

## Synthesis of bis(ferrocenylamino)glyoxime and its nickel(II) complex

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### Abstract

Bis(ferrocenylamino)glyoxime has been prepared by the reaction of amino ferrocene with *anti*-dichloroglyoxime. The nickel(II) complex of this new compound is also described.

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### Introduction

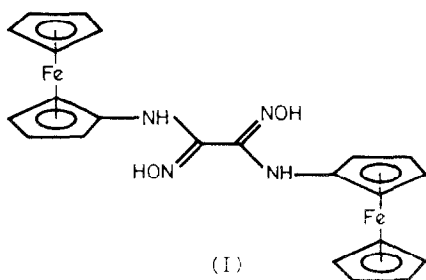
Although organometallic and coordination chemistry are regarded as being closely related, there are relatively few examples of compounds which can be considered to bridge the two fields. Our recent reports on the synthesis of compounds containing ferrocene and *vic*-dioxime groups have received considerable attention owing to the fact that *vic*-dioximes furnish suitable donor sites for binding various transition metal ions [1,2].

We have previously worked on the structures of the diaminoglyoxime complexes and investigated the effect of crown ether groups on the properties of the *vic*-dioxime complexes [3–5]. In this paper, a new approach to the diaminoglyoxime compound has been devised involving the synthesis of a diaminoglyoxime with two symmetrical ferrocene units. The Ni<sup>2+</sup> complex of this new ligand is also described.

### Results and discussion

Aminoferrocene was prepared from bromoferrocene through its reaction with copper phthalimide followed by hydrolysis of the product with hydrazine hydrate [6]. This procedure was chosen because of the ease of the various steps [7,8].

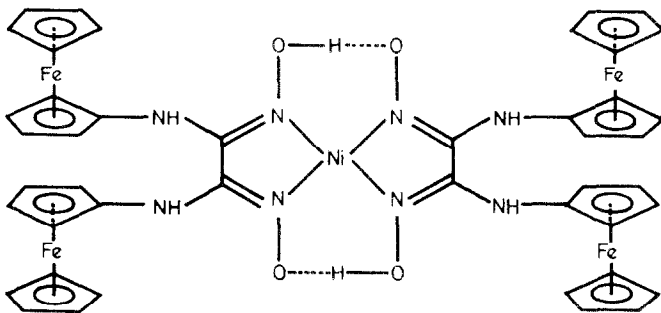
In order to introduce the *vic*-dioxime group, *anti*-dichloroglyoxime (DCGO) was used. The reaction was carried out in ethanol with NaHCO<sub>3</sub> to take up the HCl formed. Bis(ferrocenylamino)glyoxime (I) was obtained in 78% yield. I was light sensitive in solution. Its mass spectrum showed the molecular ion peak at *m/z* 486.



As for diaminoglyoxime, the *s-trans* configuration can be suggested for I on the basis of the  $^1\text{H}$  NMR data [5,9]. The signals for the O-H and N-H protons appeared at 10.2 and 7.4 ppm as singlets, which disappeared upon deuterium exchange. The presence of only one chemical shift for each of exchangeable groups implied that both NH protons and OH protons are equivalent, and this is the case only when the oxime groups are in the *s-trans* position [5,9]. The signals from  $\alpha$  and  $\beta$  protons of the bound cyclopentadienyl group appeared as two well separated triplets at 4.27 and 3.85 ppm and the free cyclopentadienyl protons appeared as a singlet at 4.07 ppm.

The IR spectrum of I shows bands due to OH, C=N, and N-O bonds of the aminoglyoxime moiety at 3360, 3250, 1640, and 920  $\text{cm}^{-1}$ , as for similar compounds [5]. The C-H out-of-plane bending vibrations of the ferrocene group gave a doublet at 820  $\text{cm}^{-1}$ .

I formed complexes with various transition metal ions very rapidly, but only the nickel(II) complex (II) was isolated in the present work. The Ni/I ratio in the complex was 1/2 even when an excess of Ni(II) salt was used. Consequently, there was no complexation through the NH groups of I. The orange complex was not soluble in common solvents, so NMR and electronic spectra could not be obtained.



In the IR spectrum the free OH stretching vibrations of the ligand at 3250  $\text{cm}^{-1}$  are absent, and a bending vibration of the O-H  $\cdots$  O bridge appears at 1720  $\text{cm}^{-1}$  as a weak band. The (C=N) bands of the oxime group were shifted to lower frequencies (1560  $\text{cm}^{-1}$ ) as a result of *N,N'*-coordination of the metal ion [10].

The reaction of hydroxyferrocene with DCGO was also investigated, but no oxime could be obtained. This may be due to the decreasing reactivity of DCGO derivatives in the order NH > SH > OH [11].

## Experimental

Aminoferrocene and *anti*-dichloroglyoxime (DCGO) were prepared by published procedures [6,12]. NMR spectra were recorded with a Bruker AC-200 FT-NMR spectrometer in the Tübitak Research Institute for Basic Sciences, Gebze, Turkey.

### *Bis(ferrocenylamino)glyoxime (I)*

To a cold solution of ferrocenylamine (0.520 g, 2.58 mmol) in ethanol (100 ml) containing an excess of solid NaHCO<sub>3</sub> (5 g) a solution of DCGO (0.220 g, 1.4 mmol) in ethanol (60 ml) was added dropwise with stirring at room temperature. The mixture was stirred for a further 1 h and then filtered. The yellow precipitate was washed with water to remove any unchanged NaHCO<sub>3</sub> then dissolved in a hot mixture of CH<sub>2</sub>Cl<sub>2</sub>/ethanol (1/5) (100 ml). The solution was boiled with activated charcoal and was filtered hot. The filtrate was kept at 0 °C overnight and gave yellow crystals which were filtered off, washed with ethanol, and dried in vacuo. Yield: 490 mg (78%). M.p. 170 °C, (dec.); MS: *m/z*, *M*<sup>+</sup> 486; IR (KBr):  $\nu_{\max}$  3360, 3250, 3100, 2880, 1640, 1620, 1500, 1400, 1280, 1100, 1000, 920, 820, 480 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  3.85 (t, 4H), 4.07 (s, 10H), 4.27 (t, 4H), 7.37 (s, 2H, NH), 10.16 (s, 2H, OH) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): 143.3, 98.9 (C<sub>b</sub>), 68.9 (C<sub>p</sub>), 63.2 (C<sub>a</sub>), 59.9 (C<sub>β</sub>) ppm. Analysis. Found: C, 54.43; H, 4.46; N, 11.81. C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>Fe<sub>2</sub> calc: C, 54.35; H, 4.56; N, 11.52%.

### *Ni*<sup>2+</sup> complex of *I*

A solution of NiCl<sub>2</sub> · 6H<sub>2</sub>O (20.4 mg, 0.086 mmol) in ethanol (20 ml) was added to a solution of *I* (83.5 mg, 0.17 mmol) in ethanol (80 ml); the solution immediately turned to red. When the pH of the solution was raised to pH 4 by addition of 0.1 *M* NaOH in ethanol the desired complex precipitated out. The orange solid was filtered off, washed first with water and then with ethanol and diethyl ether, and dried in vacuo. Yield: 47 mg (53%); M.p. > 250 °C; IR (KBr):  $\nu_{\max}$  3400, 3100, 1720, 1560, 1470, 1100, 1000, 820, 480 cm<sup>-1</sup>. Analysis. Found: C, 50.94; H, 4.08; N, 11.26. C<sub>44</sub>H<sub>42</sub>N<sub>8</sub>O<sub>4</sub>Fe<sub>4</sub>Ni calc: C, 51.36; H, 4.11; N, 10.89%.

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