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Structure and Magnetic Properties of Biferrocenyl Nitronyl Nitroxide Radicals

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Biferrocenyl nitronyl nitroxide (**1**) was prepared and its X-ray structure was determined. Magnetic susceptibility measurements on **1** showed the presence of a weak antiferromagnetic interaction ($\theta = -2$ K) in the solid state.

Keywords: biferrocene; radical; nitronyl nitroxide

INTRODUCTION

Biferrocenium salts are mixed-valence compounds showing rapid electron transfer in the solid state [1]. In order to realize molecular magnets with dielectric functions based on intramolecular electron transfer, we have investigated the solid-state properties of charge transfer complexes of various biferrocene derivatives [2]. Here we report the synthesis and solid-state properties of 2,2'-di-(1',1'''-biferrocenediyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-yl oxyl diradical (**1**), containing two radical sites. Preparation and properties of metallocene compounds containing the nitronyl nitroxide moiety are well documented [3, 4], and the metallocene moiety is

reported to work as a ferromagnetic coupler [4]. In the case of **1**, the magnetic and dielectric properties of its one-electron oxidation state, having three radical centers, should be of special interest.

EXPERIMENTAL

Compound **1** was prepared by the following scheme (Figure 1). All reactions were carried out under a dinitrogen atmosphere. Substitution of a bromine atom of 1,1'-dibromoferrocene [5] by a formyl group (yield 92%), followed by Ullmann coupling, afforded 1',1'''-biferrocene carboxyaldehyde (yield 22%). The product was reacted with 2,3-dimetyl-2,3-bis(hydroxylammonium)butane sulfate, oxidized with PbO_2, and purified by column chromatography on silica gel to give **1** (yield 18 %). Deep-green plate-like crystals were obtained by the diffusion recrystallization method from choroform/ether.

X-ray diffraction data were collected on a Rigaku AFC-5S four-circle diffractometer using Mo$K\alpha$ radiation. Crystallographic parameters for **1**: Formula $C_{34}H_{40}Fe_2N_4O_4$ monoclinic, space group $P2_1/c$, a =13.086(6) Å, b = 13.777(4) Å, c = 17.155(3), β = 94.44(2)°, V = 3084(1) Å^3, Z = 4, R = 0.049 for 7363 independent reflections. Cyclic voltammetry was measured in the presence of 0.1M n-Bu_4NClO_4 in acetonitrile/dichloromethane at a scanning rate of 200 mV/s, using $Ag/AgNO_3$ as a reference electrode. Magnetic susceptibility data on

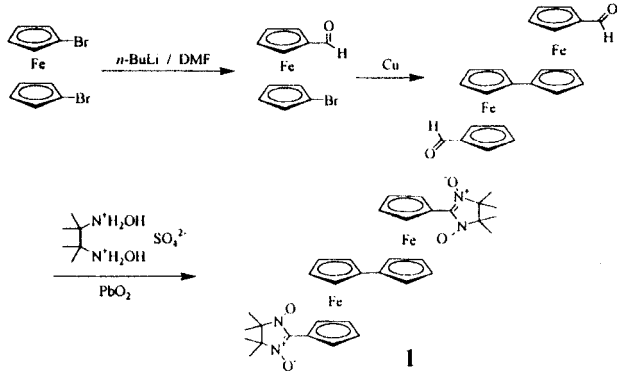

FIGURE 1 Synthetic scheme for the preparation of **1**.

microcrystalline samples were collected from 300 to 4.2K using a SQUID susceptometer in a magnetic field of 5000 G.

RESULTS AND DISCUSSION

1) Crystal Structure

The crystal structure of **1** is shown in Figure 2. The molecule has a twisted conformation in the crystal, though the imidazoline moiety of **1** keeps planarity with respect to its adjacent cyclopentadienyl ring. The nitronyl nitroxide moiety is stacked alternately with the intramolecular or intermolecular ferrocenyl moiety, and there is no spatial contact between the radical sites. No intermolecular C-H···O hydrogen bonds are found in contrast to the structures of ferrocenyl nitroxides [4].

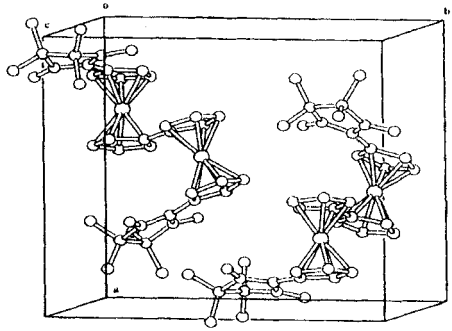

FIGURE 2 X-ray crystal structure of **1**.

2) Cyclic Voltammetry

Redox potentials of **1** showed a quasi-reversible oxidation wave at $E_{1/2}$ = + 0.55 V, and two irreversible ones at + 0.80 V and + 0.98 V (*vs* SCE). The first two waves are attributed to the oxidation of the biferrocene unit, while the third one is attributed to the nitroxide unit. This interpretation is reasonable also in comparison with the data for ferrocenyl nitronyl nitroxide [4]. The first two oxidation potentials of **1** appear at higher potentials than those for unsubstituted biferrocene (+ 0.40 V, + 0.65 V), reflecting the electron withdrawing character of the nitroxide moiety.

3) Solid State Magnetic Susceptibility

The magnetic susceptibility of microcrystals of **1** is shown in Figure 3. A Curie-Weiss-like behavior with a weak antiferromagnetic interaction (θ = - 2 K) was observed.

We also tried to obtain charge transfer salts, in combination with various electron acceptors such as I_3^-, TCNQ, DDQ, *etc*. However, only powdered products were obtained in every attempt.

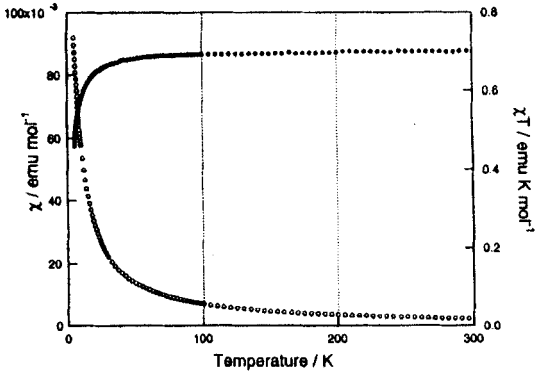

FIGURE 3 Magnetic susceptibility of **1**.

Acknowledgments

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