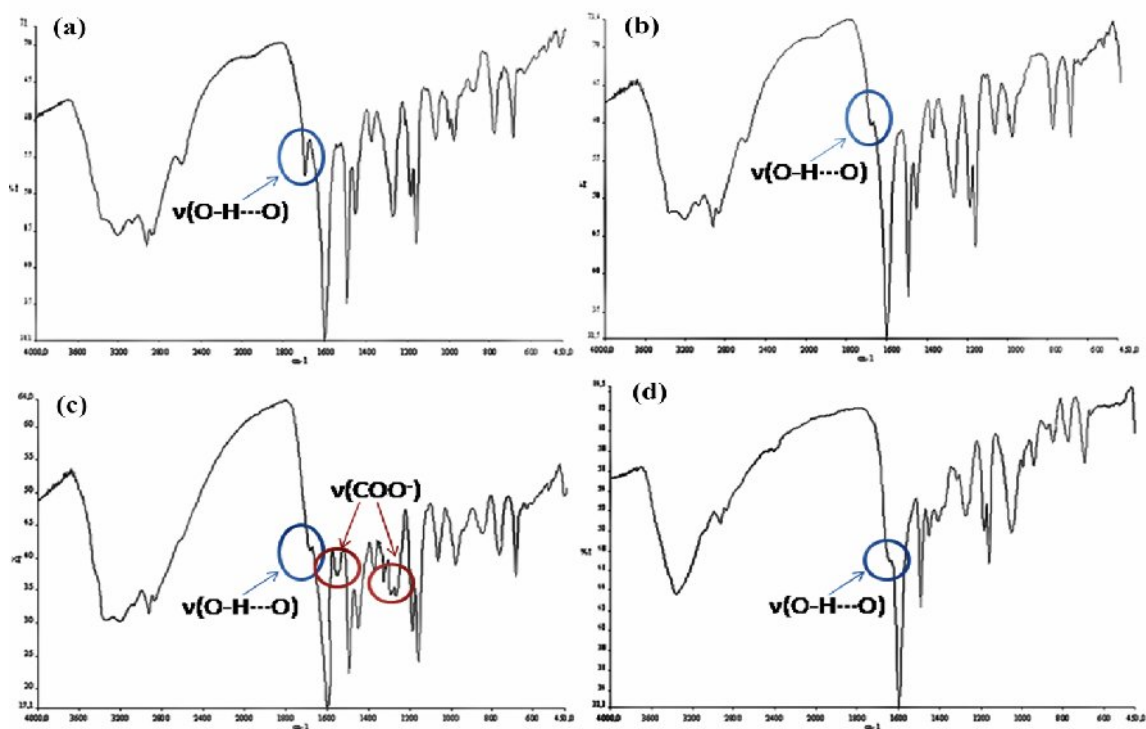


Fig. 4: FT-IR spectra of (a) $[\text{Cu}_2(\text{LH}_2)_2] \cdot 2\text{H}_2\text{O}$, (b) $[\text{Ni}_2(\text{LH}_2)_2] \cdot \text{H}_2\text{O}$, (c) $[\text{Co}_2(\text{LH}_2)_2(\text{OAc})_2]$, (d) $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.

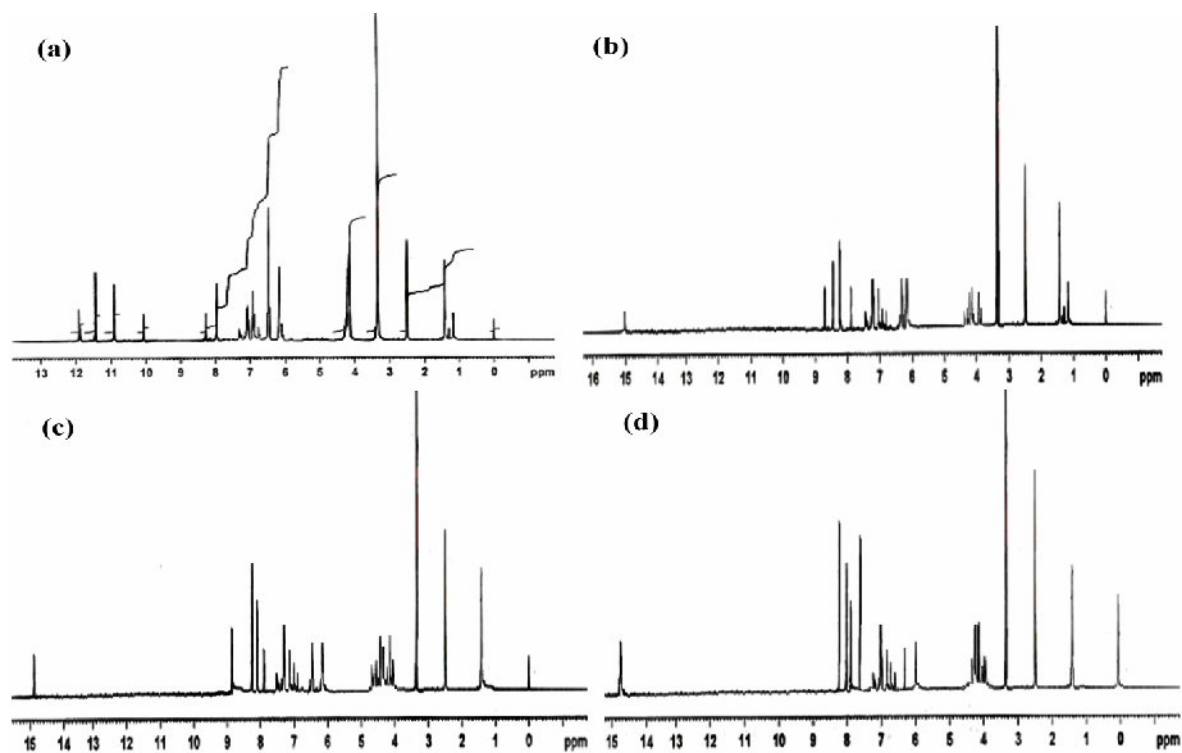


Fig. 5: ^1H -NMR spectra of (a) LH_4 , (b) $[\text{Cu}_2(\text{LH}_2)_2] \cdot 2\text{H}_2\text{O}$, (c) $[\text{Ni}_2(\text{LH}_2)_2] \cdot \text{H}_2\text{O}$, (d) $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.

The observed room-temperature magnetic moment values for all of complexes are found diamagnetic. Co^{2+} is oxidized to Co^{+3} complex by O_2 in air [16, 17].

Electronic Spectra and Magnetic Susceptibility

As observed in Fig. 6, UV-Vis spectra of LH_4 and complexes were recorded in DMSO or DMF solution in the range from 250 to 1100 nm. Based on Fig. 6, UV-Visible spectrum of free ligand contains two prominent absorption bands at 260 and 400 nm. As observed in Fig. 6, UV-visible spectra of complexes contain an absorption band at 259-268 and 304-319 nm while one other band of ligand at the region of 400 nm are shifted until to max. 800 nm. Complexation changes the ligand geometry to a large extent, in particular for N,O-type substituted amino *vic*-dioxime ligand. The UV region strong transitions are believed to originate from the intraligand $\pi\text{-}\pi^*/n\text{-}\pi^*$ transitions. The intense band in the range 369-426 nm may be considered as an oxime-based MLCT or LMCT transition. Therefore, the introduction of -N and -O units in the N,O-type substituted amino *vic*-dioxime framework of all complexes enhances the energy gap between the donor and acceptor levels.

The observed magnetic moment of the $[\text{Cu}_2(\text{LH}_2)_2]\cdot 2\text{H}_2\text{O}$ complex is diamagnetic. This stage may be the result of dimerization and strong interaction with the neighboring molecule or subsequent antiferromagnetic exchange between the Cu(II) ions [18, 19]. The electronic spectrum of this complex shows a shoulder at 800 nm assignable to d-d transition of the metal ions (Fig. 6a), suggesting a

distorted square-planar geometry around the Cu(II) ions [20, 21].

The magnetic moment of the $[\text{Ni}_2(\text{LH}_2)_2]\cdot \text{H}_2\text{O}$ complex is diamagnetic. This stage may be the result of dimerization and strong interaction with the neighboring molecule [22]. This electronic spectrum of this complex has one absorption band at 420 nm, assigned to the ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ transition (Fig. 6b), suggesting a square planar geometry [23-26].

The electronic spectrum of the $[\text{Co}_2(\text{LH}_2)_2(\text{AcO})_2]$ complex has two adsorption bands at 424 and 494 nm attributable to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ transitions (Fig. 6c). This complex is diamagnetic; indicating a low-spin octahedral configuration [27].

A presumably octahedral structure is suggested for the diamagnetic $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ complex [22]. The electronic spectrum of this complex shows a broad absorption band at 369-426 nm (Fig. 6d), which is attributed to the charge transfer transition from the ligand to metal ion (L \rightarrow M) [Error! Bookmark not defined., Error! Bookmark not defined.].

Thermal Studies

The thermal behavior of the complexes was studied at a heating rate of 10 K/min. in a nitrogen atmosphere over a temperature range of 20.00-1000.00°C (Fig. 7).

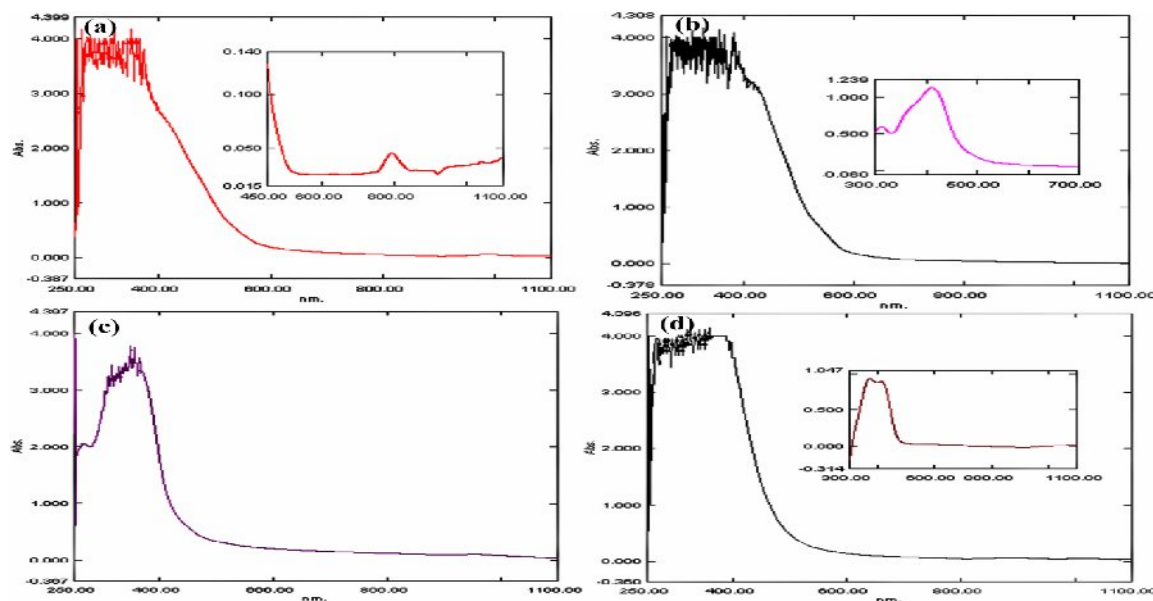


Fig. 6: UV-vis spectra of a) $[\text{Cu}_2(\text{LH}_2)_2]\cdot 2\text{H}_2\text{O}$, b) $[\text{Ni}_2(\text{LH}_2)_2]\cdot \text{H}_2\text{O}$, c) $[\text{Co}_2(\text{LH}_2)_2(\text{OAc})_2]$, d) $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$

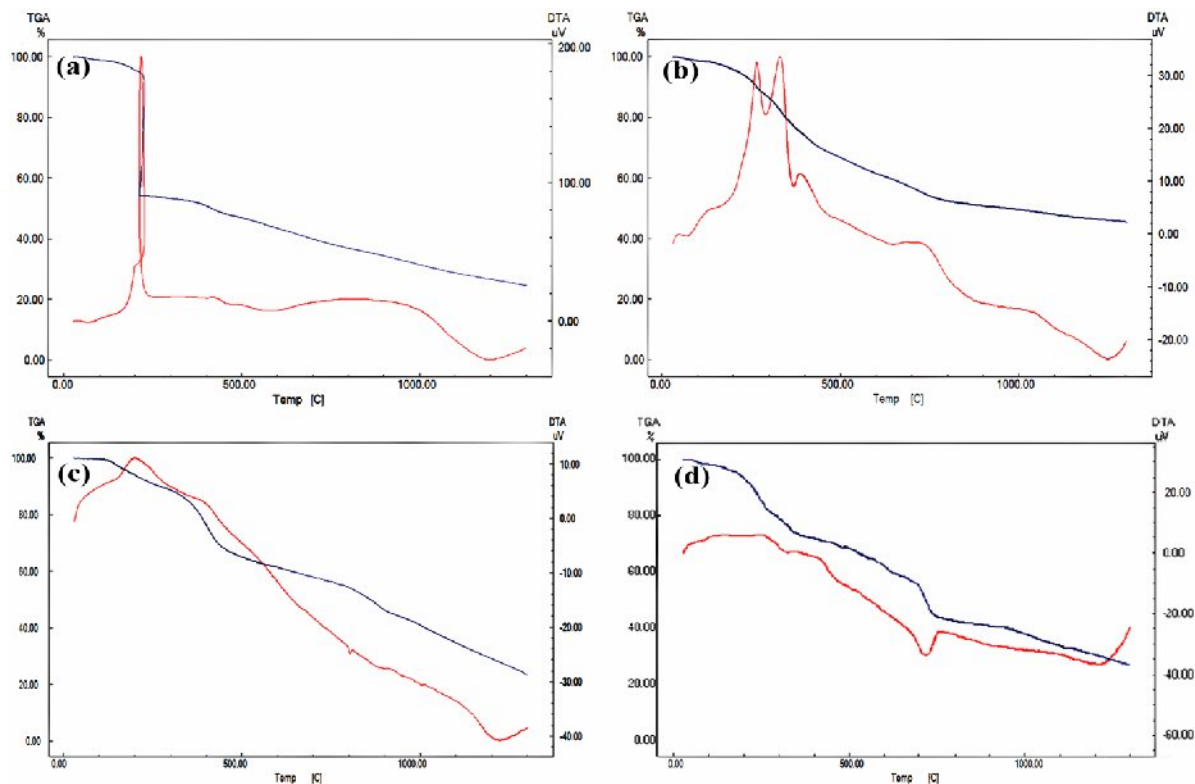


Fig. 7: TGA and DTA curves of a) $[\text{Cu}_2(\text{LH}_2)_2] \cdot 2\text{H}_2\text{O}$, b) $[\text{Ni}_2(\text{LH}_2)_2] \cdot \text{H}_2\text{O}$, c) $[\text{Co}_2(\text{LH}_2)_2(\text{OAc})_2]$, d) $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.

The decomposition temperature and weight losses of the complexes were calculated from the TGA data (Table-2). It may be seen from the TGA data that the complexes decompose in two or three steps at different temperature ranges. The DTA data (Table-3) shows that $[\text{Cu}_2(\text{LH}_2)_2] \cdot 2\text{H}_2\text{O}$, $[\text{Co}_2(\text{LH}_2)_2(\text{OAc})_2]$ and $[\text{Cd}_2(\text{LH}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complexes have two exothermic peaks while $[\text{Ni}_2(\text{LH}_2)_2] \cdot \text{H}_2\text{O}$ complex has five exothermic peaks. As observed in Table-3, all complexes have also endothermic peaks. In the TGA curves of Cu(II), Ni(II) and Cd(II) complexes, 3.64%, 2.78% and 3.20% weight losses are observed at 168.75, 137.50 and 150.00°C, respectively. The Co(III) complex has not crystal water. These results show that Cu(II), Ni(II), Co(III) and Cd(II) have 2.0, 1.5, 0 and 2.0 mole of crystal water per molecule, respectively. The IR spectra of the all complexes are characterized by the appearance of a broad band in the region of 3346-3368 cm^{-1} due to the $\nu(\text{OH})$ of water of crystallization [28, 29]. Also, these crystal water molecules were 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. All of these

complexes could not complete decomposition until at 1000°C temperature.

Conclusion

A new N,O-type substituted amino *vic*-dioxime ligand was synthesized, characterized by advance techniques and used for the complexation with some transition metal salts. The functional groups (N,O) of *vic*-dioxime were found to be effective on complexation. Also, these functional groups such as phenyl groups join into the binuclear complexation. Obtained results shown that geometries of Cu(II) and Ni(II) complexes are square-planar, Co(III) and Cd(II) complexes are octahedral. However, it was found that Co(III) and Cd(II) complexes contain μ -acetato and μ -aqua bridges, respectively, coordinating to binuclear structure. These results clearly indicate that N,O-type substituted amino *vic*-dioxime and its μ -acetato / μ -aqua bridged binuclear complexes with Cu(II), Ni(II), Co(III) and Cd(II) are an important contribution to literature.

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