

# Synthesis and Characterization of 4-(Alkylaminoisonitrosoacetyl)diphenyl ether and Some of Their Metal Complexes

Ahmet COŞKUN\* and Funda YILMAZ

*Department of Chemistry, Faculty of Education, Selçuk University, Konya-TURKEY*

*e-mail: acoskun42@selcuk.edu.tr*

Received 16.05.2007

4-(Chloroacetyl)diphenyl ether (I) was synthesized from chloroacetyl chloride and diphenyl ether in the presence of  $\text{AlCl}_3$  as catalyst in a Friedel-Crafts reaction. Subsequently, its keto oxime (II) derivative was prepared. Then 3 new substituted 4-(alkylaminoisonitrosoacetyl)diphenyl ether ligands derived from 4-(phenoxy)phenyloxylohydroxymoyl chloride and corresponding amines were synthesized. The following aromatic and aliphatic amines were used for the ligands ethanolamine, 2-amino-4-methylphenol, and 2-(aminomethyl) pyridine. Mononuclear or binuclear Co(II), Ni(II), Cu(II), and Cd(II) complexes of the ligands were synthesized. The structures of these ligands were identified by FT-IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectral data and elemental analysis, and the structures of the complexes were identified by FT-IR, ICP-AES, elemental analysis, and magnetic susceptibility measurements.

**Key Words:** Ketoxime, transition metal complexes, binuclear complexes.

## Introduction

Oximes and their metal complexes are of current interest for their rich physicochemical properties, reactivity patterns, and potential applications in many important chemical processes in the areas of medicine,<sup>1-4</sup> bioorganic systems,<sup>5,6</sup> catalysis,<sup>7,8</sup> and electrochemical and electro-optical sensors.<sup>9-11</sup> Current research concerning the structure and properties of polynuclear oxime complexes is aimed at understanding the structural and chemical features governing electronic exchange coupling through multiatomic bridging ligands. Some types of ligand systems, which can bind 2 metal ions in close proximity, were used as biomimetic studies of binuclear metalloenzyme and metalloprotein due to their interesting catalytic properties, their ability to stabilize unusual oxidation states, and possibilities for magnetic interaction between 2 metal ions. Thus, during the last 2 decades, homopolynuclear systems are of interest to both inorganic chemists and biologists

---

\*Corresponding author

investigating the structure and function of the polynuclear metal centers in protein and to physicists or physical inorganic chemists searching for new materials.<sup>12–16</sup>

This article describes the synthesis and characterization of 3 new 4-(alkylaminoisonitrosoacetyl)diphenyl ether ligands and their binuclear and mononuclear metal complexes.

## Materials and Methods

4-(Chloroacetyl)diphenyl ether (I) was prepared according to the literature procedure.<sup>17</sup> All solvents, amines, and metal salts  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  used for the synthesis and physical measurements were reagent grade and used without further purification. Elemental analyses (C, H, N) were determined using a Leco, CHNS-932 model analyzer.  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectra were recorded on a Bruker DPX-400 400 MHz High Performance Digital FT-NMR. Infrared spectra were recorded on a Perkin-Elmer model 1605 FT-IR spectrophotometer as KBr pellets. Metal contents of the compounds were determined on a Varian, Vista AX CCD simultaneous spectrophotometer. The magnetic moments of the complexes were measured using a Sherwood Scientific model MX1 Gouy magnetic susceptibility balance at room temperature. The pH values were measured on a WTW pH, 537 pH meter.

## Experimental

### Synthesis of 4-(phenoxy)phenyloxyhydroxymoyl chloride (II)

4-(Chloroacetyl)diphenyl ether (2.46 g, 10 mmol) was dissolved in  $\text{CHCl}_3$  (40 mL) with cooling, and then HCl gas was bubbled through the solution for 30 min. Butyl nitrite (1.5 mL, 11 mmol) was added dropwise to the mixture with stirring and passing HCl gas into the mixture. The mixture was left overnight to form a precipitate at room temperature. The precipitate was filtered and recrystallized from  $\text{Et}_2\text{O}$ -hexane (1:1). The crystallized product was filtered off, washed with hexane, and dried. Yield, 1.93 g (74%), mp 128 °C.

### Preparation of the ligands

The ligands ( $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$ ,  $\text{H}_2\text{L}^3$ ) were obtained by the reaction of amines [2-(aminomethyl) pyridine, 2-amino-4-methylphenol and ethanolamine] with 4-(phenoxy)phenyloxyhydroxymoyl chloride in the presence of triethylamine. The amine (16.5 mmol) and triethylamine (15 mmol) dissolved in 50 mL of ethanol was added dropwise to a solution of 4-(phenoxy)phenyloxyhydroxymoyl chloride (3.92 g, 15 mmol) in 50 mL of ethanol over 30 min at 0 °C. Precipitation and color change were observed in the reaction medium immediately. After this period, the reaction mixture was stirred for 2 h at the same temperature. Then it was allowed to stir at ambient temperature for 2 h. The powder resulting from the reaction is insoluble in ethanol and thus was filtered off, washed with aqueous sodium bicarbonate (1%), distilled water, and ethanol, and dried in air.

### Preparation of the complexes

A quantity of 1.00 mmol ligands ( $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$ ,  $\text{H}_2\text{L}^3$ ) was dissolved in 40 mL of hot ethanol. Then the solution of 1.00mmol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in 20 mL of ethanol (95%) was added dropwise with stirring. The pH of the reaction mixture was around 3.5-4.0 and

was then adjusted to 5.5-6.0 by adding 1% NaOH solution. The complex precipitated was kept in a water bath at 70 °C for 1 h in order to complete the precipitation. The precipitate was filtered off, washed with hot water, ethanol, and ether, and dried.

The colors, yield, melting points, elemental analyses, and FT-IR data of the complexes and ligands are given in Tables 1 and 2, and the <sup>1</sup>H- and <sup>13</sup>C-NMR data of the ligands in Tables 3 and 4, respectively.

**Table 1.** Physical properties and elemental analysis of the ligands and complexes.

Compounds	Color	mp (°C)	Yield (%)	Calculated/Found % of			
				C	H	N	Metals
II	Yellow	128	74	64.24/64.10	3.82/3.77	5.35/5.29	-
H <sub>2</sub> L <sup>1</sup>	Yellow	98	65	64.00/63.82	5.33/5.21	9.33/9.16	-
Co(HL <sup>1</sup> ) <sub>2</sub>	Brown	117	63	58.45/58.24	4.56/4.39	8.52/8.34	8.97/9.08
Ni(HL <sup>1</sup> ) <sub>2</sub>	Green	119	85	58.47/58.63	4.57/4.76	8.53/8.41	8.94/8.78
Cu <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Green	202	86	48.30/48.46	4.53/4.37	7.04/6.87	15.98/15.69
Cd <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Dark green	155	87	43.01/42.88	4.03/4.14	6.27/6.36	25.18/25.05
H <sub>2</sub> L <sup>2</sup>	Cream	147	61	69.61/69.74	4.97/4.81	7.73/7.89	-
Co <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Brown	254	72	55.39/55.45	4.39/4.52	6.15/6.04	12.95/12.79
Ni <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Red brown	> 300	80	55.42/55.27	4.40/4.53	6.16/6.02	12.91/12.94
Cu <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Dark brown	240	86	54.84/54.77	4.35/4.46	6.09/6.17	13.83/13.66
Cd <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Light brown	290	63	49.57/49.39	3.93/4.04	5.51/5.39	22.11/22.19
H <sub>2</sub> L <sup>3</sup>	Green yellow	101	68	69.16/69.29	4.90/4.73	12.10/11.89	-
Co(L <sup>3</sup> ) <sub>2</sub>	Light brown	212	66	63.92/63.77	4.26/4.40	11.18/11.04	7.85/7.69
Ni(L <sup>3</sup> ) <sub>2</sub>	Dark brown	287	83	63.94/63.86	4.26/4.34	11.19/11.09	7.82/7.77
Cu(L <sup>3</sup> ) <sub>2</sub>	Green	208	82	63.53/63.39	4.23/4.12	11.12/11.23	8.41/8.53
Cd(L <sup>3</sup> ) <sub>2</sub>	Brown	199	69	59.67/59.55	3.98/3.76	10.44/10.53	13.97/13.86

## Results and Discussion

4-(Chloroacetyl)diphenyl ether (I) was obtained by the reaction of chloroacetyl chloride with diphenylether in the presence of AlCl<sub>3</sub> as catalyst in a Friedel-Crafts reaction.<sup>17</sup> 4-(Phenoxy)phenyloxyhydroxymoyl chloride (II) was originally synthesized by following the methods described in the literature.<sup>18</sup> 4-(Ethanolaminoisonitrosoacetyl)diphenyl ether (H<sub>2</sub>L<sup>1</sup>), 4-(2-hydroxy-5-methylphenylaminoisonitrosoacetyl)diphenyl ether (H<sub>2</sub>L<sup>2</sup>), and 4-[2-(aminomethyl)pyridylisonitrosoacetyl]diphenyl ether (H<sub>2</sub>L<sup>3</sup>) were prepared by the condensation reaction of II with ethanolamine, 2-amino-4-methylphenol, and 2-(aminomethyl)pyridine, respectively.

We report the synthesis of new 4-(alkylaminoisonitrosoacetyl)diphenyl ethers, shown below in Scheme 1, and the metal complexes of these compounds.

The <sup>1</sup>H-NMR spectrum of 4-(phenoxy)phenyloxyhydroxymoyl chloride (II) exhibits a singlet peak for the OH protons of the oxime group at 13.60 ppm. In all ligands, a singlet peak at 9.84-10.55 ppm is also attributed to the OH proton of the oxime group. The higher shift of the OH protons of the oxime group is

typical of the condensation reaction with 4-(phenoxy)phenoxylohydroxymoyl chloride and corresponding amines. The NH protons neighboring the oxime groups were observed at 8.47-9.24 ppm, aromatic C-H protons at 6.46-7.96 ppm, aliphatic C-H protons at 2.19-4.33 ppm, and OH protons of ethanolamine and phenol at 5.52 and 6.81 ppm, respectively. These values are in good agreement with those of known oximes.<sup>19,20</sup> <sup>1</sup>H-NMR spectra of the complexes could not be obtained because of their very low solubility in organic solvents.

**Table 2.** Magnetic measurements and characteristic IR bands ( $\text{cm}^{-1}$ ) of the ligands and their complexes as KBr pellets.

Compounds	$\mu_{eff}, \mu_B$ per M(II)	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{N-O})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$
II	-	3252 b	1604 s	1022 s	-	1654 s
H <sub>2</sub> L <sup>1</sup>	-	3279 b	1606 s	996 s	3319 m	1636 m
Co(HL <sup>1</sup> ) <sub>2</sub>	3.21	3286 b	1603 s	998 w	3333 m	1638 m
Ni(HL <sup>1</sup> ) <sub>2</sub>	3.24	3288 b	1597 s	998 w	3347 m	1691 m
Cu <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> .4H <sub>2</sub> O	1.02	-	1590 s	997 w	3340 b	1688 m
Cd <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Dia	-	1604 s	998 w	3343 b	1635 m
H <sub>2</sub> L <sup>2</sup>	-	3381s, 3151 w	1608 s	987 m	3192 s	1680 s
Co <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	3.31	-	1599 s	954 w	3395 b	1645 s
Ni <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	2.17	-	1596 s	949 w	3384 b	1666 s
Cu <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	1.09	-	1580 s	964 w	3388 b	1667 s
Cd <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> .4H <sub>2</sub> O	Dia	-	1599 s	945 m	3390 b	1665 s
H <sub>2</sub> L <sup>3</sup>	-	3198 b	1597 s	1002 w	3379 m	1651 s
Co(L <sup>3</sup> ) <sub>2</sub>	4.08	-	1599 s	1004 w	3402 b	1640 m
Ni(L <sup>3</sup> ) <sub>2</sub>	2.20	-	1571 s	1004 w	3387 b	1596 m
Cu(L <sup>3</sup> ) <sub>2</sub>	1.21	-	1600 s	1005 w	3397 b	1638 m
Cd(L <sup>3</sup> ) <sub>2</sub>	Dia	-	1600 s	1006 w	3389 b	1652 m

s: strong, m: medium, w: weak

**Table 3.** <sup>1</sup>H-NMR spectral data of the ligands in DMSO-d<sup>6</sup>, ( $\delta$ , ppm).

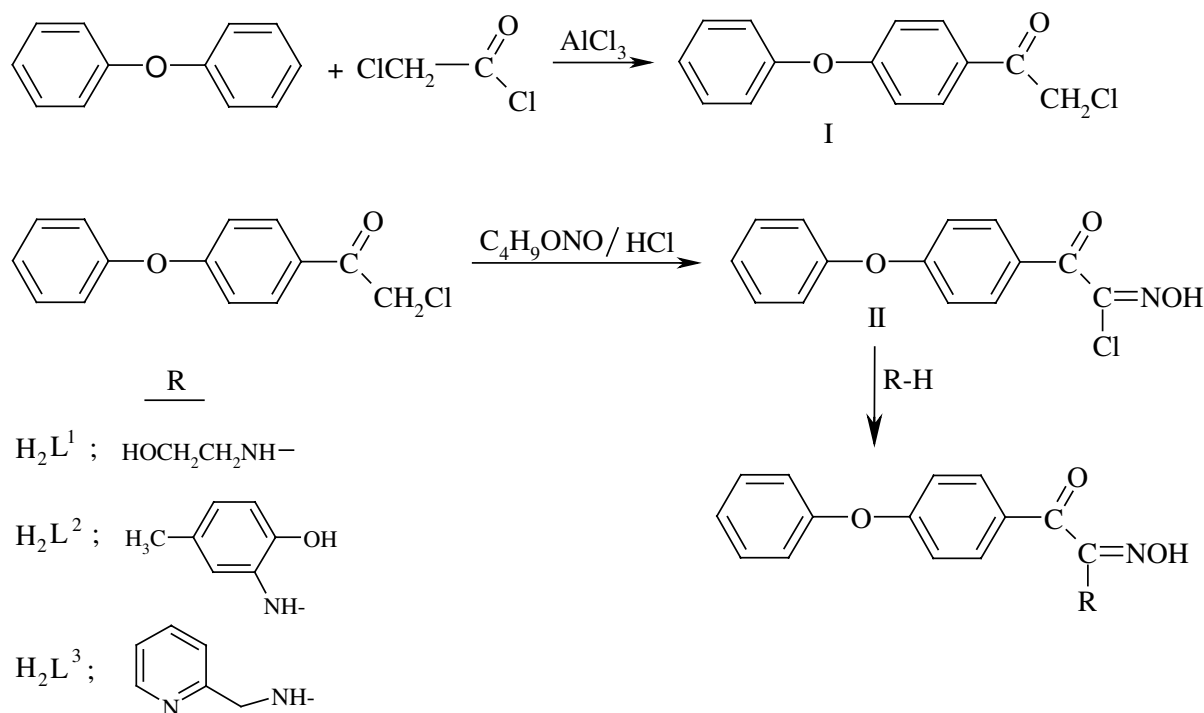
Compounds	O-H*	O-H**	C-H (arom)	C-H(aliph)	N-H
II	13.60 (s, 1H)	-	7.24-7.96 (m, 9H)	-	-
H <sub>2</sub> L <sup>1</sup>	10.36 (s, 1H)	5.52 (s, 1H)	7.29-8.02 (m, 9H)	2.88-3.84 (m, 4H)	8.52 (t, J=5.5 Hz, 1H)
H <sub>2</sub> L <sup>2</sup>	9.84 (s, 1H)	6.81 (s, 1H)	6.46-7.57 (m, 12H)	2.19 (s, 3H)	9.24 (s, 1H)
H <sub>2</sub> L <sup>3</sup>	10.55 (s, 1H)	-	7.08-7.91 (m, 13H)	4.33 (d, J=6.2 Hz, 2H)	8.47 (t, J=4.8 Hz, 1H)

\*OH of oxime group

\*\* OH of alcohol or phenol groups

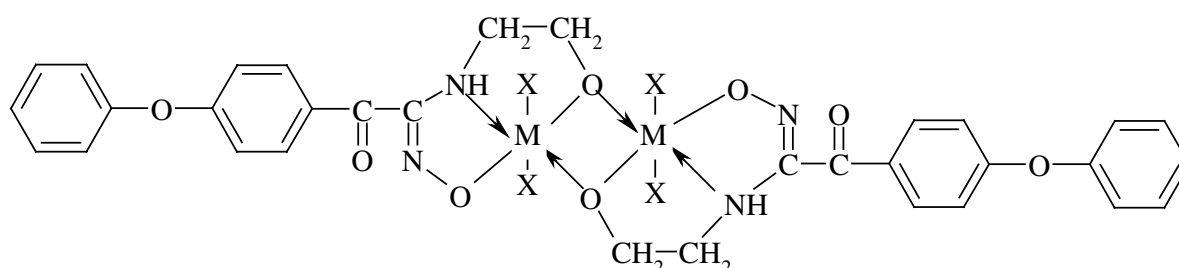
**Table 4.**  $^{13}\text{C}$ -NMR spectral data of the ligands (DMSO-  $d_6$ ).

Compounds	$\delta$ (ppm)
II	183.13, 162.36, 155.47, 136.70, 133.75, 131.10, 130.39, 125.65, 120.81, 117.54
$\text{H}_2\text{L}^1$	181.54, 157.60, 153.39, 135.66, 133.60, 131.02, 130.32, 125.44, 119.77, 117.39, 64.40, 44.98
$\text{H}_2\text{L}^2$	181.46, 157.39, 153.30, 140.26, 136.54, 134.20, 133.46, 131.25, 130.12, 129.48, 128.10, 125.05, 120.74, 119.60, 117.81, 116.54, 21.40
$\text{H}_2\text{L}^3$	181.32, 158.64, 157.26, 155.19, 154.68, 149.36, 136.80, 134.40, 133.10, 131.02, 130.20, 129.34, 126.80, 119.78, 117.81, 47.52


**Scheme 1.** The synthesis of 4-(chloroacetyl)diphenyl ether (I), 4-(phenoxy)phenyloxylhydroxymoyl chloride (II), and ligands ( $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$ ,  $\text{H}_2\text{L}^3$ ).

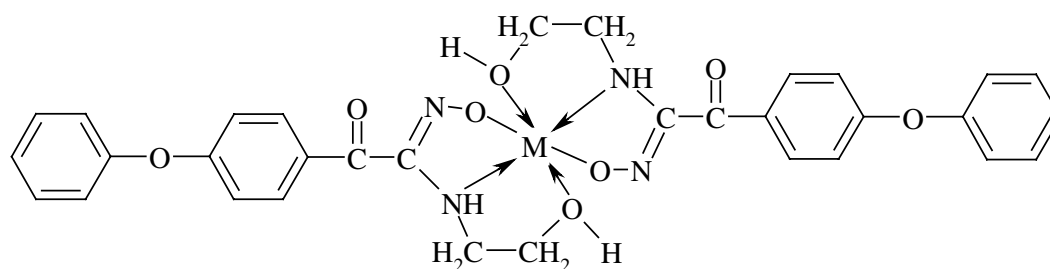
In the  $^{13}\text{C}$ -NMR spectra of the ligands II,  $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$ , and  $\text{H}_2\text{L}^3$  the signals at 162.36, 157.60, 157.39, and 157.26 ppm; and the signals at 183.14, 181.54, 181.46, and 181.32 ppm are attributed to the oxime and the carbonyl carbon atoms, respectively. All the signals in the range 116.54-157.26 ppm are assigned to the carbon atoms of the aromatic rings. The signals at 44.98, 64.40, and 47.52 ppm in the  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^3$  ligand belong to  $\text{NHCH}_2$ ,  $\text{OCH}_2$ , and  $\text{Py}-\text{CH}_2$  carbon atoms, respectively. All these values are in good agreement with the values previously reported.<sup>20</sup>

In the FT-IR spectra of these compounds, the differences between the spectral bands of  $H_2L^1$ ,  $H_2L^2$ , and  $H_2L^3$  are clearly shown by the presence of characteristic vibrations at  $3379\text{--}3192\text{ cm}^{-1}$  belonging to the NH groups. The ligands exhibit stretching frequencies OH ( $3381\text{--}3151\text{ cm}^{-1}$ ) and N-O ( $1002\text{--}996\text{ cm}^{-1}$ ) as for substituted aminooximes. In the complexes, N-H stretching vibrations are shifted to higher frequencies in the  $3402\text{--}3333\text{ cm}^{-1}$  range, and this confirms that the nitrogen atom of the amine group is coordinated to the metal ions. The coordination of the amine nitrogen to the metal ions can be inferred from the shift of  $\nu\text{C}=\text{N}$  from  $1608\text{--}1597$  to about  $1604\text{--}1571\text{ cm}^{-1}$ . In addition, the spectra of the complexes do not show hydroxyl frequencies, because the oxygen atom of the hydroxyl group is coordinated to the metal ions. The OH stretching vibrations were not observed in the spectra of the binuclear Cu(II) and Cd(II) complexes of  $H_2L^1$  (Scheme 2), which indicates the separation of OH protons of both alcohol and oxime groups.



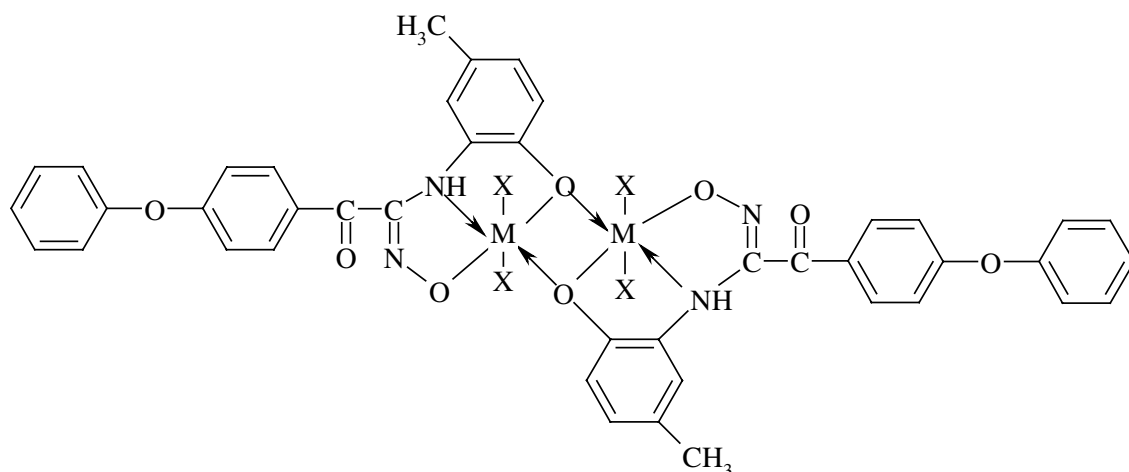
**Scheme 2.** Binuclear Cu(II) and Cd(II) complexes of  $H_2L^1$  ( $X=H_2O$ ).

In the spectra of the Co(II) and Ni(II) complexes of  $H_2L^1$  (Scheme 3), the bands at  $3286$  and  $3288\text{ cm}^{-1}$  are assigned to the ethanolic hydroxyl groups. The binuclear metal complexes of  $H_2L^2$  (Scheme 4) exhibit the disappearance of the OH stretching vibrations at  $3381$  and  $3151\text{ cm}^{-1}$ , which shows the separation of OH protons of both phenol and oxime groups.

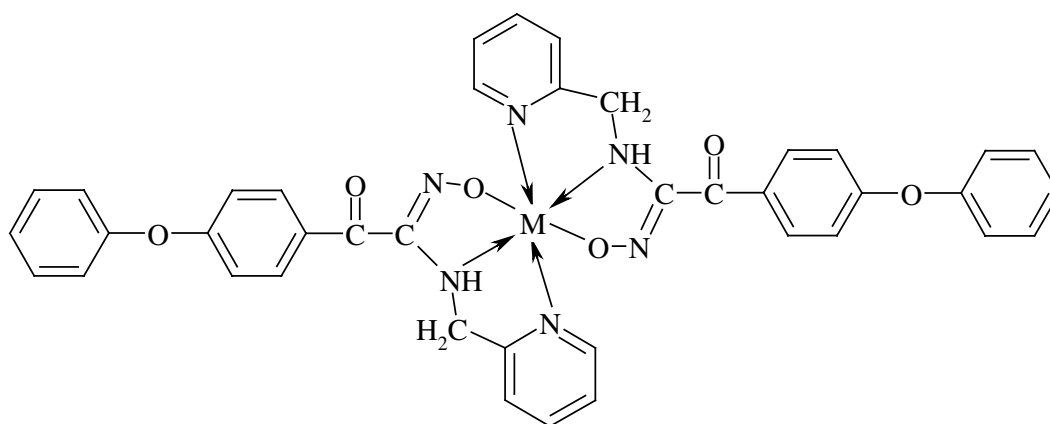


**Scheme 3.** Co(II) and Ni(II) complexes of  $H_2L^1$ .

The disappearance of the OH band at  $3198\text{ cm}^{-1}$  in the complexes of  $H_2L^3$  indicates coordination through the O atom of the oxime group. The stretching vibration of C=C pyridine rings appears at  $1477\text{ cm}^{-1}$  in  $H_2L^3$ , which shifts to the  $1529\text{--}1486\text{ cm}^{-1}$  range in their metal complexes (Scheme 5). This indicates coordination through the N atom of the pyridine ring.<sup>21</sup> In the FT-IR spectra of the metal complexes, the bands at  $1691\text{--}1596$ ,  $1604\text{--}1571$ , and  $1006\text{--}945\text{ cm}^{-1}$  belong to C=O, C=N, and N-O stretching vibrations, respectively. The FT-IR data of the ligands and their complexes are in good agreement with those of known oximes.<sup>21–24</sup>



**Scheme 4.** Binuclear Co(II), Ni(II), Cu(II) and Cd(II) complexes of  $H_2L^2$  ( $X=H_2O$ ).



**Scheme 5.** Co(II), Ni(II), Cu(II), and Cd(II) complexes of  $H_2L^3$ .

According to the FT-IR data, elemental analyses and magnetic susceptibility measurements, the mononuclear complexes have a metal to ligand ratio of 1:2, and the binuclear complexes have a metal to ligand ratio of 1:1. The room temperature magnetic moment measurements show that all Cd(II) complexes are diamagnetic, as expected, and the Cu(II) complexes are paramagnetic. The binuclear Cu(II) complexes show effective magnetic moments lower than the expected value at room temperature and their magnetic susceptibilities are 1.02 and 1.09  $\mu_B$  per  $Cu^{2+}$  ion. Magnetic susceptibility of the mononuclear Cu(II) complex is 1.21  $\mu_B$ . The Ni(II) complexes are paramagnetic with magnetic susceptibility values of 2.17-3.24  $\mu_B$ , which fit the 2-spin value, 2.83  $\mu_B$ . The results for the Ni(II) complexes fit the  $d^8$  metal ion in an octahedral structure.<sup>25,26</sup> The Co(II) complexes are paramagnetic with magnetic susceptibilities of 3.21-4.08  $\mu_B$ , which fit the tri-spin value, 3.90  $\mu_B$ . All the complexes of these ligands have an octahedral structure. The above values of FT-IR,  $^1H$ -NMR,  $^{13}C$ -NMR, elemental analyses, and magnetic susceptibility are in agreement with those of previously reported aminoglyoximes.<sup>24,27-29</sup>

## Acknowledgment

This study was supported by the Scientific Research Projects Coordinator of Selçuk University (Konya, Turkey). (Project No 2005/05401005).

## References

1. (a) G.A. Melson, **Coordination Chemistry of Macrocyclic Compounds**. New York, Plenum Press, 1979. (b) J.J. Christensen, J.J. Eatough and R.M. Izatt, **Chem. Rev.** **74**, 351-384 (1974).
2. J.R. Dilworth and S.J. Parrott, **Chem. Soc. Rev.** **27**, 43-55 (1998).
3. P.J. Blower, **Transition Met. Chem.** **23**, 109-112 (1998).
4. S.S. Jurisson and J.D. Lydon, **Chem. Rev.** **99**, 2205-2218 (1999).
5. W.A. Wolkert and T.J. Hoffman, **Chem. Rev.** **99**, 2269-2280 (1999).
6. K. Ohta, R. Higashi, M. Ikejima, I. Yamamoto and N. Kobayashi, **J. Mater. Chem.** **8**, 1979-1991 (1998).
7. P. Mitchell, **Science**, **206**, 1148-1159 (1979).
8. B.G. Malmstrom, **Acc. Chem. Res.** **26**, 332-338 (1993).
9. M.C.M. Laranleira, R.A. Marusak and A.G. Lappin, **Inorg. Chim. Acta.** **186**, 300-302 (2000).
10. M. Bakir, **J. Electroanal. Chem.** **466**, 60-66 (1999).
11. M. Bakir and J.A.M. McKenzie, **J. Electroanal. Chem.** **425**, 61-66 (1997).
12. P. Chaudhuri, **Coord. Chem. Rev.** **243**, 143-190 (2003).
13. A. Yatani, M. Fujii, Y. Nakao, S. Kashino, M. Kinoshita, W. Mori and S. Suzuki, **Inorg. Chim. Acta.** **316**, 127-132 (2001).
14. C.H. Li, R.J. Wang, H.Z. Kou and Y.D. Li, **Inorg. Chem. Commun.** **5**, 403-406 (2002).
15. N. Sengottuvelan, J. Manonmani and M. Kandaswamy, **Polyhedron.** **21**, 2767-2772 (2002).
16. F. Akagi, Y. Michihiro, Y. Nakao, K. Matsumoto, T. Sato and W. Mori, **Inorg. Chim. Acta.** **357**, 684-688 (2004).
17. G. Cavallini, E. Massarani, D. Nardi, L. Mauri, F. Tenconi and P. Mantegazza, **J. Med. Chem.** **6**, 573-578 (1963).
18. D.S. Breslow, K. Brack and H.A. Boardman, **J. Appl. Polym. Sci.** **32**, 4657-4661 (1986).
19. H.E. Ungnade, B. Fritz and L.W. Kissenger, **Tetrahedron.** **19**, 235-248 (1963).
20. H.E. Ungnade, D.C. Baham, A. Narath and L.W. Kissenger, **J. Org. Chem.** **28**, 134-136 (1963).
21. M. Tumer, H. Koksall and M.K. Sener, **Transition Met. Chem.** **24**, 414-420 (1999).
22. J.E. Caton and C.V. Banks, **Inorg. Chem.** **6**, 1670-1675 (1967).
23. A. Nakamura, A. Konishi and S. Otsuka, **J. Chem. Soc., Dalton Trans.** 488-495 (1979).
24. F. Karipcin, F. Arabali and I. Karataş, **Russ. J. Coord. Chem.** **32**, 109-115 (2006).
25. F.A. Cotton and G. Wilkinson, **Advanced Inorganic Chemistry**, New York, Wiley. 725-749 (1988).
26. M.A. Deveci and G. Irez, **Synth. React. Inorg. Met-Org. Chem.** **26**, 871-881 (1996).
27. F. Karipcin, H.I. Uçan and I. Karataş, **Transition Met. Chem.** **27**, 813-817 (2002).
28. A. Coşkun and I. Karataş, **Turk. J. Chem.** **28**, 173-180 (2004).
29. A. Coşkun, **Turk. J. Chem.** **30**, 461-469 (2006).