Asian Journal of Chemistry Vol. 19, No. 3 (2007), 1870-1874

Synthesis and Complexation Behaviour of 1,3-*Bis*(2-pyridylimino)isoindole with Nickel(II)

M. Kasim Sener
Department of Chemistry, Yüzüncü Yil University, 65080 Van, Turkey
Fax: (90)(432)2251188; E-mail: mkasimsener@gmail.com

The synthesis and complex behaviour of 1,3-*bis*(2-pyridylimino)isoindoline (**2**) with nickel(II) is reported. The new compounds were characterized by elemental analysis, FT-IR, ^{13}C NMR, ^{1}H NMR and *via* mass spectrometric analysis. Electrochemical properties of the [(4,5-*bis*(hydroxyethylmercapto)-*bis*(2-pyridylimino)-isoindoline)Ni(OAc)(H_2O)] was also studied by cyclic voltammetry.

Key Words: *Bis*(2-pyridylimino)isoindole, N- and S-Donor ligands, Nickel.

INTRODUCTION

Nitrogen donor ligands have been widely used in the transition metal catalyzed oxidation of hydrocarbons[1]. Among the acyclic polydentate ligands, *bis*(pyridylimino)isoindole (BPI) derivatives have been the focus of interest in oxidation chemistry, ever since their use in the cobalt and iron catalyzed aerobic oxidation of cyclohexane to cyclohexanone, a key intermediate in the production of polyamides[1,2]. The BPI-transition metal catalyzed oxidations generally tend to be unselective and it is therefore of interest whether the modification of the ligands by variation of their peripheral substitution pattern and the variation of the oxidizing agent may enable more selective transformations[3-12].

The protonated neutral precursors of the formally anionic BPI ligands are readily accessible in a one-step condensation reaction of a phthalonitrile derivative with two molar equivalents of 2-aminopyridine[13]. Since the synthesis of these systems follows the classical condensation of suitably substituted phthalonitriles, the preparation of substituted phthalonitriles with different groups on the aromatic system is very important[14,15]. The aim of the present paper has been to introduce *bis*(pyridylimino)isoindole containing S-donor groups and its Ni(II) complex. Electrochemical characterization of the [(4,5-*bis*(hydroxyethylmercapto)-*bis*(2-pyridylimino)-isoindoline)Ni(OAc)(H_2O)] has also been investigated.

EXPERIMENTAL

1,2-*Bis*(hydroxyethylmercapto)-4,5-dicyanobenzene (**1**) was prepared according to the published procedure[16]. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a GE QE-300 spectrometer using DMSO-d_6 as the solvent. Mass spectra were obtained on a Ultima Fourier Transform and Varian 711 mass spectrometer. Elemental analyses were performed on a Carlo Erba EAGER 200. Melting points were determined on an Electrothermal Gallenkamp apparatus. All reagents and solvents were obtained from commercial suppliers and were of reagent grade quality.

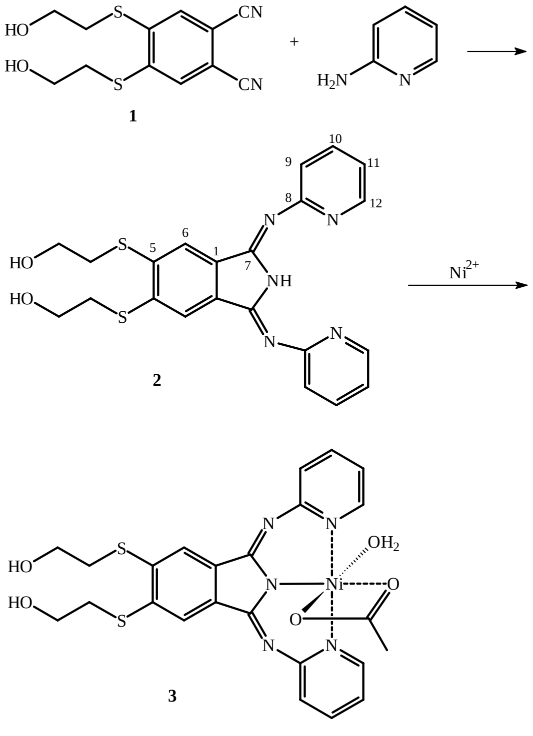
All electrochemical techniques were carried out with a Princeton Applied Research versastat II potentiostat/galvanostat controlled by an external PC utilizing a three-electrode configuration at 25ºC. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge containing saturated KCl adjacent to SCE and solvent and carrier adjacent to the solution. Ferrocene/Ferrocenium was used as universal reference. The working electrode was a Pt plate with an area of 0.10 cm^2. The surface of the working electrode was polished with a H_2O suspension of Al_2O_3 before each run. The last polishing was done with a particle size of 50 nm. Electrochemical grade tetrabutylammoniumperchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.1 $moldm^{-3}$. High purity N_2 was used for deaeration and to maintain a nitrogen blanket for at least 15 min prior to each run.

Synthesis of 4,5-*bis*(hydroxyethylmercapto)-BPI (2): 1,2-*Bis*(hydroxyethylmercapto)-4,5-dicyanobenzene (1, 0.500 g, 1.70 mmol), 2-aminopyridine (0.401 g, 4.26 mmol) and $CaCl_2$ (0.048 g, 0.43 mmol) were suspended in 1-hexanol (16 mL) and heated at reflux for 20 h. After cooling to room temperature the reaction product was isolated as a yellow solid washed with water and dried over P_4O_{10}. The product was crystallized from ethanol. Yield: 0.450 g (55 %); m.p.: 229°C. FT-IR (ν_{max}, cm^{-1}): 3184, 3060, 2992, 2879, 1614, 1570, 1551, 1456, 1430, 1359, 1208, 1055, 788. ^1H NMR (200 MHz, DMSO-d_6): δ 8.67 (dd, 2H, H-12), 7.89 (m, 2H, H-10), 7.79 (s, 2H, H-6), 7.43 (d, 2H, H-9), 7.25 (dd, 2H, H-11), 5.12 (t, 2H, OH), 3.69 (q, 4H, $HO\underline{C}H_2$-), 3.25 (t, 4H, $-C\underline{H}_2S$-), NH not seen. ^{13}C NMR (50 MHz, DMSO-d_6): δ 160.2 (C-8), 152.8 (C-7), 148.8 (C-12), 141.7 (C-10), 139.4 (C-5), 132.7 (C-1), 123.6 (C-6), 121.4 (C-11), 119.9 (C-9), 60.1 ($HO\underline{C}H_2$-), 35.6 ($-\underline{C}H_2S$-). FAB-MS: m/e 452 $[M]^+$. Anal. (%) calcd. for $C_{22}H_{21}N_5O_2S_2$: C, 58.51; H, 4.68; N, 15.50. Found: C, 58.40; H, 4.63; N, 15.63.

[(4,5-*Bis*(hydroxyethylmercapto)-BPI)Ni(OAc)(H_2O)] (3): 4,5-*Bis*(hydroxyethylmercapto)-BPI (0.063 g, 0.13 mmol) was dissolved in ethanol (10 mL). A solution of $Ni(CH_3COO)_2.4H_2O$ (0.069 g, 0.27 mmol) in ethanol (10 mL) was added to the solution with stirring. The mixture was boiled for 24 h and filtered. All volatiles were removed *in vacuo* and the residue was dissolved in toluene. The resulting reddish brown precipitate was filtered off and dried *in vacuo*. Yield, 0.075 g (92 %). FT-IR (ν_{max}, cm^{-1}): 3600-3200, 2971, 1565, 1520, 1411, 1349, 1152, 1046, 784. ^1H NMR (200 MHz, DMSO-d_6): δ 7.90-7.12 (m, 10H, aromatic H), 5.10 (br, 2H, OH), 3.83-3.21 (m, 10H, CH_2 and H_2O), 2.25 (s, 3H, CH_3). FAB-MS: m/e 589 $[M+2]^+$. Anal. (%) calcd. for $C_{24}H_{25}N_5O_5S_2Ni$: C, 49.08; H, 4.29; N, 11.92. Found: C, 49.60; H, 4.15; N, 12.09.

RESULTS AND DISCUSSION

Bis(2-pyridylimino)isoindole (BPI) ligand **2**, has been prepared by a one step reaction of 1,2-*bis*(hydroxyethylmercapto)-4,5-dicyanobenzene with the 2-aminopyridine. Conversion of *bis*(2-pyridylimino)isoindole derivative **2** into corresponding metal complex **3** was accomplished by reaction with nickel(II) acetate in ethanol (**Scheme-I**).



Scheme-I Synthesis of 4,5-*bis*(hydroxyethylmercapto)-BPI (**2**) and its nickel complex (**3**). (i) $CaCl_2$, 1-hexanol, 20 h reflux; (ii) $Ni(CH_3COO)_2.4H_2O$, ethanol, 24 h reflux

All of these new compounds were characterized by elemental analyses together with FT-IR, ^{1}H NMR, ^{13}C NMR and MASS spectroscopic techniques. Elemental analyses correspond closely with the values calculated for **2** and **3**. In compound **2**, the strong band observed at 3184 cm^{-1} can be attributed to the NH group vibration. Aliphatic and aromatic CH stretching vibrations are observed at 3060-2879 cm^{-1}. The characteristic bands of the pyridine ring are observed at 1570-1430 cm^{-1}. In ^{1}H NMR spectrum of 2 aromatic protons appear at 8.68-7.23 ppm. The OH proton is observed 5.12 ppm and CH_2 protons are observed 3.71-3.22 ppm. The ^{13}C NMR signals are found to be at 160.2 (C-8), 152.8 (C-7), 148.8 (C-12), 141.7 (C-10), 139.4 (C-5), 132.7 (C-1), 123.6 (C-6), 121.4 (C-11), 119.9 (C-9), 60.1 ($HO\underline{C}H_2$-), 35.6 (-$\underline{C}H_2S$-) ppm. FAB-MS spectrum of **2** the molecular ion peak appeared at m/e 452.

In compound **3**, broad band in the 3600-3200 cm^{-1} range may be assigned to $\nu(H_2O)$ of coordinated water molecule and OH stretching vibrations. After conversion of the **2** into the **3**, the strong peak for the NH vibration around 3184 cm^{-1} disappeared. Aromatic and aliphatic CH stretching vibrations are observed at 3074-2971 cm^{-1}. The observed bands at 1565-1411 cm^{-1}, ascribed to pyridine rings. In the complex these bands shifted to the lower frequencies, indicating that the nitrogen atom of the pyridine rings is coordinated to the metal ion. ^{1}H NMR investigation of compound **3** provided the characteristic chemical shifts for the structure expected. Aromatic protons appear at 7.90-7.12 ppm. The OH proton is observed 5.10 ppm as a broad peak. CH_2 protons are observed 3.83-3.21 ppm and CH_3 protons are observed 2.25 ppm. In the MS spectrum, a $[M+2]^+$ peak is observed at 589 for **3**.

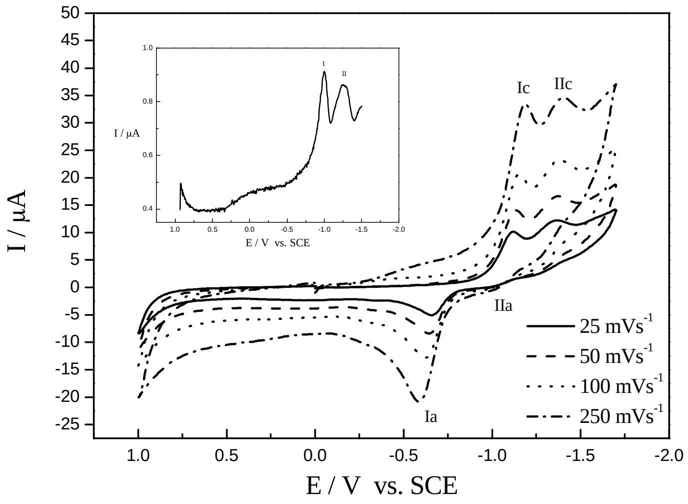


Fig. 1. Cyclic voltammograms of **3** in DMSO solution at different scan rates. Inset: Differential pulse voltammogram of **3** in DMSO solution at different scan rates

The redox properties of [(4,5-*bis*(hydroxyethylmercapto)-BPI)Ni(OAc)(H_2O)] were studied in DMSO solution containing TBAP (0.1 mol dm^{-3}). As shown in Fig. 1, the complex exhibits a quasi-reversible and an irreversible ligand based reduction processes at -0.890 and -1.210 V *vs.* SCE. The anodic and cathodic peak currents for the first reduction couple are equal, but the peak potential separation (*ca.* 0.500 V) is larger than the expected 58 mV for a reversible one-electron process. Controlled potential coulometry measurement at potentials anodic of the both reduction processes verify that these are one-electron processes with n = 1.0 ± 0.10. Differential pulse voltammetry measurements support the processes recorded with cyclic voltammetric measurements.

ACKNOWLEDGEMENT

The author is grateful to Dr. Atif Koca for cyclic voltammetry measurements.

REFERENCES

1. G.W. Parshall and S.D. Ittel, Homogeneous Catalysis, The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, Wiley-Interscience, New York (1992).
2. (a) Applied Homogeneous Catalysis with Organometallic Compounds (Hrsg.: W.A. Hermann and B. Cornils), VCH, Weinheim, Patents (1996); (b) A. Yashima, European Patent, 0164463B1 (1988); (c) J.D. Druliner, S.D. Ittel, P.J. Krusic and C.A. Tolmann, U.S. Patent, 4 326 084 (1982); (d) F. Igersheim and M. Costantini, EP 87-420322 (1988); (e) L. Saussine, A. Robine and H. Mimoun, FR 2559154 (1985).
3. M.B. Meder, B.A. Siggelkow and L.H. Gade, *Z. Anorg. Allg. Chem.*, **630**, 1962 (2004).
4. B.A. Siggelkow, M.B. Meder, C.H. Galka and L.H. Gade, *Eur. J. Inorg. Chem.*, 3424 (2004).
5. B.A. Siggelkow and L.H. Gade, *Z. Anorg. Allg. Chem.*, **631**, 2575 (2005).
6. M.B. Meder and L.H. Gade, *Eur. J. Inorg. Chem.*, 2716 (2004).
7. M.B. Meder, I. Haller and L.H. Gade, *Dalton Trans.*, 1403 (2005).
8. M.B. Meder, C.H. Galka and L.H. Gade, *Monatsh. Chem.*, **136**, 1693 (2005).
9. W.O. Siegl, *J. Org. Chem.*, **42**, 1872 (1977).
10. R.R. Gagne, W.A. Marritt, D.N. Marks and W.O. Siegl, *Inorg. Chem.*, **20**, 3260 (1981).
11. R.R. Gagne, R.S. Gall, G.C. Lisensky, R.E. Marsh and L.M. Speltz, *Inorg. Chem.*, **18**, 771 (1979).
12. D.N. Marks, W.O. Siegl and R.R. Gagne, *Inorg. Chem.*, **21**, 3140 (1982).
13. (a) W.O. Siegl, *Inorg. Nucl. Chem. Lett.*, **10**, 825 (1974); (b) W.O. Siegl, *J. Heterocycl. Chem.*, **18**, 1613 (1981).
14. S.Ö. Yildirim, M. Akkurt, M.K. Sener, M.B. Koçak and H.-K. Fun, *Acta Cryst.*, E61, 4101 (2005).
15. M.K. Sener, A. Gül and M.B. Koçak, *J. Porphyrins Phthalocyanines*, **7**, 617 (2003).
16. A.G. Gürek and Ö. Bekaroglu, *J. Porphyrins Phthalocyanines*, **1**, 227 (1997).

(*Received*: 16 March 2006; *Accepted*: 13 October 2006) AJC-5193