Synthesis and characterization of a new vic-dioxime ligand and its complexes with cobalt(II), nickel(II) and copper(II)

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Received 4 March 2003; revised 29 January 2004

A new vic-dioxime ligand (LH₁), 1,10-phenanthrolino-5,6-bis(2,3-dihydroxyimino-1-aza) propane has been synthesized from the reaction of 5,6-diamino-1,10-phenanthroline with anti-chloromethylglyoxime. The ligand reacts with Co(II), Ni(II) and Cu(II) salts to form complexes. The complexes have been characterized by FTIR, ¹H NMR (DMSO-d₆), elemental analyses and magnetic measurements. Protonation constants of the ligand and overall formation constants of the complexes have been calculated from potentiometric data using the program TITFIT.

IPC Code: Int.Cl.⁷ C01G 51/00, C01G 3/00, C01G 53/00

1,10-Phenanthroline (phen) has been extensively used as a ligand in both analytical and preparative coordination chemistry. Systematic studies of substituted derivatives of phen and other ε-diimines have been successfully undertaken⁴. The photochemical and redox properties of complexes can be varied systematically through appropriate substitution on the phenanthroline rings²-⁴.

In the literature, the synthesis of substituted amino and diaminoglyoximes and their various derivatives have been a subject of study for a long period of time⁵-¹⁴. Metal complexes of vic-dioximes have been widely investigated as analytical reagents and models for biological systems such as vitamin B₁₂ (ref. 15-16).

Potentiometric titration alone can be effectively applied to estimate the complex species in different pH ranges by carefully applying different mathematical procedures related to least square regression. The computer programs enable one to calculate overall protonation or formation constants which minimize the sum of the square residual between observed and calculated potential values.

The present note deal with the synthesis of a new vic-dioxime (I) and its reactions with various metal ions. We report herein the synthesis and characterization of a 5,6-diamino-1,10-phenanthroline substituted dioxime ligand, namely 1,10-phenanthro-

Experimental

Doubly distilled and deionized water was used throughout in the potentiometric experiments which were carried out under an atmosphere of purified nitrogen. All other chemicals employed were of the highest grade available. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. High purity potassium nitrate (Merck) was used as supporting electrolyte. The ionic medium was 0.1 mol/dm³ KNO₃ at the beginning of each potentiometric titration.

The IR spectra (KBr discs) were recorded in the 4000-400 cm⁻¹ range on a Mattson 1000 FT-IR spectrometer. Proton NMR spectra were recorded on a Bruker AC-200 MHz (DMSO-d₆) spectrometer. The elemental analyses and mass spectra (FAB-MS) were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). Melting points were obtained with a Gallenkamp CAP MPD-350 apparatus in open capillaries. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance. Potentiometric measurements were carried out using a titration system with a Metrohm E-415 dosimeter and a Metrohm E-510 pH meter. A Metrohm 6.0204.000 combined glass electrode was used for potentiometric titrations, pH and EMF measurements. A
The thermostated titration vessel of 100 mL capacity was used. The electrode system was calibrated using standard buffer solutions of pH 4.00 and 7.00.

The following solutions were prepared to obtain the pH-titration curves: Solution A: HClO₄ (2.5 mL, 0.1 M), KNO₃ (5 mL, 1.0 M). Solution B: Solution A + solution of LH₄ in ethanol (2.5 mL, 0.01 M). Solution C-F: Solution B + 2.5 mL, 0.01 M metal salt solution (i.e. CuCl₂2H₂O, NiCl₂6H₂O, CoCl₂6H₂O) in ethanol.

Sufficient amounts of ethanol were added to make up the total volume Vₒ, which was 25±0.1 mL and thermostated at 25.0 ± 0.1°C⁵,⁶,¹¹-¹³.

**Synthesis of 1,10-phenanthrolino-5,6-bis(2,3-dihyroximinio-1-aza)propane**

To solution of 5,6-diamino-1,10-phenanthroline (0.315 g, 1.5 mmol) in 100 mL of absolute ethanol was added solid NaHCO₃ (0.336 g, 4.0 mmol) and stirred for 10 min. Thereafter, anti-chloromethylglyoxime (0.409 g, 3.0 mmol) in 10 mL of absolute ethanol and this solution was added dropwise to the above mixture during 60 min and then was stirred for 90 min at 65°C. The hot solution which contained solid NaCl was filtered washed with absolute ethanol (ca. 20 mL) until the filtrate became colourless. The combined ethanol filtrates were evaporated to 1/3 of their volume and petroleum ether (10 mL) was added at room temperature and a yellow precipitate was obtained. It was filtered and washed with diethyl ether. Yield 0.319 g (52%); m.p. > 360°C. The product is very slightly soluble in ethanol, chloroform and soluble OM. Since the solubility of the complex in organic solvents is very low, IH NMR spectra could not be taken. Anal. Calcd. for (C₃₅H₃₆N₁₆O₃CUJ¹)₆: C, 78.37; H, 3.61; N, 22.68. Found: C, 78.29; H, 3.59; N, 22.61.

**Synthesis of Cu(II) complex**

LH₄ (0.082 g, 0.2 mmol) was dissolved in a absolute ethanol (100 mL) and NiCl₂6H₂O (0.0952 g, 0.4 mmol) in 10 mL of absolute ethanol was added to this solution. After addition of 0.05 N NaOH solution in ethanol to raise the pH to 8.0-8.5, a light-brown complex precipitated very rapidly. The mixture was stirred on a water bath at 65°C for 30 min. It was filtered, washed with absolute ethanol and dried with diethyl ether. The product was very slightly soluble in ethanol and chloroform and DMSO. Yield, 425 mg (42.67%); m.p. >360°C; IR (KBr): 3412 (NH), 3234 (OH), 3080 (Ar-CH), 2978, 2927 (CH₃), 1625 (C=N), 1012 (N-O) cm⁻¹. Since the solubility of the complex in organic solvents is very low, IH NMR spectra could not be taken. Anal. Calcd. for (C₃₅H₃₆N₁₆O₃CUJ¹)₆: C, 43.37; H, 3.61; N, 22.49. Found: C, 43.29; H, 3.42; N, 22.30. The complex is diamagnetic.

**Synthesis of Cu(II) complex**

The Cu(II) complex was prepared in a similar way from LH₄ (0.082 g, 0.2 mmol) and CuCl₂2H₂O (0.0682 g, 0.4 mmol) in 10 mL of absolute ethanol. This complex was prepared as Co(II) and Ni(II) complexes. The brown product is very slightly soluble in ethanol and chloroform and DMSO. Yield, 455 mg (45.05%); m.p. >360°C; IR (KBr): 3412 (NH), 3208 (OH), 3080 (Ar-CH), 2978-2927 (CH₃), 1625 (C=N), 1012 (N-O). Since the solubility of the complex in organic solvents is very low, IH NMR spectra could not be taken. Anal. Calcd. for (C₃₅H₃₆N₁₆O₃CUJ)₆: C, 42.72; H, 3.56; N, 22.18. Found: C, 42.81; H, 3.49; N, 22.35. The product is diamagnetic.
Results and discussion

5,6-Diamino-1,10-phenanthroline\textsuperscript{2,3,18,19} and anti-chloromethylglyoxime\textsuperscript{20,21} were synthesized according to reported procedures. The new vic-dioxime ligand, 1,10-phenanthroline-(5,6-b)-2,3-dihydroxymino-1,4-diazin (LH\textsubscript{4}) was synthesized from 5,6-diamino-1,10-phenanthroline and anti-dichloroglyoxime, in a good yield (ca. 52\%), as shown in Structure I.

Elemental analyses of LH\textsubscript{4} and its Co(II), Ni(II) and Cu(II) complexes show good agreement with the proposed structures.

IR data gave further useful information on the structure of the LH\textsubscript{4} ligand, clearly indicating the presence of H-N and O-H stretching bands at 3412 and 3182 cm\textsuperscript{-1}, respectively C=N and N-O vibrations at 1574 and 1012 cm\textsuperscript{-1}. In the IR spectra of the complexes, the C=N higher frequency indicates the formation of coordination bonds between the metal and nitrogen atoms of the ligands. The values are in harmony with the previously reported diaminoglyoxime derivatives\textsuperscript{3-14}.

The \textsuperscript{1}H NMR spectrum of LH\textsubscript{4} in DMSO-\textit{d}_6 confirmed the proposed structure showing two D\textsubscript{2}O-exchangeable protons of \(\delta\) 11.90, 12.45 ppm for the OH and 9.20 ppm for the NH groups. Two singlet peaks were observed for the O-H protons in substituted aminomethylglyoximes because of difference in the neighbouring groups at 11.90 (CH\textsubscript{3}-N-OH) and 12.45 ppm (the other -N-OH). Aromatic C-H protons at 7.72-9.38 ppm as multiplet and aliphatic C-H protons at 2.20 ppm as singlet are observed.

The solubility of the metal complexes in organic solvents was insufficient to obtain \textsuperscript{1}H NMR spectra and further investigations were not possible.

Protonation constants of the ligand were calculated with a potentiometric titration method and the TITFIT program\textsuperscript{17}. The calculated protonation and formation constants of the ligand are given in Table 1. In the normal aqueous titration range, the amphoteric oxime ligand releases two protons from the four OH groups of the oxime.

The ligand forms H\textsubscript{4}L between pH: 2-7, H\textsubscript{3}L\textsuperscript{-} between pH: 4-8.5, H\textsubscript{2}L\textsuperscript{2-} between pH: 5-10 and HL\textsubscript{3} - between pH: 8-12.

Some general observations about the various systems are as follows: In the case of the Co(II)-LH\textsubscript{4} system, complexation begins at pH = 2.0 with the formation of CoLH\textsubscript{2}. CoLH appears at pH values between pH: 7-11 and the CoL complex begins to form at pH: 8.

It is observed that for the complexes forming in solutions containing Ni(II) ions and LH\textsubscript{4}, complexation begins at pH = 2 with the formation of NiLH\textsubscript{2} and then the NiLH complex at pH = 6 showing a maximum at pH = 8. The NiL complex begins to form at pH = 7 followed by NiLOH complex which begins to form at pH = 8.

It is seen that for the complex formation in solutions containing Cu(II) ions and LH\textsubscript{4}, complexation begins at pH = 2.0 with the formation of CuLH\textsubscript{2}. Then the CuLH complex begins to form at pH = 3.5 showing a maximum at pH = 6.5 followed by CuL complex which begins to form at pH = 6.5.

Magnetic susceptibility measurements provide sufficient information to characterize the complexes. The complexes have magnetic moments of 4.01 B.M.

Table 1—Protonation and overall formation constants of the LH\textsubscript{4} ligand and its complexes at 25\°C and ionic strength (I): 1.0 M KNO\textsubscript{3}

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<th>Metal ion</th>
<th>Species</th>
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<tr>
<td>H\textsuperscript{+}</td>
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for Co(II), 1.49 B.M. for Cu(II) and Ni(II) is diamagnetic. Our studies show that Cu(II) have tetrahedral and for Ni(II) square-planar geometries, while Co(II) complex is octahedral with chlor atoms as axial ligands Structure II. The formation of LH₄-Co is verified by MS (positive FAB, solution in DMSO); m/z: 1175.8 [2L + 3Co + 5Cl]⁺ corresponding to a dimeric species of the polymeric compound.

Acknowledgement
We wish to acknowledge the financial support by the "Yıldız Technical University Research Fund" (Project No: 20-01-02-01).

References