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Preparation and structures of biferrocenes with alicyclic substituents: Order-disorder of substituents in the crystal structures of cyclohexenylbiferrocene and its charge-transfer salt

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Abstract

Biferrocene derivatives with cyclohexyl, cyclohexenyl, and cyclopentenyl substituents were prepared and crystallographically characterized. The cyclohexenyl substituents exhibited twofold disorder in the crystals. A charge-transfer salt of 1′-cyclohexenylbiferrocene with $[Ni(mnt)_2]$ was prepared. The biferrocenium cation in this salt was in a valence-trapped state owing to electrostatic interactions with the anion. The cyclohexenyl substituent in the $[Ni(mnt)_2]$ salt exhibited no disorder because of closer packing in the salt.

Keywords: Biferrocene; Cycloalkene; Cycloalkane; Crystal structures; Redox potentials; Charge-transfer salts; Mixed-valence compound

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1. Introduction

It is understood that the valence state of the biferrocenium cation is influenced by its substituents as well as the packing environment [1]. To investigate this phenomenon, a variety of substituents has been introduced to biferrocene. In our previous work, we found an electron-transfer phase transition in the dineopentylbiferrocenium salt of F1TCNQ [2], in which the bulky substituent plays an important role. In this study, our aim is to introduce conformational flexibility to biferrocenium salts. To this end, we prepared biferrocene derivatives with alicyclic substituents. Cyclohexane derivatives can adopt various conformations, and these materials often exhibit glass transitions as well as phase transitions in the solid state [3]. In crystals of cyclohexene compounds, conformational disorder is frequently found in the form of two half-chair conformers (Chart 1), which has been interpreted as either dynamic or static [4]. In the case of charge-transfer complexes, conformational flexibility in six-membered rings allows control of physical properties; in the salts of bis(ethylenedithio)tetrathiafulvalene (= BEDT-TTF), the order-disorder of the ethylene groups is reflected in their electrical conductivities [5]. Because of this, we decided to introduce a cyclohexenyl substituent into biferrocenium salts. Cyclopentenyl groups do not generally show disorder, while disorder is often seen in perfluorocyclopentene derivatives [6].

Here, we report the preparation and properties of 1′-(1-cyclohexenyl)biferrocene (**1a**), 1′,1‴-di-1-cyclohexenylbiferrocene (**1b**), 1′-cyclohexylbiferrocene (**2a**), 1′,1‴-dicyclohexylbiferrocene (**2b**), 1′-(1-cyclopentenyl)biferrocene (**3a**), and 1′,1‴-di-1-cyclopentenylbiferrocene (**3b**), as shown in Chart 2. We also prepared and structurally characterized a charge-transfer salt, [**1a**][Ni(mnt)$_2$]. The versatile [M(mnt)$_2$] anion (mnt = $S_2C_4N_2^{2-}$ = maleonitriledithiolate) is interesting from the viewpoint of solid-state physical properties [7, 8] and crystal engineering [9] of charge-transfer salts. [**1a**][Ni(mnt)$_2$] exhibited a valence-trapped state for the biferrocenium cation due to electrostatic interactions between the cation and the anion. The conformational freedom of the cyclohexenyl substituents in **1a** and [**1a**][Ni(mnt)$_2$] was compared.

2. Results and discussion

*2.1. Preparation and properties of **1a–3b***

Several methods of introducing alicyclic substituents into ferrocene have been reported [10], and we chose to adapt the reaction of lithioferrocene with cyclohexanone [11]. Compounds **1a** and **1b** were prepared according to Scheme 1 in 20–30% yield. This procedure gave a mixture of mono- and disubstituted biferrocenes, which were separated by gel permeation chromatography (GPC). Compounds **3a** and **3b** were prepared by the same method, with yields of about 17%. Alternatively, **1b** could be obtained by coupling of bromo-1-cyclohexenylferrocene. Compounds **2a** and **2b** were readily obtained by hydrogenation of **1a** and **1b**, respectively.

The thermal properties of **1a–3b** were investigated by means of differential scanning calorimetry (DSC). Melting points and entropies of melting are listed in Table 1. The melting points of the cyclopentenyl compounds (**3a** and **3b**) were higher than those of the cyclohexenyl compounds (**1a** and **1b**), and those of the di-substituted compounds were higher those of the mono-substituted compounds. In **2a**, melting was not reversible; melting occurred at 365 K, and a glass transition was observed on cooling. On heating the material, a glass transition occurred at 245 K, and on further heating, crystallization was observed at 294 K. The supercooling characteristic of **2a** may be attributed to its asymmetric, bent molecular structure, which prevents crystallization. No phase transitions were observed in the solid state in any of the compounds.

The redox potentials of **1a–3b** were measured by means of cyclic voltammetry (CV) and are listed in Table 2 (*vs*. $FeCp_2^{0/+}$). The first half-wave potentials of these compounds were lower than that of biferrocene, which indicates that electron-donating ability was increased by the substituents. No difference was observed between the redox potentials of the cyclohexyl and cyclohexenyl compounds. The first waves of the compounds containing five-membered rings (**3a** and **3b**) were slightly higher than those with six-membered rings (**1a–2b**). The $\Delta E_{1/2}$ value was larger than that of biferrocene in every case. The $\Delta E_{1/2}$ values of the mono-substituted compounds were greater than those of the di-substituted compounds, which is ascribable to the effect of asymmetry.

2.2. *Crystal structures of **1a**, **1b**, and **2b***

The crystal structures of **1a**, **1b**, and **2b** were determined by X-ray crystallography at 173 K. ORTEP [12] drawings of their molecular structures are shown in Fig. 1. The cyclohexenyl groups in **1a** and **1b** are disordered, and are oriented parallel to the adjacent ferrocenyl moiety within the molecule. In contrast, the cyclohexyl group in **2a** is much bulkier, and extends outside the ferrocenyl ring.

In **1a**, the average Fe(1)–C(Cp) and Fe(2)–C(Cp) distances are 2.045 Å and 2.042 Å, respectively. The central Cp–Cp rings in the biferrocenyl moiety are twisted by 5.6°. The cyclohexenyl substituent is nearly planar, and is in a face-to-face orientation with the other ferrocenyl moiety within the molecule (Fig. 1a). The cyclohexenyl ring exhibits twofold disorder, as shown in Chart 1: the ethylene carbons (–C23–C24– and –C27–C28–) opposite the double bond (–C21=C26–) are disordered in a 1:1 ratio. In the crystal, the molecules form a centrosymmetric dimer via intermolecular face-to-face contact between a Cp ring and a cyclohexenyl ring, as shown in Fig. 2a. The centroid-centroid distance between the neighboring Cp ring and the cyclohexene ring is 4.43 Å.

In the crystal of **1b**, the molecule is located on the inversion center. The average Fe–C(Cp) distance is 2.050 Å. Similarly to **1a**, the cyclohexenyl substituent is nearly planar and exhibits twofold disorder in a 1:1 ratio (Fig. 1b). The substituents are in a face-to-face orientation with the ferrocenyl moieties in the molecule. In the crystal, the molecules are arranged almost perpendicular to each other, and no face-to-face intermolecular contacts are present between the Cp rings and/or the cyclohexene rings.

The molecule of **2b** has no inversion symmetry, and the central Cp–Cp rings in the biferrocenyl moiety are twisted by 19.4°. The average Fe(1)–C(Cp) and Fe(2)–C(Cp) distances are 2.054 Å and 2.050 Å, respectively. The cyclohexyl group adopts a chair conformation (Fig. 1c), and no disorder was observed. The substituent is largely twisted with respect to the Cp plane to which it is attached;

the torsion angles are about 58° and 45° for the substituents at Fc1 and Fc2, respectively. In the crystal, the molecules are stacked in a columnar arrangement along the [101] direction. In the column, each cyclohexyl group faces the Cp ring of an adjacent molecule.

*2-3. Structure and valence states of [**1a**][Ni(mnt)$_2$]*

The charge-transfer salt [**1a**][Ni(mnt)$_2$] was prepared by reacting **1a** with [Fe(C_5H_4Br)$_2$][Ni(mnt)$_2$], followed by vapor diffusion of pentane into the solution. Attempts to prepare [Ni(mnt)$_2$] salts with other donors were unsuccessful. TCNQ derivatives afforded no crystalline charge-transfer complexes.

The packing diagram of the complex, as determined by X-ray crystallography, is shown in Fig. 3a. The crystallographically independent unit consists of one biferrocenium cation and one [Ni(mnt)$_2$] anion. The anions are stacked along the *a*-axis. The IR spectrum showed CN stretching bands characteristic of the [Ni(mnt)$_2$] monoanion [13] at 2208 cm^{-1}. The intramolecular bond lengths of the anion are virtually identical to those of (N^nBu$_4$)[Ni(mnt)$_2$] [14]; the intramolecular Ni–S distances are 2.1390(6)–2.1463(6) Å (average: 2.143 Å). The anion is not planar, and exhibits a slight distortion toward a tetrahedral shape, with an angle between the metallacycle mean planes of 8.1° around the Ni atom.

The donor molecule was a mixed-valence cation which exhibited a valence-trapped state. The Fe(1)–C(Cp) distances of the donors were within the range 2.056(2)–2.153(2) Å (average value: 2.088 Å), which is comparable to those in the ferrocenium cation (2.08 Å) [15]. The Fe(2)–C(Cp) distances are within the range 2.038(2)–2.056(2) Å (average value: 2.048 Å), which is comparable to those in neutral ferrocene (2.04 Å) [16]. This charge localization may be ascribed to electrostatic interactions between the donor and acceptor in the crystal, as seen in other [M(mnt)$_2$] salts [8]. The local arrangement of the donor and acceptor is shown in Fig. 3b. The shortest CN...Fe distances around Fe(1) and Fe(2) are 4.369 Å and 4.629 Å, respectively. The former, shorter distance stabilizes the cationic charge on the Fe(1) atom. The higher electron-donating ability of the Fe(1) site induced by the cyclohexyl group also favors charge localization on Fe(1). Owing to the asymmetric crystal environment, it is unlikely that the salt exhibits valence-detrapped state even at higher temperatures. However, valence-detrapping might occur if non-coordinating anions are used.

Interestingly, the cyclohexenyl unit is disordered in **1a** but not in [**1a**][Ni(mnt)$_2$]. The suppression of disorder in the latter compound is probably attributed to closer packing in the ionic crystal, caused by Coulomb attractions. As in the case of **1a** (Fig. 2a), the donor molecules in the salt form centrosymmetric dimers via Cp–cyclohexenyl face-to-face contact (Fig. 2b). Comparison of the structures shows that the Cp ring and the cyclohexene ring face each other more closely in the salt, which is probably related to suppression of disorder. The distance from the centroid of the cyclohexene ring to the mean Cp–cyclohexene plane of the neighboring molecule is shorter in [**1a**][Ni(mnt)$_2$] (3.95 Å) than in **1a** (4.03 Å). Another difference is the intramolecular Cp–Cp torsion angle in the fulvalenide moiety, which is 5.6° in **1a** and 8.0° in [**1a**][Ni(mnt)$_2$]. The larger angle in the salt may be associated with the fixed conformation of the substituent.

The acceptors form dimers in the column. The intradimer and interdimer Ni…Ni distances are 4.677 Å and 6.241 Å, respectively (Fig. 3a). The shortest Ni…S and S…S distances in the dimer are 4.064 Å and 3.769 Å, respectively, and those between dimers are 5.230 Å and 4.251 Å, respectively. Between the molecules, there was no interatomic distance shorter than the sum of the van der Waals radii. The overlap integrals between the LUMOs of the acceptors were $S_1 = 14.4 \times 10^{-3}$ and $S_2 = 3.52 \times 10^{-3}$ for the intradimer and interdimer interactions, respectively; the interdimer value was about 1/4 of the intradimer one.

DSC measurements of [**1**][Ni(mnt)$_2$] showed no indication of a phase transition, and only a broad exothermic peak was observed above 150 K, which probably corresponds to decomposition.

3. Conclusion

In this study, biferrocenes with five- and six-membered alicyclic substituents were synthesized in order to introduce conformational freedom into biferrocenium complexes. X-ray structure analysis revealed that the shapes of the resulting molecules were significantly influenced by the substituents; cyclohexenyl units were positioned parallel to the ferrocene moiety, while cyclohexyl groups were much more bulky and extended outward from the molecule. In addition, a salt of cyclohexenylbiferrocene with $[Ni(mnt)_2]$ anion was obtained. Here, the donor was a mixed-valence monocation which exhibited a valence-trapped state due to electrostatic interactions between the cation and the anion. In the crystal of cyclohexenylbiferrocene, the substituent exhibited twofold disorder, but the disorder was suppressed in the $[Ni(mnt)_2]$ salt due to closer packing of the ionic crystal. The introduction of cyclohexenyl rings was thus shown to be useful in inducing changes in conformational freedom in the crystal.

4. Experimental

4.1. General methods

1,1′-Dibromobiferrocene [17], $[Fe(C_5H_4Br)_2][Ni(mnt)_2]$ [8], and 1-bromo-1′-(1-hydroxycyclohexyl)ferrocene [11] were prepared by literature methods. Other reagents and solvents were commercially available. All reactions were carried out under a nitrogen atmosphere. JAI LC-908 was used for gel permeation chromatography (GPC). NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer using KBr pellets. UV-vis spectra were recorded on a JASCO V-570 UV-vis/NIR spectrometer. Cyclic voltammograms were recorded using an ALS/chi electrochemical analyzer, model 610C. Redox potentials were measured at a scan rate of 0.1 V s^{-1} in acetonitrile containing 0.1 mol dm^{-3} n-Bu_4NClO_4 as a supporting electrolyte. An Ag/Ag^+ reference electrode and a platinum working electrode were used, and the potentials were referenced to a $FeCp_2/FeCp_2^+$ couple. Intermolecular overlap integrals were calculated by the extended Hückel molecular orbital method [18]. Differential scanning calorimetry was performed on a TA Instruments Q100 calorimeter from 103 K to 473 K at a scan rate of 10 K min^{-1}.

*4.2. 1'-Cyclohexenylbiferrocene (**1a**) and 1',1'''-dicyclohexenylbiferrocene (**1b**)*

A. Preparation from 1,1'-dibromobiferrocene (Scheme 1). *n*-BuLi (4.8 mL, 7.63 mmol, 1.59 mol dm^{-3} in *n*-hexane) was added to a THF (40 mL) solution of 1,1 -dibromobiferrocene (2.0 g, 3.79 mmol) in a dropwise manner. The solution was stirred for 30 min, after which cyclohexanone (1.12 mL, 11.9 mmol) was added slowly. After stirring for 90 min at room temperature, the reaction was quenched by adding a small amount of water. The solution was extracted with ether and washed with water, and the organic layer was separated and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure afforded a red oil (2.0 g), which was found to be a mixture of ′1,1‴ -bis(1-hydroxycyclohexyl)biferrocene and ′1 -(1-hydroxycyclohexyl)biferrocene. The product was separable by column chromatography (alumina), but the mixture was subjected to the dehydration reaction without separation. A toluene solution (40 mL) of *p*-toluene sulfonic acid (4.0 mg) was added to the mixture (1.0 g), and the solution heated at 110 ºC for 3 h. The mixture was cooled to room temperature and washed with water, and the organic layer was separated and dried over anhydrous magnesium sulfate. The crude product was a mixture of **1a**, **1b**, and biferrocene, which were separated by gel permeation chromatography (eluent: chloroform). Compound **1a** was obtained as red-orange crystals, 0.27 g (yield 31%). ^{1}H NMR (CDCl$_3$) $\delta = 1.58$ (m, 2H), 1.64 (m, 2H), 2.00 (m, 2H), 2.13 (m, 2H), 3.97 (s, 5H), 4.00 (s, 2H), 4.12 (s, 4H), 4.15 (t, 2H, $J = 3.6$ Hz), 4.23 (s, 2H), 4.31 (t, 2H, $J = 3.6$ Hz), 5.72 (s, 1H). Anal. Calcd for $C_{26}H_{26}Fe_2$: C, 69.36; H, 5.82. Found: C, 69.11; H, 5.81. Compound **1b** was obtained as red-orange crystals, 0.20 g (yield 20% based on dibromobiferrocene). ^{1}H NMR (CDCl$_3$) $\delta = 1.64$ (m, 8H), 2.13 (m, 8H), 4.01 (s, 4H), 4.13 (s, 8H), 4.22 (s, 4H), 5.68 (s, 2H). Anal. Calcd for $C_{32}H_{34}Fe_2$: C, 72.47; H, 6.46. Found: C, 72.22; H, 6.52. Biferrocene was isolated in 15% yield. The products were recrystallized from dichloromethane–hexane (1:1 v/v).

*B. Preparation of 1',1'''-dicyclohexylbiferrocene (**1b**) via Ullman coupling.* A toluene solution (40 mL) of *p*-toluene sulfonic acid (7 mg) was added to 1-bromo-1′-(1-hydroxycyclohexyl)ferrocene

(1.5 g, 4.1 mmol), and the mixture heated at 80 ºC for 2 h. After cooling to room temperature, the solution was washed with water, and the organic layer was separated**,** and dried over anhydrous magnesium sulfate. Evaporation of the solution afforded 1-bromo-1′-cyclohexenylferrocene as a brown oil, 0.86 g (yield 61%). ^{1}H NMR ($CDCl_3$) δ= 1.66 (m, 2H), 1.75 (m, 2H), 2.07 (m, 2H), 2.32 (m, 2H), 4.02 (t, 4H, J = 3.6 Hz), 4.21 (t, 4H, J = 3.6 Hz), 4.27 (t, 4H, J = 3.6 Hz), 4.33 (t, 4H, J = 3.6 Hz), 5.95 (q, 1H, J = 9.0 Hz). The 1-bromo-1′-cyclohexenylferrocene thus obtained (0.15 g, 4.35×10^{-4} mol) was heated with copper powder (0.28 g, 4.4×10^{-3} mol) at 135 ºC for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane and filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane–dichloromethane 5:1 v/v) to give **1b** as red-orange crystals (0.027 g, yield 11%).

*4.3. 1′-Cyclohexylbiferrocene (**2a**) and 1′,1‴-dicyclohexylbiferrocene (**2b**)*

Palladium carbon (7 mg) was added to an ethanol solution (15 mL) of **1a** (60 mg, 1.34×10^{-4} mol), and the solution was vigorously stirred overnight under an atmosphere of hydrogen. The reaction was quenched by adding water (3 mL), and the mixture was filtered to remove insoluble materials. The filtrate was evaporated under reduced pressure, and passed through a short column of silica gel (eluent: hexane-dichloromethane 1:1 v/v). Recrystallization from dichloromethane and hexane gave **2a** as red-orange crystals (46 mg, yield 76%). ^{1}H NMR ($CDCl_3$) δ= 1.08–1.30 (m, 6H), 1.72 (m, 2H), 1.86 (m, 2H), 2.05 (m, 1H), 3.86 (s, 4H), 3.97 (s, 5H), 4.12 (t, 2H, J = 3.6 Hz), 4.16 (t, 2H, J = 3.6 Hz), 4.28 (t, 2H, J = 3.3 Hz), 4.33 (t, 2H, J = 3.3 Hz). Anal. Calcd for $C_{26}H_{28}Fe_2$: C, 69.05; H, 6.24. Found: C, 69.30; H, 6.20. Compound **2b** was obtained, via the same method, as orange needle crystals (32 mg, yield 53%). ^{1}H NMR ($CDCl_3$) δ= 1.08–1.30 (m, 12H), 1.72 (m, 4H), 1.85 (m, 4H), 2.04 (m, 2H), 3.85 (s, 8H), 4.12 (t, 4H, J = 3.6 Hz), 4.26 (t, 4H, J = 3.6 Hz). Anal. Calcd for $C_{32}H_{38}Fe_2$: C, 71.92; H, 7.16. Found: C, 71.07; H, 7.11. These compounds could be also obtained by reduction of 1′,1‴-bis(1-hydroxycyclohexyl)biferrocene and

1′-(1-hydroxycyclohexyl)biferrocene by $LiAlH_4$ in the presence of $AlCl_3$.

*4.4. 1'-Cyclopentenylbiferrocene (**3a**) and 1',1'''-dicyclopentenylbiferrocene (**3b**)*

These compounds were prepared by the same method as **1a** and **1b**, except that twice the amount of cyclopentanone was used, and the reaction time was prolonged to overnight. The product was a mixture of **3a**, **3b**, and biferrocene, which were separated by gel permeation chromatography and recrystallized from chloroform. Compound **3a** was obtained as red-orange crystals (yield 17%). ^{1}H NMR ($CDCl_3$) δ = 1.84 (m, 4H), 2.29 (m, 4H), 2.36 (m, 4H), 4.00 (s, 4H), 4.09 (s, 8H), 4.16 (s, 4H), 5.54 (s, 2H). Anal. Calcd for $C_{25}H_{22}Fe_2$: C, 69.10; H, 5.57. Found: C, 68.87; H, 5.61. Compound **3b** was obtained as red-orange crystals (yield 18%). ^{1}H NMR ($CDCl_3$) δ = 1.84 (m, 2H), 2.29 (m, 2H), 2.36 (m, 2H), 3.96 (s, 5H), 4.02 (s, 2H), 4.11 (s, 4H), 4.15 (t, 2H, J = 3.6 Hz), 4.22 (s, 2H), 4.29 (t, 2H, J = 3.6 Hz), 5.57 (s, 1H). Anal. Calcd for $C_{30}H_{30}Fe_2$: C, 71.73; H, 6.02. Found: C, 71.09; H, 6.12. Biferrocene was isolated in 18% yield.

*4.5. Charge transfer salt [**1a**][Ni(mnt)$_2$]*

An acetone solution (2 mL) of $[Fe(C_5H_4Br)_2][Ni(mnt)_2]$ (3.2 mg, 4.7 mmol) and a dichloromethane solution (2 mL) of **1a** (5 mg, 4.7 mmol) were mixed, and pentane vapor was diffused into the resulting solution at room temperature under a nitrogen atmosphere. Black prismatic crystals of [**1a**][Ni(mnt)$_2$] formed within a few days, with a yield of approximately 40%. IR (KBr, cm^{-1}): 2208, 1712, 1620, 1529, 1473, 1417, 1157, 1109, 1039, 850, 821. Anal. Calcd for $C_{34}H_{26}Fe_2N_4NiS_4$: C, 51.74; H, 3.32; N, 7.10. Found: C, 51.54; H, 3.49; N, 6.36.

4.6. X-ray crystallographic analysis

Single crystals of **1a**, **1b**, and **2b** suitable for X-ray structure analysis were obtained by slow evaporation of acetone solutions. Single crystals of [**1a**][Ni(mnt)$_2$] were obtained as described above. Crystallographic parameters are listed in Table 3. X-ray diffraction data were collected at

173 K on a Bruker SMART APEX CCD diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). The data were corrected for absorption using the SADABS program [19]. The structures were solved by the direct method (SHELXS 97 [20]) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at the calculated positions and allowed to ride on their respective parent atoms.

Acknowledgments

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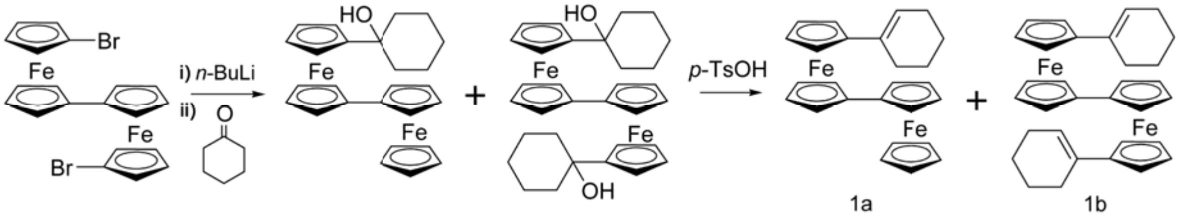
Appendix A. Supplementary materials

CCDC 619892–619895 contain the supplementary crystallographic data for **1a**, **1b**, **2b**, and [**1a**][Ni(mnt)$_2$]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version.

Scheme 1. Preparation of **1a** and **1b**.



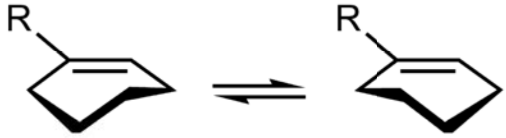


Chart 1.

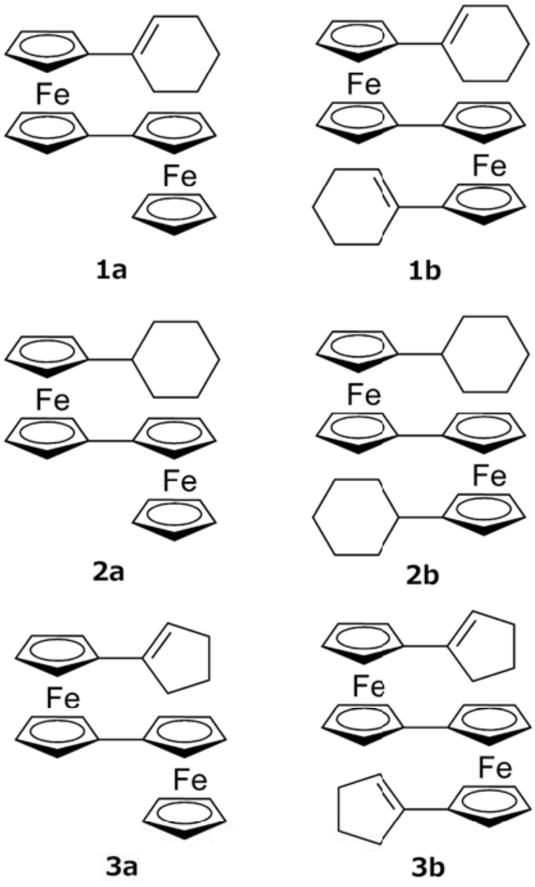


Chart 2.

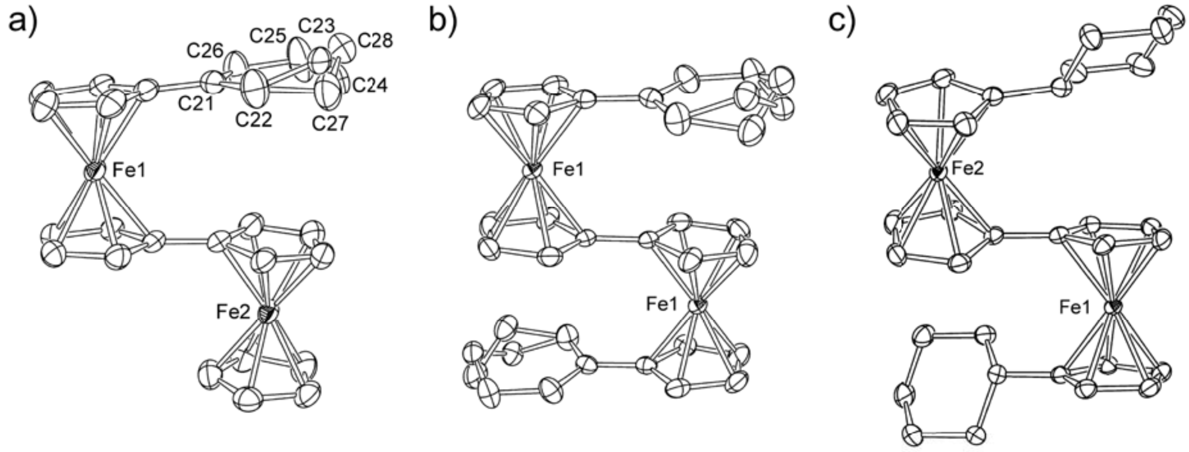


Fig. 1. Molecular structures of (a) 1′-cyclohexylbiferrocene (**1a**), (b) 1′,1‴-dicyclohexenylbiferrocene (**1b**), and (c) 1′,1‴-dicyclohexylbiferrocene (**3b**) at 173 K.

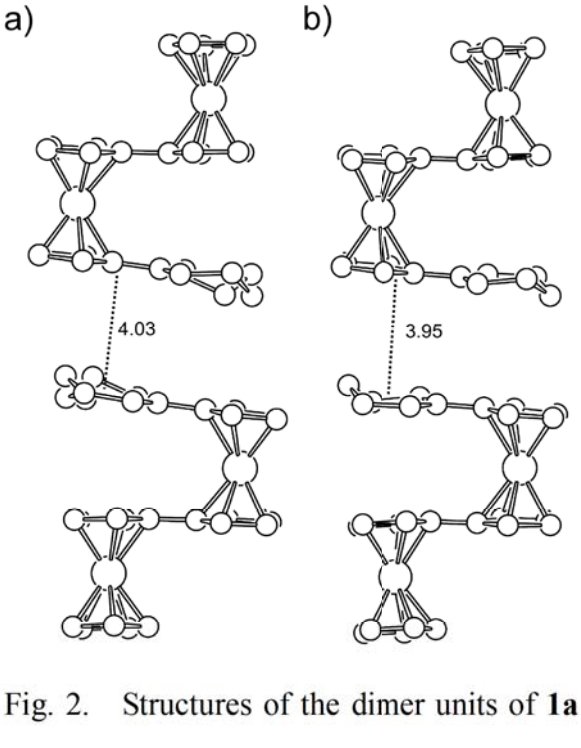


Fig. 2. Structures of the dimer units of **1a** in crystals of (a) **1a** and (b) [**1a**][Ni(mnt)$_2$] at 173 K. Interplane distances (Å) are also shown. Dashed lines are a guide to the eye.

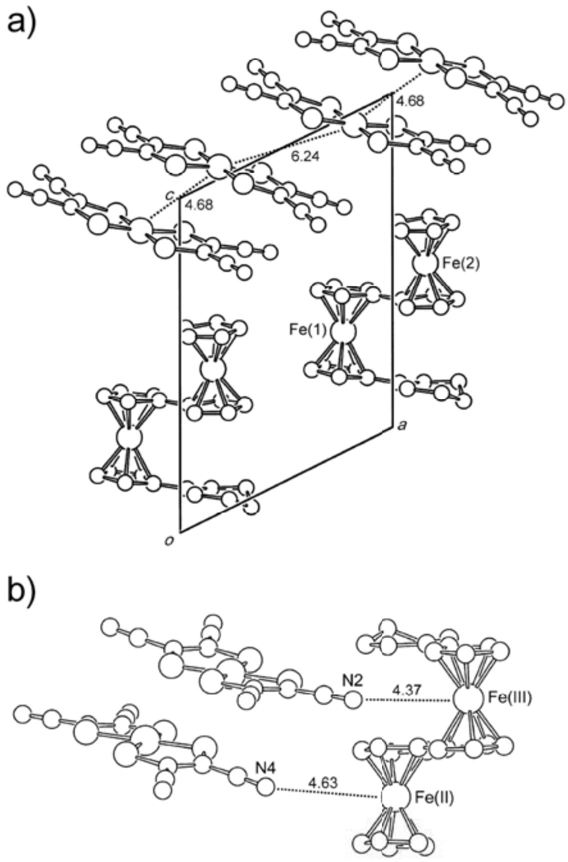


Fig. 3. Crystal structure of [**1a**][Ni(mnt)$_2$] at 173 K. (a) Packing diagram viewed along the *b*-axis; (b) local arrangements of the cation and anion. Intermolecular Ni…Ni and Fe…NC distances (Å) are also shown. Dashed lines are a guide to the eye.

Table 1

Melting points (T_m), melting enthalpies (ΔH_m), and melting entropies (ΔS_m) for **1a**–**3b**.

Compound	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**
T_m/K	398.9	418.3	365.0	423.5	426.4	462.1
ΔH_m/kJmol^{-1}	35.2	41.6	27.0	53.3	32.8	52.1
ΔS_m/JK^{-1}mol^{-1}	87.9	99.0	73.2	125.0	75.9	112.4

Table 2

Redox potentials of **1a**–**3b** and biferrocene (V *vs*. $FeCp_2^{0/+}$).

Compound	$E_{1/2}(\text{Bifc}^{+/0})$	$E_{1/2}(\text{Bifc}^{2+/+})$	$\Delta E_{1/2}{}^{a}$
1a	-0.17	0.22	0.39
1b	-0.19	0.17	0.36
2a	-0.17	0.22	0.39
2b	-0.19	0.18	0.37
3a	-0.15	0.22	0.37
3b	-0.17	0.19	0.36
Biferrocene	-0.11	0.22	0.33

[a] $\Delta E_{1/2} = E_{1/2}(\text{Bifc}^{2+/+}) - E_{1/2}(\text{Bifc}^{+/0})$

Table 3

Crystallographic parameters.

	1a	**1b**	**2b**	[**1b**][Ni(mnt)$_2$]
Empirical Formula	$C_{26}H_{26}Fe_2$	$C_{32}H_{34}Fe_2$	$C_{32}H_{38}Fe_2$	$C_{34}H_{26}Fe_2N_4NiS_4$
Formula weight	450.17	530.29	534.32	789.24
T (K)	173	173	173	173
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1
a (Å)	9.3738(6)	9.6398(6)	11.3466(12)	10.7386(7)
b (Å)	8.0953(5)	7.5594(5)	11.0705(11)	12.9359(9)
c (Å)	25.8271(17)	16.9248(11)	19.538(2)	14.0845(10)
α (°)				99.0470(10)
β (°)	91.6510(10)	106.2680(10)	96.916(2)	109.9100(10)
γ (°)				113.3510(10)
V (Å^3)	1959.0(2)	1183.95(13)	2436.3(4)	1589.19(19)
Z	4	2	4	2
Reflections collected	14168	8492	17748	11940
Independent reflections	4869	2924	6039	7830
Refl. / Parameter ratio	17.9	17	13.3	19.3
Density (gcm^{-3})	1.526	1.488	1.457	1.649
R_1, R_w ($I > 2\sigma$)	0.0374, 0.1023	0.0330, 0.0987	0.0268, 0.0571	0.0349, 0.0906
R_1, R_w (all data)	0.0459, 0.1089	0.0361, 0.1022	0.0297, 0.0584	0.0439, 0.0963
Goodness-of-fit	1.044	1.024	1.001	1.03

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