Journal of Organometallic Chemistry, 335 (1987) 105–108
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis of a novel [10]ferrocenophanedioxime with bridge heteroatoms and of its nickel(II) complex

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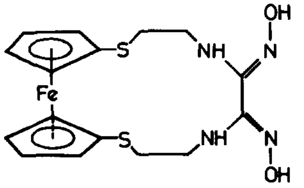
(Received April 21st, 1987)

Abstract

1,10-Dithia-4,7-diaza-5,6-bis(hydroxyimino)[10](1,1′)ferrocenophane has been prepared by the reaction of S,S'-bis(aminoethyl)(1,1′)dithiaferrocene with *anti*-dichloroglyoxime. The nickel(II) complex of the new ligand has been isolated.

Introduction

We have recently described synthetic and structural aspects of compounds containing *vic*-dioximes and ferrocene groups simultaneously [1–3]. As part of a study on ferroceneoximes, we were interested in extending the ferrocenophanes to include compounds containing sulfur and nitrogen as bridging heteroatoms. In this paper, we describe the synthesis of 1,10-dithia-4,7-diaza-5,6-bis(hydroxyimino)[10]-(1,1′)ferrocenophanedioxime (I) and its nickel(II) complex. This compound was expected to show whether ferrocenophane, in which a ferrocene nucleus was incorporated in the framework of a macro-heterocyclic ring, was capable of complexing with transition metal ions as the *vic*-dioximes.



(I)

0022-328X/87/$03.50

Results and discussion

The synthesis is shown in Scheme 1 [4].

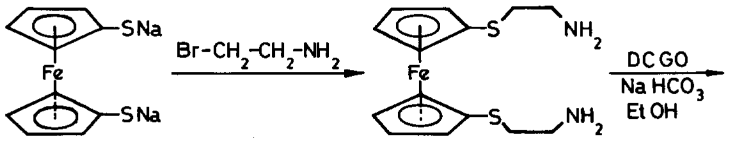
Compound II was treated with 1-amino-2-bromoethane in ethanol to give *S*,*S*′-bis(aminoethyl)(1,1′)dithiaferrocene (III); owing the fast decomposition of III, no attempt was made to purify it. Compound III reacted with *anti*-dichloroglyoxime (DCGO) in 1/1 ratio in the presence of sodium bicarbonate to give the [10]-ferrocenophanedioxime (I), which was purified by flash chromatography. The satisfactory elemental analysis results and the FAB mass spectrum of I, which shows a molecular ion at *m*/*e* 420, confirm the proposed structure and rule out an undesired polymeric form. In the IR spectrum characteristic bands appeared at 3380 (ν(NH)), 3230 (ν(OH)), 3090 (ν(C–H)Cp), 2960, 2920 (ν(CH)), 1640 (ν(C=N)), 1605 (δ(NH)), 1410 (δ(OH)), and 950 (ν(N–O)) cm^{-1}.

The ^1H NMR data 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 (δ 9.8 ppm, 2H) [5,6]. The signals from the protons of the ferrocene group appeared at δ 4.27 and 4.14 ppm as two close singlets and those of the ethylene bridges at δ 3.0 ppm as a singlet [7]. The NH proton signals were observed at higher field (δ 6.0 ppm) than those from the similar amidoximes [5]. The signals from both OH and NH protons disappeared upon D_2O exchange. In the ^{13}C NMR spectrum the signals from the C atoms of the oxime groups appeared at 146.35 ppm as expected [5]. The signal from the bridge-head carbon atom of the cyclopentadienyl ring was shifted downfield (δ 85.34 ppm).

The Ni^{2+} complex of I had a metal/ligand ratio of 1/2, as is the case for most *anti*-dioximes (Fig. 1). Even when excess Ni^{2+} salt was added to complex with the donor groups of the ferrocenophanes as well, only one type of complex was obtained.

A molecular model of I shows that the donor groups (two thia and two aza groups) of the ferrocenophane lie in a distorted plane which is unsuitable for complex formation. In addition to this steric hindrance, thia groups attached directly to the cyclopentadienyl ring are thought to interact with the Fe ion of the ferrocene unit, the lone pair electrons of S-atoms were being suggested to engage in a d_π–p_π interaction [7,8]. Both of the steric and electronic effects may hinder complexation of the ferrocenophane.

The structure of the Ni^{2+} complex of I is confirmed by its IR and ^1H NMR spectra. The absence of the ν(OH) band at 3230 cm^{-1} in the IR spectrum is as expected. The formation of hydrogen bridges (O–H---O) is confirmed by the very



(II) (III)

Scheme 1

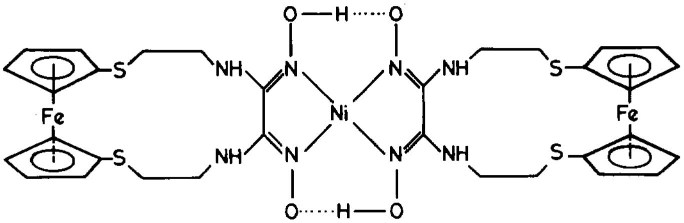


Fig. 1. Structure of the nickel(II) complex of compound I.

low shift of the deuterium-exchangeable oxime protons in the ^1H NMR spectrum (δ 17.04 ppm), and bending frequencies of 1750 cm^{-1} in the IR spectrum [5,9].

Experimental

Reactions were carried out under purified argon. All solvents were purged with argon before use. (1,1′)Ferrocenedithiol and *anti*-dichoroglyoxime (DCGO) were prepared by published methods [4,10]. ^1H NMR spectra were recorded on a Bruker AC-200 FT-NMR spectrometer in the TUBITAK Research Institute for Basic Sciences, Gebze, Turkey.

S,S′-Bis(aminoethyl)(1,1′)dithiaferrocene (III)

A solution of 1-amino-2-bromethane hydrobromide (1.55 g, 7.5 mmol) in 40 ml of ethanol was neutralized with 0.8 ml of 40% aqueous NaOH then added dropwise with stirring at room temperature to a solution of disodium (1,1′)ferroceceneditiolate prepared from (1,1′)ferrocenedithiol (0.95 g, 3.8 mmol) and 40% aqueous NaOH (0.62 ml) in 60 ml of ethanol. The mixture was stirred overnight and then evaporated under vacuum. The residue was dissolved in CH_2Cl_2 and the solution filtered. Complex III was obtained as a brown oil by evaporating the solvent. Yield: 1.0 g (78%).

1,10-Dithia-4,7-diaza-5,6-bis(hydroxyimino)[10](1,1′)ferrocenophane (I)

A solution of III (1 g, 2.97 mmol) (prepared as above) in 100 ml of ethanol and a solution of DCGO (0.47 g, 3 mmol) in 100 ml of ethanol were added dropwise at the same rate, with stirring during 1 h at room temperature to ethanol (200 ml) containing $NaHCO_3$ (5 g). Stirring was continued for another 2 h, then the mixture was filtered and the filtrate evaporated under vacuum. Flash chromatography of the condensed residue on silica, with 5/1 CH_2Cl_2/ethanol as eluant, gave 0.312 g of I (25%) as orange crystals; m.p. 212 °C (dec.). ^1H NMR (DMSO-d_6): δ 3.00 (s, 8H); 4.14 (s, 4H); 4.27 (s, 4H); 6.00 (s, 2H, NH); 9.80 (s, 2H, OH) ppm. ^{13}C NMR (DMSO-d_6): 146.35, 85.34 (C_b), 72.18 (C_α), 68.22 (C_β), 41.72, 37.16 ppm. Analysis. Found: C, 45.99; H, 4.91; N, 13.56. $C_{16}H_{20}N_4S_2O_2Fe$ calcd.: C, 45.72; H, 4.80; N, 13.33%.

Preparation of the nickel(II) complex of I (Fig. 1)

A solution of $NiCl_2 \cdot 6H_2O$ (14 mg, 0.059 mmol) in ethanol (10 ml) was added to a solution of I (50 mg, 0.12 mmol) in ethanol (40 ml). The solution was warmed to 60 °C and 0.1 *N* KOH in EtOH was added until the pH of the solution was 4.5. The precipitated brown complex was filtered off, washed successively with ethanol, hot water, and hot acetone, and then dried under vacuum. Yield; 30 mg (56%), m.p. $> 210\,^\circ C$ (dec.). ^1H NMR (DMSO-d_6): δ 3.34 (s, 16H), 4.75 (d, 16H), 6.50 (s, 4H), 17.04 (s, 2H) ppm. Analysis. Found: C, 43.10; H, 4.35; N, 12.76. $C_{32}H_{38}N_8S_4O_4Ni$-Fe_2 calc: C, 42.83; H, 4.27; N, 12.50%.

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