ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 1, pp. 66–70. © Pleiades Publishing, Ltd., 2016.

Coordination Chemistry of Some New Cu(II), Ni(II) and Co(II) Macroacyclic (N_2O_4) Schiff Base Complexes: X-ray Crystal Structure of Cu(II) Complex[1]

M. Rezaeivala[a], *, R. Golbedaghi[b], and M. Khalili[b]

[a] Department of Chemical Engineering, Hamedan University of Technology, Hamedan, 65155 Iran
[b] Chemistry Department, Payame Noor University, 19395-4697 Tehran, Iran
*e-mail: mrezaeivala@gmail.com; mrezaeivala@hut.ac.ir

Received February 11, 2015

Abstract—Six new Cu(II), Ni(II) and Co(II) macroacyclic Schiff base complexes $[M^{II}(H_2L)](ClO_4)_2$ (L = L^1 and L^2) (I–VI) were prepared by the reaction of two new N_2O_4 Schiff base ligands in equemolar ratios. The ligands H_2L^1 and H_2L^2 were synthesized by reaction of 2-[2-(2-formyl phenoxy)ethoxy]benzaldehyde (A^1) and/or 2-[2-(3-formylphenoxy)propoxy]benzaldehyde (A^2) and ethanol amine and characterized with IR and ^1H, ^{13}C NMR spectroscopy. All complexes were characterized by microanalysis, IR and mass spectrometry, whereas complex **I** was also characterized by single crystal X-ray (CIF file CCDC no. 1020055). The X-ray structure of complex **I** revealed that all nitrogen and oxygen atoms of ligand (N_2O_4) have coordinated to the metal ion. However, Cu^{2+} ion is in six coordination environment that can bedescribed as a distorted octahedral geometry.

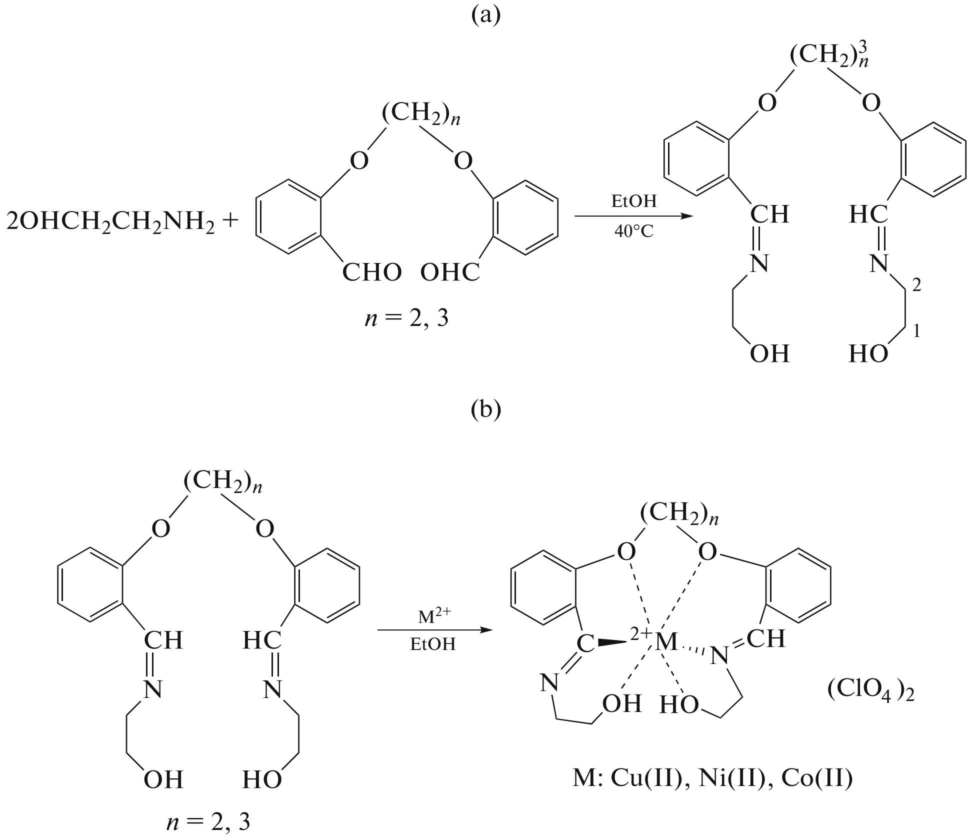
DOI: 10.1134/S1070328415120064

INTRODUCTION

Schiff base complexes of transition metal ions have receivedgreat attention for their medicinal, industrial, catalytic activities and as antibacterial [1–11]. The key Schiff base condensation reaction involves simply the reaction of an amine with aldehyde to eliminate water and give an imine. They are named after Hugo Schiff who first reported this type of reaction in 1864 [12]. Complexation with metals often improvesthe stability of the Schiff bases [1]. A review was published on the chemistry of these systems and there is also an extensive review ontheir complexation behavior with many metals [13]. The ligands must be sophisticatedly designed so that their preferred conformation is appropriate for the desired complexation and architecture, especially in the integrated systems, such as helicates, which are accomplished by self-assembly. Recently, we reported synthesis and characterization of several mono and dinuclear macrocyclic and macroacyclic Schiff base ligands and related metal complexes [3–5, 14–17]. In this paper, we report the study of the various complexes which show characteristic architecture and properties depending on the conformation of the Schiff base ligand. Herein, we report the synthesis and characterization of Cu(II), Ni(II), and Co(II) complexes of two linear Schiff base ligands derived from the 2-[2-(2-formyl phenoxy)ethoxy]benzaldehyde and/or 2-[2-(3-formyl phenoxy)ethoxy]benzaldehyde and ethanol amine (Scheme). The resulting complexes were characterized by elemental analysis and IR in all cases and single crystal X-ray diffraction in the case of complex $[Cu(H_2L^1)](ClO_4)_2$ (**I**). Syntheses of the Schiff base ligands H_2L^1 and H_2L^2 (a) and related complexes (b) are given in Scheme:

---

[1] The article is published in the original.



Scheme.

EXPERIMENTAL

General information. Hydrated metal salts and ethanol amine were obtained from Aldrich and were used without further purification. IR and NMR spectra were measured on a Perkin Elmer FT-IRGX and a Bruker DPX 300 spectrometer, respectively.

2-[2-(2-Formyl phenoxy)ethoxy]benzaldehyde (A^1) and/or 2-[2-(3-formylphenoxy) propoxy] benzaldehyde (A^2) were prepared according to literature method [18].

Synthesis of ligand H_2L^1. Aldehyde (0.27 g, 1 mmol) and ethanol amine (0.122 g, 2 mmol) were mixed and heated in the 40°C for 30 min in EtOH (30 mL). The solution was filtered and the filtrate was reduced to ~10 cm^3. Yellow crystalline compound was obtained washed with cooled ethanol and dried. The yield was 60%.

For $C_{20}H_{24}N_2O_4$

anal. calcd, %:	C, 67.40;	H, 6.79;	N, 7.86.
Found, %:	C, 67.36;	H, 6.77;	N, 17.76.

IR (ν, cm^{-1}): 1642 ν(C=N Schiff base), 1492 ν(C=C), 3160 ν(OH). ^1H NMR (DMSO; 300 MHz; δ, ppm): 3.66 (s., 4H), 3.54 (t., 4H), 3.85 (t., 4H), 6.98 (m., 2H), 7.40 (m., 2H) 7.96 (m., 2H), 7.99 (m., 2H), 870 (s., 2H). ^{13}C NMR (DMSO; 300 MHz; δ, ppm): 60.78(C-1), 63.81(C-2), 67.64 (C-3), 112.64, 120.38, 124.02, 126.63, 131.94, 136.43, 156.67, 157.66 (aromatic rings), 168.87 (Schiff base).

Synthesis of ligand H_2L^2 was carried out by an analogous method used for H_2L^1. The yield was 54%.

For $C_{21}H_{26}N_2O_4$

anal. calcd, %:	C, 67.85;	H, 6.84;	N, 7.91.
Found, %:	C, 67.44;	H, 6.79;	N, 17.81.

IR (ν, cm^{-1}): 1638 ν (C=N Schiff base), 1490 ν (C=C), 3365 ν (OH). ^1H NMR (DMSO; 300 MHz; δ, ppm): 2.36 (m., 2H), 3.71 (t., 4H), 3.82 (t., 4H), 4.25 (t., 4H), 6.99 (m., 2H), 7.40 (m., 2H) 7.96 (m., 2H), 7.99 (m., 2 H), 875 (s., 2H). ^{13}C NMR (DMSO; 300 MHz; δ, ppm): 62.48 (C-1), 63.57 (C-2), 65.03 (C-3), 76.73(C-4), 77.05(C-5), 112.20, 121,09, 125.62, 125,74, 126.84, 127.40, 132.16 (aromatic rings), 158.88 (Schiff base).

Synthesis of complex $[Cu(H_2L^1)](ClO_4)_2$ (I) was carried out by reaction of ligand H_2L^1 and $Cu(ClO_4)_2 \cdot$

$6H_2O$. Ligand H_2L^1 (0.178 g, 0.5 mmol) was solved in 10 mL methanol and the solution was stirred at 30–40°C. $Cu(ClO_4)_2 \cdot 6H_2O$ (0.185 g, 0.5 mmol) dissolved in MeOH (5 mL) was subsequently added. The mixture was stirred at 50–60°C for 24 h. The solution was filtered and the filtrate was reduced to ~10 cm^3. A crystalline compound was obtained by slow diffusion of Et_2O vapor into this solution. The yield of complex I was 0.16 g (55%).

For $C_{20}H_{24}N_2O_{12}Cl_2Cu$

anal. calcd., %:	C, 38.82;	H, 3.91;	N, 4.53.
Found, %:	C, 38.95;	H, 3.50;	N, 4.10.

IR (ν, cm^{-1}): 3442 ν(OH), 1637 ν(C=N, Schiff base), 1486 ν(C=C), 1120, 625 ν(ClO_4).

Synthesis of complex $[Ni(H_2L^1)](ClO_4)_2$ (II) was carried out by an analogous method used for **I**. Ligand H_2L^1 (0.370 g, 1 mmol) was solved in 10 mL methanol and the solution was stirred at 30–40°C. $NiCl_2 \cdot 6H_2O$ (0.236 g, 1 mmol) dissolved in MeOH (5 mL) was subsequently added. The mixture was stirred at 50–60°C for 24 h, then $NaClO_4$ (0.28 g, 2 mmol) was added. The solution was filtered and the filtrate was reduced to ~10 cm^3. A crystalline compound was obtained by slow diffusion of Et_2O vapor into this solution. The yield of complex **II** was 0.13 g (52%).

For $C_{20}H_{24}N_2O_{12}Cl_2Ni$

anal. calcd., %:	C, 39.12;	H, 3.94;	N, 4.56.
Found, %:	C, 38.95;	H, 3.65;	N, 4.41.

IR (ν, cm^{-1}): 3432 ν(OH), 1637.27 ν(C=N, Schiff base), 1484.92 ν(C=C); 1061, 624.6 ν(ClO_4).

Synthesis of complex $[Co(H_2L^1)](ClO_4)_2$ (III) was carried out by an analogous method used for **II** only used $Co(CH_3CO_2)_2 \cdot 6H_2O$. The yield of complex **III** was 15 g (58%).

For $C_{20}H_{24}N_2O_{12}Cl_2Co$

anal. calcd., %:	C, 39.12;	H, 3.94;	N, 4.56.
Found, %:	C, 38.90;	H, 3.55;	N, 4.21.

IR (ν, cm^{-1}): 3428 ν(OH); 1636 ν(C=N, Schiff base); 1486 ν(C=C); 1109, 626 ν(ClO_4).

Synthesis of complex $[Cu(H_2L^2)](ClO_4)_2$ (IV) was carried out by reaction of ligand H_2L^2 and $Cu(ClO_4)_2 \cdot 6H_2O$. The yield of complex **IV** was 75%.

For $C_{21}H_{26}N_2O_{12}Cl_2Cu$

anal. calcd., %:	C, 39.85;	H, 4.14;	N, 4.42.
Found, %:	C, 39.50;	H, 3.90;	N, 4.10.

IR (ν, cm^{-1}): 3412.4 ν(OH); 1637.27 ν(C=N, Schiff base); 1488.06 ν(C=C); 1073.19, 623.58 ν(ClO_4).

Synthesis of complex $[Ni(H_2L^2)](ClO_4)_2$ (V) was carried out by an analogous method used for **I**. The yield of complex **V** was 67%.

For $C_{21}H_{26}N_2O_{12}Cl_2Ni$

anal. calcd., %:	C, 40.16;	H, 4.17;	N, 4.46.
Found, %:	C, 39.90;	H, 4.01;	N, 4.30.

IR (ν, cm^{-1}): 3420 ν(OH), 1652.7 ν(C=N, Schiff base), 1487.8 ν(C=C), 1108.9, 625.79 ν(ClO_4).

Synthesis of complex $[Co(H_2L^2)](ClO_4)_2$ (VI) was carried out in an analogous method to **I**. The yield of complex **VI** was 75%.

For $C_{21}H_{26}N_2O_{12}Cl_2Co$

anal. calcd., %:	C, 40.14;	H, 4.17;	N, 4.45.
Found, %:	C, 39.99;	H, 4.02;	N, 4.23.

IR (ν, cm^{-1}): 3431.7 ν(OH); 1637.7 ν(C=N, Schiff base); 1487.9 ν(C=C); 1085.6, 625.79 ν(ClO_4).

X-ray structure determination. Single crystal X-ray data on complex **I** was collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [19]. The data integration and reduction were carried out with SAINT [20] software. Empirical absorption correction was applied to the collected reflections with SADABS [21] and the space group was determined using XPREP [22]. The structure was solved by the direct methods using SHELXTL-97 [23] and refined on F^2 by full-matrix least-squares using the SHELXL-97 program [24] package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1020055; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

All complexes **I–VI** were readily synthesized by the reaction of Schiff base H_2L^1 and/or H_2L^2 and Cu(II), Ni(II) or Co(II) metal ions, respectively (Scheme). These compounds are quite stable in air and can be stored in a desiccator for long periods of time without decomposition. The resulting compounds were characterized by IR, elemental analysis in all cases and X-ray diffraction in the case of complex **I**.

Table 1. Crystallographic data and structure refinement for complex **I**

Parameters	Value
Fw	618.86
Temperature, K	100(2)
Crystal system	Monoclinic
Space group	*C*2/*c*
a, Å	19.230(5)
b, Å	10.432(4)
c, Å	15.010(5)
β, deg	125.486(5)
V, Å^3	2451.8(14)
Z	4
ρ_{calcd}, g/cm^3	1.677
μ, mm^{-1}	1.176
F(000)	1268
Reflections collected	6466
Independent reflections	2276
GOOF	1.112
Final *R* indices, ($I > 2\sigma(I)$)	$R_1 = 0.0421$, $wR_2 = 0.1084$
R indices, all data	$R_1 = 0.0496$, $wR_2 = 0.1301$
Largest difference peak/hole, *e*/Å^3	0.576–0.648

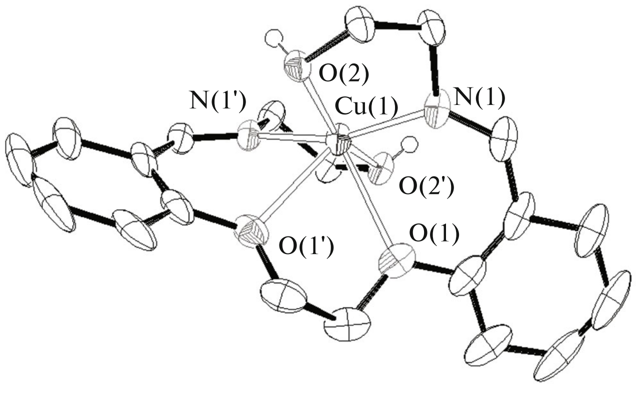
Table 2. Selected bond lengths (Å) and bond angles (deg) for compound **I**

Bond	*d*, Å	Angle	ω, deg
Cu(1)–N(1)	1.956(3)	O(1)Cu(1)O(1')	64.14(3)
Cu(1)–O(1)	2.486(2)	O(1)Cu(1)N(1)	75.82(2)
Cu(1)–O(2)	2.014(2)	O(2)Cu(1)N(1)	93.14(6)
O(1)–C(1)	1.367(5)	N(1)Cu(1)N(1')	159.51(19)
O(1)–C(7)	1.441(5)	O(1')Cu(1)O(2)	118.08(4)
O(2)–C(10)	1.450(4)	O(2)Cu(1)O(2')	156.93(16)
N(1)–C(9)	1.476(5)		

Condensation of all the primary amino group is confirmed by the lack of N–H stretching bands in the IR region (3150–3450 cm^{-1}) and the presence of strong C=N (Schiff base) stretching bands at 1642 and 1638 cm^{-1} for Schiff base ligands H_2L^1 and H_2L^2, respectively. Also the stretching bands of C=N (imine) complexes **I**–**VI** have been observed at in the range of 1635–1652 cm^{-1}. As it can be seen the bands related to the imine groups in Schiff bases have been shifted in the IR for all complexes and it can shows that the donor atoms in ligands have been coordinated to the metal ions and the complexes have been formed. A broad intense band at ~1100 cm^{-1} due to ClO_4^- shows no splitting, indicating the absence of coordination of ClO_4^- for all complexes [25, 26]. The NMR studies of Schiff base ligands are completely consistent with their formulation.

Suitable crystals of **I** were obtained by slow diffusion of diethyl ether vapor into a methanol-ethanol solution of complex **I**. A summary of the details of the crystal data, data collection and refinement details for **I** is given in Table 1. ORTEP diagram of the molecular structure of **I** is shown in figure with the atomic numbering, selected bond lengths and bond angles are listed in Table 2. Complex **I** is on the crystallographic axis 2.

The crystal structure of **I** consists of a copper metal center coordinated to two nitrogen and four oxygen donor atoms from Schiff base ligand H_2L^1. On the basis of the observed angles (NCuN, NCuO, and OCuO), complex **I** adopts a slightly distorted octahedral geometry. The two Cu–O distances (2.486(2) and 2.014(2) Å) in the Cu(II) complex differ substantially, one being short and the other long. The Cu–N distances are in the normal range (1.956(3) Å) [27]. The bond distance Cu(1)–N(1) 1.956(3) Å. The X-ray crystal structure showed that there are five rings: three are five membered whereas two are six-membered. The six-membered rings almost are *trans* together, there are no manly different between the bond angles in all rings, just the angle of N(2)CuO(3) (72.65°) is longer than another angles in other chelate rings.



Ortep view (pictured at 50% probability) of asymmetric unit of **I**.

ACKNOWLEDGMENTS

We are grateful to the department of Chemical Engineering, Hamedan University of Technology and Payame Noor University for financial supports.

REFERENCES

1. Rezaeivala, M. and Keypour, H., *Coord. Chem. Rev.,* 2014, vol. 280, p. 203.
2. Gupta, K.C. and Sutar, A.K., *Coord. Chem. Rev.,* 2008, vol. 252, p. 1420.
3. Keypour, H., Shayesteh, M., Rezaeivala, M., et al., *Spectrochim. Acta, A,* 2013, vol. 101, p. 59.
4. Keypour, H., Shayesteh, M., Rezaeivala, M., et al., *J. Mol. Struct.,* 2013, vol. 1032, p. 62.
5. Rezaeivala, M., Keypour, H., Rezaeivala, M., et al., *J. Iran Chem. Soc.,* 2014, vol. 11, p. 431.
6. Cyriac, A., Jeon, J.Y., Varghese, J.K., et al., *Dalton Trans.,* 2012, vol. 41 p, p. 1444.
7. da Silva, J.A.L., da Silva, J.J.R.F., and Pombeiro, A.J.L., *Coord. Chem. Rev.,* 2011, vol. 255, p. 2232.
8. Ebrahimpour, M., *Coord. Chem. Rev.,* 2005, vol. 249, p. 2156.
9. Romanowski, G., *J. Mol. Catal., A,* 2013, vols. 368–369, p. 137.
10. Borisova, N.E., Reshetova, M.D., and Ustynyuk, Y.A., *Chem. Rev.,* 2007, vol. 107, p. 46.
11. Rao, G.K., Kumar, A., Kumar, B., et al., *Dalton Trans.,* 2012, vol. 41, p. 1931.
12. Schiff, H., *Ann. Chem.,* 1864, vol. 131, p. 118.
13. Radecka-Paryzeka, W., Patroniaka, V., and Lisowski, J., *Coord. Chem. Rev.,* 2005, vol. 249, p. 2156.
14. Keypour, H., Jamshidi, A.M., Rezaeivala, M., et al., *Polyhedron,* 2013, vol. 52, p. 872.
15. Keypour, H., Rezaeivala, M., and Dehghani-Firouzabadi, A.A., *J. Chem. Res.,* 2009, p. 126.
16. Rezaeivala, M. and Daftari, S., *Eur. J. Chem.,* 2014, vol. 5, no. 2, p. 343.
17. Golbedaghi, R., Salehzadeh, S., Keypour, H., et al., *Polyhedron,* 2010, vol. 29, p. 850.
18. Atkinson, I.M., Byriel, K.A., Chia, P.S.K., et al., *Aust. J. Chem.,* 1998, vol. 51, p. 985.
19. *International Tables for X-ray Crystallography,* Birmingham: Kynoch, 1952.
20. *SAINT, Version 6.02,* Madison (WI, USA): Bruker AXS, 1999.
21. Sheldrick, G.M., *SADABS, Empirical Absorption Correction Program,* Göttingen (Germany): Univ. of Göttingen, 1997.
22. *XPREP, Version 5.1,* Madison (WI, USA): Siemens Industrial Automation Inc., 1995.
23. Sheldrick, G.M., *SHELXTL, Version 5.1, Reference Manual,* Madison (WI, USA): Bruker AXS, 1997.
24. Sheldrick, G.M., *SHELXL-97, Program for Crystal Structure Refinement,* Göttingen (Germany): Univ. of Göttingen, 1997.
25. Hataway, A.J. and Underhill, D.E., *J. Chem. Soc.,* 1961, p. 3091.
26. Rosenthal, M.F., *J. Chem. Educ.,* 1973, vol. 50, p. 331.
27. Zabierowski, P., Szklarzewicz, J., Kurpiewska, K., et al., *Polyhedron,* 2013, vol. 49, p. 74.