

The synthesis and characterization of some new vic-dioximes and their transition metal complexes

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Abstract In this study, three new *vic*-dioximes, [L¹H₂], N-(5-chloro-2-methoxyphenyl)amino-1-acetyl-1-cyclohexenylglyoxime, [L²H₂], N-(3-chloro-4-methoxyphenyl)amino-1-acetyl-1-cyclohexenylglyoxime and [L³H₂], N-(3-chloro-2-methoxyphenyl)amino-1-acetyl-1-cyclohexenylglyoxime were synthesized from 1-acetyl-1-cyclohexenylglyoxime and the corresponding substituted aromatic amines. Metal complexes of these ligands were also synthesized with Ni(II), Cu(II) and Co(II) salts. The structures of these new compounds (ligands and complexes) were characterized with FT-IR, magnetic susceptibility measurement, molar conductivity measurements, mass spectrophotometer measurements, thermal methods (TGA), ¹H NMR and ¹³C NMR spectral data and elemental analyses.

Keywords *vic*-Dioximes · Ligands · Ni(II) · Cu(II) and Co(II) complexes

Introduction

One of the major interests in coordination chemistry is to study the interaction of a central atom with surrounding atoms, ions or molecules. *Vic*-dioximes, have a great importance since they are used as chelating agents because they form stable complexes with transition metals, also they have been widely studied as analytical reagents [1, 2]. Various *vic*-dioximes and their metal complexes have been reported [3–10]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make *vic*-dioximes

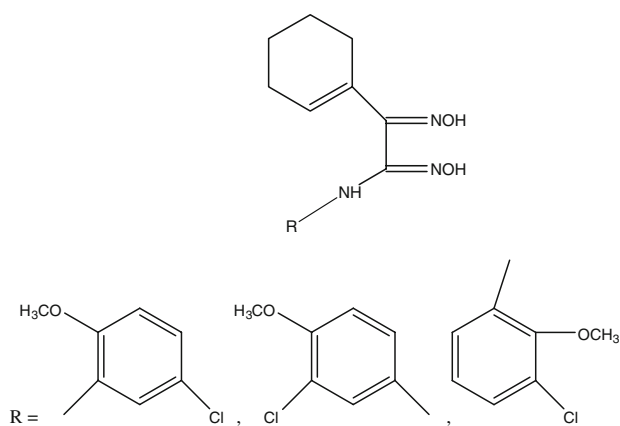
amphoteric ligands that form corrin-type, square planar, square pyramidal and octahedral complexes with transition metal ions such as Ni(II), Cu(II), Co(II) and Co(III) as central atoms [10]. Transition metal complexes of *vic*-dioximes have been of particular interest in biological model compounds and have been investigated extensively for their similarity with vitamin B₁₂ [3, 4].

In recently reviewed data shows that oximes, (although being classical ligands) display a variety of reactivity modes unusual even for the coordination chemistry [11–14]. The study of the exchange interaction between paramagnetic metal centers through polyatom bridges has been one of the most interesting research areas in coordination chemistry, the goal being to understand basic factors governing the magnetic properties of transition metal complexes and to find appropriate systems applicable to the improvement of design of new materials [15]. One of the best strategies for designing and preparing polynuclear species is to use mononuclear complexes as ligands containing potential donor sites for another metal ion [16]. In the present work, I synthesized three new unsymmetric ligands and their complexes with Ni(II), Cu(II) and Co(II) metal ions; spectral, magnetic and thermal properties of the new compounds were studied in detail. The molecular structure of ligands and their complexes are given Scheme 1, 2, respectively.

Experimental

Elemental analyses (C, H and N) were realized using Carlo-Erba 1106 model analyzer and analyses for metals were determined using an Emler AAS 700 spectrometer, ¹H NMR and IR spectras were obtained with Bruker 200 MHz spectrometer and Jasco FT/IR-300 instrument, respectively. M.p.s's were measured on an Electrothermal IA 9100 digital

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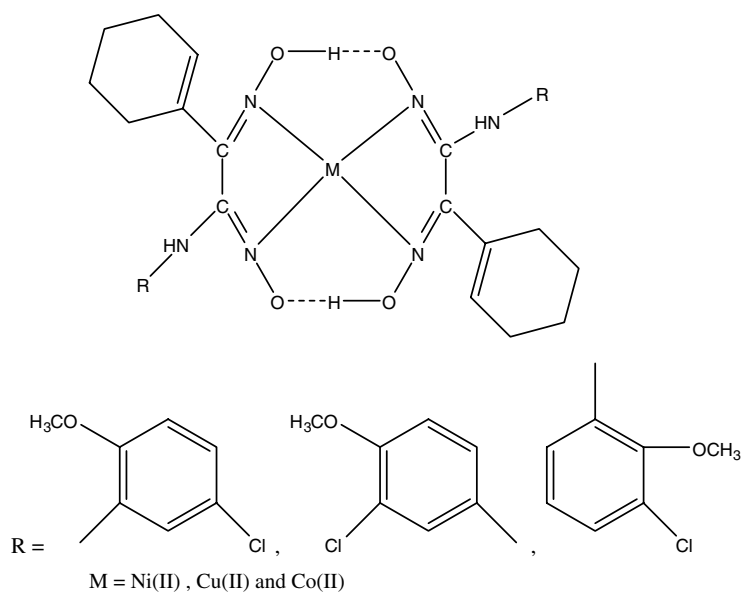
Scheme 1 Ligands formula

melting point apparatus. The pH of the solutions were adjusted and controlled with WTW pH-537 pH meter. Molar conductivity of the ligands and their metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. TGA curves were recorded with Shimadzu TG-50 thermo balance. Mass spectra were recorded with MS 12 mass spectrometer (Kratos) at 70 eV and 220 °C (ion source temperature), with electron impact ionization. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility balance (Model MK1) at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a standard; diamagnetic corrections were calculated from Pascal's constants.

Synthesis

1-acetyl-1-cyclohexene was bought ready made from Sigma. *Anti*-1-acetyl-1-cyclohexenylglyoxime was prepared by reported procedures [17].

Scheme 2 Complexes formula



[*N*-(5-chloro-2-methoxyphenyl), *N*-(3-chloro-4-methoxyphenyl) and *N*-(3-chloro-2-methoxy)amino-1-acetyl-1-cyclohexenylglyoxime]

To 1-acetyl-1-cyclohexene chloroglyoxime (2.025 g, 10 mmol) dissolved in absolute ethanol (50 mL), a solution of freshly distilled 5-chloro-2-methoxyaniline (1.576 g, 10 mmol) and 3-chloro-4-methoxyaniline (1.576 g, 10 mmol), 3-chloro-2-methoxyaniline (1.576 g, 10 mmol) in absolute ethanol (30 mL) were added dropwise at 25 °C with constant stirring. The reaction mixture was further stirred for 2–3 h. at 25 °C. The pH of the solution was adjusted to 4.0–5.0 with 1% KOH solution in ethanol. Ligands were precipitated by the addition of H_2O with continuous stirring. The precipitated ligands was filtered and washed with cold ethanol. The ligands were recrystallized from an ethanol solution and dried in vacuum at 70 °C.

[L^1H_2]: yield: 1.941 g (60.0%). Melting point: 180 °C, color: White. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}$: C, 55.64, H, 5.56, N, 12.98. Found: C, 55.78, H, 5.31, N, 13.27. Selected IR data (KBr, $\nu\text{ cm}^{-1}$): 3415 $\nu(\text{N-H})$, 3350 $\nu(\text{OH})$, 3065 $\nu(\text{C-H}_{\text{Arom}})$, 1655 $\nu(\text{C=N})$, 962 $\nu(\text{NO})$. Selected ^1H NMR (DMSO $-\text{d}_6$; δ ppm): 11.70–11.20 (O–H), 6.50–6.80 (H_{arom}), 8.45 (N–H), 2.20 (CH_2 , 2H). Selected ^{13}C NMR (DMSO $-\text{d}_6$; δ ppm): 140.15, 158.64 (C=N(OH)), 55.02 (OCH_3). Mass spectral data: $m/z = 323.5\text{ M}^+$,

[L^2H_2]: yield: 1.844 g (57.0%). Melting point: 185 °C, color: White. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}$: C, 55.64, H, 5.56, N, 12.98. Found: C, 55.32, H, 5.32, N, 12.78. Selected IR data (KBr, $\nu\text{ cm}^{-1}$): 3417 $\nu(\text{N-H})$, 3350 $\nu(\text{OH})$, 3072 $\nu(\text{C-H}_{\text{Arom}})$, 1664 $\nu(\text{C=N})$, 970 $\nu(\text{NO})$. Selected ^1H NMR (DMSO $-\text{d}_6$; δ ppm): 11.50–11.10 (O–H),

6.60–6.80 (H_{arom}), 8.51 (N–H), 2.22 (CH_2 , 2H). Selected ^{13}C NMR (DMSO $-d_6$; δ ppm): 141.25, 158.75 (C=NOH), 55.25 (OCH_3). Mass spectral data: $m/z = 323.5 \text{ M}^+$,

[L^3H_2]: yield: 1.779 g (55.0%). Melting point: 195 °C, color: White Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}$: C, 55.64, H, 5.56, N, 12.98. Found: C, 55.11, H, 5.72, N, 12.71. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3400 $\nu(\text{N-H})$, 3345 $\nu(\text{OH})$, 3068 $\nu(\text{C-H}_{\text{Arom}})$, 1651 (C=N), 965 $\nu(\text{NO})$. Selected ^1H NMR (DMSO $-d_6$; δ ppm): 11.60–11.20 (O–H), 6.50–6.90 (H_{arom}), 8.38 (N–H), 2.24 (CH_2 , 2H). Selected ^{13}C NMR (DMSO $-d_6$; δ ppm): 141.10, 158.15 (C=NOH), 54.15 (OCH_3). Mass spectral data: $m/z = 323.5 \text{ M}^+$,

[Ni(L^1H_2) $_2$]

A solution of metal salts $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.4756 g, 2.0 mmol), dissolved in 60 mL absolute ethanol were added to a stirred solution of ligands L^1H_2 (1.294 g 4.0 mmol), L^2H_2 (1.294 g, 4.0 mmol) and L^3H_2 (1.294 g, 4.0 mmol) dissolved in absolute ethanol 60 mL. With the addition of these solutions, the pH values of the solution decreased from 5–6 to 3.0–3.5. The pH was increased up to 5–5.5 with the addition of 1% KOH. The mixtures were

stirred for an hour at 50 °C in water bath in order to participate of complexes. The precipitated complexes was filtered, washed with H_2O and diethylether and dried in vacuum at 50 °C. The Formula weights, colors, melting point, yields, magnetic susceptibilities, elemental analyses of the ligands and their complexes are given in Table 1, and TGA data of the complexes are given in Table 2.

Yield: 0.747 g (55%). Color: red. M.p.: >300 °C. μ_{eff} , BM: diamagnetic. Anal. Calcd for $\text{NiC}_{30}\text{H}_{34}\text{N}_6\text{O}_6\text{Cl}_2$: C, 51.16, H, 4.83, N, 11.94, Ni, 8.34 Found: C, 51.11, H, 4.48, N, 11.52, Ni, 8.62. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3330 $\nu(\text{N-H})$, 3058 (C-H_{Arom}), 1755 $\nu(\text{O}\cdots\text{H-O})$, 1610 $\nu(\text{C=N})$, 970 $\nu(\text{N-O})$. Selected ^1H NMR data (DMSO- d_6 , δ ppm): 6.60–7.10 (Ar. –H, 8H), 8.80 (–NH, 2H), 2.26 (CH_2 , 4H), 3.90 (– CH_3O , 6H), 15.90 ($\text{O}\cdots\text{H-O}$, 2H).

The experiments at the following were made due to process at the below, with taking $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.3408 g, 2.0 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.4760 g, 2.0 mmol)

[Cu(L^1H_2) $_2$]

Yield: 0.850 g (60%). Color: Dark gren. M.p.: >300 °C. μ_{eff} , BM: 1.77. Anal. Calcd for $\text{CuC}_{30}\text{H}_{34}\text{N}_6\text{O}_6\text{Cl}_2$: C,

Table 1 Colors, molecular weights, magnetic moments, m.p.s, yield and elemental analytical results for the ligands and their complexes

Compounds	Color and M.W	Yield (%)	M.p. (°C)	μ_{eff} (BM) ⁱ	Calcd. (found), %			
					C	H	N	M
$\text{L}^1\text{-H}_2$	White	60	180	–	55.64 (55.78)	5.56 (5.31)	12.98 (13.27)	–
$\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}$	323.5							
[Ni(HL^1) $_2$]	Red	55	>300	Dia	51.16 (51.11)	4.83 (4.48)	11.94 (11.52)	8.34 (8.62)
$\text{C}_{30}\text{H}_{34}\text{NiN}_6\text{O}_6\text{Cl}_2$	703.7							
[Cu(HL^1) $_2$]	Dark Green	60	>300	1.77	50.81 (51.15)	4.79 (4.32)	11.86 (11.15)	8.96 (8.12)
$\text{C}_{30}\text{H}_{34}\text{CuN}_6\text{O}_6\text{Cl}_2$	708.5							
[Co(HL^1) $_2$]	Dark Brown	50	>300	2.75	51.14 (51.02)	4.83 (4.52)	11.85 (11.54)	8.37 (8.56)
$\text{C}_{30}\text{H}_{34}\text{CoN}_6\text{O}_6\text{Cl}_2$	703.9							
$\text{L}^2\text{-H}_2$	White	57	185	–	55.64 (55.32)	5.56 (5.32)	12.98 (12.78)	–
$\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}$	323.5							
[Ni(HL^2) $_2$]	Red	50	>300	Dia	51.16 (51.27)	4.83 (4.41)	11.94 (11.52)	8.34 (8.46)
$\text{C}_{30}\text{H}_{34}\text{NiN}_6\text{O}_6\text{Cl}_2$	703.7							
[Cu(HL^2) $_2$]	Green	50	>300	1.74	50.81 (51.57)	4.79 (4.28)	11.86 (11.72)	8.96 (9.02)
$\text{C}_{30}\text{H}_{34}\text{CuN}_6\text{O}_6\text{Cl}_2$	708.5							
[Co(HL^2) $_2$]	Dark Brown	55	>300	2.25	51.14 (51.42)	4.83 (4.42)	11.85 (11.49)	8.37 (8.57)
$\text{C}_{30}\text{H}_{34}\text{CoN}_6\text{O}_6\text{Cl}_2$	703.9							
$\text{L}^3\text{-H}_2$	White	55	165	–	55.64 (55.11)	5.56 (5.72)	12.98 (12.71)	–
$\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}$	323.5							
[Ni(HL^3) $_2$]	Red	55	>300	Dia	51.16 (51.58)	4.83 (4.65)	11.94 (11.66)	8.34 (8.73)
$\text{C}_{30}\text{H}_{34}\text{NiN}_6\text{O}_6\text{Cl}_2$	703.7							
[Cu(HL^3) $_2$]	Brown	50	>300	1.68	50.81 (51.41)	4.79 (4.72)	11.86 (11.63)	8.96 (8.46)
$\text{C}_{30}\text{H}_{34}\text{CuN}_6\text{O}_6\text{Cl}_2$	708.5							
[Co(HL^3) $_2$]	Dark Brown	53	>300	2.55	51.14 (51.31)	4.83 (4.53)	11.85 (11.43)	8.37 (8.24)
$\text{C}_{30}\text{H}_{34}\text{CoN}_6\text{O}_6\text{Cl}_2$	703.9							

Table 2 TGA data of the complexes

Compounds	First step (°C) weight loss calcd. (found), %	Second step(°C) weight loss calcd. (found), %	Third step (°C) weight loss calcd. (found), %	Weight loss calcd. (found), %	Residue (NiO, CuO) calcd. (found), %
[Ni(HL ¹) ₂]	465–583 35.03 (35.43) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N + 2OH + NO	583–801 39.15 (39.52) Cl–CH ₃ O–C ₆ H ₃ –N=CH + C ₆ H ₉ –C≡N	801–1086 15.21 (15.42) C ₆ H ₉ –C≡N	89.39 (90.37)	10.61 (10.63) NiO
[Cu(HL ¹) ₂]	394–580 34.79 (34.65) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N+2OH + NO	580–780 38.84 (38.39) Cl–CH ₃ O–C ₆ H ₃ –N=CH + C ₆ H ₉ –C≡N	780–1064 15.10 (15.58) C ₆ H ₉ –C≡N	88.73 (88.62)	11.27 (11.38) CuO
[Co(HL ¹) ₂]	415–586 35.02 (34.57) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N+2OH+NO	586–628 39.14 (39.45) Cl–CH ₃ O–C ₆ H ₃ –N=CH+C ₆ H ₉ –C≡N	628–1004 15.20 (15.18) C ₆ H ₉ –C≡N	89.36 (89.20)	10.64 (10.80) CoO
[Ni(HL ²) ₂]	463–578 35.03 (35.33) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N+2OH + NO	578–806 39.15 (39.52) Cl–CH ₃ O–C ₆ H ₃ –N=CH + C ₆ H ₉ –C≡N	806–1095 15.21(15.42) C ₆ H ₉ –C≡N	89.39 (90.27)	10.61 (10.73) NiO
[Cu(HL ²) ₂]	401–585 34.79 (34.85) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N+2OH+NO	585–792 38.84 (38.43) Cl–CH ₃ O–C ₆ H ₃ –N=CH+C ₆ H ₉ –C≡N	792–1072 15.10 (15.48) C ₆ H ₉ –C≡N	88.73 (88.76)	11.27 (11.24) CuO
[Co(HL ²) ₂]	409–579 35.02 (35.24) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N + 2OH + NO	579–634 39.14 (39.16) Cl–CH ₃ O–C ₆ H ₃ –N=CH+C ₆ H ₉ –C≡N	634–1012 15.20 (15.25) C ₆ H ₉ –C≡N	89.36 (89.65)	10.64 (10.35) CoO
[Ni(HL ³) ₂]	470–580 35.03 (35.41) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N + 2OH + NO	580–811 39.15 (39.32) Cl–CH ₃ O–C ₆ H ₃ –N=CH + C ₆ H ₉ –C≡N	811–1083 15.21 (15.11) C ₆ H ₉ –C≡N	89.39 (89.84)	10.61 (10.06) NiO
[Cu(HL ³) ₂]	400–579 34.79 (34.28) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N + 2OH + NO	579–786 38.84 (38.36) Cl–CH ₃ O–C ₆ H ₃ –N=CH + C ₆ H ₉ –C≡N	786–1069 15.10 (15.58) C ₆ H ₉ –C≡N	88.73 (88.22)	11.27 (11.78) CuO
[Co(HL ³) ₂]	404–582 35.02 (35.23) Cl–CH ₃ O–C ₆ H ₃ –NH–C≡N + 2OH + NO	582–638 39.14 (39.03) Cl–CH ₃ O–C ₆ H ₃ –N=CH + C ₆ H ₉ –C≡N	638–1019 15.20 (15.35) C ₆ H ₉ –C≡N	89.36 (89.61)	10.64 (10.39) CoO

50.81, H, 4.79, N, 11.86, Cu, 8.96 Found: C, 51.15, H, 4.32 N, 11.15, Cu, 8.12. Selected IR data (KBr, ν cm⁻¹): 3340 ν (N–H), 3055 ν (C–H_{Arom}), 1760 ν (O···H–O), 1605 ν (C=N), 980 ν (N–O).

[Co(L¹H₂)₂]

Yield: 0.704 g (50%). Color: Dark brown. M.p.: >300 °C. μ_{eff} , BM: 2.75. Anal. Calcd for CoC₃₀H₃₄N₆O₆Cl₂: C, 51.14, H, 4.83, N, 11.93, Co, 8.37 Found: C, 51.02, H, 4.52 N, 11.54, Co, 8.56. Selected IR data (KBr, ν cm⁻¹): 3350,

ν (N–H), 3040 ν (C–H_{Arom}), 1765 ν (O···H–O), 1615 ν (C=N), 960 ν (N–O).

[Ni(L²H₂)₂]

Yield: 0.679 g (50%). Color: red. M.p.: >300 °C. μ_{eff} , BM: diamagnetic. Anal. Calcd for NiC₃₀H₃₄N₆O₆Cl₂: C, 51.16, H, 4.83, N, 11.94, Ni, 8.34 Found: C, 51.27, H, 4.41 N, 11.52, Ni, 8.46. Selected IR data (KBr, ν cm⁻¹): 3345 ν (N–H), 3063 ν (C–H_{Arom}), 1770 ν (O···H–O), 1600 ν (C=N), 965 ν (N–O). Selected ¹H NMR data (DMSO –d₆, δ ppm):

6.60–7.20 (Ar. –H, 8H), 8.80 (–NH, 2H), 2.27 (CH₂, 4H), 3.85 (–CH₃O, 6H), 15.80 (O⋯H–O, 2H).

[Cu(L²H₂)₂]

Yield: 0.708 g (50%). Color: Gren. M.p.: >300 °C. μ_{eff} , BM: 1.74. Anal. Calcd for CuC₃₀H₃₄N₆O₆Cl₂: C, 50.81, H, 4.79, N, 11.86, Cu, 8.96 Found: C, 51.57, H, 4.28 N, 11.72, Cu, 9.02. Selected IR data (KBr, ν cm⁻¹): 3335 ν (N–H), 3059 ν (C–H_{Arom}), 1750 ν (O⋯H–O), 1615 ν (C=N), 975 ν (N–O).

[Co(L²H₂)₂]

Yield: 0.774 g (55%). Color: Dark brown. M.p.: >300 °C. μ_{eff} , BM: 2.25. Anal. Calcd for CoC₃₀H₃₄N₆O₆Cl₂: C, 51.14, H, 4.83, N, 11.93, Co, 8.37 Found: C, 51.42, H, 4.42 N, 11.49, Co, 8.57. Selected IR data (KBr, ν cm⁻¹): 3340, ν (N–H), 3038 ν (C–H_{Arom}), 1740 ν (O⋯H–O), 1615 ν (C=N), 970 ν (N–O).

[Ni(L³H₂)₂]

Yield: 0.747 g (55%). Color: red. M.p.: >300 °C. μ_{eff} , BM: diamagnetic. Anal. Calcd for NiC₃₀H₃₄N₆O₆Cl₂: C, 51.16, H, 4.83, N, 11.94, Ni, 8.34 Found: C, 51.58, H, 4.65 N, 11.66, Ni, 8.73. Selected IR data (KBr, ν cm⁻¹): 3325 ν (N–H), 3055 ν (C–H_{Arom}), 1745 ν (O⋯H–O), 1610 ν (C=N), 960 ν (N–O). Selected ¹H NMR data (DMSO –d₆, δ ppm): 6.70–7.00 (Ar. –H, 8H), 9.00 (–NH, 2H), 3.95, 2.27 (CH₂, 4H), (–CH₃O, 6H), 15.85 (O⋯H–O, 2H).

[Cu(L³H₂)₂]

Yield: 0.708 g (50%). Color: Brown. M.p.: >300 °C. μ_{eff} , BM: 1.78. Anal. Calcd for CuC₃₀H₃₄N₆O₆Cl₂: C, 50.81, H, 4.79, N, 11.86, Cu, 8.96 Found: C, 51.41, H, 4.72 N, 11.63, Cu, 8.46. Selected IR data (KBr, ν cm⁻¹): 3345 ν (N–H), 3044 ν (C–H_{Arom}), 1755 ν (O⋯H–O), 1605 ν (C=N), 965 ν (N–O).

[Co(L³H₂)₂]

Yield: 0.746 g (53%). Color: Dark brown. M.p.: >300 °C. μ_{eff} , BM: 2.55. Anal. Calcd for CoC₃₀H₃₄N₆O₆Cl₂: C, 51.14, H, 4.83, N, 11.93, Co, 8.37 Found: C, 51.31, H, 4.53 N, 11.43, Co, 8.24. Selected IR data (KBr, ν cm⁻¹): 3320 ν (N–H), 3051, ν (C–H_{Arom}), 1740 ν (O⋯H–O), 1610 ν (C=N), 980 ν (N–O).

Results and discussion

In this study, the reaction of anti-1-acetyl-1-cyclohexenylglyoxime [17, 18] with three different arylamines

in ethanol at 25 °C gave three new substituted amino-1-acetyl-1-cyclohexenylglyoxime L¹H₂, L²H₂, and L³H₂.

Ligands and complexes were characterized by elemental analyses, IR, ¹³C NMR, ¹H NMR, TGA. The crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common solvents.

The Ni(II), Cu(II) and Co(II) complexes of the three new ligands were prepared in ethanol by addition of a 1 % KOH solution in ethanol to raise the pH to 5.0–5.5. The metal–ligand ratio in all these complexes were 1:2. Consequently, square–planar coordination for the Ni(II), Cu(II) and Co(II) complexes was proposed. The red color for the Ni(II) complexes of the ligands indicates that these ligands are in the (E, E) form [18] and also the anti-form of the ligands.

As the most part of vic-dioximes, Ni(II) complexes of ligands L¹H₂, L²H₂ and L³H₂ are planar, and *N,N'*-coordination is verified by the diamagnetism of this compound, since it is known that a d⁸ metal complexes has no unpaired electrons in square–planar field [18, 19].

In the ¹H NMR spectra of the ligands, two peaks are present for the OH protons of the substituted amino-1-acetyl-1-cyclohexenylglyoximes because of the difference in the neighboring oxime groups. These two deuterium exchangeable singlets correspond to two nonequivalent OH protons, which also indicate the anti configuration of the OH groups relative to each other [17–22]. When the chemical shifts of the two OH groups are compared for three different ligands, the shifts in a lower field showed a similarity to each other (11.70, 11.50, 11.60 ppm), whereas a considerable difference was observed for the shift in the higher field (11.20, 11.10, 11.20 ppm). The D₂O exchangeable NH protons of the aminoglyoximes were measured at 8.45, 8.51, 8.38 ppm as singlets. The addition of D₂O cause the disappearance of the NH and OH peak. The values were in agreement with the similar vic-dioximes [9, 23, 24].

The ¹H NMR spectrum of the diamagnetic Ni(II) complexes indicate O⋯H–O bridge formation resulting in a strong shift of the protons to lower field (15.90, 15.80, 15.85 ppm) compared to the free ligands [22–27]

As a consequence of the unsymmetry in the ligands, the complexes are expected to form two isomers. TLC (siligagel-G) was employed with different solvent mixtures and varying polarities but only spot appears in each case. These results showed the formation of only one isomer under these reaction conditions. The ¹H NMR spectrum of the Ni(II) complexes can be evaluated to determine the isomer formed, since the different chemical environments will show two peaks for the O⋯H–O bridging protons in the *cis*-form but only one peak for the bridging protons in the *trans*-structure. Since only one signal occurs at 15.90, 15.80 and 15.85 ppm, respectively, for Ni(II) complexes of

the ligands, the *trans*-form of these complexes is confirmed. This is in agreement with similar vic-dioxime complexes in the literature [25–27]. The Cu(II) and Co(II) complexes paramagnetic; for this reason, they are not suitable for ^1H NMR study.

In the ^{13}C NMR spectrum of L^1H_2 , L^2H_2 and L^3H_2 , carbon resonances of the oxime groups were observed around 140.15–158.75 ppm. Observation of vic-dioximes and OH protons in the ^1H NMR and of dioxime carbons in the ^{13}C NMR spectra at two different frequencies in each case indicates that the *vic*-dioximes has an anti structure [28].

In the IR spectra of the ligands, NH (3417–3400 cm^{-1}), OH^- (3350–3345 cm^{-1}), C=N (1664–1651 cm^{-1}), and NO (970–962 cm^{-1}) exhibit stretching frequencies of for substituted aminoglyoximes [1, 2].

The IR spectra of the complexes supported the structure of Ni(II), Cu(II), and Co(II) complexes by the weak bending vibration of the $\text{O}\cdots\text{H}-\text{O}$ bridges at ca. 1740–1770 cm^{-1} and shift of the C=N vibration to lower frequencies (1600–1615 cm^{-1}) due to *N*, *N'*-metal coordination [9, 23, 29, 30]. Also, the bands observed at 980, 970, 960 in the free ligands assigned to the $\nu(\text{N}-\text{O})$ is shifted to lower frequency after complexation. The mononuclear complexes of ligands with Ni(II), Cu(II), and Co(II) have a metal: ligands ratio of 2 as found for most of the vic-dioximes [9, 10, 31].

The TGA curves for the Ni(II), Cu(II) and Co(II) complexes were obtained at a heating rate of 10 $^\circ\text{C}/\text{min}$. In N_2 atmosphere between the temperature of 394–1095 $^\circ\text{C}$. It was seen from the TGA results that decomposition of Ni(II), Cu(II), and Co(II) complexes began between 394–470 $^\circ\text{C}$ and finished between 628–1095 $^\circ\text{C}$. Ni(II), Cu(II), and Co(II) complexes decompose to NiO, CuO, and CoO in three steps in the temperature ranges. These results are in agreement with other literatures [32–35]. When the Table 2 was investigated, it was easily seen that the experimental and theoretical data's were similar in each case in the point of the view of weight lost.

The molar conductivity values of the synthesized ligands and their complexes were measured and by the way it was seen that all the complexes were non-electrolytes. The M^+ values of ligands in mass spectrum were 287, 315, and 289, respectively and this position also confirmed the proposed structure. The molecular ion peak indicated the formula weight of the ligands. Magnetic susceptibility measurements provide sufficient data to characterize the structure of the complexes (Table 1). The mononuclear complexes of Ni(II) are diamagnetic as expected for d^8 metal ions in a square-planar field [11], whereas the Cu(II) and Co(II) complexes paramagnetic [25] and their magnetic susceptibility values are 1.74–1.78 and 2.25–2.75, respectively. For these complexes, additional physical and analytical data are given Table 1, according to these

results, the Cu(II) and Co(II) complexes have a square-planar geometry [23, 26].

Conclusions

In this work, It has been synthesized and characterized three new dioxime, ligands and their new Ni(II), Cu(II) and Co(II) complexes. Also, these compounds synthesized were characterized by IR, NMR, TGA, and elemental analyses methods. The investigations of metal selectivities and biological activities of these synthesized compounds are thought to be the next studies of our group. In order to evacuate of these compounds which will be available for pharmacology.

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