# Co(II), Ni(II) AND Cu(II) COMPLEXES OF 1,4-DI-(1-HYDROXYIMINO-2-PHENYL-2-OXO-ETHYLAMINO)BENZENE
## Synthesis, characterization and thermal studies

*M. Taş*[1][*] *and H. Batı*[2]

[1]Karadeniz Technical University, Giresun Faculty of Art and Sciences, Department of Chemistry, 28049 Giresun, Turkey
[2]Ondokuz Mayis University, Art-Science Faculty, Department of Chemistry, 55139 Samsun, Turkey

The ligand has been prepared from ω-chloroisonitrosoacetophenone and 1,4-phenylenediamine in the presence of NaHCO$_3$. The ligand have a C=O group and an –NH–R group adjacent to the oxime group. The Ni(II), Cu(II) and Co(II) complexes of the synthesized ligand were prepared and their structures were identified using FTIR, UV-Vis spectral data, elemental analysis, thermal analysis and magnetic moment measurements. The metal-ligand ratios were found to be 3:2. The ligands were found to coordinate to the metal ions via the oxime nitrogen, oxime oxygen, one of the carbonyl group and amide nitrogen atoms. Thermal analyses data reveals that the water in the complexes was found to be non-coordinated to the metal ions. In the trinuclear structures, the metals have the tetrahedral environments.

*Keywords: amide oxime, carbonyl oxime, oxime, thermal analysis, trinuclear complex*

## Introduction

Organic chelating ligands containing the –C=N–OH group have been named as oxime compounds (Fig. 1a) [1, 2]. Tscugaeff first introduced dimethylglyoxime as a gravimetric reagent for nickel and since then oxime ligands and their transition metal complexes have been extensively studied [1–3]. Oximes derivatives are very important compounds because of their biological activity, such as insecticidal, miticidal, nematocidal activities, antidote activities for organophosphor poison. Some oxime complexes have anticancerogenic activities [4–6]. Oximes and their derivatives have also been used in analytical applications, such as determination and extraction of the metals [7–12].
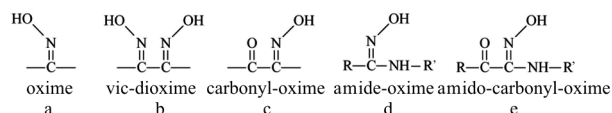


**Fig. 1** Oximes and dioxime derivatives

Vic-dioxime (Fig. 1b), carbonyl-oxime (Fig. 1c), amide-oxime ligands (Fig. 1d) and their metal complexes have been studied extensively, but the work done on amido-carbonyl-oximes (Fig. 1e), which have –C=O and –NH–R' groups in the same molecule in vicinal position with oxime groups are rather few [13–18]. This type of compounds is a new research area on the oxime ligands and their complexes.

In present work, a newly synthesized amido-carbonyl-oxime ligand which contains two oxime groups, two carbonyl groups and two –NH-groups, and their Ni(II), Cu(II), Co(II) complexes were studied.

## Experimental

### Materials

Synthesis of the 1,4-di-(1-hydroxyimino-2-phenyl-2-oxo- ethylamino)benzene (LH$_4$)

The ligand was prepared from the reaction of ω-chloro-isonitrosoaceto-phenone [19] with 1,4-phenylene-diamine (Scheme 1) and can be named alternatively as 1-phenyl-2-[4-(1-hydroxyimino-2-phenyl-2-oxo-ethyl-amino)phenylamino]-2-hydroxyimino ethane-1-one.

A solution of 0.015 mol 1,4-phenylenediamine (1.62 g) in EtOH (20 mL) was added dropwise to a solution of ω-chloroisonitrosoacetophenone (0.030 mol, 5.5 g) in EtOH, and then solid NaHCO$_3$ (0.030 mol, 2.52 g) was added to the mixture. After 4 h, H$_2$O (20 mL) was added dropwise to the mixture. The precipitated product was filtered, washed with water and cold EtOH and dried on air.

### Ni(II), Cu(II), Co(II) complexes

The solutions of metal salts (3 mmol) (Ni(CH$_3$COO)$_2$·4H$_2$O, Cu(CH$_3$COO)$_2$·H$_2$O and Co(CH$_3$COO)$_2$·4H$_2$O) in 15 mL H$_2$O were added to a solution of the ligands

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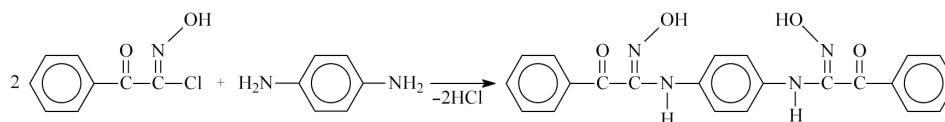* Author for correspondence: murattas@ktu.edu.tr

(3 mmol) dissolved in 30 mL EtOH. The color of the ligand solutions were changed immediately from yellow to black for complex formation. In order to isolate complexes by precipitation, concentrated $NH_3$ (0.1 mL) were added. The precipitates were filtered, washed with water and EtOH and dried on air. The colors, melting points, molecular masses, magnetic measurements and elemental analysis data are given in Table 1.

*Methods*

All starting materials were commercially available and were reagent grade. The $^1H$–NMR spectra was recorded on a Bruker AC-200 FT-NMR spectrometer, utilizing deuterated dimethylsulphoxide as a solvent and TMS was used as an internal standard. IR spectra (4000–200 cm$^{-1}$) were recorded on a Jasco-430 FTIR spectrophotometer with sample prepared as KBr pellets. The magnetic moments of the complexes were measured using a Sherwood scientific MX1 model Gouy magnetic susceptibility balance at room temperature. UV-Vis spectra were recorded with a Unicam UV2 UV-Visible spectrometer in dimethylsulphoxide solution. TG and DTA curves were recorded simultaneously in static air atmosphere with a Rigaku TG8110 thermal analyzer. The heating rate was 10ºC min$^{-1}$ and the temperature ranges were between 20–1000ºC using platinum crucibles. Highly sintered $\alpha$-$Al_2O_3$ was used as a reference.

## Results and discussion

Ligand was prepared from the reaction of $\omega$-chloro-isonitrosoacetophenone [19] with the 1,4-phenylene-diamine in the presence of $NaHCO_3$. Metal complexes
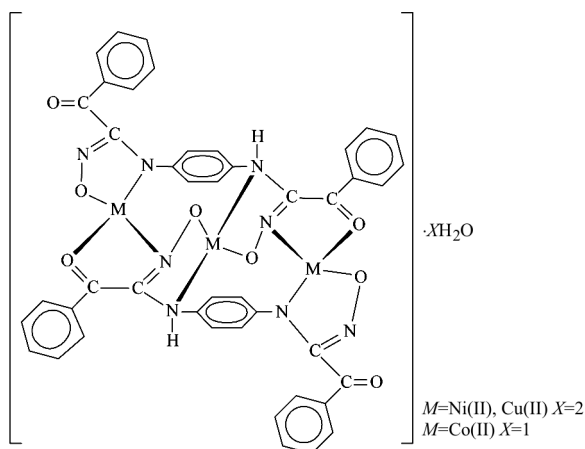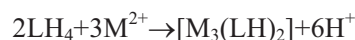


**Fig. 2** Suggested structure for Co(II), Ni(II) and Cu(II) complexes of the ligand

of the ligand were synthesized by treating the ligand and the metal salts in the presence of ammonia. The general reaction for the formation of metal complexes is shown below and their structures are given in Fig. 2.

$$2LH_4 + 3M^{2+} \rightarrow [M_3(LH)_2] + 6H^+$$

where $M$=Ni(II), Cu(II) and Co(II).

The structures of the ligand and their complexes have been verified by IR, UV-Vis, $^1H$ NMR spectral data, magnetic measurements, thermal analyses and elemental analyses (Tables 1–3).

The ligand was prepared in a good yield. However, the complexes of the ligand were prepared in lower yields. The complexes are paramagnetic with experimental magnetic moments of 9.63, 6.32 and 4.21 BM for Co(II), Ni(II) and Cu(II) complexes (Table 1), respectively. These magnetic moments correspond to six, four and three unpaired electrons that suitable for



**Scheme 1** Synthesis route of the ligand

**Table 1** Magnetic measurements, physical properties and elemental analyses of the ligand and complexes

| Compound | $\mu_{eff}$*/BM | Molecular mass/g mol$^{-1}$ | D.p.**/°C | Color yield/% | Calculated (found)/% | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | H | N |
| LH$_4$ C$_{22}$H$_{18}$N$_4$O$_4$ | – | 402.41 | 175 | yellow 80 | 65.67 (65.74) | 4.51 (4.83) | 13.92 (13.72) |
| [Co$_3$(LH)$_2$]·H$_2$O [Co$_3$(C$_{44}$H$_{30}$N$_8$O$_8$)]·H$_2$O | 9.63 | 993.59 | 112 | black 26 | 53.19 (53.46) | 3.25 (3.05) | 11.28 (11.48) |
| [Ni$_3$(LH)$_2$]·2H$_2$O [Ni$_3$(C$_{44}$H$_{30}$N$_8$O$_8$)]·2H$_2$O | 6.32 | 1010.28 | 120 | black 20 | 52.28 (52.66) | 3.39 (3.37) | 11.08 (10.91) |
| [Cu$_3$(LH)$_2$]·2H$_2$O [Cu$_3$(C$_{44}$H$_{30}$N$_8$O$_8$)]·2H$_2$O | 4.21 | 1025.44 | 109 | black 23 | 51.54 (51.86) | 3.34 (2.98) | 10.93 (11.25) |

*The magnetic moments of the complexes; **Decomposition points of the compounds

**Table 2** Thermal analyses data of the complexes in static air atmosphere

| Complex | Stage | $T_{range}$ /°C | $DTA_{max}$ /°C | Mass loss/% found (calcd.) | Removal group | Total mass loss/% | Residue/% |
|---|---|---|---|---|---|---|---|
| | | | | | | found (calcd.) | |
| [Ni$_3$(C$_{44}$H$_{30}$N$_8$O$_8$)]·2H$_2$O | 1 | 44–120 | 102 | 3.2 (3.6) | 2 mol H$_2$O | 79.8 (77.9) | NiO 20.2 (22.1) |
| | 2 | 120–262 | – | 11.6 | C$_{44}$H$_{34}$N$_8$O$_7$ | | |
| | 3 | 262–316 | 295 | 11.8 | C$_{44}$H$_{34}$N$_8$O$_7$ | | |
| | 4 | 316–417 | 395–411 | 53.1 | C$_{44}$H$_{34}$N$_8$O$_7$ | | |
| [Cu$_3$(C$_{44}$H$_{30}$N$_8$O$_8$)]·2H$_2$O | 1 | 40–109 | 101 | 3.6 (3.5) | 2 mol H$_2$O | 74.9 (76.7) | CuO 25.1 (23.3) |
| | 2 | 109–225 | 184 | 13.3 | C$_{44}$H$_{34}$N$_8$O$_7$ | | |
| | 3 | 225–303 | – | 11.3 | C$_{44}$H$_{34}$N$_8$O$_7$ | | |
| | 4 | 303–384 | 351 | 46.7 | C$_{44}$H$_{34}$N$_8$O$_7$ | | |
| [Co$_3$(C$_{44}$H$_{30}$N$_8$O$_8$)]·H$_2$O | 1 | 45–112 | 105 | 2.2 | 1 mol H$_2$O | 78.6 (77.4) | CoO 21.4 (22.6) |
| | 2 | 112–255 | 207 | 15.4 | C$_{44}$H$_{32}$N$_8$O$_6$ | | |
| | 3 | 255–420 | 390–420 | 60.9 | C$_{44}$H$_{32}$N$_8$O$_6$ | | |

**Table 3** IR spectra of the ligand and complexes in KBr pellets (cm$^{-1}$)

| Compounds | O–H$_{water}$ | N–H | O–H | C=O$_{non–coord.}$ | C=O$_{coord.}$+ C=N$_{non–coord.}$ | C=N | C–N– | N–O | M–O | M–N |
|---|---|---|---|---|---|---|---|---|---|---|
| LH$_4$ | – | 3348 | 3234 | 1664 | – | 1637 | 1311 | 962 | – | – |
| [Co$_3$(LH)$_2$]·H$_2$O | 3670–3350 | 3332 | – | 1670 | 1653 | 1618 | 1336 | 941 | 523 | 339–316 |
| [Ni$_3$(LH)$_2$]·2H$_2$O | 3670–3345 | 3340 | – | 1670 | 1651 | 1618 | 1344 | 939 | 516 | 362–327 |
| [Cu$_3$(LH)$_2$]·2H$_2$O | 3670–3360 | 3332 | – | 1668 | 1658 | 1619 | 1363 | 937 | 524 | 339–318 |

tetrahedral geometry of metal environments, for Co(II), Ni(II) and Cu(II) complexes, respectively.

### $^1$H-NMR spectra of the ligand

In the $^1$H-NMR spectra of the ligand a singlet peak for the OH protons of oxime group is observed at 11.06 ppm (2 H). The N–H protons adjacent to the oxime groups in the ligand resonate at 8.44 ppm (2 H). The aromatic C–H protons resonate at 7.94–6.51 ppm (14 H). The O–H and N–H peaks of the ligand disappeared with the addition of deuterium oxide to the solutions. These results are in good agreement with those of known oximes [4, 14, 20].

### Thermal analyses of the complexes

Both the elemental (Table 1) and thermal analyses data (Table 2) of the complexes coincide with each other and metal-ligand ratios were found to be 3:2 for all complexes. Based on the elemental and thermal analyses data, general structures for all complexes found as [M$_3$(LH)$_2$]·XH$_2$O. The thermal analyses curves (TG and DTA) of the complexes are shown in Figs 3–5 and the mass losses are summarized in Table 2. The TG and DTA data and IR spectra show that the first stages in the decomposition process of all complexes are related to dehydration. For all complexes, water is removed up to 120°C. This is indicated that the waters in the complexes are non-coordi-

nated waters and these are hydrated waters [21–23]. According to the TG and DTA curves, the dehydration process takes place in a single step which corresponds exactly to loss of the crystal waters and the Co(II) and Ni(II) complexes decompose in a similar manner. The dehydration temperature of the complexes lies in the range of 40–120°C. On the basis of
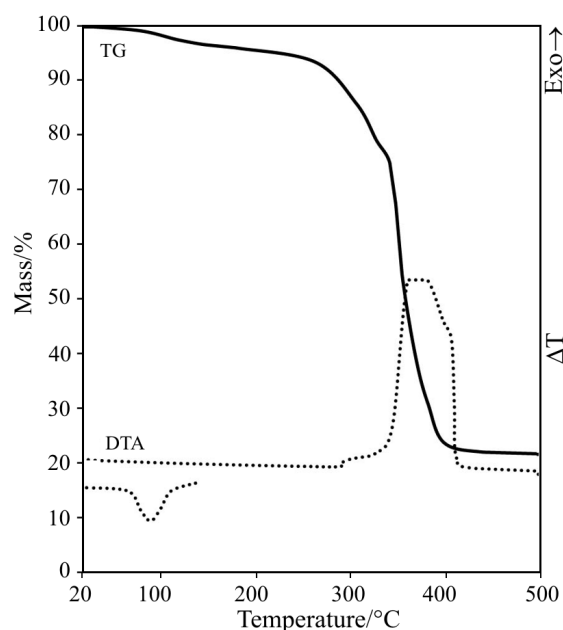


**Fig. 3** Thermal analyses curves of the [Ni$_3$(LH)$_2$]·2H$_2$O complex
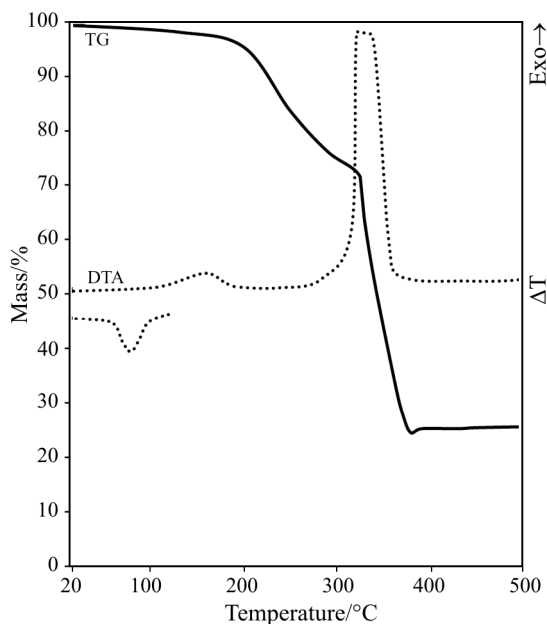
**Fig. 4** Thermal analyses curves of the $[Cu_3(LH)_2] \cdot 2H_2O$ complex



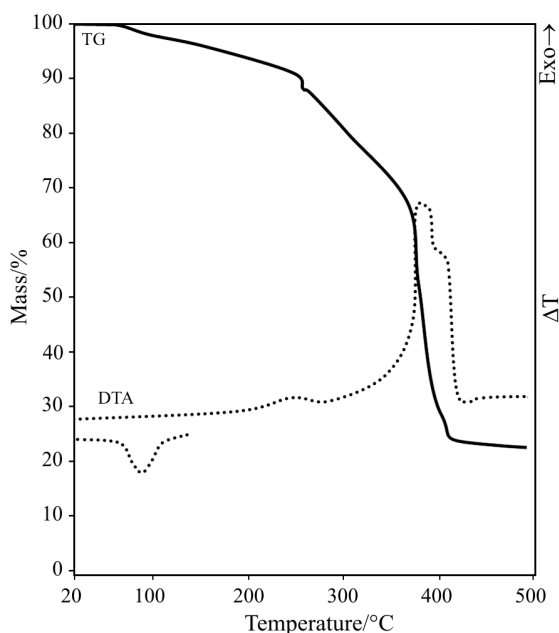**Fig. 5** Thermal analyses curves of the $[Co_3(LH)_2] \cdot H_2O$ complex

the $DTA_{max}$, the thermal stability of the hydrated complexes follows the order: Co(II)(105ºC)> Ni(II)(102ºC)≅Cu(II) (101ºC).

After dehydratation, the pyrolysis of the ligand takes place in the anhydrous complexes in three steps. But decomposition stages are not differentiated from each other exactly. Maximum exothermic decomposition of the ligand occurred at 390, 395 and 351ºC for the Co(II), Ni(II) and Cu(II) complexes, respectively. For Co(II) and Ni(II) complexes, at the last decomposition stage, another exothermic decomposition is ac-

companied with the pyrolysis of the ligand (at 420 and 411ºC for the Co(II) and Ni(II) complex, respectively).

Total loss of masses were found to be 78.6% (calc.=77.4%), 79.8% (calc.=77.9%), 74.9% (calc.=76.7%) for Co(II), Ni(II) and Cu(II) complexes, respectively. The results in calculated and found total mass losses coincide with each other and are suitable for the proposed general structure, $[M_3(LH)_2] \cdot XH_2O$. The final decomposition products, namely MO [$M$=Ni(II), Cu(II) and Co(II)] were identified by IR spectroscopy with corresponding spectra obtained under the same conditions as the pure oxides.

*IR spectra of the ligand and complexes*

In the IR spectra of the ligand, bands at 3348, 3234, 1664, 1637, 1367 and 962 cm$^{-1}$ belong to N–H, O–H, C=O, C=N, –C–N– and N–O vibrations, respectively. These values are in accord with those of previously reported substituted oximes [5, 7, 14, 20]. IR spectra of ligand and complexes were summarized in Table 3.

Based on the elemental and thermal analyses data found for three moles $M^{2+}$ ions and two moles ligand, the ligand must have –3 negative charge. For this, two protons of the oxime groups and one proton of the C–N–H groups should be separated upon complex formation as expected. The IR results support the separated oxime protons. A broad band for C–N– vibrations, shifted to higher frequencies than the free ligand, indicated that some of the N–H protons were deprotonated upon complex formation and bonded to metals.

The complexes showed a broad band due to hydrated water between 3345–3670 cm$^{-1}$. In the IR spectra of the complexes, the peaks at 3332–3340, 1670–1668, 1658–1651, 1619–1618, 1363–1336, 941–937 cm$^{-1}$ are attributed to N–H, non-coordinated C=O, both coordinated C=O and non-coordinated C=N, coordinated C=N, C–N– and N–O vibrations, respectively. In the complexes, shifting to lower frequencies for N–H vibrations showed nitrogen of the N–H group coordinated to the metals. This is supported by the shifting to higher frequencies than the free ligand (at 1311 cm$^{-1}$), for C–N– as the broad band (1336, 1344, 1363 cm$^{-1}$ for Co(II), Ni(II) and Cu(II) complexes, respectively) [24]. These bands belong to both neutrally coordinated C–N–H and ionically bonded C–N– vibrations and otherwise the peak for C–N– should be sharp. Shifting to higher frequencies than the free ligand for C–N vibrations indicates the nitrogen atoms of the amide groups bonded to the metal ions [14, 24]. The O–H vibrations of the oxime groups disappeared in the IR spectra of the complexes indicated that the oxime protons were separated upon complex formation and bonded to the metals. This result is supported by shifting N–O vibrations to lower frequencies (941, 939, 937 cm$^{-1}$ for Co(II), Ni(II) and Cu(II) complexes, respectively) than the free ligand

(at 962 cm$^{-1}$) [14, 20]. Based on IR spectra results, one of the carbonyl groups (C=O) of the ligands remained non-coordinated to the metals as C=O stretching vibrations shifted to higher frequencies and the other one coordinated to the metal ions as C=O stretching vibrations shifted to lower frequencies [5, 7, 14]. For C=N vibrations, the spectra of the complexes had one peak at 1619–1618 cm$^{-1}$ indicated the oxime nitrogen coordinated to the metals [5, 7, 14, 20]. But, one of the oxime nitrogens should coordinate to the metals because of steric hindrance [24]. So, there must be two peaks for C=N vibrations, the one at the higher frequency indicating non-coordinated and the other one at the lower frequency indicating coordinated position. However, the peaks indicating coordinated C=N were seen in the IR spectra whereas the peaks of non-coordinated oxime nitrogen were not discerned. The peaks may be suppressed by the C=O peaks that indicating coordinating C=O group. In the IR spectra of the complexes, metal-oxygen and metal-nitrogen bonds were identified between 524–516 and 362–316 cm$^{-1}$, respectively [14, 20, 25].

Consequently, the ligand coordinated to the metal ions through nitrogen of the C–N–H group, one of the carbonyl group, nitrogen and oxygen atoms of the oxime groups and, nitrogen atoms of deprotonated amide groups (Fig. 2) [1–5, 7, 14].

*UV-Vis spectra*

The ligand showed an absorption band for π→π* at 256 nm (ε=19044 M$^{-1}$ cm$^{-1}$) and for n→π* at 327 nm (ε=1749 M$^{-1}$ cm$^{-1}$) in the UV-Vis spectra. For complexes, *d*→*d* transitions were not observed; because of the peaks were under the charge transfer bands. The charge transfer bands were at 476 nm (ε=5466), 400 (ε=4009), 460 (ε=16293) for cobalt, nickel and copper complexes, respectively.

## Acknowledgements

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