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Mükerrem Kurtoğlu & Selahattin Serin

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SYNTHESIS AND COMPLEX FORMATION OF DI[4-(11-CHLORO-3,6,9-TRIOXAUNDECYLOXY)-PHENYLAMINO]GLYOXIME

Mükerrem Kurtoğlu[1] **and Selahattin Serin***,[1,2]

[1]Department of Chemistry, University of
Kahramanmaraş Sütçü İmam, 46100,
Kahramanmaraş, Turkey
E-mail: mkurtoglu@ksu.edu.tr
[2]Department of Chemistry, University of Çukurova,
01130, Adana, Turkey
E-mail: serin@ksu.edu.tr

ABSTRACT

Di[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylamino]glyoxime (LH_2) has been prepared from 1-amino-4-(11-chloro-3,6,9-trioxaundecyloxy)benzene, *anti*-dichloroglyoxime, and sodium carbonate in ethanol. Nickel(II), copper(II) and cobalt(II) complexes of the ligand were synthesized. The Cu(II), Ni(II) and Co(II) complexes of the *vic*-dioxime ligand LH_2 have a metal/ligand ratio of 1:2 and the ligand coordinates only through the *N, N* atoms, as do most vicinal dioximes. The structures of the ligand and its complexes were investigated by elementel analyses, magnetic susceptibility measurements, ^{1}H NMR, IR and U.V.-Visible spectroscopy.

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*Corresponding author.

INTRODUCTION

Even though the chemistry of transition metal complexes with *vic*-dioxime ligands has been well studied and has been the subject of several reviews, only a few examples of the ligands with two *vic*-dioxime groups have been reported[1–4]. *Vic*-dioximes have received considerable attention as model compounds which mimic biofunctions such as the reduction of vitamin B_{12}[1,5]. Oxime metal chelates are biologically active[6] and semiconducting[7,8].

Both *anti*-dichloroglyoxime and cyanogendi-*N*-oxide, have been used to prepare *vic*-dioxime derivatives[9–15]. The addition reaction of either of these two reactants with diamino compounds gives heterocyclic or macroheterocyclic dioximes. The first five-membered heterocyclic *vic*-dioxime, 1,3-diphenyl-2-thioxa-4,5-bis(hydroximino)-imidazoline, was synthesized by the reaction of diphenyl-1-thiourea with cyanogendi-*N*-oxide[12]. The (E,E)- and (E,Z)-stereoisomers of *vic*-dioximes coordinate through their *N,N* or *N,O* sites and, in a few cases, interconversion of (E,E)- and (E,Z)-complexes[16–18] is possible. In this article we describe the synthesis of a novel (E,E)-dioxime (Fig. 1) and its complexes with the transition metal ions Ni(II), Cu(II) and Co(II).

EXPERIMENTAL

Materials

All chemicals and solvents were of analytical grade and were used without further purification. Dichloroglyoxime was prepared using known procedures[19,20]. 1-Amino-4-(11-chloro-3,6,9-trioxaundecyloxy)benzene was

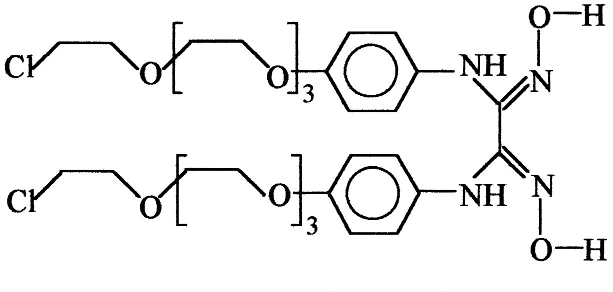
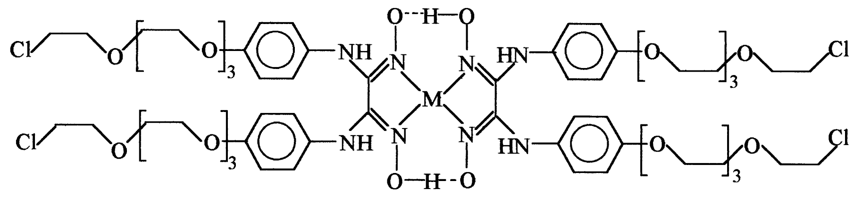


Figure 1. Structure of the ligand, LH_2.



M = Ni(II), Cu(II) and Co(II)

Figure 2. Proposed structure of the metal complexes.

prepared according to the literature method[21]. Cyanogen-di-*N*-oxide was prepared as described by Grundmann *et al.*[9]

Physical Measurements

The elemental analyses were carried out with a Carlo Erba 1106 instrument. The ^1H NMR spectrum of the ligand was obtained in DMSO-d_6 on a Bruker Ar X250 MHz spectrometer. The electronic absorption spectra of DMSO solutions of the ligand and complexes in the range 200–800 nm were measured on a Shimadzu UV-160A spectrometer. IR spectral measurements were taken on a Shimadzu FT-IR 8300 spectrometer.

Synthesis of Di[4-(11-chloro-3,6,9-trioxaundecyloxy)-phenylamino]glyoxime, LH_2

To a solution of 1-amino-4-(11-chloro-3,6,9-trioxaundecyloxy) benzene (0.45 g, 1.48 mmol) in 50 mL of ethanol was added a solution of cyanogen-di-*N*-oxide which was obtained by treating a suspension of *anti*-dichloroglyoxime (0.091 g, 0.576 mmol) in dichloromethane with 1 N Na_2CO_3 at −10 °C. The mixture was stirred at the same temperature for 8 h. The volume of the reaction mixture was reduced to 30 mL and the crystallization completed at low temperature (−30 °C). The white crystals were filtered off, washed with cold ethanol and dried. The ligand was soluble in hot ethanol and DMSO. Yield, 0.522 g (51%). M.p., 73–74 °C. ^1H NMR (ppm, DMSO-d_6): 3.55–3.65 (t, J = 5.8, 4H, $-CH_2Cl$), 3.67–3.75 (m, 20H, γ-η-CH_2), 3.86 (t, J = 4.8, 4H, β-CH_2), 4.15 (t, J = 4.8, 4H, α-CH_2), 6.60 (d, J = 2.3, 4H, Ar-H), 6.75 (d, J = 2.3, 4H, Ar-H), 9.20 (s, 2H, N-H), 10.85 (s, 2H, OH). Uv.-Vis. (nm, DMSO, $M^{-1}.cm^{-1}$): 370 ($\varepsilon = 14,000$), 275 ($\varepsilon = 12,200$), 270

($\varepsilon = 11,150$). IR (KBr, cm^{-1}): 3440 m (N-H), 3180 s (OH), 3045 w (Ar-C-H), 2962 s (CH_2CH_2), 1640 m (C=N), 1225 s (Ar-O-C), 1118 s (C-O-C), 930 m (N-O). Elemental analyses for $C_{30}N_4H_{44}O_{10}Cl_2$ (MW 691 g/mol)): Calcd: C, 52.10; N, 8.10; H, 6.37%. Found: C, 52.26; N, 8.22; H, 6.12%.

Synthesis of Ni(LH)$_2$

A solution of $NiCl_2.6H_2O$ (0.043 g, 0.181 mmol) in ethanol (20 mL) was added to a solution of di[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylamino]- glyoxime, LH_2, (0.25 g, 0.363 mmol) in ethanol (25 mL). The reaction mixture was stirred at 45 °C for 31/2 h. A solution of 0.1 M NH_3 in alcohol (10 mL) was then added (pH = 3.5) and the resulting red precipitate was filtered off, washed with water and ethanol and dried. Yield, 0.411 g (79%). M. p. 130–132 °C. Uv.-Vis. (nm, DMSO, M^{-1}.cm^{-1}): 407 ($\varepsilon = 22,300$), 272 ($\varepsilon = 16,500$), 260 ($\varepsilon = 14,300$). IR (KBr, cm^{-1}): 3451 m (N-H), 3053 w (Ar-C-H), 2960 s (CH_2CH_2), 1637 w (C=N), 1211 s (Ar-O-C), 1127 s (C-O-C), 925 m (N-O). Elemental analyses for $C_{60}N_8H_{86}O_{20}Cl_4Ni$ (MW. 1438.5): Calcd: C, 50.05; N, 7.78; H, 5.90; Ni, 4.08%. Found: C, 49.88; N, 7.93; H, 6.05, Ni, 4.37%.

Synthesis of Cu(LH)$_2$

Di[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylamino]glyoxime (0.47 g, 0.68 mmol) was dissolved in ethanol. To this solution was added a solution of $CuCl_2.2H_2O$ (0.0578 g, 0.34 mmol) in ethanol (15 mL). While stirring and heating, a 1% NaOH solution in ethanol was added until the pH became 4 and the mixture was then heated on a water bath for 4 h. The formed dark brown complex was filtered, washed with alcohol and ether, then dried. This complex is soluble in DMSO and DMF. Yield, 0.72 g (73%). M. p. 123–124 °C. μ_{eff}(B.M): 1.85. Uv.-Vis. (nm, DMSO, M^{-1}.cm^{-1}): 370 ($\varepsilon = 18,000$), 275 ($\varepsilon = 15,200$), 270 ($\varepsilon = 14,350$). IR (KBr, cm^{-1}): 3451 w (N-H), 3053 w (Ar-C-H), 2960 s (CH_2CH_2), 1630 w (C=N), 1211 s (Ar-O-C), 1127 s (C-O-C), 925 m (N-O). Elemental analysis for $C_{60}N_8H_{86}O_{20}Cl_4Cu$ (MW, 1438.5): Calcd: C, 49.88; N, 7.76; H, 5.96; Cu, 4.43%. Found: C, 49.72; N, 7.84; H, 5.85, Cu, 4.61%.

Synthesis of Co(LH)$_2$

Di[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylamino]glyoxime (0.25 g, 0.363 mmol) was dissolved in ethanol (15 mL) and to this solution was added a solution of $CoCl_2.6H_2O$ (0.043 g, 0.181 mmol) in ethanol. The solution was treated with 1% NaOH solution in alcohol until the *p*H became 4. Then the mixture was heated on a water bath for 4 h and allowed to stand overnight. A brown complex was precipitated with ether. Yield, 0.395 g (75%). M.p.: 136–138 °C. μ_{eff}(B. M): 2.03. Uv.-Vis. (nm, DMSO, $M^{-1}.cm^{-1}$): 395 ($\varepsilon = 18,550$), 267 ($\varepsilon = 15,150$), 260 ($\varepsilon = 13,750$). IR (KBr, cm^{-1}): 3449 w (N—H), 3041 w (Ar-C-H), 2964 s (CH_2CH_2), 1633 w (C=N), 1223 s (Ar-O-C), 1120 s (C-O-C), 927 m (N—O). Elemental analyses for $C_{60}N_8H_{86}O_{20}Cl_4Co$ (MW, 1439): Calcd: C, 52.10; N, 8.19; H, 6.37; Co, 4.42%. Found: C, 52.21; N, 8.19; H, 6.45, Co, 4.23%.

RESULTS AND DISCUSSION

Synthesis of Compounds

The ligand used for this study, di[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylamino]glyoxime, contains two long chain polyether groups and a *vic*-dioxime group. Its synthesis was accomplished in 51% yield by the reaction of cyanogen-di-N-oxide which was obtained from (E,E)-dichloroglyoxime and 1 N aqueous Na_2CO_3 solution and 1-amino-4-(11-chloro-3,6,9-trioxaundecyloxy)- benzene in ethanol. The structure of the ligand is shown in Fig. 1. The structure of LH_2 ligand was confirmed by a combination of elemental analyses, ^1H NMR, IR and UV-Vis spectral data.

The *vic*-dioxime ligand LH_2 has been reacted with Ni(II), Cu(II) and Co(II) chlorides to give the complexes as described by the following equation.

$$MCl_2.mH_2O + 2LH_2 \rightarrow M(LH)_2 + 2HCl + mH_2O$$
$$M = Ni(II), Cu(II) \quad \text{and} \quad Co(II)$$

The experimental results of the elemental analyses of the ligand and complexes are in agreement with theoretical expectations. The analytical data show that the ligand LH_2 forms 1:2 complexes with Ni(II), Cu(II) and Co(II) ions. All of the metal complexes are stable in air and soluble in dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO). Magnetic susceptibility measurements revealed that the complex $Ni(LH)_2$ is diamagnetic which is an expected property for nickel(II) complexes and that the complexes $Cu(LH)_2$ and $Co(LH)_2$ are paramagnetic[13,22]. Magnetic susceptibility measurements were determined at 293 K on a Gouy balance. Experimental magnetic susceptibilities were corrected for diamagnetism. The magnetic susceptibility value of the $Ni(LH)_2$ complex was calculated by the spin-only formula. The μ_{eff} values of the complexes, $Cu(LH)_2$ and $Co(LH)_2$, are 1.85 and 2.03 B.M., respectively.

^1H NMR Spectra

The ^1H NMR data of the ligand indicate an *anti*-configuration for the *vic*-dioxime by virtue of the presence of only one singlet for N-OH protons at the lower field of the spectrum (10.85 ppm, 2H)[12]. In the case of *amphi*-dioximes, one of the OH proton is directed towards the N atom of the adjacent hydroximino group and is participating in intramolecular hydrogen bonding ($O\text{-}H\cdots N$). This results in two singlets observed for the OH protons[16]. The N—H proton signals were observed at higher field (9.20 ppm, 2H). The signals of the protons of the aromatic group appeared at 6.75 and 6.60 ppm as two close doublets. The ^1H NMR spectrum of the ligand showed two triplets at 3.86 and 4.15 ppm for the $Ar\text{-}OCH_2CH_2$ protons[23]. The rest of the ether methylene protons appeared as multiplets at 3.55–3.63 and 3.67–3.75 ppm. The results are consistent with those reported for oxyethylene groups attached to a benzene ring in crown ethers or chains.

IR Spectra

In the IR spectrum of the LH_2 ligand, the O-H stretching vibration is observed at 3180 cm^{-1} as a broad absorption band. Ar-CH, C=N and N-O stretches are observed at 3045, 1640 and 960 cm^{-1}, respectively[24,25]. In addition to these, a narrow band at about 3440 cm^{-1} implies the presence of a N-H group. These values are in harmony with previously reported diaminoglyoxime derivatives. The bands at 1225 and 1118 cm^{-1} in the spectrum of the LH_2 *vic*-dioxime ligand are the bands corresponding to the streching of Ar-O-C and C-O-C ether groups[26–28]. In the IR spectra of the metal complexes, $Ni(LH)_2$, $Cu(LH)_2$ and $Co(LH)_2$, the weak bands at 1720, 1710, 1715 cm^{-1}, respectively, may be assigned to intramoleculer hydrogen bridge ($O\text{-}H\cdots O$) bending vibrations[29]. The disappearence of the stretching vibrations of the OH band at 3180 cm^{-1}, which was present in the free ligand, is further evidence for $O\text{-}H\cdots O$ bond formation.

UV-Visible Spectra

The UV-Visible spectra of all compounds were measured in DMSO solutions. In the UV-Visible spectrum of LH_2, the band belonging to the C=N group is observed at 370 nm. β-Bands belonging to aromatic rings appear at 275 nm. In the spectra of the metal complexes, the bands in the 275–270 nm range can be attributed to the $\pi \rightarrow \pi^*$ transitions of the benzenoid rings. In a like manner, the bands observed in the 429–362 nm range are also assigned to charge-transfer bands.

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