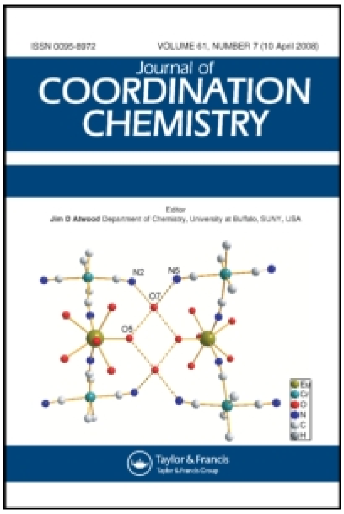


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The synthesis and characterization of three new <i>vic</i>-dioximes and their nickel(II), copper(II) and cobalt(II) complexes

Ersın Güler[a]
[a] Department of Chemistry, Faculty of Arts and Sciences, Selcuk University, Konya, Turkey

To cite this Article Güler, Ersın(2009) 'The synthesis and characterization of three new **<i>vic</i>**-dioximes and their nickel(II), copper(II) and cobalt(II) complexes', Journal of Coordination Chemistry, 62: 7, 1143 — 1150, First published on: 29 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970802492047

URL: http://dx.doi.org/10.1080/00958970802492047

Journal of Coordination Chemistry
Vol. 62, No. 7, 10 April 2009, 1143–1150

Taylor & Francis
Taylor & Francis Group

The synthesis and characterization of three new *vic*-dioximes and their nickel(II), copper(II) and cobalt(II) complexes

ERSİN GÜLER*

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

(*Received 7 May 2008; in final form 21 July 2008*)

Three new *vic*-dioximes, [L^1H_2], *N*-(4-ethylphenyl)amino-1-acetyl-1-cyclohexenylglyoxime, [L^2H_2], *N*-(4-butylphenyl)amino-1-acetyl-1-cyclohexenylglyoxime, and [L^3H_2], *N*-(4-methoxyphenyl)amino-1-acetyl-1-cyclohexenylglyoxime were synthesized from 1-acetyl-1-cyclohexeneglyoxime and the corresponding substituted aromatic amines. Metal complexes of these ligands were also synthesized with Ni(II), Cu(II), and Co(II) salts. These new compounds (ligands and complexes) were characterized with FT–IR, magnetic susceptibility measurement, molar conductivity measurements, mass spectrometry measurements, thermal methods (e.g. thermal gravimetric analysis), ^{1}H NMR (Nuclear Magnetic Resonance) and ^{13}C NMR spectral data and elemental analyses.

Keywords: *vic*-Dioximes; Ligands; Ni(II), Cu(II) and Co(II) complexes

1. Introduction

vic-Dioximes are used as chelating agents forming stable complexes with transition metals and also 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 nitrogens 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) [10]. Transition metal complexes of *vic*-dioximes are of particular interest in biological model compounds and have been investigated extensively for their similarity with vitamin B_{12} [3, 4].

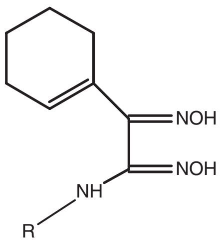
Recently reviewed data show that oximes, although being classical ligands, display a variety of reactivity modes unusual even for the coordination chemistry [11–15]. Oximes and their metal complexes are of interest for applications in medicine [16], bioorganic systems [17], catalysis [18], electrochemical and, electrooptical sensors [19].

In the present work, I synthesized three new unsymmetric ligands containing weak and strong electron donor groups and their complexes with Ni(II), Cu(II), and Co(II). Spectral, magnetic, and thermal properties of the new compounds indicate the structures given in scheme 1 (ligands) and scheme 2 (complexes).

---

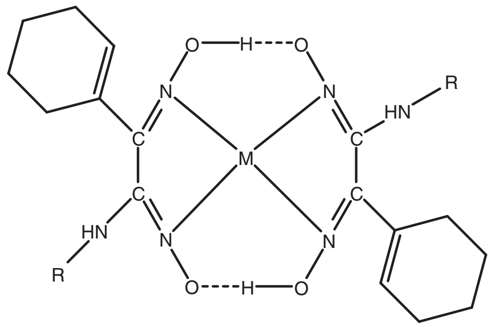
*Email: eguler66@gmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802492047



R = CH_3–CH_2–Ph–, CH_3–CH_2–CH_2–CH_2 Ph–, CH_3O–Ph–

Scheme 1. Ligands formula.



R = CH_3–CH_2–Ph–, CH_3–CH_2–CH_2–CH_2–Ph–, CH_3O–Ph–
M = Ni(II), Cu(II), and Co(II)

Scheme 2. Complexes formula.

2. Experimental

2.1. *Methods*

Elemental analyses (C, H, and N) were realized using a Carlo-Erba 1106 model analyzer and analyses for metals were determined using an Emler AAS 700 spectrometer, ^{1}H NMR (Nuclear Magnetic Resonance) and Infrared (IR) spectra were obtained with a Bruker 200 MHz spectrometer and a Jasco FT/IR-300, respectively. Melting points were measured on an Electrothermal IA 9100 digital melting point apparatus. The pH of the solutions were adjusted and controlled with WTW pH-meter pH 537. Molar conductivities of the ligands and their metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. Thermal Gravimetric Analysis (TGA) curves were recorded with a Shimadzu TG-50 thermo balance. Mass spectra were recorded with a 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 $Hg[Co(SCN)_4]$ as a standard; diamagnetic corrections were calculated from Pascal's constants.

2.2. *Chemical and starting materials*

1-Acetyl-1-cyclohexene and anilines were purchased from Sigma. Anti-1-acetyl-1-cyclohexeneglyoxime was prepared by reported procedures [20].

2.3. *Synthesis of [N-(4-ethylphenyl), N-(4-butylphenyl) and N-(4-ethoxy-phenyl) 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 4-ethylaniline (1.250 mL, 10 mmol, $\delta = 0.970\,\mathrm{g\,cm^{-3}}$) and 4-butylaniline (1.49 g, 10 mmol), 4-ethoxyaniline (1.23 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 in ethanol. Ligands precipitated by addition of H_2O with continuous stirring. The precipatated ligand 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: 1.58 g (55.0%). M.p.: 115°C, color: primrose yellow. Anal. Calcd for $C_{16}H_{21}N_3O_2$: C, 66.90; H, 7.32; N, 14.63. Found: C, 66.57; H, 7.05; N, 14.11. Selected IR data (KBr, $\upsilon\,\mathrm{cm^{-1}}$): 3415 υ(N–H), 3208 υ(OH), 3065 υ(Ar–CH), 2940 υ(Alph. CH), 1645 υ(C=N), 992 υ(NO). Selected ^1H NMR (DMSO-d_6; δ ppm): 12.17–11.68 (O–H), 6.5–6.9 (H_{arom}), 8.17 (N–H), 1.8 (CH_3). Selected ^{13}C NMR (DMSO-d_6; δ ppm): 138.95, 157.74 (C=NOH), 28.33 (CH_2), 15.02 (CH_3). Mass spectral data: $m/z = 287\,M^+$.

[L^2H_2]: yield: 1.89 g (60.0%). M.p.: 175°C, color: yellow. Anal. Calcd for $C_{18}H_{25}N_3O_2$: C, 68.57; H, 7.93; N, 13.34. Found: C, 68.18; H, 7.81; N, 13.45. Selected IR data (KBr, $\upsilon\,\mathrm{cm^{-1}}$): 3430 υ(N–H), 3185 υ(OH), 3072 υ(Ar–CH), 2972 υ(Alph. CH), 1664 υ(C=N), 980 υ(NO). Selected ^1H NMR (DMSO-d_6; δ ppm): 11.95–10.78 (O–H), 6.5–6.9 (H_{arom}), 8.59 (N–H), 1.8 (CH_3). Selected ^{13}C NMR (DMSO-d_6; δ ppm): 140.15, 157.65 (C=NOH), 33.72, 33.45, 23.22, (CH_2), 14.87 (CH_3). Mass spectral data: $m/z = 315\,M^+$.

[L^3H_2]: yield: 1.65 g (57.0%). M.p.: 185°C, color: white Anal. Calcd for $C_{15}H_{19}N_3O_3$: C, 62.29; H, 6.57; N, 14.53. Found: C, 62.54; H, 6.75; N, 14.18. Selected IR data (KBr, $\upsilon\,\mathrm{cm^{-1}}$): 3402 υ(N–H), 3340 υ(OH), 3077 υ(Ar–CH), 1610 υ(C=N), 942 υ(NO). Selected ^1H NMR (DMSO-d_6; δ ppm): 11.40–10.50 (O–H), 6.5–6.9 (H_{arom}), 7.90 (N–H), 1.8 (CH_3). Selected ^{13}C NMR (DMSO-d_6; δ ppm): 141.10, 158.15 (C=NOH), 53.15 (CH_3O). Mass spectral data: $m/z = 289\,M^+$.

2.4. *Synthesis of complexes*

A solution of metal salt $NiCl_2 \cdot 6H_2O$ (0.7134 g, 3.0 mmol), $CuCl_2 \cdot 2H_2O$ (0.5112 g, 3.0 mmol) or $CoCl_2 \cdot 6H_2O$ (0.7140 g, 3.0 mmol) dissolved in 60 mL absolute ethanol was added to a stirred solution of ligand L^1H_2 (1.7220 g 6.0 mmol), L^2H_2 (1.8900 g, 6.0 mmol), or L^3H_2 (1.7340 g, 6.0 mmol) dissolved in absolute ethanol 60 mL. With the addition of these solutions, the pH of the solution decreased from 5–6 to 3.0–3.5 and was increased to 5.0–5.5 with the addition of 1% KOH. The mixtures were stirred for an hour at 50°C in a water bath in order to precipitate complexes, which were filtered, washed with H_2O and diethylether, and dried in vacuum at 50°C. Formula weights,

Table 1. Colors, molecular weights, magnetic moments, melting points yield and elemental analytical results for the ligands and their complexes.

Compounds	Color and MW	Yield (%)	M.p. (°C) (dec)	μ_{eff} (BM)$^{\dot{I}}$	Calcd (Found) % C	H	N	M
$L^1 \cdot H_2$ $C_{16}H_{21}N_3O_2$	Primrose yellow 287	55	115	–	66.90 (66.57)	7.32 (7.05)	14.63 (14.11)	–
$[Ni(HL^1)_2]$ $C_{32}H_{40}NiN_6O_4$	Red 630.7	60	>300	Dia	60.88 (60.45)	6.34 (6.54)	13.32 (14.02)	9.31 (9.18)
$[Cu(HL^1)_2]$ $C_{32}H_{40}CuN_6O_4$	Dark green 635.5	60	>300	1.80	60.42 (60.86)	6.29 (6.14)	13.22 (13.41)	10.00 (10.45)
$[Co(HL^1)_2]$ $C_{32}H_{40}CoN_6O_4$	Dark brown 630.9	50	>300	2.82	60.87 (60.59)	6.34 (6.42)	13.31 (13.42)	9.34 (10.38)
$L^2 \cdot H_2$ $C_{18}H_{25}N_3O_2$	Yellow 315	60	175	–	68.57 (68.18)	7.93 (7.81)	13.34 (13.45)	–
$[Ni(HL^2)_2]$ $C_{36}H_{48}NiN_6O_4$	Red 686.7	65	>300	Dia	62.91 (62.68)	6.99 (6.87)	12.23 (12.49)	8.55 (9.51)
$[Cu(HL^2)_2]$ $C_{36}H_{48}CuN_6O_4$	Green 691.5	63	>300	1.78	62.47 (62.04)	6.94 (7.16)	12.15 (12.65)	9.18 (9.53)
$[Co(HL^2)_2]$ $C_{36}H_{48}CoN_6O_4$	Dark brown 686.9	51	>300	2.23	62.90 (63.18)	6.99 (6.75)	12.22 (12.43)	8.57 (9.55)
$L^3 \cdot H_2$ $C_{15}H_{19}N_3O_3$	White 289	57	185	–	62.29 (62.54)	6.57 (6.75)	14.53 (14.18)	–
$[Ni(HL^3)_2]$ $C_{30}H_{36}NiN_6O_6$	Red 634.7	63	>300	Dia	56.72 (57.06)	5.67 (5.43)	13.23 (13.56)	9.25 (9.46)
$[Cu(HL^3)_2]$ $C_{30}H_{36}CuN_6O_6$	Green 639.5	60	>300	1.96	56.30 (56.56)	5.63 (5.37)	13.13 (13.44)	9.93 (10.24)
$[Co(HL^3)_2]$ $C_{30}H_{36}CoN_6O_6$	Dark brown 634.9	52	>300	2.52	56.70 (57.03)	5.67 (5.54)	13.23 (13.02)	9.28 (9.53)

colors, melting point, yields, magnetic susceptibilities, and elemental analyses of the ligands and their complexes are given in table 1; TGA data of the complexes are given in Supplementary Material.

2.5. *Spectral characterization of [Ni(L^1H_2)$_2$]*

Yield: 1.135 g (60%). Color: red. M.p.: >300°C. μ_{eff}, BM: diamagnetic. Anal. Calcd for $NiC_{32}H_{40}N_6O_4$: C, 60.88; H, 6.34; N, 13.32; Ni, 9.31. Found: C, 60.45; H, 6.54; N, 14.02; Ni, 9.18. Selected IR data (KBr, $\upsilon\,cm^{-1}$): 3403 υ(N–H), 3058 υ(Ar–CH), 1780 υ(O$\cdots$H–O), 1632 υ(C=N), 2948 υ(Alph.–CH), 983 υ(N–O). Selected ^1H NMR data (DMSO-d_6; δ ppm): 2.52 (–CH_2 4H), 1.05 (–CH_3, 6H), 6.40–7.10 (Ar–H, 8H), 16.15 (O$\cdots$H–O, 2H).

2.6. *Spectral characterization of [Cu(L^1H_2)$_2$]*

Yield: 1.144 g (60%). Color: dark green. M.p.: >300°C (dec.). μ_{eff}, BM: 1.80. Anal. Calcd for $CuC_{32}H_{40}N_6O_4$: C, 60.42; H, 6.29; N, 13.22; Cu, 10.00. Found: C, 60.86;

H, 6.14; N, 13.41; Cu, 10.45. Selected IR data (KBr, $\upsilon\,\text{cm}^{-1}$): 3390 υ(N–H), 3055 υ(Ar–CH), 1785 υ(O···H–O), 1635 υ(C=N), 2940 υ(Alph.–CH), 975 υ(N–O).

2.7. *Spectral characterization of* $[Co(L^1H_2)_2]$

Yield: 0.946 g (50%). Color: dark brown. M.p.: >300°C (dec.). μ_{eff}, BM: 2.82. Anal. Calcd for $CoC_{32}H_{40}N_6O_4$: C, 60.87; H, 6.34; N, 13.31; Co, 9.34. Found: C, 60.59; H, 6.42; N, 13.42; Co, 10.38. Selected IR data (KBr, $\upsilon\,\text{cm}^{-1}$): 3398 υ(N–H), 3040 υ(Ar–CH), 1805 υ(O···H–O), 1622 υ(C=N), 2955 υ(Alph.–CH), 978 υ(N–O).

2.8. *Spectral characterization of* $[Ni(L^2H_2)_2]$

Yield: 1.340 g (65%). Color: red. M.p.: >300°C (dec.). μ_{eff}, BM: diamagnetic. Anal. Calcd for $NiC_{36}H_{480}N_6O_4$: C, 62.91; H, 6.99; N, 12.23; Ni, 8.55. Found: C, 62.68; H, 6.87; N, 12.49; Ni, 9.51. Selected IR data (KBr, $\upsilon\,\text{cm}^{-1}$): 3415 υ(N–H), 3063 υ(Ar–CH), 1832 υ(O···H–O), 1640 υ(C=N), 2963 υ(Alph.–CH), 968 υ(N–O). Selected ^{1}H NMR data (DMSO-d_6; δ ppm): 2.73 (–H_2 4H), 1.05 (–CH_3, 6H), 6.50–6.85 (Ar–H, 8H), 15.75 (O···H–O, 2H).

2.9. *Spectral characterization of* $[Cu(L^2H_2)_2]$

Yield: 1.307 g (63%). Color: green. M.p.: >300°C (dec.). μ_{eff}, BM: 1.78. Anal. Calcd for $CuC_{36}H_{48}N_6O_4$: C, 62.47; H, 6.94; N, 12.15; Cu, 9.18. Found: C, 62.04; H, 7.16; N, 12.65; Cu, 9.53. Selected IR data (KBr, $\upsilon\,\text{cm}^{-1}$): 3400 υ(N–H), 3059 υ(Ar–CH), 1798 υ(O···H–O), 1643 υ(C=N), 2958 υ(Alph.–CH), 969 υ(N–O).

2.10. *Spectral characterization of* $[Co(L^2H_2)_2]$

Yield: 1.051 g (51%). Color: dark brown. M.p.: >300°C (dec.). μ_{eff}, BM: 2.23. Anal. Calcd for $CoC_{36}H_{48}N_6O_4$: C, 62.90; H, 6.99; N, 12.22; Co, 8.57. Found: C, 63.18; H, 6.75; N, 12.43; Co, 9.55. Selected IR data (KBr, $\upsilon\,\text{cm}^{-1}$): 3412 υ(N–H), 3028 υ(Ar–CH), 1803 υ(O···H–O), 1636 υ(C=N), 2967 υ(Alph.–CH), 983 υ(N–O).

2.11. *Spectral characterization of* $[Ni(L^3H_2)_2]$

Yield: 1.200 g (63%). Color: red. M.p.: >300°C. μ_{eff}, BM: diamagnetic. Anal. Calcd for $NiC_{30}H_{36}N_6O_6$: C, 56.72; H, 5.67; N, 13.23; Ni, 9.25. Found: C, 57.06; H, 5.43; N, 13.56; Ni, 9.46. Selected IR data (KBr, $\upsilon\,\text{cm}^{-1}$): 3338 υ(N–H), 1755 υ(O···H–O), 1610 υ(C=N), 981 υ(N–O). Selected ^{1}H NMR data (DMSO-d_6; δ ppm): 6.80–7.00 (Ar–H, 8H), 7.80 (–NH, 2H), 3.90 (–CH_3O, 6H), 16.00 (O···H–O, 2H).

2.12. *Spectral characterization of* $[Cu(L^3H_2)_2]$

Yield: 1.151 g (60%). Color: brown. M.p.: >300°C (dec.). μ_{eff}, BM: 1.96. Anal. Calcd for $CuC_{30}H_{36}N_6O_6$: C, 56.30; H, 5.63; N, 13.13; Cu, 9.93. Found: C, 56.56; H, 5.37; N, 13.44; Cu, 10.24. Selected IR data (KBr, υ cm^{-1}): 3340 υ(N–H), 1745 υ(O$\cdots$H–O), 1660 υ(C=N), 974 υ(N–O).

2.13. *Spectral characterization of [Co(L^3H_2)$_2$]*

Yield: 0.9904 g (52%). Color: dark brown. M.p.: >300°C (dec.). μ_{eff}, BM: 2.52. Anal. Calcd for $CoC_{30}H_{36}N_6O_6$: C, 56.70; H, 5.67; N, 13.23; Co, 9.28. Found: C, 57.03; H, 5.54; N, 13.02; Co, 9.53. Selected IR data (KBr, υ cm^{-1}): 3390 υ(N–H), 1740 υ(O$\cdots$H–O), 1625 υ(C=N), 965 υ(N–O).

3. Results and discussion

Reaction of anti-1-acetyl-1-cyclohexenylglyoxime [20, 21] with three different arylamines in ethanol at 25°C gave three new substituted amino-1-acetyl-1-cyclohexenylglyoxime L^1H_2, L^2H_2, and L^3H_2. The yield of the ligands and complexes were between 50 and 65%. These results were in harmony with the literature [20–22].

Ligands and complexes were characterized by elemental analyses, IR, ^{13}C NMR, ^{1}H NMR, and TGA. Crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most 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 was 1 : 2 and square-planar coordination for Ni(II), Cu(II), and Co(II) complexes was proposed. The red colors for the Ni(II) complexes indicate that these ligands are in the (E,E) form [21] and also the anti-form of the ligands.

Ni(II) complexes of L^1H_2, L^2H_2, and L^3H_2 are planar, and *N,N′*-coordination is verified by the diamagnetism of this compound, since it is known that d^8 metal complexes have no unpaired electrons in square-planar field [21, 23].

In ^{1}H NMR spectra of the ligands, two peaks are present for OH of the substituted amino1-acetyl-1-cyclohexenylglyoximes because of the difference in the neighboring oxime groups. These two deuterium exchangeable nonequivalent OH protons indicate anti-configuration of the OH groups relative to each other [20, 24, 25]. Comparing the chemical shifts of the two OH groups for the different ligands, the shifts of the lower field resonance showed similarity (12.17, 11.95, and 11.40 ppm), whereas considerable difference was observed for the higher field resonance (11.68, 10.78, 10.50 ppm). The D_2O exchangeable NH protons of the aminoglyoximes were at 8.17, 8.59, and 7.90 ppm as singlets. The values are in agreement with similar *vic*-dioximes [9, 26, 27].

The ^{1}H NMR spectrum of the diamagnetic Ni(II) complexes indicate O$\cdots$H–O bridge formation resulting in a strong shift to lower field (16.15, 15.75, 16.00 ppm) compared to the free ligands [28–30].

As a consequence of the asymmetry in the ligands, the complexes are expected to form two isomers. Thin layer chromatography (silicagel-G) was employed with different solvent mixtures and varying polarities. The obtained results showed the formation of one isomer under its reaction conditions. The ^{1}H NMR spectra of the Ni(II) complexes can be evaulated 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 for the bridging protons in the *trans*-structure. Since only one signal occurs at 16.15, 15.75, and 16.00 ppm, respectively, for Ni(II) complexes of the ligands, the *trans*-form of these complexes is confirmed, in agreement with similar *vic*-dioxime complexes in the literature [28–30].

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 138.95–158.15 ppm. OH protons in the ^{1}H NMR and dioxime carbons in the ^{13}C NMR spectra at two different frequencies indicate an anti-structure [31].

In the IR spectra of the ligands, NH (3430–3402 cm^{-1}), OH^- (3340–3185 cm^{-1}), C=N (1664–1610 cm^{-1}), and NO (992–942 cm^{-1}) exhibit stretching frequencies for substituted aminoglyoximes [1, 2].

The IR spectra of the complexes show weak bending vibration of the O···H–O bridges at ca. 1740–1832 cm^{-1} and shift of the C=N vibration to lower frequencies (1610–1660 cm^{-1}) due to *N*,*N*′-metal coordination [9, 26, 32, 33]. Also, the bands at 992, 980, and 942 in the free ligands assigned to υ(N–O) are shifted to lower frequency after complexation [9, 34, 35].

The TGA curves for the Ni(II), Cu(II), and Co(II) complexes were obtained at a heating rate of 10°C min^{-1} in N_2 between 365 and 1013°C, from 365–428°C and finished between 701–1013°C. Ni(II), Cu(II), and Co(II) complexes decompose to NiO, CuO, and CoO in three steps, in agreement with other literatures (Supplementary Material) [36-39]. When the table in the Supplementary Material was investigated it was easily seen that the experimental and theoretical datas were similar in each case in the point of the view of weight lost.

Molar conductivity values of the ligands and their complexes were measured and all were nonelectrolytes. The M^+ values of ligands in mass spectrum were 287, 315, and 289, respectively, confirming the proposed structure. Magnetic susceptibility measurements provide data to characterize the structure of the complexes (table 1). The mononuclear complexes of Ni(II) are diamagnetic as expected for d^8 square-planar complexes [11]. Cu(II) and Co(II) complexes are paramagnetic [28] with magnetic susceptibility values of 1.78–1.96 and 2.23–2.82, respectively [40]. Additional physical and analytical data given in table 1 show the Cu(II) and Co(II) complexes are also square planar [26, 29].

Acknowledgement

The author is grateful for the kind financial support provided by Selcuk University Research Foundation (SUAF).

References

[1] Y. Gok. *New J. Chem.*, **20**, 971 (1996).
[2] S. Serin, Y. Gok, S. Karabocek, N. Gultekin. *Analyst*, **119**, 1629 (1994).
[3] A. Chakravorty. *Coord. Chem. Rev.*, **13**, 1 (1974).
[4] G.N. Schrauzer, R.J. Windgassen. *J. Am. Chem. Soc.*, **89**, 1999 (1967).

[5] M. Ekerc. *Synth. React. Inorg. Met. Org. Chem.*, **29**, 487 (1999).
[6] I. Gurol, V. Ahsen, O. Bekaroglu. *J. Chem. Soc., Dalton Trans.*, 2283 (1992).
[7] H.E. Ungnade, L.W. Kissinger, A. Narath, D.C. Barham. *J. Org. Chem.*, **28**, 134 (1963).
[8] H.C. Sevindir, R. Mirzaoglu, E. Ozcan, S. Ertul, E. Guler. *Synth. React. Inorg. Met. Org. Chem.*, **24**, 613 (1994).
[9] A. Gul, O. Bekaroglu. *J. Chem. Soc., Dalton Trans.*, 2587 (1983).
[10] Y. Gok, H. Kantekin. *Chem. Ber.*, **123**, 1479 (1990).
[11] E.G. Ozkan, E. Canpolat, M. Kaya. *Russ. J. Coord. Chem.*, **31**, 506 (2005).
[12] V.Y. Kukushkin, D. Tudela, A.J.L. Pombeiro. *Coord. Chem. Rev.*, **156**, 333 (1996).
[13] A.N. Nesmeyanow, N.A. Nesmeyanow. *Fundamentals of Organic Chemistry*, p. 167, MIR Publishers, Moscow (1981).
[14] Y.Z. Voloshin, N.A. Kostromina, R. Kramer. *Chlatrochelats: Synthesis, Structure and Properties*, Elsevier, Amsterdam (2002).
[15] D.A. Garnovskii, V.Y. Kukushkin. *Russ. Chem. Rev.*, **75**, 111 (2006).
[16] S.S. Jurisson, J.D. Lydon. *Chem. Rev.*, **99**, 2205 (1999).
[17] W.A. Volkert, T.J. Hoffman. *Chem. Rev.*, **99**, 2269 (1999).
[18] K. Ohta, R. Higashi, M. Ikejima, I. Yamamoto, N. Kobayashi. *J. Mater. Chem.*, **8**, 1979 (1998).
[19] M.C.M. Laranleira, R.A. Marusak, A.G. Lappin. *Inorg. Chim. Acta*, **186**, 300 (2000).
[20] E. Ozcan, E. Karapinar, N. Karapinar. *Russ. J. Coord. Chem.*, **30**, 491 (2004).
[21] M. Kocak, O. Bekaroglu. *Synth. React. Inorg. Met. Org. Chem.*, **14**, 689 (1984).
[22] M. Kocak, O. Bekaroglu. *Synth. React. Inorg. Met. Org. Chem.*, **15**, 479 (1985).
[23] S.B. Pedersen, E. Larsen. *Acta Chem. Scand.*, **27**, 3291 (1973).
[24] E. Ozcan, E. Karapinar, N. Karapinar. *Russ. J. Coord. Chem.*, **31**, 1163 (2001).
[25] H.C. Sevindir. *Synth. React. Inorg. Met. Org. Chem.*, **30**, 183 (2000).
[26] E. Ozcan, R. Mirzaoglu. *Synth. React. Inorg. Met. Org. Chem.*, **18**, 559 (1988).
[27] H. Bati, M. Tas, B. Bati. *Synth. React. Inorg. Met. Org. Chem.*, **28**, 137 (1988).
[28] E. Canpolat, M. Kaya. *J. Coord. Chem.*, **55**, 961 (2002).
[29] E. Canpolat, M. Kaya. *J. Coord. Chem.*, **55**, 1419 (2002).
[30] A. Zulfikaroglu, M. Tas, H. Bati, B. Bati. *Synth. React. Inorg. Met. Org. Chem.*, **33**, 625 (2003).
[31] A. Cukurovali, E. Tas. *Synth. React. Inorg. Met. Org. Chem.*, **28**, 449 (1998).
[32] J.V. Burakevic, A.M. Lore, G.P. Volpp. *J. Org. Chem.*, **36**, 1 (1971).
[33] E. Karapinar. *J. Incl. Phenom. Macromol. Chem.*, **53**, 171 (2005).
[34] B.L. Shaw, I. Shepherd. *Dalton Trans.*, **10**, 1634 (1979).
[35] Y. Gok, H. Kantekin. *Polyhedron*, **16**, 2413 (1997).
[36] H. Arslan. *J. Therm. Anal. Calorim.*, **60**, 399 (2001).
[37] H. Arslan, N. Ozpozan, T. Ozpozan. *Thermochim. Acta*, **329**, 57 (1999).
[38] H. Arslan, N. Kulcu. *Turk. J. Chem.*, **27**, 55 (2003).
[39] E. Canpolat, M. Kaya. *Turk. J. Chem.*, **28**, 235 (2004).
[40] E. Karapınar, N. Karapınar, E. Özcan. *Russ. J. Coord. Chem.*, **32**, 885 (2006).