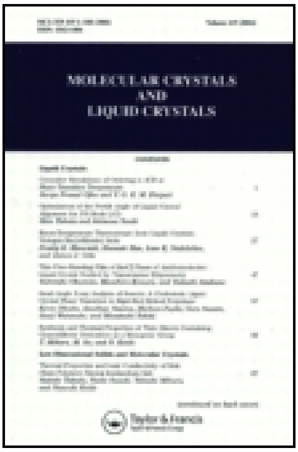

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Structures and Mixed-valence State in Ni(mnt) 2 Salts of Biferrocenes

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Structures and Mixed-valence State in $Ni(mnt)_2$ Salts of Biferrocenes

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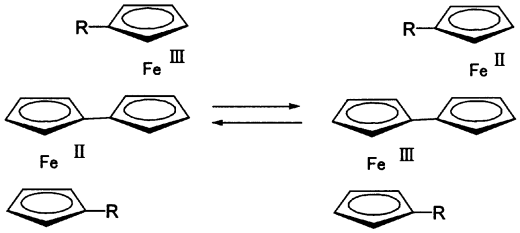
$Ni(mnt)_2$ salts of 1',1'''-diisopropyl-1,1''-biferrocene (**1**) and 1',1'''-dibenzyl-1,1''-biferrocene (**2**) have been prepared. Both complexes show segregated-stack crystal structure, consisting of a mixed-valent biferrocenium monocation and a $Ni(mnt)_2$ monoanion. The D-A ratio is 1:1 in both compounds. The trapped-valence state is demonstrated for **2** at room temperature.

Keywords Biferrocenium salts; Mixed-valence state; Electron transfer; $Ni(mnt)_2$ salts

INTRODUCTION

The electron transfer phenomena in mono-oxidized biferrocene derivatives in the solid state have drawn considerable attention, especially from a Mössbauer spectroscopic point of view [1]. However, most of the salts contain inorganic anions, such as I_3^-, and only several examples of organic charge-transfer salts have been reported. We consider that a design of magnets accompanying dielectric functions would be possible by combining biferrocenium cation and organic acceptors, taking advantage of the mobile electrons in biferrocenium salts [2]. From this point of view, we have synthesized a series of new biferrocenium salts with TCNQ type acceptors [3], though they often afford non-mixed valence salts consisting only of Fe(III) ions. Thus, in order to synthesize mixed-valence salts, here we employed metathesis or anion exchange methods to successfully obtain salts of biferrocenium monocations with Ni(mnt)$_2^-$ anion, **1** and **2**. The Ni(mnt)$_2$ anion has been selected as the counter ion (mnt = $S_2C_4N_2^{2-}$ = dimercaptomaleodinitrilato-), since the anion has drawn attention in connection with their magnetic and electrical conducting properties, even affording a ferromagnet of (NH$_4$)[Ni(mnt)$_2$]-H$_2$O (T_C = 4.5 K) [4]. Several Ni(mnt)$_2$ salts of ferrocene derivatives have recently been synthesized and characterized [5]. Here we present the structure and properties of **1** and **2**.



1: R=*i*-C_3H_7, **2**: R=CH_2Ph

EXPERIMENTAL

Tetrafluoroborate salts of 1',1'''-diisopropylbiferrocene and 1',1'''-dibenzylbiferrocene were synthesized according to the literature methods [6]. Compounds **1** and **2** were synthesized by the metathesis of the biferrocenium salts and (N^nBu$_4$)[Ni(mnt)$_2$], purchased from Tokyo Kasei Kogyo *Co. Ltd.* Single crystals were grown by a diffusion of ether into CH$_2$Cl$_2$ solutions, after which the solids were washed with methanol to remove bi-products. Crystallographic parameters for **1**: triclinic $P1$, a = 13.052(7)Å, b = 18.085(8)Å, c = 11.542(5)Å, α =91.36(4)°, β = 109.63(4)°, γ = 82.13(5)°, V = 2541(2)Å^3, Z = 3. **2**: triclinic $P1$, a = 15.287(4)Å, b = 22.461(1)Å, c = 12.504(4)Å, α =105.47(4)°, β= 103.57(2)°, γ= 88.64(3)°, V = 4019(3)Å^3, Z = 4. The X-ray diffraction measurements were performed on a Rigaku AFC-5S four-circle diffractometer using Mo*K*α radiation. The structures were solved and refined by using the teXsan software package [7]. ^{57}Fe Mössbauer spectra was measured on Wissel MDU-1200, DFG-1200 and MVT-1000, using ^{57}Co/Rh as the source. Isomer shifts are measured with respect to α-Fe foil at 296 K.

RESULTS AND DISCUSSION

1) Structure and Properties of (Diisopropylbiferrocene)[Ni(mnt)$_2$](**1**)

Figure 1 shows the packing diagram of **1**. The D-A stoichiometry is 1:1, forming a segregated-stack structure. The acceptor molecule is forming a regular column, though a slight dimerization is observed. The formal charge of the Ni(mnt)$_2$ anion is –1, evidenced by the infrared –CN stretch vibration appearing at 2207 cm^{-1}, at the same position in [N^nBu$_4$][Ni(mnt)$_2$]. The intramolecular Ni - S distances of 2.152 Å and 2.143 Å in the anion are consistent with the corresponding values in Ni(mnt)$_2$ monoanion [8]. The anions form dimers and are stacked in columnar fashion along the *c*-axis.

On the other hand, the biferrocene molecule is in a mixed-valence state, having a formal charge of +1. There are two kinds of crystallographically independent biferrocenium cations. One of them sits on the center of symmetry, having two crystallography ically equivalent Fe atoms. The average Fe(3) - C(*C*p) distance is 2.066 Å, which is in-between the value for neutral ferrocene (2.035 Å) and ferrocenium cation (2.075 Å) [9] [10], thus it is highly probable that a fast

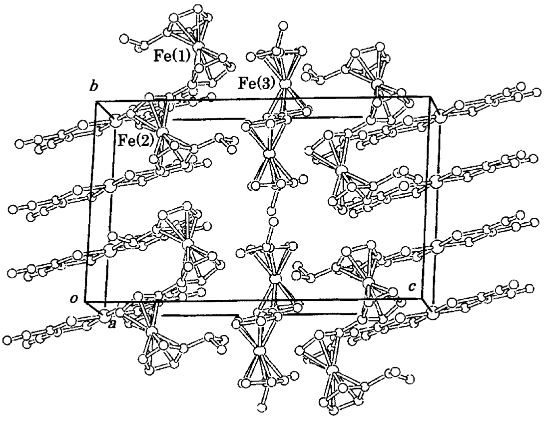


FIGURE 1 Packing diagram of **1**.

electron transfer is occurring in this molecule. On the other hand, the other biferrocene molecule does not have the center of symmetry, and the molecular structure is slightly asymmetric. The average Fe(1)-C(Cp) and Cp-Cp distances in the ferrocene unit involving Fe(1) are 2.077 Å and 3.385 Å, respectively, whereas the corresponding values for the other ferrocene unit involving Fe(2) are 2.056 Å and 3.340 Å, respectively. These values indicate that Fe(1) is somewhat closer to Fe(III), whereas Fe(2) is to Fe(II). Thus the electron transfer process, if any, is occurring in an asymmetrical potential, or it is more likely that the molecule is in a trapped valence state. The origin for the valence asymmetry should be ascribed to the electrostatic stabilization, since Fe(1), located nearer to the anion, is more strongly interacting with the anion than Fe(2).

Measurements of electrical conductivity revealed that the material is an insulator, being consistent with the electronic structure of the acceptor columns as shown above.

2) Structure and Properties of (Dibenzylbiferrocene)[Ni(mnt)$_2$](**2**)

The packing diagram of (dibenzylbiferrocene)[Ni(mnt)$_2$] (**2**) is shown in Figure 2. The D-A ratio is 1:1, forming a segregated-stack structure along the *a*-axis. The overall features of the complex are somewhat similar to those in **1**. The acceptor molecule is forming a tetramer-like arrangement, in which a slight dimerization is observed. The acceptor molecule has a formal charge of –1, as evidenced by the molecular geometries and the IR spectra. The material is an insulator, in accordance with these structural features.

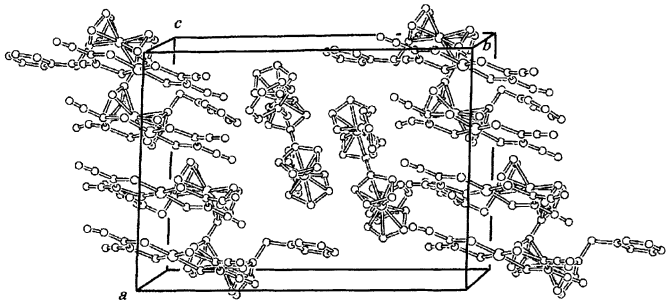
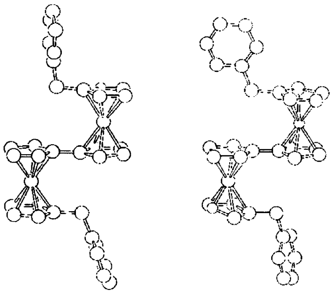


FIGURE 2 Packing diagram of **2**.

The biferrocene molecule is in a mixed-valence state, with a formal charge of +1. Though the compound forms a segregated-stack structure, the π-π stacking interaction between the biferrocene units is small, in contrast to **1**. There are two kinds of crystallographically independent donor molecules, as shown in Figure 3. In both molecules, the molecular structure is asymmetric.

Figure 4 shows the ^{57}Fe Mössbauer spectra of **2** recorded at room temperature. The spectrum consists of two quadrupole-split doublets [11], one characteristic of an Fe(II) ferrocene with a quadrupole splitting of ΔE_Q = 1.923 mm/s, δ= 0.4403 mm/s and the other characteristic of an Fe(III) ferrocene with ΔE_Q = 0.378 mm/s, δ= 0.4081. Thus the compound is shown to have the trapped-valence state at room temperature.



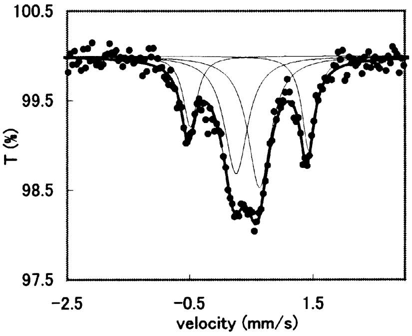


FIGURE 3 (left) Molecular structures of the crystallographically independent cations in **2**.

FIGURE 4 (right) ^{57}Fe Mössbauer spectrum of **2** at 300 K.

In conclusion, we have prepared $Ni(mnt)_2^-$ salts of biferrocenes, **1** and **2**, which are the first examples of 1:1 mixed-valence biferrocenium charge transfer salts showing segregated-stack structure. Another example of mixed-valence segregated stack complexes known to date is a family of TCNQ salts of dialkylbiferrocenes, showing the D:A stoichiometry of 1:3, which are semiconductors [3]. Preliminary magnetic measurements showed that **1** and **2** are paramagnets with small antiferomagnetic interactions. Detailed results of Mössbauer studies and magnetic measurements will be reported elsewhere.

Acknowledgment
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