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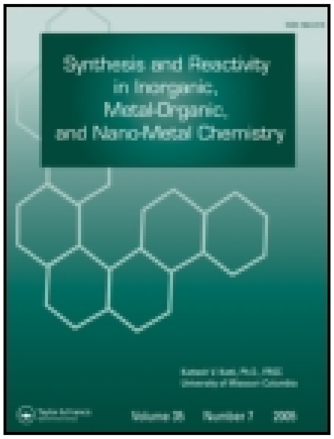

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SYNTHESES AND CHARACTERIZATION OF 4-(11-CHLORO-3,6,9-TRIOXAUNDECYLOXY) PHENYLAMINO-GLYOXIME AND ITS COMPLEXES WITH COPPER(II), NICKEL(II), AND COBALT(II)

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SYNTHESES AND CHARACTERIZATION OF 4-(11-CHLORO-3,6,9-TRIOXAUNDECYLOXY)PHENYLAMINO-GLYOXIME AND ITS COMPLEXES WITH COPPER(II), NICKEL(II), AND COBALT(II)

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ABSTRACT

A novel *vic*-dioxime ligand containing ethyleneoxy groups, 4-(11-chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoxime (LH_2) has been prepared from 1-amino-4-(11-chloro-3,6,9-trioxaundecyloxy)benzene and monochloro *anti*-glyoxime. Its complexes, $Ni(LH)_2$, $Cu(LH)_2$ and $Co(LH)_2$, have been synthesized. The analytical data show that the metal to ligand ratio in the complexes is 1:2. The complexes are formed by

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coordination of N,N atoms of the ligand. The structures of the oxime ligand (LH_2) and its complexes were elucidated by ^1H NMR, IR, UV.-Visible and elemental analyses techniques.

INTRODUCTION

Vic-dioximes have received considerable attention as model compounds which mimic biofunctions such as the reduction of vitamin B_{12}[1,2]. Oxime metal chelates are biologically active and semiconducting[3].

The coordination chemistry of *vic*-dioximes is an intensive area of study and numerous transition metal complexes of this group of ligands have been investigated[4–6]. The presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make vicinal dioximes amphoteric ligands which form corrin-type, square-planar, square-pyramidal or octahedral complexes with transition metal ions such as copper(II), nickel(II), palladium(II), cobalt(II) and cobalt(III) as central atoms[7,8]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding. The high stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for various purposes, including model compounds for vitamin B_{12} or trace metal analyses[9].

In the present study, we report the syntheses and complex formation of 4-(11-chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoxime (LH_2) which was synthesized by the reaction of l-amino-4-(3,6,9-trioxaundecyloxy)-benzene with monochloro *anti*-glyoxime at room temperature. The reaction of l-amino-4-(3,6,9-trioxaundecyloxy)benzene with monochloro *anti*-glyoxime may be represented as shown in Fig. 1. We examined its complexing ability with Ni(II), Cu(II) and Co(II) salts.

EXPERIMENTAL

Materials

1-Amino-4-(11-chloro-3,6,9-trioxaundecyloxy)benzene[10] and monochloro *anti*-glyoxime were prepared according to the literature[11]. $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$ (Merck) were used as purchased. All solvents were reagent grade and used without further purification. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer. The electronic absorption spectra of ethanol solutions of the ligand and complexes in the range 200–800 nm were measured on a Shimadzu

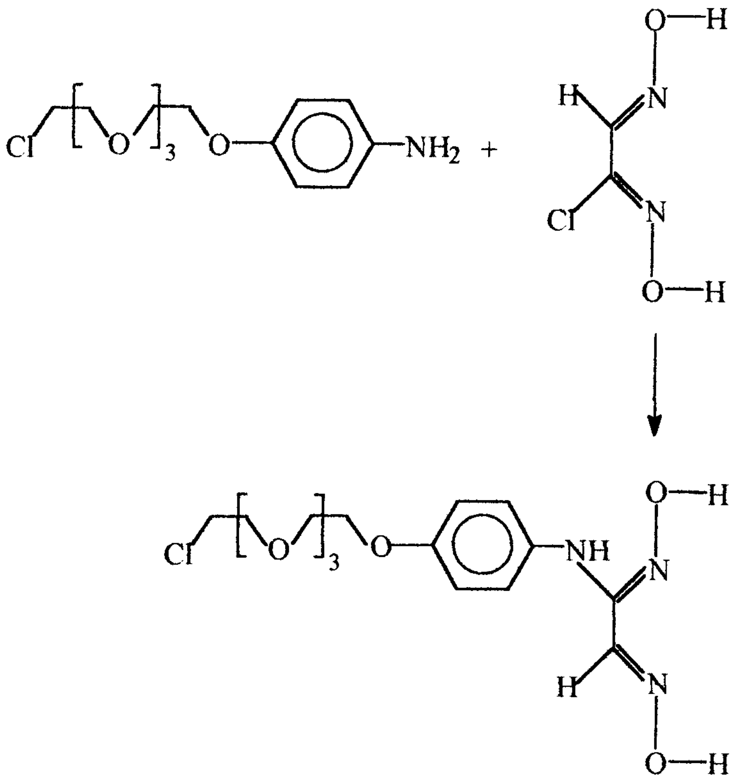


Figure 1. Synthesis reaction of 4-(11-Chloro-3,6,9-trioxaundecyloxy)phenylamino-glyoxime.

UV-160A spectrometer. The elemental analyses and ^1H NMR spectra of the ligand were determined at TUBITAK (Center of Science and Technology Research of Turkey).

Synthesis of 4-(11-Chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoxime, LH_2

A solution of l-amino-4-(11-chloro-3,6,9-trioxaundecyloxy)benzene (0.400 g, 1.318 mmol) in 25 mL of alcohol was added dropwise with stirring into a solution of monochloro *anti*-glyoxime (0.161 g, 1.318 mmol) in 35 mL of methylene chloride at room temperature. Stirring was continued for 11/2 h after the precipitation started. A quantity of 15 mL of cold ethanol was added and the precipitate was filtered and washed with cold ethanol and dried in *vacuo*; it is soluble in hot ethanol, DMSO and DMF and slightly soluble in chloroform and water. Yield, 0.395 g (77%); M. p.: 63–65 °C. Elemental Analyses for $C_{16}H_{24}N_3ClO_6$ (MW 389.5 g/mol); Calcld. (%): C, 49.29; H, 6.16; N, 10.78. Found (%): C, 49.47; H, 6.03; N, 10.91. IR (KBr, cm^{-1}): 3440 m (N-H), 3180 s (O-H), 3045 w (Ar-C-H), 2960 s ($-CH_2CH_2-$), 1640 m (C=N), 1225 s (Ar-O-C), 1118 s (C-O-C). UV-Vis. (λ_{max}, nm): 385, 290, 272. ^1H NMR (DMSO-d_6): 3.55–3.65 (m, 2 H, $-CH_2Cl$), 3.65–3.75 (m, 10 H, γ-η-CH_2), 3.86 (t, J = 4.8, 2 H, β-CH_2), 4.15 (t, J = 4.8 Hz, 2 H, α-CH_2), 6.60–6.75 (m, 4 H, Ar-H), 8.30 (s, 1 H, HC=N), 9.20 (s, 1 H, NH), 10.85 (s, 2 H, OH).

Synthesis of Bis[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoximato]nickel(II), Ni(LH)$_2$

A solution of $NiCl_2 \cdot 6H_2O$ (0.125 g, 0.53 mmol) in ethanol (20 mL) was added to a solution of LH_2 (0.412 g, 1.05 mmol) in hot ethanol (10 mL). The reaction mixture was stirred at 45 °C for 3 1/2 h. A 0.1 M solution of NH_3 in alcohol (10 mL) was then added (pH = 3.5) and the resulting precipitate was filtered, washed with water and ethanol and dried. Yield, 0.713 g (80%); M. p.: 145–147 °C. Elemental Analyses for $C_{32}H_{46}N_6Cl_2O_{12}N$ (MW 835.5 g/mol); Calcld. (%): C, 45.96; H, 5.51; N, 10.05. Found (%): C, 46.09; H, 5.64; N, 10.25. IR (KBr, cm^{-1}): 3430 m (N-H), 3050 w (Ar-C-H), 2960 s ($-CH_2CH_2-$), 1640 w (C=N), 1225 s (Ar-O-C), 1118 s (C-O-C). UV-Vis. (λ_{max}, nm): 390, 285, 270.

Synthesis of Bis[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoximato]copper(II), Cu(LH)$_2$

LH_2 (0.389 g 1.0 mmol) was dissolved in 10 mL of ethanol. To this solution was added a solution of $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.5 mmol) in ethanol (10 mL). While stirring and heating, a 0.1 N solution of NaOH in ethanol was added until the pH became 4.5 and then was heated on a water bath for 4 h. The dark brown complex was filtered, washed with alcohol and ether, then dried in *vacuo*. Yield, 0.70 g (83%); M. p.: 133–134 °C; μ_{eff}.: 1.82 B. M. Elemental Analyses for $C_{32}H_{46}N_6Cl_2O_{12}Cu$ (MW 840.5 g/mol); Calcld. (%): C, 45.68; H, 5.47; N, 9.99. Found (%): C, 45.77; H, 5.53; N, 9.78. IR (KBr, cm^{-1}): 3435 w (N-H), 3035 w (Ar-C-H), 2964 s ($-CH_2CH_2-$), 1642 w (C=N), 1225 s (Ar-O-C), 1120 s (C-O-C). UV-Vis. ($\lambda_{max,}$ nm): 410, 380, 285.

Synthesis of Bis[4-(11-chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoximato]cobalt(II), Co(LH)$_2$

LH_2 (0.389 g, 1 mmol) was dissolved in 10 mL of ethanol and to this solution was added a solution of $CoCl_2 \cdot 6H_2O$ (0.119 g, 0.5 mmol) in ethanol

(10 mL). The solution was treated with a 0.1 N NaOH solution in alcohol until the *p*H became 4.5. Then the mixture was heated on a water bath for 4 h and allowed to stand overnight. The brown complex was precipitated with ether. The product was dried in *vacuo*. Yield, 0.625 g (77%); M. p.: 158–160 °C; μ_{eff}.: 2.12 B. M. Elemental Analyses for $C_{32}H_{46}N_6Cl_2O_{12}Co$ (MW 836 g/mol); Calcld. (%): C, 45.93; H, 5.50; N, 10.05. Found (%): C, 46.07; H, 5.41; N, 10.17. IR (KBr, cm^{-1}): 3450 w (N-H), 3047 w (Ar-C-H), 2958 s (-CH_2CH_2-), 1637 w (C=N), 1224 s (Ar-O-C), 1117 s (C-O-C). UV-Vis. (λ_{max}, nm): 405, 383, 261.

RESULTS AND DISCUSSION

The synthesis of 4-(l1-chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoxime, the *vic*-dioxime ligand LH_2, is described in Fig. 1. The *vic*-dioxime was obtained in 77% yield by reacting monochloro *anti*-glyoxime with 1-amino-4-(11-chloro-3,6,9-trioxaundecyloxy)benzene. The structure of LH_2 was determined by a combination of elemental analyses, ^1H NMR, IR and UV-Vis. spectral data.

The reaction of the *vic*-dioxime ligand with $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $CoCl_2{\cdot}6H_2O$ salts give product with a metal ligand ratio of 1:2 according to elemental analysis data. The Ni(II), Cu(II) and Co(II) complexes of the LH_2 *vic*-dioxime ligand have been isolated and their structures have been investigated. The formation of these complexes is shown by the following general equation.

$$\begin{aligned}&MCl_2{\cdot}mH_2O + 2LH_2 \longrightarrow M(LH)_2 + mH_2O + 2HCl\\&\quad M = Ni(II),\ Cu(II)\ \text{or}\ Co(II)\\&\quad LH_2 = \text{4-(11-chloro-3,6,9-trioxaundecyloxy)phenylaminoglyoxime}\end{aligned}$$

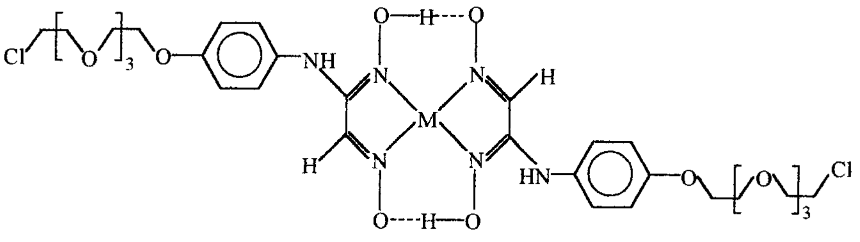
The ^1H NMR spectrum of LH_2 in DMSO-d_6 resulted in peaks corresponding to the aromatic protons at 6.63 ppm and 675 ppm as doublets. In the spectrum of LH_2 the N-H protons next to the oxime groups are a singlet at 9.25 ppm. The singlet at 10.80 ppm is assigned to hydroxy protons of *vic*-dioxime[12,16]. The spectrum also show three triplets at 3.55–3.63 ppm, 3.80 ppm and 4.20 ppm for -CH_2Cl, β-CH_2- and α-CH_2- protons, respectively[13,14]. The other ether methylene protons appeared as multiplets at 3.63–3.75 ppm. These results were consistent with those reported for oxyethylene groups attached to a benzene ring as in crown ethers or chains[15–17].

In the IR spectrum of LH_2, the OH stretching vibrations are observed at 3180 cm^{-1} as a broad absorption. Bands due to N-H, C=N and N-O stretches are at 3440, 1640 and 1010 cm^{-1}, respectively, in good agreement with values reported for similar compounds[18]. The bands at 1225 cm^{-1} and 1118 cm^{-1}in the spectrum of LH_2 correspond to the asymmetric and symmetric stretching of the C-O-C ether groups[19,20]. Aromatic C-H and aliphatic C-H bands occurred at 3045 cm^{-1} and 2960 cm^{-1}. The $Ni(LH)_2$, $Cu(LH)_2$ and $Co(LH)_2$ complexes have IR spectra very similar to those of LH_2, except for the disappearence of the OH stretching frequencies. Weak bands at *ca.* 1700 cm^{-1} indicate OH-O bridges, while the C=N vibrations are at lower wave numbers, as expected for *N*,*N*-chelated vicinal dioxime complexes.

The UV-Visible spectra of the *vic*-dioxime ligand and its metal complexes, $Ni(LH)_2$, $Cu(LH)_2$ and $Co(LH)_2$, were measured in ethanol. The data of the ligand and the complexes are reported in the experimental part. The UV.-Visible peaks corresponding to the C=N group and the aromatic ring in the vicdioxime ligand were observed at 385 nm and 290 nm. The peaks belonging to the C=N group in the spectra of the $Ni(LH)_2$, $Cu(LH)_2$ and $Co(LH)_2$ complexes appeared at 390 nm, 380 nm and 383 nm, respectively.

Magnetic susceptibility measurements provided sufficient data to characterize the structures. The complex of Ni(II), $Ni(LH)_2$ is diamagnetic as expected for a d^8 metal ion in a square-planar field[21].

The magnetic moment value of 2.12 BM observed for the Co(II) complex, $Cu(LH)_2$, reveals a square-planar geometry around the Co(II) ion.



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

Figure 2. Proposed structure of the metal complexes.

The effective magnetic moment of 1.82 B.M. for Cu(II) complex suggested a square-planar geometry around the Cu(II) ion[22–25].

The synthesized complexes are suggested to have the general structural formulas as shown in Fig. 2.

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