$\mathbf{COORDINATION} \ \mathbf{COMPOUNDS} =$ 

## The Synthesis of Two New Isonitrosoacetophenone Derivatives and Investigation of Their Ni(II), Co(II), Cu(II), and Zr(IV) Complexes<sup>1</sup>

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**Abstract**—In the present study, two new ligands, 4-chlorobenzal-azino-isonitrosoacetophenone  $(L_1)$ , 4-methylbenzal-azino-isonitrosoacetophenone  $(L_2)$  and their metal complexes were synthesized using acetophenone as a starting material. The coloured complexes were prepared by the addition of chloride salts of Ni(II), Co(II), Cu(II) and Zr(IV) ions to a solution of ligands. In conclusion, the structures of the obtained ligands and their complexes were characterized by FT-IR, and <sup>1</sup>H NMR spectra, AAS (atomic absorption spectrum) analysis, magnetic susceptibilities as well as elemental analysis.

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Recently, due to the increasing use of the coordination compound in analytical, bioinorganic, pigment and medicinal chemistry, many researchers have studied these topics, especially, the important role of the complexes of oximes in coordination chemistry [1–6]. Oximes and hydrazones are two important classes of inorganic ligands owing to their wide application in industry, medicine, detection and determination of various metal ions [7, 8]. Schiff base hydrazone derivatives and their complexes have been studied for their antifungal and antibacterial activity, and as antiviral drugs [9].

Oximes are amphoteric materials containing weak acidic –OH groups and basic >C=N– groups. Generally, the geometrical isomers of oximes and their derivatives are syn and anti structures. However, 1,2– dioximes have three isomers which are syn, anti and amphi forms [10, 11], Usually, the stability order of them is anti > amphi > syn configuration, but there are some exceptions [12, 13]. The high stability of the complexes prepared with vic-dioxime ligands has been extensively used for various purposes including model compounds for vitamin  $B_{12}$  or trace metal analysis. The successful design and synthesis of ligands capable of forming heteronuclear complexes has been receiving attention for their magnetic, optical and electrical properties [14].

In the present study, two new imino oximes were synthesized, and their complexes with Cu(II), Ni(II), Co(II) and Zr(IV) ions were prepared. Besides, structural properties of ligands and their complexes were investigated.

## **EXPERIMENTAL**

All reagents were purchased from Merck and used without further purification. Isonitrosoacetophenone were prepared according to the procedures reported in literature [1, 4].<sup>1</sup>H NMR spectra and elemental analyses were carried out at laboratories of the Scientific and Technical Research Council of Turkey (TUBITAK). IR spectra were recorded on a Perkin-Elmer 1605 FT-IR spectrophotometer as KBr pellets. pH of solutions was monitored with a WTW 537 pH meter. Magnetic Susceptibilities of metal samples were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus, and magnetic measurements were carried out by the Gouy method using  $Hg[Co(SCN)_4]$  as calibrant. Metal contents in complexes were determined with a Unicam-929 AAS (atomic absorption spectrometer).

Synthesis of Isonitrosophenylhydrazine (Fig. 1). A solution of isonitrosoacetophenone (2.98 g, 20 mmol) in 20 mL of ethanol was added dropwise to a stirred solution of hydrazinehydrate (4 g, 80 mmol) in 20 mL of ethanol at  $-5^{\circ}$ C followed by addition of acetic acid (pH 8.5). Then the mixture was diluted with distilled water and allowed to stand 2 days in the refrigerator. The precipitate was filtered, dried in a vacuum at 65°C and weighed 2.75 g in 77% yield, m.p. 114°C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz)  $\delta$ : 5.92 (s, 2H), 7.45–7.90 (m, *J* = 7.3 Hz, 5H), 8.15 (s, 1H), 11.32 (s, 1H); IR (KBr) v: 3460, 3000, 1640, 1610, 1460 cm<sup>-1</sup>.

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Fig. 1. Synthesis of isonitrosophenylhydrazine.

Anal, calcd. for C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>O: C 58.85, H 5.58, N 25.76; found C 58.67, H 5.39, N 25.54.

Synthesis of 4-chlorobenzal-hydrazine (Fig. 2). To a stirred solution of hydrazinehydrate (1 g, 80 mmol) in 20 mL ethanol at  $-5^{\circ}$ C was added dropwise to a solution of p-chlorobenzaldehyde (2.8 g, 20 mmol) in 20 mL ethanol. Then the mixture was diluted with distilled water (20 mL) and allowed to stand two days in the refrigerator. The precipitate was filtered, dried in a vacuum at 65°C and afforded 2.51 g of product in 81% yield, m.p. 145°C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) & 4.84 (s, 2H), 7.54–7.81 (m, *J* = 8.4 Hz, 4H), 8.42 (s, 1H); IR (KBr) v: 3380, 3290, 1650, 1610, 760 cm<sup>-1</sup>. Anal. calcd. for C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub>: C 54.36, H 4.57, N 18.13; found C 54.22, H 4.46, N 17.95.

Synthesis of 4-chlorobenzal-azino-isonitrosoacetophenone  $(L_1)$  (Fig. 3). 4-chlorobenzalhydrazine (0.77 g, 5 mmol) was dissolved in 20 mL ethanol, then a solution of isonitrosoacetophenone (0.69 g, 5 mmol) in 20 mL ethanol was added dropwise to above solution. After  $K_2CO_3$  (0.69 g, 5 mmol) was added to reaction mixture, it was refluxed for 1 h. Then mixture was left to cool to r.t. Distilled water was added to mixture with stirring until precipitate was formed. After 2 h, precipitated solid was filtered off, washed with water, dried in vacuum at 65°C and afforded 0.90 g of product as a light vellow solid in 63% yield. The final product was soluble in dioxane, chloroform, diethylether and DMF. m.p. 209°C; <sup>1</sup>H NMR (DMSO- $d_6$ , 300 MHz)  $\delta$ : 7.08–8.29 (m, J = 8.2 Hz, 9H), 8.58 (s, 1H), 8.77 (s, 1H), 11.65 (s, 1H); IR (KBr) v: 3560, 3020, 1612, 1642, 1656, 1470, 920 cm<sup>-1</sup>. Anal. calcd. for C<sub>15</sub>H<sub>12</sub>ClN<sub>3</sub>O: C 63.05, H 4.23, N 14.70; found C 62.86, H 3.99, N 14.59.

**Preparation of Ni(II) complex of L<sub>1</sub>:** 4-chlorobenzalazino-isonitrosoacetophenone (0.057 g, 0.2 mmol) was dissolved in 20 mL of dioxane. Then, 10 mL of aqueous solution of NiCl<sub>2</sub>  $\cdot$  6H<sub>2</sub>O (0.12 g, 0.5 mmol) was added dropwise to above solution by stirring. The pH of the reaction mixture was adjusted to 5.0–5.5 by adding an aqueous solution of NaOH (1%, wt). Precipitated solid was kept on a water bath at 60°C for 30 min, then filtered, washed with distilled water, ethanol and diethyl ether, and dried in vacuum at 60°C. The product was obtained as a light green solid in 74% yield (0.092 g). m.p. 237°C (with degradation); IR (KBr) v: 3520, 2940, 1615, 1645, 1663, 1410, 960, 515, 430 cm<sup>-1</sup>. Anal. calcd. for  $C_{30}H_{22}Cl_2N_6O_2Ni$ : C 57.36, H 3.52, N 13.37 Ni 9.34; found C 57.17, H 3.25, N 13.67 Ni 9.18.

**Preparation of Cu(II) complex of L<sub>1</sub>.** This compound was prepared by the procedure mentioned for the preparation of  $(L_1)_2$ Ni. The product was obtained as a green solid in 83% yield (0.105 g). m.p. 227°C (with degradation); IR (KBr) v: 3500, 2950, 1617, 1645, 1665, 1465, 1000, 520, 440 cm<sup>-1</sup>. Anal. calcd. for C<sub>30</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>Cu: C 56.92, H 3.50, N 13.27 Cu 10.04; found C 56.62, H 3.39, N 13.06 Cu9.95.

**Preparation of Co(II) complex of L<sub>1</sub>.** Complexes of L<sub>1</sub> with Co(II) ion was prepared by the procedure above mentioned for the preparation of  $(L_1)_2$ Ni. The product was obtained as a grey solid in 78% yield (0.098 g). m.p. 214°C (with degradation); IR (KBr) v: 3620, 2940, 1619, 1650, 1664, 1420, 975, 528, 435 cm<sup>-1</sup>. Anal. calcd. for C<sub>30</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>4</sub>Co: C 57.34, H 3.53, N 13.37 Co 9.38; found C 57.30, H 3.45, N 13.30, Co 9.31.

**Preparation of Zr(IV) complex of L**<sub>1</sub>. Complexes of L<sub>1</sub> with Zr(IV) ion was prepared by the procedure above mentioned for the preparation of (L<sub>1</sub>)<sub>2</sub>Ni. The product was obtained as a yellow solid in 89% yield (0.118 g). m.p. 269°C (with degradation); IR (KBr) v: 3500, 2960, 1618, 1640, 1670, 1460, 950, 535, 420 cm<sup>-1</sup>. Anal. calcd. for C<sub>30</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>ZrCl<sub>2</sub>: C 49.25, H 3.03, N 11.49, Zr 12.47; found C 49.00, H 2.97, N 11.50 Zr 12.35.

Synthesis of 4-methylbenzal-azino-isonitrosoacetophenone (L<sub>2</sub>) (Fig. 4). A solution of isonitrosophenylhydrazine (0.815g, 5 mmol) in 20 mL of ethanol was added slowly to a solution of 4-methylbenzaldehyde (0.6 g, 5 mmol) in 20 mL of ethanol. The mixture was refluxed for 1 h and then diluted with distilled water. The mixture was stirred for 2 h and precipitate was filtered, washed with water, dried in vacuum at  $60-70^{\circ}$ C. The final product was weighed 1.06 g as a yellow solid in 80% yield. The final product was soluble in ethanol, chloroform, acetone, DMSO, and DMF. m.p. 133°C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ: 2.50 (s, 3H), 7.06–8.80 (m, J = 7.7 Hz, 9H), 9.34 (s, 1H), 9.57 (s, 1H), 12.16 (s, 1H); IR (KBr) v: 3440, 3000, 1610, 1635, 1660, 1460, 975 cm<sup>-1</sup>. Anal. calcd. for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O: C 72.43, H 5.69, N 15.83; found C 72.29, H 5.48, N 15.45.



Fig. 2. Synthesis of 4-chlorobenzal-hydrazine.



Fig. 3. Synthesis of 4-chlorobenzal-azino-isonitrosoacetophenone  $(L_1)$ .



Fig. 4. Synthesis of 4-methylbenzal-azino-isonitrosoacetophenone (L<sub>2</sub>).

**Preparation of Ni(II) complex of L**<sub>2</sub>. 4-methylbenzalazino-isonitrosoacetophenone (0.052 g, 0.2 mmol) was dissolved in 20 mL of ethanol. Then, 10 mL of aqueous solution of NiCl<sub>2</sub>  $\cdot$  6H<sub>2</sub>O (0.12 g, 0.5 mmol) was added dropwise to above solution by stirring. The pH of the reaction mixture was adjusted to 5.0–5.5 by adding an aqueous solution of NaOH (1%, wt). Precipitated solid was kept on a water bath at 60°C for 30 min, then filtered, washed with distilled-water, ethanol and diethyl ether, and dried in vacuum at 60°C. The product was obtained as a pale red solid in 90% yield (0.104 g). m.p. 198°C (with degradation); IR (KBr) v: 3440, 2900, 1612, 1640, 1665, 1420, 900, 536, 450 cm<sup>-1</sup>; Anal. calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>6</sub>O<sub>2</sub>Ni: C 65.44, H 4.80, N 14.30 Ni 9.99; found C 65.28, H 4.66, N 14.12 Ni 9.96.

**Preparation of Cu(II) complex of L**<sub>2</sub>. Complexes of L<sub>2</sub> with Cu(II) ion was prepared by the procedure above mentioned for the preparation of  $(L_2)_2$ Ni. The product was obtained as a green solid in 83% yield (0.096 g). m.p. 228°C (with degradation); IR (KBr) v: 3490, 2920, 1614, 1630, 1663, 1490, 980, 530, 448 cm<sup>-1</sup>. Anal. calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>6</sub>O<sub>2</sub>Cu: C 64.90, H 4.76, N 14.19 Cu 10.73; found C 64.66, H 4.57, N 13.95, Cu 10.70.

**Preparation of Co(II) complex of L<sub>2</sub>.** Complex of L<sub>2</sub> with Co(II) ion was prepared by the procedure above mentioned for the preparation of  $(L_2)_2$ Ni. The product

Compounds	0-Н	C-H (ar)	C=N <sup>a</sup>	C=N <sup>b</sup>	C=N <sup>c</sup>	C-H (aliph)	N-0	M–N	М-О	B.M. <sup>d</sup>
L <sup>1</sup>	_	3020	1612	1642	1656	1470	920	—	_	_
$L_2^1 Ni$	_	2940	1615	1645	1663	1410	960	515	430	Dia
$L_2^1$ Cu	—	2950	1617	1645	1665	1465	1000	520	440	1.90
$L_2^1$ Co	_	2940	1619	1650	1664	1420	975	528	435	2.43
$L_2^1$ ZrCl <sub>2</sub>	_	Weak	1618	1640	1670	1460	950	535	420	Dia
L <sup>2</sup>	3240	3000	1610	1635	1660	1460	975	—	—	_
$L_2^2 Ni$	_	2900	1612	1640	1665	1420	900	536	450	Dia
$L_2^2Cu$	—	2920	1614	1630	1663	1490	980	530	448	1.85
$L_2^2$ Co	_	2940	1620	1645	1666	1490	960	540	442	2.65
$L_2^2 Zr Cl_2$	_	2920	1618	1640	1670	1450	950	538	445	Dia

**Table 1.** Magnetic moment and the FT-IR spectral data of ligands and their metal complexes (cm<sup>-1</sup>) (KBr pellets)

<sup>a</sup> Oxime (C=N).

<sup>b</sup>Azomethine (C=N).

<sup>c</sup>Azine (C=N).

<sup>d</sup> Magnetic moment per metal atom.





Fig. 5. The suggested geometries of complexes.

was obtained as a brown solid in 91% yield (0.105 g). m.p. 233°C (with degradation); IR (KBr) v: 3620, 2940, 1620, 1645, 1666, 1490, 960, 540, 442 cm<sup>-1</sup>. Anal. calcd. for  $C_{32}H_{28}N_6O_2Co$ : C 65.41, H 4.80, N 14.30 Co 10.03; found C 64.94, H 4.70, N 14.08, Co 9.97.

**Preparation of Zr(IV) complex of L<sub>2</sub>.** Complex of L<sub>2</sub> with Zr(IV) ion was prepared by the procedure above mentioned for the preparation of  $(L_2)_2$ Ni. The product was obtained as a yellow solid in 92% yield (0.112 g). m.p. 189°C (with degradation); IR (KBr) v: 3500, 2920, 1618, 1640, 1670, 1450, 950, 538, 445 cm<sup>-1</sup>. Anal. calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>6</sub>O<sub>2</sub>ZrCl<sub>2</sub>: C 55.64, H 4.09, N 12.17, Zr 13.21; found C 55.60, H 4.05, N 12.13, Zr 13.19.

## **RESULTS AND DISCUSSION**

In this study, acetophenone was used as a starting material. Isonitrosoacetophenone was prepared according to published methods [1, 4]. Isonitrosophenylhydrazine was prepared by the coupling reaction of isonitrosoacetophenone with hydrazine hydrate. Then, 4-chloro-benzal-azino-isonitrosoacetophenone ( $L_1$ ) and 4-methyl-benzal-azino-isonitrosoacetophenone ( $L_2$ ) were synthesized from the reaction of isonitrosophenylhydrazine with 4-chlorobenzalde-

**Table 2.** Data of the <sup>1</sup>H NMR spectra of the ligands in DMSO- $d_6(\delta, \text{ppm})$ 

Com- pounds	O–H <sup>a</sup>	C–H*	C-H*	H (ar)	CH <sub>3</sub>
L <sup>1</sup>	11.65 s (1H)	8.77 s (1H)	8.58 s (1H)	7.08–8.29 m (10H)	—
L <sup>2</sup>	12.16 s (1H)	9.57 s (1H)	9.34 s (1H)	7.06–8.80 m (10H)	2.50 s (3H)

hyde and 4-methylbenzaldehyde. These compounds are derivatives of Schiff base and oxime. Transition metal complexes of them with Cu(II), Ni(II), Co(II) and Zr(IV) ions were prepared. Structures of ligands and their complexes were confirmed by IR, <sup>1</sup>H NMR spectra AAS and elemental analysis as well as physical methods.

In the IR spectra of the ligands (Table 1),  $C=N^{a}$ stretching in  $L_2$  was appeared at region of 1610 cm<sup>-1</sup>, while C=N<sup>a</sup> stretching in L<sub>1</sub> at 1612 cm<sup>-1</sup>. C=N<sup>b</sup> stretching in  $L_2$  were appeared at region of 1635 cm<sup>-1</sup>, while  $C = N^b$  stretching in L<sub>1</sub> at 1642 cm<sup>-1</sup>. In the IR spectra of the ligands,  $C=N^{c}$  stretching in  $L_{2}$  were appeared at region of 1660 cm<sup>-1</sup>, while C=N<sup>c</sup> stretching in  $L_1$  at 1656 cm<sup>-1</sup>. O–H and C–H (ar) stretchings in  $L_2$  give sharp peaks. Due to the existence of chloride group bound to benzene ring in Li, peaks of O-H and C-H (ar) interfere with each other. C-H (ar) frequencies range from 3000 to 3200 cm<sup>-1</sup>. O-H frequencies belonging to oxime were appeared at  $3400-3620 \text{ cm}^{-1}$ . These values are in agreement with literature [21]. In the IR spectra of the complexes, Cu(II), Ni(II) and Co(II) complexes demonstrated weaker C=N absorption than that of the ligands and no changes in N–O bonds. In all complexes, the bands in the region of 534–461 and 461–420 cm<sup>-1</sup> can be attributed to the M–N and M–O stretching modes [15].

The magnetic susceptibility of the complexes (Table 1) was measured at room temperature. The magnetic moments of the nickel(II) complex of the  $L_1$  and  $L_2$  have got four coordination of d<sup>8</sup> configuration and the diamagnetic nature of the compounds shows that it acquires an square planner structure [16]. It has been observed that the complexes of Co(II) and Cu(II) have got paramagnetic properties. The magneticness of the Co(II) complexes having d<sup>7</sup> configuration was measured and found as 2.35–2.65 B.M. These

values are within the normal range (2.20-2.70 B.M.) reported for square planar geometry [17]. The magneticness of the Cu(II) complexes having d<sup>9</sup> configuration was measured and found as 1.83-1.90 B.M.. These data show that the complexes has a square planner structures [18]. The magnetic moment of complexes of the Zr(IV) has got diamagnetic properties and shows that it acquires an octahedral structure [19]. These data are in agreement with the literature [2, 20-22].

The synthesized ligands have been characterized using <sup>1</sup>H NMR (Table 2) spectroscopy. Chemical shifts of O–H groups in  $L_1$  and  $L_2$  were appeared at 11.65 and 12.16 ppm, respectively. The chemical shift changes result from the effects of the electron-withdrawing and donating of substituents. Due to the existence of chlorine group in  $L_1$  signal of O–H is shifted. Likewise, the downfield shift of O-H signal in  $L_2$  is due to the existence of methyl group. Two different C-H signals were observed in two ligands. Proton signal of C–H adjacent to benzene ring bound methyl group in  $L_2$  is more obvious than that of oxime group. Aromatic protons in ligands were appeared at approximately expected regions. The chemical shift of methyl substituent in  $L_2$  was observed at 2.5 ppm as a singlet. Also, peaks at 11–12 ppm were disappeared when the ligands were treated with  $D_2O$ . This show that these values belong to protons of O–H.

<sup>1</sup>H NMR spectra of complexes could not be taken because they have not good solubility in common organic solvents. Thus, their structures were confirmed by IR spectra, AAS and elemental analysis. As seen from the results, it was determined that coordination geometries of complexes are square plane and octahedral. The suggested structures are given in Fig. 5.

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