Asian Journal of Chemistry Vol. 20, No. 8 (2008), 6523-6528

Synthesis of Complexes of Co, Ni, Cu and Zn with N,N'-Ethylene-*bis*(2-phenyl)glycinonitrile Ligand

HAMID GOLCHOUBIAN* and ALI RAZINATAJ
Department of Chemistry, University of Mazandaran
P.O. Box 453, Babolsar, Iran
E-mail: h.golchobian@umz.ac.ir

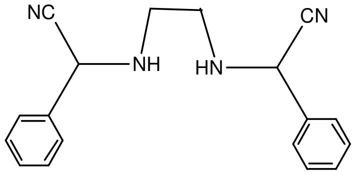
The new chelating ligand N,N'-ethylene-*bis*(2-phenyl)-glycinonitrile and its corresponding complexes with bivalent metals of Co, Ni, Cu and Zn were prepared and characterized by IR, NMR, UV/Vis spectroscopy and elemental analysis.

Key Words: N,N'-Ethylene-*bis*(2-phenyl)glycinonitrile, Aminonitrile, Cobalt, Nickel, Zinc, Copper.

INTRODUCTION

Transition metal coordination compounds of multidentate nitrogen ligands have attracted wide attention due to their use in industrial catalysis, biology and medicinal fields and so on, because of its novel conformation, multiple fashions of band constitution and paramagnetic behaviour[1,2]. The construction of functional system compound lies on the character of mutual effect in reagents. The important development of multidentate nitrogen organic corporation is inducting organic compound as oriented reagent to inorganic framework by self-assembly of covalent bond, assort bond and hydrogen bond in order to form compound with novel conformation[3,4]. Aminonitrile are compounds that containing nitrile and amine groups in their skeleton. They are used as starting materials for synthesis of amino acids[5], polyamid polymers[6] and diamines[7]. Ethylenediamine and its derivatives have been studied as ligands largely on account of their presence in salen type ligands in which studied extensively due to their important biological activities that are often augmented on complex formation with metal ions[8,9].

In this paper, the synthesis and characterization of a new ligand N,N'-ethylene-*bis*(2-phenyl)glycinonitrile and its *3d* bivalent metal complexes are reported. Based on the best of our knowledge, such investigations have not been employed on any aminonitrile ligands yet.



Structure of N,N'-ethylene-*bis*(2-phenyl)glycinonitrile (L)

EXPERIMENTAL

All chemicals and solvents are obtained from Merck and Fluka and used without further purification. The solvent used for the measurements were of spectrophotometric grade or reagent grade. Elemental analyses were performed by a LECO CHN-600 elemental analyzer. Absolute metal percentages were determined by an atomic absorption-flame spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 500 DRX Fourier transform spectrometer. The UV-Vis solution spectra were obtained on a Cicil CE5501 spectrophotometer using Omnisolv grade solvents. Infrared spectra were recorded in KBr mixture by a single beam Bruker VECTOR22 FTIR. Mass spectra were obtained on a VG 70E double focusing high-resolution spectrometer. Conductance measurements were made at 25 ºC with a Jenway 400 conductance meter on 1.0×10^{-3} M samples in nitromethane. All samples were dried to constant weight under high vacuum prior to analysis.

Preparation of N,N'-ethylene-*bis*(2-phenyl)glycinonitrile (L): A mixture 5.2 g (0.05 mol) sodium bisulfite solution in 5 mL water and 1 mL (0.01 mol) of benzaldehyde was added to 0.34 mL (0.005 mol) ethylenediamine. The resulted mixture was stirred at *ca.* 50 to 60 °C for 7 h. Then a solution of 0.66 g (0.01 mol) sodium cyanide in 10 mL water was added. The N,N'-ethylene-*bis*(2-phenyl)glycinonitrile was precipitated almost immediately. The desired product was filtered and washed with water and ethanol and diethyl ether, respectively and dried in vacuum. The yield of the reaction after recrystallization from hot ethanol was 83 %. m.p. 101-103 ºC, anal. calcd. for $C_{18}H_{18}N_4$ (%): C, 74.46; H, 6.25; N, 19.30. Found: C, 74.66; H, 5.88; N, 19.20. ^{1}H NMR (500 MHz in $CDCl_3$) δ: 1.89 (s, 2H, N-H), 2.97 (s, 4H, NCH_2CH_2N), 4.83 (m, 2H, PhCHCN), 7.4 (m, 10H, Ph-H). Upon adding a drop of D_2O to the solution the singlet peak at 1.89 ppm which corresponds to N-H was disappeared. ^{13}C NMR (126.77 MHz in $CDCl_3$) δ: 49.79 (CH_2-NH-), 53.72 (CH-Ph), 117.59 (-CN), 125.67, 128.76, 131.01 (aromatic carbons). IR (KBr, ν_{max}, cm^{-1}): 1440 (CH_2 *bend.*), 1500 (C=C *str.* aromatic); 2230 (C≡N *str.*); 2800 (C-H *str.* aliphatic): 3000 (C-H *str.* aromatic); 3300 (N-H *str.*). UV-Vis (nm; ε_{max}) 258 (5360). Mass spectrum showed the dominant peak at m/e 264 corresponding to lost of a CN moiety from molecular formula of $C_{18}H_{18}N_4$.

Preparation of $ZnLCl_2$: $ZnCl_2$ (0.136 g, 1 mmol) in ethanol (5 mL) was added to 0.290 g (1 mmol) of ligand L in hot ethanol (10 mL). The reaction mixture was stirred for 10 min at room temperature. $ZnLCl_2$ was formed and precipitated immediately as a colourless solid. The product was separated by filtration and washed with water (2 × 5 mL), ethanol (2 × 5 mL) and ether (2 × 5 mL) respectively and dried in vacuum (340 mg, 80 %). The prepared compound is sparingly soluble in common solvents. Anal. calcd. for $C_{34}H_{37}N_7O_{10}Cl_2Zn$ (%): C, 41.04; H, 3.75; N, 9.85; Zn, 6.43. Found: C, 40.89; H, 3.61: N 10.02; Zn 6.33. FT-IR (KBr, ν_{max}, cm^{-1}): 3303 (N-H *str.*), 2200 (C≡N *str.*), 1445 (CH_2 *bend.*).

Preparation of $[ZnL(H_2O)_2](ClO_4)_2$: To the suspension of $ZnLCl_2$ (0.426 g, 1 mmol) in methanol (10 mL) was added a solution of $AgNO_3$ (0.338 g, 2 mmol) in methanol (10 mL). The resulting white AgCl precipitate was separated by filtration. The resulting colourless solution was concentrated to one-third of its original volume and a saturated solution of $LiClO_4$ in methanol was added. $[ZnL(H_2O)_2](ClO_4)_2$ precipitate as a colourless solid. The yield of reaction after recrystallization from methanol was 48 %. Λ_m = 172 Ω^{-1} mol^{-1} cm^2 (standard values for a 1:2 electrolyte type in CH_3NO_2 is in the range of 150-180 Ω^{-1} cm^2 mol^{-1} at 25 ºC). Anal. calcd. for $C_{18}H_{22}N_4O_{10}Cl_2Zn{\cdot}CH_3OH$ (%): C, 36.65; H, 4.21; N, 9.00. Found: C, 35.89; H, 3.61: N 9.53. FT-IR (KBr, ν_{max}, cm^{-1}): 3202 (N-H *str.*), 2170 (C≡N *str.*), 1446 (CH_2 *bend.*) 1103 (ClO_4 *str.*). ^1H NMR (500.13 MHz, $CDCl_3$): δ = 2.92 (s, 4H), 4.43 (s, H), 4.71 (s, H), 7.01-7.74 (m, 10H). ^{13}C NMR (126.77 MHz in CD_3CN): δ = 44.97, 55.17, 83.97, 115.57, 125.50, 127.30, 129.94, 130.44, 136.29, 143.36, 188.95.

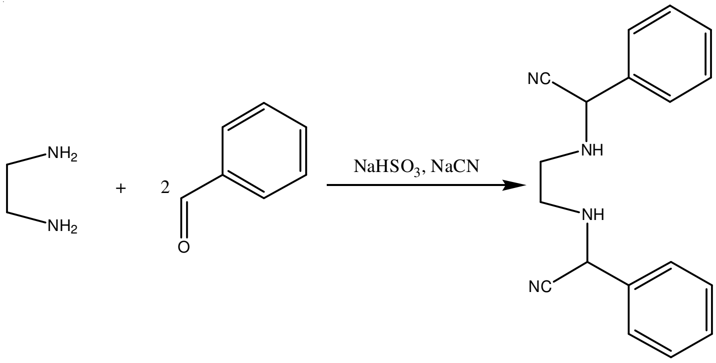
Preparation of $CoLCl_2$: $CoLCl_2$ was prepared by the general procedure described for $ZnLCl_2$ except that initial precipitate was blue but turn pale brown while washed with solvent to remove the starting materials impurities (80 %). This compound is sparingly soluble in common solvents. Anal. calcd. for $C_{18}H_{18}N_4Cl_2Co$ (%): C, 51.54; H, 4.32; N, 13.33. Found: C, 50.68; H, 4.95; N, 14.23. FT-IR (KBr, ν_{max}, cm^{-1}): 3251 (N-H *str.*), 2167 (C≡N *str.*), 1380 (CH_2 *bend.*).

Preparation of $CuLCl_2$: $CuLCl_2$ was prepared by the general procedure described for $ZnLCl_2$. The copper complex was formed as green solid (83 %). This compound is also sparingly soluble in common solvents. Anal. calcd. for $C_{18}H_{18}N_4Cl_2Cu$ (%): C, 50.89; H, 4.27; N, 13.19. Found: C, 50.01; H, 4.84; N, 13.91. FT-IR (KBr, ν_{max}, cm^{-1}): 3211 (N-H *str.*), 2198, 2136 (C≡N *str.*), 1448 (CH_2 *bend.*).

Preparation of $NiLCl_2$: $NiLCl_2$ was prepared by the general procedure described for $ZnLCl_2$. The nickel complex was formed as green solid (853 %). This compound is sparingly soluble in common solvents. Anal. calcd. for $C_{18}H_{18}N_4Cl_2Ni$ (%): C, 51.48; H, 4.32; N, 13.98. Found: C, 50.64; H, 4.88; N, 14.49. FT-IR (KBr, ν_{max}, cm^{-1}): 3216 (N-H *str.*), 2170 (C≡N *str.*), 1395 (CH_2 *bend.*).

RESULTS AND DISCUSSION

The ligand N,N'-ethylene-*bis*(2-phenyl)glycinonitrile was prepared in aqueous media by mixing of 2 moles of aldehyde with a mole ethylenediamine and 2 moles sodium cyanide in present of sodium bisulfite as shown in **Scheme-I**. Tetranitrile derivative of ethylenediamine was prepared by Frost *et al.*[10] which require low temperature, inert atmosphere and introduction of the poisonous HCN gas but, our method used milder condition and higher yield with using sodium cyanide salt as the source of -CN.



Scheme-I

The $MLCl_2$ complexes were prepared easily according to **Scheme-II** by mixing of equimolar ligand and metal(II) chloride salt in solvent of ethanol in acceptable yield (80 %). These compounds are sparingly soluble in common solvents at concentrations sufficient for characterization purposes. As a result, the $ZnLCl_2$ complex was converted to $[ZnL(H_2O)_2](ClO_4)_2$ which is more soluble than its counterpart due to ion pair formation. In this way dechlorination was carried out by $AgNO_3$ and then the desired compound was obtained by addition of $LiClO_4$ to the resulting solution.

$$\mathbf{L + M''Cl_2 \xrightarrow{EtOH} MLCl_2}$$

$$\mathbf{ZnLCl_2 \xrightarrow[2)\ LiClO_4]{1)\ AgNO_3} [ZnL(H_2O]_2](ClO_4)_2}$$

Scheme-II

Attempts to produce X-ray-quality crystals of compounds have been frustrated by the limited solubility of these compounds in suitable solvents. In the IR spectra of compounds $MLCl_2$ several bands appear in the region 700-3600 cm^{-1} that are also observed, although with minor shifts, in the spectra of the free ligands. The absorption band around 2200 ± 20 cm^{-1} is probably due to the stretching vibration of C=N bond[11]. This band is shifted to the lower energy along with an increase in its intensity in metal complexes in comparison with free ligand due to interaction with metal ion. The strong bands at 1450-1384 cm^{-1} are very likely associated with the scissoring vibration of $-CH_2-$ groups[12]. The band at around 750 cm^{-1} that in the spectra of free diamine ligands appears broader and is split in two in region of 730-790 cm^{-1} may be due to the rocking vibration of CH_2 groups[13]. The stretching vibrations of $N-CH_2$ groups in the free ligands and the well-known bands in the region 2850 ± 100 cm^{-1} that are associated with it, are more important since they serve as an indication of coordination of diamine ligand. Upon covalent bond formation, these absorption bands apparently lose intensity, become shifted to the higher frequencies and mix with other C-H absorption bands. Dependence on coordination is also exhibited by the intense and narrow band occurring at 3245 ± 45 cm^{-1} which is associated with N-H vibration and is observed at around 3300 cm^{-1} and broader in the free diamine ligands. As the lone pair of electrons of the donor nitrogen atoms become involved in the metal-ligand bond, the transfer of electron density to the metal and the subsequent polarization of the ligands involves electron depopulation of the N-H bond which culminates in a shift to lower frequencies.

The presence of the ClO_4^- group in $[ZnL(H_2O)_2](ClO_4)_2$ is observed by the appearance of two intense bands at 1110 and 630 cm^{-1} which are attributed to the anti-symmetric stretching and anti-symmetric bending vibration modes, respectively[14].

The molar conductivity value of complex $[ZnL(H_2O)_2](ClO_4)_2$ in solvent of CH_3NO_2 show 1:2 electrolyte[15] and is in agreement with the expectation from the spectral data. Based on the results obtained the proposed structure for $[ZnL(H_2O)_2](ClO_4)_2$ is shown in Fig. 1.

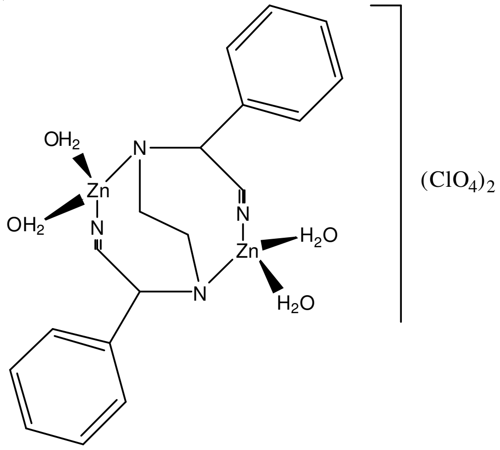


Fig. 1. Proposed structure for $[ZnL(H_2O)_2](ClO_4)_2$

Conclusion

It can be concluded that the ligand N,N'-ethylene-*bis*(2-phenyl)-glycinonitrile and its bivalent complexes were prepared in satisfactory yield with a simple and convenient method. The general low solubility of these complexes has hindered a more extensive spectroscopic and physical characterization.

ACKNOWLEDGEMENT

The authors are grateful for the financial support of Mazandaran University of the Islamic Republic of Iran.

REFERENCES

1. (a) H. Golchoubian, W.L. Waltz and J.W. Quail, *Can. J. Chem.*, **37**, 77 (1999); (b) H. Golchoubian and W.L. Waltz, *Synth. Commun.*, **28**, 3907 (1998).
2. (a) A. Ghaffarinia and H. Golchoubian, *Polish J. Chem.*, **79**, 83 (2005); (b) A.N. Rahnama, H. Golchoubian and R. Pritchard, *Bull. Chem. Soc. (Japan)*, **78**, 1047 (2005); (c) A. Ghaffarinia, H. Golchoubian and R. Hosseinzadeh, *J. Chin. Chem. Soc.*, 52, 531 (2005); (d) F. Farsavi and H. Golchoubian, *Phosphorus, Sulfur, Silicon Rel. Elem.*, **181**, 1277 (2006); (e) Y. Khaniani and H. Golchoubian, *Phosphorus, Sulfur, Silicon Rel. Elem.*, **181**, 2817 (2006); (f) H. Golchoubian, E. Baktash and R. Welter, *Inorg. Chem. Commun.*, **10**, 120 (2007); (g) H. Golchoubian, E. Baktash and R. Welter, *Inorg. Chem. Commun.*, **10**, 1035 (2007).
3. D. Gejihi, Y.-G. Lee and R.-D. Huang, *Inorg. Chem. Commun.*, **6**, 1091 (2003).
4. Y. Lu, E.-B. Wango and M. Yuang, *J. Mol. Struct.*, **649**, 649 (2003).
5. D. Putzing, E. Donald, E. McBrid, D. Fransis and H. Quang, *US Patent*, 16080834 (2000).
6. M. Periasmy and K. Square, *J. Organometal. Chem.*, **37**, 609 (2000).
7. D.A. House, in eds.: G. Wilkinson, R.D. Gillard and J.A. McCleverty, Comprehensive Coordination Chemistry, Pergamon, Oxford Vol. 2, p. 2 (1987).
8. E. Tenor and R. Ludwig, *Pharmazie*, **26**, 534 (1971).
9. H.J. Zawadzki, *Polish J. Chem.*, **68**, 1293 (1994).
10. A.E. Frost and H.H. Freedman, *J. Org. Chem.*, 1905 (1959).
11 M. Handa, A. Farida, L.K. Thompson, C. Hayashibara, T. Sugimori, I. Hiromitsu and K. Kasuga, *Mol. Cryst. Liq. Crtst.*, **342**, 75 (2000).
12. C. Tsiamis and M. Themeli, *Inorg. Chim. Acta*, **206**, 105 (1993).
13. X.M. Chen, B.H. Ye, X.C. Huang and Z.T. Xu, *J. Chem. Soc., Dalton Trans.*, 3465 (1996).
14. H. Asadi, H. Golchoubian and R. Welter, *J Mol. Struct.*, **779**, 30 (2005).
15. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

(*Received*: 17 March 2008; *Accepted*: 21 July 2008) AJC-6715