

## A NOVEL DITHIOFERROCENOPHANE WITH A *vic*-DIOXIME MOIETY IN THE BRIDGING CHAIN

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### Summary

The *amphi* and *anti* isomers of 1,4-dithia-2,3-bis(hydroxyimino)[4](1,1')ferrocenophane were prepared by the reaction of disodium 1,1'-ferrocenedithiolate with *anti*-dichloroglyoxime. The Ni<sup>II</sup> complex of the *amphi* isomer was also isolated and characterized.

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### Introduction

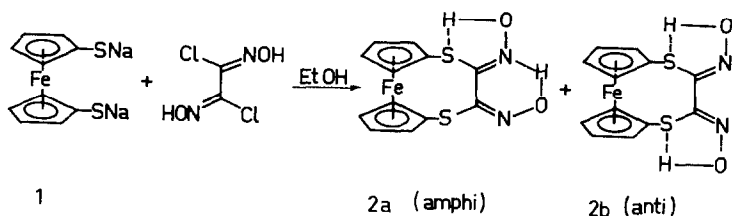
The structure and chemistry of ferrocenophanes have recently received considerable attention [1]. Many [*n*]ferrocenophanes have been prepared [2], but to the best of our knowledge no ferrocenophane with a monoxime or dioxime moiety in the bridging chain has been reported. The synthesis of various *vic*-dioximes and their transition metal complexes have been the main goal of recent research in our laboratory [3], and during our current studies of the preparation of novel systems which combine the features of both coordination and ferrocene chemistry [4] we obtained a dithiaferrocenophane containing a *vic*-dioxime group in its bridging chain. This new ligand and its Ni<sup>2+</sup> complex are described here.

### Results and discussion

Disodium 1,1'-ferrocenedithiolate (**1**), prepared by the reaction of 1,1'-ferrocenedithiol with 40% aqueous sodium hydroxide in ethanol [5] and treatment with

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\* Dedicated to Prof. H.A. Staab on the occasion of his 60th birthday.



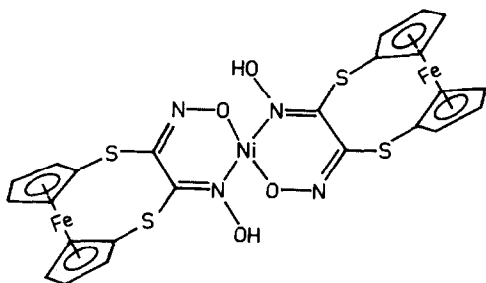
SCHEME 1

*anti*-dichloroglyoxime in ethanol under dilute conditions gave an orange product mixture, which was separated by flash chromatography. The first band yielded the *amphi*-form of 1,4-dithia-2,3-bis(hydroxyimino)[4](1,1')ferrocenophane (**2a**) in 58.7% yield, and the second band gave the *anti* isomer (**2b**) in trace amounts (Scheme 1). Because only a very small amount of **2b** was obtained we were only able to carry out the structural characterization of the *amphi*-form **2a**. The identification of **2b** as the *anti* isomer is based on the observation that it reacts with  $\text{Ni}^{2+}$  ions to give a "usual" red complex [6].

In the  $^1\text{H}$  NMR spectrum of **2a** the  $\alpha$ - and  $\beta$ -protons of the ferrocene rings appeared as two triplets ( $\delta$  4.28, 4H,  $J$  1.8 Hz,  $\text{H}_\alpha$ ; 4.55, 4H,  $J$  1.8 Hz,  $\text{H}_\beta$ ), suggesting that there is a little tilt-deformation in the two cyclopentadienyl rings [5]. The OH proton was observed as a broad singlet at 13.28, which disappeared when the solution was shaken with  $\text{D}_2\text{O}$ .

In the IR spectrum bands at 3365 and 2850  $\text{cm}^{-1}$  were respectively assigned to the intramolecular  $\text{N} \cdots \text{H}-\text{O}$  and  $\text{S} \cdots \text{H}-\text{O}$  linkages. The  $\text{C}=\text{N}$  band was at 1620  $\text{cm}^{-1}$ , and the characteristic bands of a bridged ferrocene were also present. The mass spectrum of **2a** showed the molecular ion peak at  $m/z$  334 and the elemental analysis (C,H,N,Fe) was in excellent accord with the proposed structure.

It should be noted that two separate signals would be expected for the OH protons in the  $^1\text{H}$  NMR spectrum of **2a**; the observation of one signal can only be accounted for in terms of chance coincidence of the relevant chemical shifts. Compound **2a** gives a yellow-greenish complex with  $\text{Ni}^{2+}$  salts and we suggest for this the structure shown in Fig. 1, in which the ligand forms a six-membered chelate ring by coordinating to Ni through the N and O atoms. This type of coordination is usual in *amphi*-dioximes [7].

Fig. 1. Structure of  $\text{Ni}^{2+}$  complex of **2a**.

The  $^1\text{H}$  NMR spectrum of the Ni complex could not be obtained owing to its very low solubility in organic solvents, but the IR spectrum confirmed the proposed structure; the peaks for the intramolecular bridging hydrogens of the ligand were absent, and bands due to  $\nu(\text{OH})$  at  $3440$  and  $\nu(\text{C}=\text{N})$  at  $1620\text{ cm}^{-1}$  were observed.

## Experimental

Reactions were carried out under prepurified argon. Absolute ethanol was purged with argon before use. 1,1'-Ferrocenedithiol and *anti*-dichloroglyoxime (DCGO) were prepared by published procedures [8,9].

### *1,4-Dithia-2,3-bis(hydroxyimino)[4](1,1')ferrocenophane (2a)*

A solution of disodium 1,1'-ferrocenedithiolate, prepared from 1,1'-ferrocenedithiol (0.34 g, 1.36 mmol) and 40% aqueous sodium hydroxide (0.23 ml) in ethanol (50 ml), and a solution of DCGO (0.22 g, 1.4 mmol) in ethanol (50 ml) were added dropwise with stirring at the same time during 3 h to ethanol (100 ml). The mixture was stirred overnight, the solvent was evaporated under vacuum, and the residue then subjected to flash chromatography on silica. Elution with dichloromethane/ethanol = 20/1 gave first **2a** (266 mg, 58.7%) and then a trace of **2b**. Compound **2a** was recrystallized from ethanol, as orange plates, m.p. ( $130^\circ\text{C}$  (dec.)) (Found: C, 43.20; H, 2.99; N, 8.50; Fe, 17.11.  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_2\text{Fe}$  calc.: C, 43.12; H, 3.01; N, 8.38; Fe, 16.71%).

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

A solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (23.8 mg, 0.1 mmol) in ethanol (20 ml) was added to a solution of **2a** (66.8 mg, 0.2 mmol) in ethanol (60 ml). The temperature of the mixture was raised to  $60^\circ\text{C}$ , and 0.1 N NaOH was added to adjust the pH to 5.0. The precipitated yellow-greenish complex was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. Yield: 87 mg (60%); m.p. ( $> 250^\circ\text{C}$  (dec.)) (Found: C, 40.13; H, 2.75; N, 8.01.  $\text{C}_{24}\text{H}_{18}\text{N}_4\text{S}_4\text{O}_4\text{Fe}_2\text{Ni}$  calc.: C, 39.75; H, 2.50; N, 7.72%).

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