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Synthesis and Characterization of New *vic*-Dioximes with Benzo-15-crown-5 Derivatives and Their Nickel(II), Copper(II), Cobalt(II) Complexes

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Benzo-15-crown-5-*p*-toluidino-glyoxime (**1**) and N(1-naphthyl)amino-benzo-15-crown-5-glyoxime (**2**) were synthesized by classical methods. Their structures were confirmed by spectral techniques. Both of them were capable of forming complexes with various metal ions (Co^{2+}, Cu^{2+} and Ni^{2+}). The structure of the complexes was confirmed by FT-IR, mass spectra and elemental analyses.

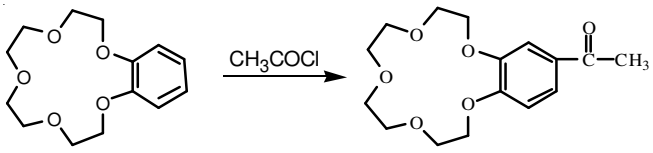
Key Words: Macrocyclic ether, Cation binding, NMR spectroscopy, Glyoxime, Cation complexes, Solubility.

INTRODUCTION

Tschugaeff[1] discovered the *vicinal*-dioxime-metal complex-*bis*-dimetyl-glyoxime of nickel(II), initiating an area of coordination chemistry which has been widely explored during the past century. The first *vic*-oxime quasi-macro cyclic complexes were prepared by Uhling *et al.*[2]. Recently, a copper-oxime complex was used to oxidize anthracene[3]. Metal containing oxime complexes are utilized as well[4-6].

In some recent studies, *vic*-dioxime complexes of platinum have been tested as antitumour agents in chemotherapy[7]. Further applications include column packing material in chromatographic separation of nucleotides and nucleosides after bonding to natural resins as functional groups[8].

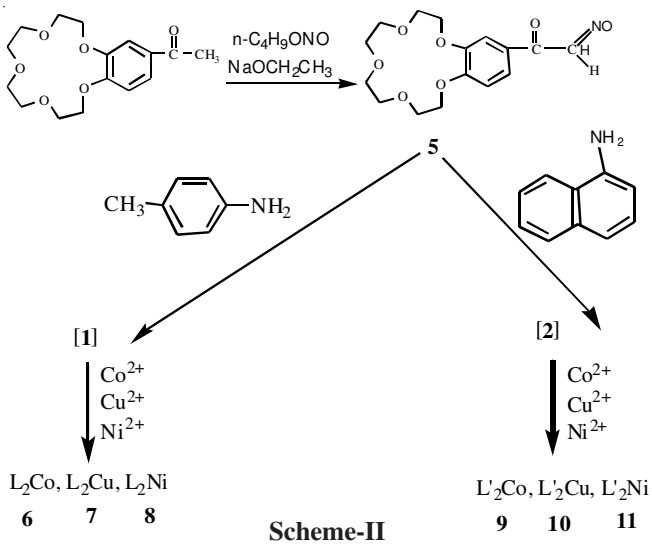
At the same time, the acetylation of benzo-15-crown-5 yields 4'-acetyl-benzo-15-crown-5 (**Scheme-I**) which is a key intermediate for a variety of technology products including complexon for the separation of radioactive cations, ionophore antibiotics and phase transfer catalysts[9].



Scheme-I

This acetylation can be performed in a Friedel-Crafts type reaction with $AlCl_3$. this method gives some problems during reaction. Because of them, the acetylation was performed in presence of polyphosphoric acid as catalysts[10]. 4'-Acetyl-benzo-15-crown-5 was converted into *iso*-nitroso derivative by *n*-butylnitrite and sodium ethoxide[11] (**Scheme-II**).

As a new approach to the synthesis of *p*-toluidino-benzo-15-crown-5 glyoxime (**1**) and N(1-naphthyl)amino-benzo-15-crown-5-glyoxime (**2**), we have synthesized benzo-15-crown-5-chlorooxime (5) (**Scheme-II**).



Scheme-II

In the present study, complexes [**1**] and [**2**] of Cu(II), Co(II) and Ni(II) are studied and their structures were confirmed by FT-IR and mass spectroscopy. Some complexes weren't determined by NMR spectroscopy because of their poor solubility.

EXPERIMENTAL

Tetraethylene glycol was purchased from Fluka and purified according to literature[12,13]. The others were purchased from Merck. Infrared absorption spectra were obtained from a Jasco FTIR spectra spectrometer in KBr discs and were recorded in cm^{-1} units. Elemental analyses were performed on a Leco CHNS-932 analyzer. The ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as a internal standard. Mass spectra were obtained on a VG-2APSPEC spectrometer with on ion source temperature of 240 ºC.

Synthetic procedures

Tetraethylene glycol dicholoride: Tetraethylene glycol dichloride was synthesized from the reaction of tetraethylene glycol and $SOCl_2$ according to the published procedure[14].

Benzo-15-crown-5: Benzo-15-crown-5 was synthesized from the reaction of 1,2-dihydroxybenzene and tetraethylene glycol dichloride according to the published procedure[14].

4'-Acetyl-benzo-15-crown-5: 4'-Acetyl-benzo-15-crown-5 was synthesized from the reaction of poly-phosphoric acid and benzo-15-crown-5-according to the published procedure[15].

4'-(Isonitroso)-acetyl-benzo-15-crown-5: 4'-(Isonitroso)-acetyl-benzo-15-crown-5 (**4**) was synthesized from the reaction of sodium, *n*-isonitrosobutyl and 4'-acetyl-benzo-15-crown-5 according to the published procedure[16].

Benzo-15-crown-5-glyoxime (3): To a solution of sodium acetate (5 g, 60.98 mmol) and hydroxylamine-hydrochloride (6.5 g 93.53 mmol) in water (50 mL) was slowly added dropwise to ethanolic solution of 4'-(isonitroso)-acetyl-benzo-15-crown-5 (17 g, 50 mmol) during 1 h with vigorous stirring. The reaction mixture was refluxed and stirred for an additional 4 h. The reaction was monitored by using TLC, it was then cooled to room temperature. White crystal was filtered and washed with chloroform. The crude product was separated by column chromatography eluting with $CHCl_3/CCl_4$ (1:2) to give **3** (14.3 g, 81%), m.p.> 142 ºC, [Found; C, 54.17; H, 6.34; N, 7.28 $C_{16}H_{22}N_2O_7$ requires C, 54.13; H, 6.20; N, 7.89]; (KBr, ν_{max}, cm^{-1}) 3460, 3040, 1690, 1540, 1050, 1020, 820; δ_H: (250 MHz, DMSO-d_6), δ 6.9 (2H, m,Ph), 6.3 (1H, s, Ph), 12.0 (1H, s, Ph CNOH, CHNOH) 10.6 (1H, s, Ph CNOH, CHNOH), 8.5 (1H,s, Ph CNOHCHNOH), 3.8-2.8 (16 H, m, CH_2-O).

Benzo-15-crown-5-choloroglyoxime: This compound is synthesized according to the modified method of Ponzio[12]. Benzo-15-crown-5-glyoxime (**5**) (5 g, 14.12 mmol) was dissolved in 150 mL of freshly distilled $CHCl_3$. Chloride gas was slowly passed, during 1 h to this mixture with stirring at 25 ºC. Reaction was monitored by using TLC, the excess of Cl_2 was separated by adding distilled water of 200 mL. The $CHCl_3$ layer was dried over $MgSO_4$ and the $CHCl_3$ was evaporated. The crude product was separated by column chromatography eluting with $CHCl_3/CCl_4$ (1:2) to give **5** (3.88 g, 71 %), m.p. > 149 ºC, [Found; C, 49.02; H, 5.23; N, 7.09 $C_{16}H_{21}N_2O_7Cl$ requires C, 49.36; H, 5.40; N, 7.20]; (KBr, ν_{max}, cm^{-1}) 3320, 3100, 1660, 1580, 1100, 1040, 780; δ_H: (250MHz, DMSO-d_6), δ 6.9 (2H, m,Ph), 6.3 (1H, s, Ph), 12.0 (1H, s, Ph CNOH, NOHCl), 10.8 (1H, s, Ph CNOH, CNOHCl), 8.5 (1H,s, Ph CNOHCHNOH), 3.8-3.2 (16 H, m, CH_2-O).

Benzo-15-crown-5-*p*-toluidino- glyoxime (1): Benzo-15-crown-5-choloroglyoxime (**5**) (1.3 g, 3.33 mmol) was dissolved in 50 mL ethanol. *p*-Aminotoluene (0.358 g, 3.35 mmol) in 30 mL ethanol was slowly added and stirred for 0.5 h at 25 ºC. The reaction mixture was stirred for an additional 3 h. The reaction was monitored by using TLC. After that, distilled water (100 mL) was added. The mixture was extracted with $CHCl_3$ (3 × 50 mL). Organic layer was dried over $MgSO_4$, filtered and the solvent evaporated. The residue was separated by column chromatography eluting with petrol ether/$CHCl_3$ (1:1) to give **1** as a dark yellow, (1.19 g, 78 %), m.p. > 132 ºC, [Found; C, 59.78; H, 6.01; N, 8.99 $C_{23}H_{29}N_3O_7$ requires C, 60.07; H, 6.31; N, 9.14]; (KBr, ν_{max}, cm^{-1}): 3380, 2860, 1640, 1560, 1180, 1170, 970, 740; δ_H: (250 MHz, DMSO-d_6), δ 7.00-6.30 (7H, m,Ph), 11.80 (1H, s, PhCNOH CNOH-), 8.40 (1H, s, Ph-NH) 4.00-3.00 (16H, m, CH_2-O), 4.40 (3H, broad s, CH_3-Ph).

Synthesis of nickel(II) complexes (6-8) from benzo-15-crown-5-*p*-toluidino-glyoxime (1): Compound (**1**), (0.459 g, 1 mmol) was dissolved in methanol (30 mL) and $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.249 g, 1 mmol) was added to this mixture and boiled during 2 h. It was cooled to room temperature a dark green powder was obtained. Resulting solid was washed several times with hot methanol to dissolve any unreacted metal salt. Further purification was accomplished by column chromatography on alumina and methanol; chloroform (1:20). Dark green solid (0.79 g, 82 %; (m.p. > 132 ºC, [Found; C, 56.38; H, 5.52; N, 8.45 $(C_{23}H_{28}O_7)_2Ni$ (**6**) requires C, 56.58; H, 5.74; N, 8.60]; (KBr, ν_{max}, cm^{-1}): 3290, 3090, 1670, 1650, 1600, 1260, 1200, 950, 750; δ_H: (250 MHz, DMSO-d_6), δ 7.20-6.50 (14H, m, aromatic), 8.01 (2H, s, NH), 3.80-3.20 (32H, m, CH_2-O) 13.80 (2H, s, OH---O), 4.40 (6H, broad, s, -CH_3).

The same procedure was used to synthesize L_2Cu (**7**) and $L_2Co(H_2O)_2$ (**8**).

Compound (**7**) claret red solid (0.80 g, 81 %; (m.p. > 192 ºC, [Found; C, 56.04; H, 5.37; N, 8.48 $(C_{23}H_{28}N_3O_7)_2Cu$ (**6**) requires C, 56.35; H, 5.72; N, 8.59]; (KBr, ν_{max}, cm^{-1}): 3320, 3100, 1700, 1630, 1540, 1180, 1150, 960, 750.

Compound (**8**) brown solid (0.78 g, 77 %; (m.p. > 181 ºC, [Found; C, 54.48; H, 6.01; N, 8.12 $(C_{23}H_{28}N_3O_7)_2Co(H_2O)_2$ requires C, 54.49; H, 5.93; N, 8.30]; (KBr, ν_{max}, cm^{-1}): 3330, 3100, 1700, 1630, 1580, 1210, 1200, 1000, 790.

N-(1-Naphthyl)amino-benzo-15-crown 5-glyoxime (2): Benzo-15-crown-5-choloroglyoxime (**5**) (1 g, 2.58 mmol) was dissolved in 50 mL ethanol. 1-Amino-naphthalene (0.369 g, 1 mmol) in 30 mL ethanol was slowly added and stirred, during 0.5 h at 25 ºC. The reaction mixture was stirred for an additional 3 h. The reaction was monitored by using TLC. After drying in vacuum at 25 ºC pink powder was obtained. The resulting solid was filtered and washed several times with water to dissolve any unreacted compounds. The crude product was recrystallized from ethanol, water (1:2). Pink solid; (1.02 g, 80 %), m.p. > 112 ºC, [Found; C, 62.76; H, 5.73; N, 8.24 $C_{26}H_{29}N_3O_7$ requires C, 62.94; H, 5.85; N, 8.47]; (KBr,

ν_{max}, cm^{-1}): 3420, 3140, 1670, 1590, 1240, 1220, 810; δ_H: (250 MHz, DMSO-d_6), δ 6.80-6.20 (10H, m, aromatic), 11.90 (Ph-CNOH CNOH-), 10.60 (Ph-CHNOH-CNOH-), 8.20 (1H, s, Ph-CNOH-CNOH-NH-naphthyl), 3.90-3.00 (16H, m, $-CH_2-O$).

Synthesis of metal complexes (9-11) from N-(1-naphthyl)-amino-benzo-15-crown-5-glyoxime (2): Compound (**2**), (0.300 g, 0.61 mmol) was dissolved in methanol (30 mL) and $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.163 g, 1 mmol) was added to this mixture and boiled during 1 h. After it was cooled to room temperature a dark green powder was obtained. Resulting solid was washed several times with hot methanol to dissolve any unreacted metal salt. Further purification was accomplished by column chromatography on natural alumina and methanol; chloroform (1:20). Dark green solid (0.51 g, 81 %; (m.p. > 216 ºC, [Found; C, 59.94; H, 5.43; N, 7.92 $(C_{26}H_{28}O_7)_2$ Ni requires C, 59.55; H, 5.34; N, 8.02]; (KBr, ν_{max}, cm^{-1}): 3380, 3070, 1680, 1640, 1530, 1200, 1180, 940, 800.

The same procedure was used to synthesized for L'_2Cu (**10**) and $L'_2Co(H_2O)_2$ (**11**).

Compound (**10**) claret red solid (0.50 g, 80 %; (m.p. > 192 ºC, [Found; C, 52.44; H, 5.07; N, 7.82 $(C_{26}H_{28}N_3O_7)_2Cu$ requires; C, 52.49; H, 5.33; N, 7.99]; (KBr, ν_{max}, cm^{-1}): 3410, 3120, 1680, 1650, 1550, 1190, 1120, 1040, 790.

Compound (**11**) brown solid (0.53 g, 82 %; (m.p. > 202 ºC, [Found; C, 51.10; H, 5.34; N, 7.87 $(C_{26}H_{28}N_3O_7)_2Co(H_2O)_2$ requires C, 50.95; H, 5.54; N, 7.75]; (KBr, ν_{max}, cm^{-1}): 3400, 3090, 1690, 1660, 1600, 1190, 1130, 1060, 820.

RESULTS AND DISCUSSION

In this study, we have made use of the potential for exchanging the acids. -CH-proton of glyoxime (**3**) first with chloride group of Cl_2 and then in further reaction with *p*-amino-toluene and 1-amino-naphthalene. Treatment of the product (**5**) with *p*-amino-toluene and 1-amino-naphthalene give benzo-15-crown-5-*p*-toluidino-glyoxime (**1**) and N-(1-naphthyl)-amino-benzo-15-crown-5-glyoxime (**2**). Under moderately and conveniently conditions. Cu(II) complexes (**8**), (**11**) were prepared from (**1**) and (**2**) respectively.

Spectral data on the newly synthesized (**1**), (**2**) and their metal complexes are consistent with the proposed structures. For example; in compound (**1**) we observed C=N at 1640 cm^{-1}, N-O at 970 cm^{-1}, O-H at 3380 cm^{-1}, C-O-C at 1180 cm^{-1}, $C_{aromatic}$-H at 2860 cm^{-1}. The IR spectra of **1** and ML_2 (M = Co, Cu, Ni) was similar and 2860 cm^{-1} had disappeared in each case. In the ^1H NMR spectrum of **1**, the etheral protons of the crown ether group 2.80-3.80 ppm have been assigned on the basis of the result of **1**. All compounds which have been synthesized consist of benzo-15-crown-5 structure. According to the literature, this type of compounds give 3.60-4.05 ppm peaks of etheral protons. The aromatic protons of benzo-15-crown-5 moiety and phenyl protons appear at 6.30-7.2 ppm. In the ^1H NMR spectrum is similar to the corresponding signals in the **1**.

Many oxime-containing ligands stabilize Ni(III) and Ni(IV) as well as Cu(III), which usually have six donor atoms in the case of nickel and four in the case of copper[17]. Here we looked at spectral properties of Ni(II) and Cu(II) complexes with ligands that have five donors. These combine the effects of a oxime nitrogen donors with (b), either H-bond oxime quasi-macrocyclization or covalent macrocyclization (O-H--O). These indicate that the geometry is square planar for Ni(II) and Cu(II) complexes. At the same time, according to difference spectral properties of Ni(II) and Cu(II) complexes between Co(II) complexes. Co(II) complexes have octahedral geometry. In IR spectrums of these, O-H peaks give highly broad band at 3400-3200 cm^{-1}. In the mass spectrum of compound (**8**) we observed a moleculer ion peak at m/z 1011.233. Indeed, structure is confirmed by spectral technics. We should also mention that the general applicability of the synthetic procedure outlined here as a practical method to combine the versatility of crown ethers with many functional groups.

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