# Synthesis and Characterization of Some Metal Complexes of Isonitroso-2-acetylnaphthalene Derivative<sup>1</sup>

## S. Y. Uçan, M. Uçan\*, and İ. Demir

Department of Chemistry, Faculty of Arts and Sciences, Niğde University, 51200 Niğde, Turkey \*e-mail: selma.y.ucan@gmail.com

#### Received September 30, 2015

**Abstract**—Nickel(II), copper(II), and zinc(II) complexes with the Schiff base obtained from isonitroso-2acetylnaphthalene and 1,2-phenylenediamine were synthesized. The compounds were characterized by elemental analyses, FT-IR, UV-Vis, and <sup>1</sup>H and <sup>13</sup>C NMR spectra, conductance measurements, magnetic susceptibility measurements, and thermal analysis. The results suggest tetradentate coordination of the symmetrical Schiff base ligand through the two oxime oxygen atoms and two azomethine nitrogen atoms. The molar conductance data showed that the synthesized complexes are non-electrolytes.

Keywords: isonitroso-2-acetylnaphthalene, Schiff bases, metal chelates

**DOI:** 10.1134/S1070363216080235

Synthesis of imine oximes and their complexes is one of the challenging areas in the field of the oxime coordination chemistry. Imine oximes have been extensively studied because of their biological and structural importance which lies mainly in their specific and selective reactions with metal ions [1-7]. On the other hand, metal complexes of Schiff bases derived from aromatic carbonyl compounds are of great interest in inorganic chemistry. Schiff bases of diamines and their complexes have a variety of applications, including biological, clinical, and analytical [8-10]. In recent years, many Schiff bases and their metal complexes have been synthesized and reported to exhibit biological activity [11-18]. In this paper, we report the synthesis and spectral characterization of Ni(II), Cu(II), and Zn(II) complexes of the Schiff base derived from isonitroso-2-acetylnaphthlene [2-hydroxyimino-1-naphthalen-2-yl)ethanone] and 1,2-phenylenediamine (Scheme 1).

The analytical and physical data of Schiff base ligand L and its complexes 1-3 are given in Table 1. The complexes are soluble in DMF and DMSO and are insoluble in ethanol, acetone, and chloroform. The elemental analyses of the Schiff base and its complexes are consistent with those calculated from their empirical formulas.

The IR spectrum of the ligand showed bands at  $3265-3260 \text{ cm}^{-1}$  due O–H stretching,  $3090-3085 \text{ cm}^{-1}$ 

due to C–H<sub>arom</sub> stretching, and 990–980 cm<sup>-1</sup> due to N–O stretching [10–13]. The spectrum also contained characteristic C=N stretching band in the region 1645–1620 cm<sup>-1</sup>, which shifted to lower frequencies in the spectra of complexes **1–3** (1625–1585 cm<sup>-1</sup>). Metal complexes **1–3** displayed in the IR spectra new bands in the regions 470–420 and 520–470 cm<sup>-1</sup> due to formation of M–O and M–N bonds, respectively [3, 8, 19].

The <sup>1</sup>H NMR spectrum of the ligand showed a broad singlet at  $\delta$  9.20–9.00 ppm from the oxime OH protons [2–4] and a singlet at  $\delta$  8.75–8.72 ppm due to the N=CH protons [13–17]. Aromatic protons resonated as multiplet signals in the regions  $\delta$  8.50–7.59 ppm. Unlike free ligand **L**, the spectra of metal complexes **1–3** lacked OH proton signal, and the N=CH signal was observed in a slightly stronger field ( $\delta$  8.68 ppm for Zn complex **1**). In the <sup>13</sup>C NMR spectrum of the ligand, the signals at  $\delta_C$  189.79 and 171.26 ppm were assigned to the azomethine and oxime carbon atoms respectively [5, 14]. All signals in the region  $\delta_C$  150.84–125.10 ppm corresponded to aromatic carbons.

The molar conductances of complexes 1-3 were measured at 25°C in DMF solutions with a concentration of  $10^{-3}$  M. Taking into account the obtained values (10.3–18.4 W<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>; Table 1), the complexes may be regarded as non-electrolytes.

The magnetic moment of copper(II) complex **2** is 1.81 B.M. suggesting its square planar geometry [11].

<sup>&</sup>lt;sup>1</sup> The text was submitted by the authors in English.





**1**, M = Ni, n = 4; **2**, M = Cu, n = 1; **3**, M = Zn, n = 2.

The magnetic moment of complex **1** was estimated at 3.01 B.M., which is typical of tetrahedral Ni(II) complexes (2.9–3.9 B.M.) [4, 5]. Zinc(II) complex **3** is diamagnetic, as expected for  $d^{10}$  metal ion in a tetrahedral geometry [20].

The electronic spectra of complexes 1–3 were recorded from  $10^{-3}$  M solutions in DMF at room temperature. The free ligand displayed two absorption bands with their maxima at  $\lambda$  257–269 and 329–346 nm. These bands were attributed to  $\pi \rightarrow \pi^*$  transitions, the first involving the aromatic ring, and the second, the imino group. In the spectra of complexes 1–3, the second absorption band was shifted to longer wavelengths as a result of coordination. The electronic spectrum of Cu(II) complex 2 showed absorption bands in the  $\lambda$  ranges 500–553 and 650–709 nm assignable, respectively, to  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transitions of a square planar structure [17]. Nickel(II) complex 1 was characterized by an absorption band at  $\lambda$  660–690 nm which may be attributed to the  ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(F)$  transition presumably arising from a tetrahedral geometry [15]. The spectrum of zinc(II) complex **3** showed an absorption band at  $\lambda$  418–423 nm due to ligand-to-metal charge transfer, which is consistent with its tetrahedral structure. No *d*–*d* transition is expected for *d*<sup>10</sup> Zn(II) complexes [12].

Thermogravimetric analysis data for complexes 1-3 are given in Table 2. The results showed a good agreement with their elemental analyses (Table 1). Weight losses for each chelate were calculated within the corresponding temperature ranges (Fig. 1). Thermal behavior of the complexes was studied using thermogravimetric analysis from ambient temperature to 900°C in a nitrogen atmosphere. Nickel(II) complex 1 decomposed in two steps. The first step was observed in the range 30–450°C with a weight loss of 36.50%, which was assigned to partial elimination of a C<sub>13</sub>H<sub>8</sub>N<sub>2</sub> fragment. The second step was found in the temperature range 450–900°C with a weight loss of 49.31%, which was assigned to removal of C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O.

Comp. no.	Yield, %	mp, °C	Found, %			Earmula	Calculated, %			М	L <sub>m</sub> ,
			С	Н	Ν	Formula	С	Н	Ν	M	$W^{-1} mol^{-1} cm^2$
L	86	143	76.48	4.42	11.79	$C_{30}H_{22}N_4O_2$	76.58	4.71	11.91	470.53	_
1	80	198	68.22	3.63	10.43	$C_{30}H_{20}N_4NiO_2$	68.35	3.82	10.63	527.20	15.8
2	87	129	67.63	3.60	10.40	$C_{30}H_{20}CuN_4O_2$	67.72	3.79	10.53	532.06	18.4
3	76	164	67.38	3.51	10.35	$C_{30}H_{20}N_4O_2Zn$	67.49	3.78	10.49	533.90	10.3

 Table 1. Yields, melting points, elemental analyses, and molar conductances of Schiff base ligand L and complexes 1–3



Fig. 1. Thermal analysis of complexes (a) 1, (b) 2, and (c) 3.

The final weight of the residue corresponds to nickel oxide. Copper(II) complex **2** decomposed in two steps. The first step was observed in the range  $30-450^{\circ}$ C with a weight loss of 36.59%, which was assigned to partial elimination of a  $C_{13}H_{10}N_2$  fragment. The second step corresponded to removal of  $C_{17}H_{10}N_2O$  molecule with a weight loss of 48.46%. The residue was identified as CuO. Zinc(II) complex **3** decomposed in two steps. The first step in the temperature range  $30-550^{\circ}$ C with a weight loss of 47.19% was assigned to removal of the naphthalene rings ( $C_{20}H_{12}$ ). The second

step found in the range 550–900°C with a weight loss of 37.47% was assigned to removal of  $C_{10}H_8N_4O$  molecule. The weight of the residue corresponded to ZnO.

Scanning electron microscopy analysis of the ligand and transition metal complexes 1–3 showed that the original morphology of Schiff base ligand L disappeared and that aggregates of amorphous pieces of irregular size appeared (Fig. 2).

In summary, Ni(II), Cu(II), and Zn(II) complexes of the Schiff base derived from isonitroso-2-acetyl-

Comp.	Formula	Temperature	Weight	loss, %	Lost frogmont	Inorganic residue (MO), %	
no.	Forniula	range, °C	found	calculated	Lost magnitud	found	calculated
1	$C_{30}H_{20}N_4NiO_2$	30–450 450–900	36.50 49.31	36.46 49.37	$\begin{array}{c} C_{13}H_8N_2\\ C_{17}H_{12}N_2O\end{array}$	14.19	14.17
2	$C_{30}H_{20}CuN_4O_2$	30–450 450–900	36.59 48.46	36.51 48.58	$\begin{array}{c} C_{13}H_{10}N_2\\ C_{17}H_{10}N_2O\end{array}$	14.95	14.94
3	$C_{30}H_{20}N_4O_2Zn$	30–550 550–900	47.19 37.47	47.26 37.50	$\begin{array}{c} C_{20}H_{12} \\ C_{10}H_8N_4O \end{array}$	15.34	15.24

**Table 2.** Thermal analysis of the complex compounds

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 86 No. 8 2016



Fig. 2. Scanning electron micrographs of (a) ligand L and complexes (b) 1 (c) 2, and (d) 3.

naphthlene and 1,2-phenylenediamine have been synthesized in good yields and characterized by spectral data, molar conductance and magnetic moment measurements, and thermogravometric analysis. The results suggest a square–planar geometry of the Cu(II) complex and tetrahedral geometry of the Ni(II) and Zn(II) complexes.

#### EXPERIMENTAL

All reagents were of analytical grade and were used without further purification. Isonitroso-2-acetylnaphthalene was prepared according to our previous procedure [19, 20]. Benzene-1,2-diamine, Ni(OAc)<sub>2</sub> · 4H<sub>2</sub>O, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O were purchased from Merck and Sigma–Aldrich. All solvents were obtained from Merck. The elemental analyses (C, H and N) were determined using a Carlo Erba 1106 analyzer. The magnetic susceptibilities of the complexes in the solid state were determined using a Gouy balance at room temperature using copper sulfate as calibrant. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of were recorded on a Varian T 200–A spectrometer in CDCl<sub>3</sub> using TMS as internal standard. The FT IR spectra were recorded in KBr using a Pye-Unicam SP 1025 instrument. The electronic spectra were measured on a Shimadzu 160 UV-Vis spectrophotometer in the wavelength range 200–600 nm. The molar conductivities were measured in DMF with a WTW LF 330 conductivity meter. Thermal gravimetric analysis was carried out on a Shimadzu TGA-50 instrument.

(2*E*,2*'E*)-2,2'-(1,2-Phenylenediazanylylidene)bis [(naphthalen-2-yl)acetaldehyde] dioxime (L). A solution of 1.081 g (10 mmol) of 1,2-phenylenediamine in 10 mL of methanol was added to a solution of 3.984 g (20 mmol) of isonitroso-2-acetylnaphthalene in 20 mL of methanol. The mixture was stirred for 3 h and left overnight at 25°C. The precipitate was filtered off, washed with cold ethanol, recrystallized from methylene chloride, and dried under reduced pressure. Its purity was checked by TLC. IR spectrum, v, cm<sup>-1</sup>: 3265 (O–H), 1640–1620 (C=N), 990 (N–O). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 9.00 s (2H, NOH), 8.72 s (2H, CH=N), 8.17–7.59 m (18H, H<sub>arom</sub>). <sup>13</sup>C NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta_{C}$ , ppm: 189.79 (C=NOH), 171.26–171.16 (CH=N), 150.84–125.10 (C<sub>arom</sub>). Metal complexes 1–3 (general procedure). A solution of 1 mmol of the corresponding transition metal acetate [0.248 g of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, 0.199 g of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, or 0.219 g of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O] in 20 mL of ethanol was added to a solution of 1 mmol (0.470 g) of Schiff base L in 30 mL of ethanol. The mixture was stirred for 2 h at 60°C. After cooling, the precipitate was filtered off, washed with cold ethanol, and dried under vacuum over CaCl<sub>2</sub>.

**Nickel complex 1.** IR spectrum, v, cm<sup>-1</sup>: 1625–1600 (C=N), 920 (N–O), 480 (M–N), 430 (M–O).

**Copper complex 2.** IR spectrum, v, cm<sup>-1</sup>: 1620– 1590 (C=N), 925 (N–O), 520 (M–N), 470 (M–O).

**Zinc complex 3.** IR spectrum, v, cm<sup>-1</sup>: 1610–1585 (C=N), 915 (N–O), 490 (M–N), 440 (M–O). <sup>1</sup>H NMR spectrum (DMSO–*d*<sub>6</sub>),  $\delta$ , ppm: 8.68 s (2H, CH=N), 8.09–7.29 m (18H, H<sub>arom</sub>).

#### ACKNOWLEDGMENTS

The authors thank the Research Foundation of the Nigde University (BAP) for financial support of this work (P.N. FEB 2007–05).

### REFERENCES

- Chakravorty, A., Coord. Chem. Rev., 1974, vol. 13, no. 1, p. 1. doi 10.1016/S0010-8545(00)80250-7.
- Akagi, F., Michihiro, Y., Nakao, Y., Matsumoto, K., Sato, T., and Mori, W., *Inorg. Chim. Acta*, 2004, vol. 357, no. 3, p. 684. doi 10.1016/j.ica.2003.08.022.
- Achiwawanich, S., Duangthongyou, T., Kitiphaisalnont, P., and Siripaisarnpipat, S., *J. Mol. Struct.*, 2014, vol. 1072, p. 149. doi 10.1016/j.molstruc.2014.04.090.
- Dede, B., Karipcin, F., Arabalı, F., and Cengiz, M., *Chem. Pap.*, 2010, vol. 64, no. 1, p. 25. doi 10.2478/ s11696-009-0095-6.
- Uçan, S.Y. and Mercimek, B., Synth. React. Inorg. Met.-Org. Nano-Met. Chem., 2005, vol. 35, no. 3, p. 197. doi 10.1081/SIM-200037249.
- Çolak, A.T., Irez, G., Mutlu, H., et al., J. Coord. Chem., 2009, vol. 62, no. 6, p. 1005. doi 10.1080/

00958970802345831.

- Uçan, S.Y., Uçan, M., and Mercimek, B., Synth. React. Inorg. Met.-Org. Nano-Met. Chem., 2005, vol. 35, no. 5, p. 417. doi 10.1081/SIM-200059233.
- Raman, N., Jeyamurugan, R., Subbulakshmi, M., Boominathan, R., and Yuvarajan, C. R., *Chem Pap.*, 2010, vol. 64, no. 3, p. 318. doi 10.2478/s11696-010-0003-0.
- El-Sherif, A.A. and Eldebss, T.M.A., Spectrochim. Acta, Part A, 2011, vol. 79, no. 5, p. 1803. doi 10.1016/j.saa.2011.05.062.
- Taha, Z.A., Ajlouni, A.M., Al-Hassan, K.A., Hijazi, A.K., and Faiq, A.B., *Spectrochim. Acta, Part A*, 2011, vol. 81, no. 1, p. 317. DOI:10.1016/j.saa.2011.06.018.
- Singh, K., Barwa, M.S., and Tyagi, P., *Eur. J. Med. Chem.*, 2006, vol. 41, no. 1, p. 147. doi 10.1016/j.ejmech.2005.06.006.
- Al-Ne'aimi, M.M., and Al-Khuder, M.M., Spectrochim. Acta, Part A, 2013, vol. 105, p. 365. doi 10.1016/ j.saa.2012.10.046.
- 13. Eltayeb, M.A.Z. and Sulfab, Y., *Polyhedron*, 2007, vol. 26 no.1, p. 1. doi 10.1016/j.poly.2006.04.019.
- Keypour, H., Rahpeyma, N., Arzhangi, P., Rezaeivala, M., Elerman, Y., Buyukgungor, O., and Valencia, L., *Polyhedron*, 2010, vol. 29, p. 1144. doi 10.1016/ j.poly.2009.12.005.
- Kılıc, A., Tas, E., Gümgüm, B., and Yılmaz, İ., *Transi*tion Met. Chem., 2006, vol. 31, p. 645. doi 10.1007/ s11243-006-0043-z.
- Naeimi, N., Safari, J., and Heidarnezhad, A., *Dyes Pigm.*, 2007, vol. 73, p. 251. doi 10.1016/ j.dyepig.2005.12.009.
- Tümer, M., Deligönül, N., Gölcü, A., Akgün, E., Dolaz, M., Demirelli, H., and Dığrak, M., *Transition Met. Chem.*, 2006, vol. 31, no. 1, p. 1. doi 10.1007/s11243-005-6249-7.
- Uçan, S.Y., Russ. J. Gen. Chem., 2014, vol. 84, no. 9, p. 1819. doi 10.1134/S1070363214090308.
- Yıldırım, S., Pekacar, A. İ., and Uçan, M., Synth. React. Inorg. Met.-Org. Nano-Met. Chem., 2003, vol. 33, no. 5, p. 873. doi 10.1081/SIM-120021654.
- Yıldırım, S., Pekacar, A.İ., and Uçan, M., Synth. React. Inorg. Met.-Org. Nano-Met. Chem., 2003, vol. 33, no. 7, p. 1. doi 10.1081/SIM-120023496.