

Synthesis and X-Ray Crystal Structure of Two Novel Ester Ferrocenophanes

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Two novel ester ferrocenophanes have been prepared by esterification of 1,1'-ferrocene-di(carbonyl chloride) with glycol and 1,4-butanediol, respectively. Both of them have been characterized by IR, elemental analysis, MALDI-TOF MS and ^1H NMR spectroscopic methods, and their structures have been elucidated by X-ray diffraction. The intermolecular associations based on $\text{C-H}\cdots\text{O}$ hydrogen bonds have also been discussed. These molecules are assembled into chains, and the chains are further assembled into a 3D structure through several hydrogen bonds.

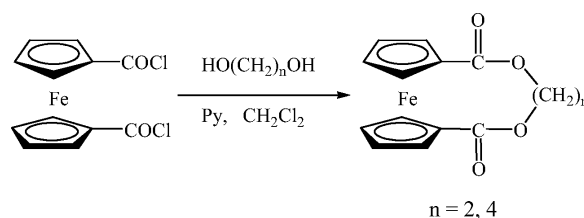
Key words: Ester Ferrocenophanes, Synthesis, X-Ray Crystal Structure, Hydrogen Bonds

Introduction

The most prevalent organometallic analogues of cyclophanes are the ferrocenophanes, in which the two cyclopentadienyl rings of ferrocene are joined by a mono- or polyatomic bridge. In this type of compounds, many of the important properties of the parent ferrocene are retained, such as high electron density, aromaticity and reversible redox characteristics. These ferrocenophanes are expected to show unique chemical properties owing to the functionality of the sidearm [1–6].

Many different classes of ferrocenophanes have been investigated. Most of them possess only carbon-based bridges [7], while others have bridges comprising heteroatoms O, N, S, P, Si, *etc.* as donor atoms. Studies of these ligands are important because they have potential properties interesting for many research areas, such as redox or non linear optical properties, charge transport, liquid crystals, electrochemical recognition or catalysis [8–14]. In these applications formation of hydrogen bonds between the host ferrocenophanes and the guests or between two appropriate substituents on the ferrocene itself often plays a crucial role. Ester ferrocenophanes can be used as cation receptors due to the formation of hydrogen bonds [15–16].

So far only one ester ferrocenophane has been prepared by the condensation of hydroquinone with 1,1'-ferrocene-di(carbonyl chloride) [17]. Herein, we report the synthesis of two novel ester ferrocenophanes



Scheme 1.

(Scheme 1), the single-crystal structure analyses of which are presented.

Results and Discussion

The starting material 1,1'-ferrocene-di(carbonyl chloride) was prepared according to literature procedures [18]. Ester ferrocenophanes **1** and **2** were synthesized by condensation reactions in dry dichloromethane with good yields. In this way we finally obtained yellow soluble solids, **1** and **2**. The preparation is summarized in Scheme 1. Both of the final compounds had elemental analyses, IR, MALDI-TOF MS and ^1H NMR spectra which were in accordance with the proposed structures. A view of the molecules **1** and **2** is shown in Fig. 1. A summary of cell constants and data collection parameters of the crystal structures are included in Table 1.

There are four molecules in the unit cells of both complexes **1** and **2**. Thus, molecules of **1**, crystallizing in space group $C2/c$, have crystallographically imposed C_2 symmetry while those of **2**

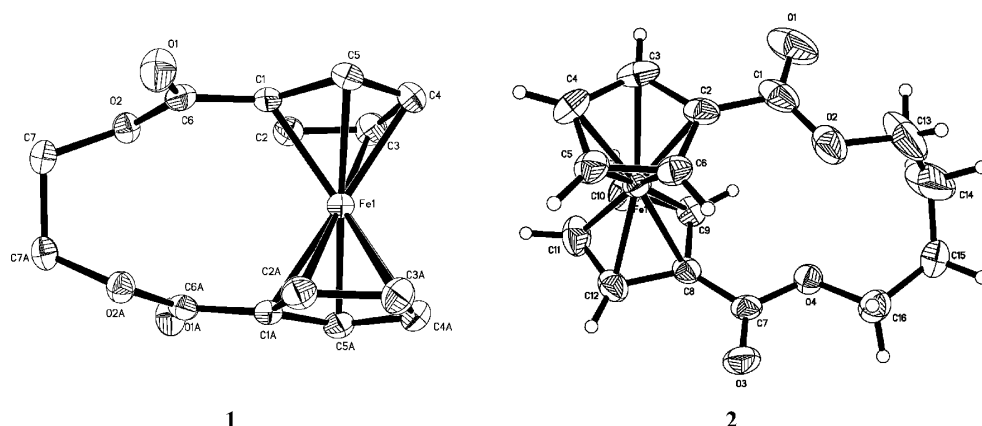


Fig. 1. The molecular structures of **1** and **2** showing the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Crystallographic data for **1** and **2**.

Compound	1	2
Empirical formula	C ₁₄ H ₁₂ FeO ₄	C ₁₆ H ₁₆ FeO ₄
Formula weight	300.09	328.14
Crystal size, mm	0.28 × 0.21 × 0.14	0.42 × 0.38 × 0.21
Temperature, K	296(2)	296(2)
Wavelength, Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	C2/c (No.15)	P2 ₁ /c (No.14)
<i>a</i> , Å	11.2347(1)	10.1819(9)
<i>b</i> , Å	14.0636(2)	8.2323(7)
<i>c</i> , Å	7.5422(8)	17.2876(2)
β , deg	92.375(1)	103.320(1)
Volume, Å ³	1190.6(2)	1410.1(2)
<i>Z</i>	4	4
Calculated density, mg m ⁻³	1.674	1.546
<i>F</i> (000)	616	680
Reflections collected	2951	6839
Reflections unique	1064	2506
<i>R</i> _{int}	0.0221	0.0165
<i>R</i> 1, <i>wR</i> 2(<i>I</i> ≥ 2σ(<i>I</i>))	0.0260, 0.0648	0.0411, 0.1042

(space group *P*2₁/c) have no crystallographic symmetry. Selected bond lengths and angles are listed in Table 2.

In the structure of **1**, the relative tilt angle α of the two cyclopentadienyl rings is 3.3°. The distance between the Fe atom and the centroid of the Cp rings (Cg) is 1.679 Å, and the angle δ Cg1–Fe–Cg2 is 164.6°. Compound **2** has similar values (Table 3). The relative orientation of the two cyclopentadienyl rings with respect to each other, as characterized by the twist angle γ [20], is 43.0° in **1**, while in **2** this value is 59.2° (Table 3). When there are no strong intermolecular forces in the crystal structures of unbridged 1,1'-disubstituted ferrocenes, the molecules frequently adopt a 1,3'-conformation (108° < γ < 180°) [20]. However, when intermolecular forces are present, the γ

Table 2. Selected bond lengths (Å) and angles (°) for complex **1** and **2**.

1		2	
Fe(1)–C(1)	2.022(2)	Fe(1)–C(2)	2.028(3)
Fe(1)–C(2)	2.035(2)	Fe(1)–C(3)	2.046(3)
Fe(1)–C(3)	2.064(2)	Fe(1)–C(4)	2.061(3)
Fe(1)–C(4)	2.066(2)	Fe(1)–C(5)	2.057(3)
Fe(1)–C(5)	2.044(2)	Fe(1)–C(6)	2.029(3)
O(1)–C(6)	1.202(3)	C(1)–C(2)	1.473(5)
O(2)–C(6)	1.355(2)	O(1)–C(1)	1.209(5)
O(2)–C(7)	1.447(2)	O(2)–C(1)	1.334(6)
		O(2)–C(13)	1.459(5)
C(1)–Fe(1)–C(1) ^{#1}	111.1(1)	C(8)–Fe(1)–C(2)	116.3(1)
C(1)–Fe(1)–C(5) ^{#1}	140.6(9)	C(2)–Fe(1)–C(9)	107.8(1)
C(1)–Fe(1)–C(2) ^{#1}	109.9(9)	C(2)–Fe(1)–C(12)	149.6(2)
C(2)–Fe(1)–C(2) ^{#1}	137.3(1)	C(6)–Fe(1)–C(12)	116.1(2)
C(5) ^{#1} –Fe(1)–C(5)	178.0(1)	C(9)–Fe(1)–C(3)	117.7(2)
C(6)–O(2)–C(7)	116.2(2)	C(12)–C(8)–C(7)	124.6(3)
O(1)–C(6)–C(1)	124.9(2)	C(9)–C(8)–C(7)	127.0(3)
O(1)–C(6)–O(2)	123.8(2)	O(1)–C(1)–C(2)	122.8(5)
O(2)–C(6)–C(1)	111.3(2)	O(1)–C(1)–O(2)	124.9(4)
O(2)–C(7)–C(7) ^{#1}	107.8(1)	C(1)–O(2)–C(13)	117.0(5)

Symmetry transformations used to generate equivalent atoms: $-x+2, y, -z+1/2$.

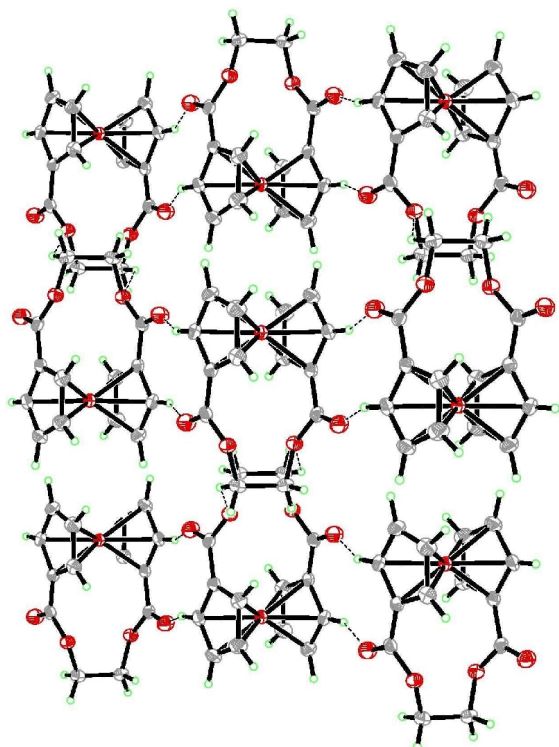
Table 3. Structural features for **1** and **2**.

	1	2
α , deg	3.3	3.0
δ , deg	164.6	165.7
γ , deg	43.0	59.2
Fe–Cg, Å	1.679	1.675

value may lie well outside this range [20]. This has been found to be the result of, *e. g.*, strong intermolecular hydrogen bonds [19,20]. Although complexes **1** and **2** also show interesting hydrogen bond patterns, these are built up by weak C–H...O interactions which are further discussed below. Characteristic data for them are listed in Table 4. As they can only be considered to be very weak, we rather see the origin of

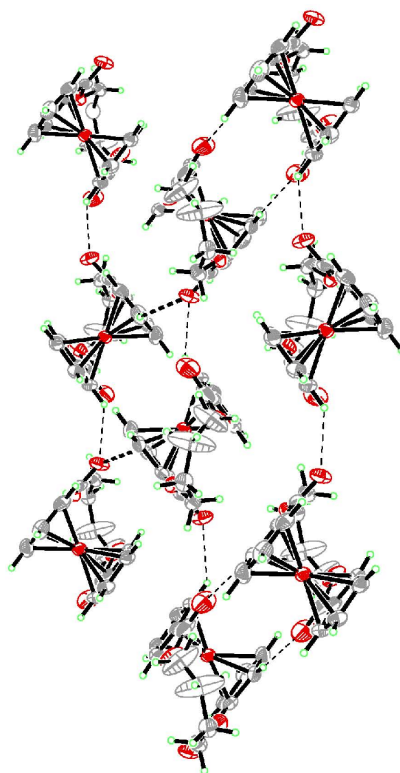
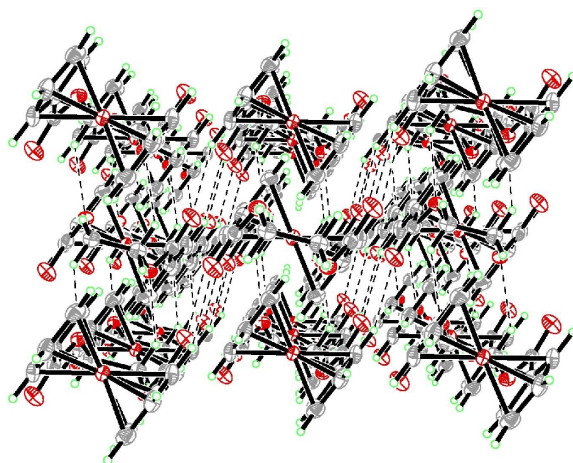
Table 4. C–H···O hydrogen bond data for **1** and **2** (Å and deg).

	D–H···A	D–H	H···A	D···A	D–H···A
1	C5–H5···O1	0.98	2.53	3.448(3)	156
	C7–H7B···O2	0.97	2.53	3.310(3)	137
2	C3–H3···O3	0.98	2.47	3.244(4)	136
	C9–H9···O1	0.98	2.35	3.225(5)	148
	C11–H11···O3	0.98	2.59	3.276(5)	127

Fig. 2. Projection of the two-dimensional layer of chains held together by C–H···O=C hydrogen bonds onto the *ab* plane in crystals of **1**.

the small twist angles γ in **1** and **2** in the bridging of the Cp rings by the 6- and 8-membered C/O chains, respectively, which force the rings into the observed conformations with the substituted C atoms being relatively close together.

In the solid state, compound **1** displays an infinite one-dimensional alignment *via* C5–H5···O1 hydrogen bonds. These one-dimensional chains are parallel, and connected *via* C7–H7B···O2 hydrogen bonds along the *c* direction to form two-dimensional sheets (shown in Fig. 2). At the same time, along the *b* direction there are C7–H7B···O2 hydrogen bonds between neighboring sheets. In the solid state structure of **2**, each molecule is connected by intermolecular

Fig. 3. Projection of the two-dimensional layer of the chains held together by C–H···O=C hydrogen bonds onto the *bc* plane in crystals of **2**.Fig. 4. The packing diagram of **1** shown along the *b* axis.

hydrogen bonds C3–H3···O3 to form chains. These one-dimensional chains are connected with their two neighbors by C9–H9···O1 and C11–H11···O3 hydrogen bonds along the *a* direction forming a two-dimensional sheet (Fig. 3). Along the *b* direction, there

are C11–H11...O3 hydrogen bonds which lead to a three-dimensional network (Fig. 4).

Experimental Section

Solvents and reagents were purified and dried by standard methods. The melting points were determined on a XT-4 micro melting point apparatus and are uncorrected. IR spectra were recorded on a EQUINOX-55 spectrometer in a KBr matrix. ^1H NMR spectra were recorded on a INOVA-400 NMR spectrometer, using TMS as internal standard and CDCl_3 as a solvent. Elemental analyses were performed on a Vario EL III CHNOS analyzer. Electrospray mass spectra were obtained with an MALDI-TOF Mass Spectrometer (Kratos Analytical Inc.). 100–200 mesh silica gel was used for column chromatography.

1,1'-Ferrocene-di(carbonyl chloride)

A mixture of 10.0 g (0.035 mol) of 1,1'-ferrocenedicarboxylic acid, 150 mL of dry dichloromethane and 3.0 mL (0.035 mol) of pyridine was stirred in the dark, and to this freshly distilled oxalyl chloride (8.9 g, 70 mmol) was added dropwise at 0 °C. The reaction mixture was then stirred at r.t. for 8 h. All volatiles were evaporated under reduced pressure. The residue was extracted at 80 °C with petroleum ether (b.p. 60–90 °C) to yield 1.4 g (62 %) product. Recrystallization from petroleum ether yielded red crystals melting at 95–96 °C. Lit. [18]: 98–100 °C.

Ester ferrocenophanes **1** and **2**

A mixture of 2 g (0.006 mol) of 1,1'-ferrocene-di(carbonyl chloride), 500 mL of dry dichloromethane, and 1 mL (0.012 mol) of pyridine was stirred in the dark at r.t. under a nitrogen atmosphere. To this solution 0.006 mol of glycol, or 1,4-butanediol in dichloromethane was added dropwise over 1 h. The mixture was stirred for 24 h

at r.t. and then refluxed for another 8 h (monitored by TLC). About 400 mL of the solvent were removed under atmospheric pressure, and the residual solution was washed 4 times with 50 mL of water and dried over CaCl_2 . The solvent was removed to leave a crude product. The residue was then purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate/acetone (10:2:1).

1: Yield 52 %. M.p. 187–189 °C. – ^1H NMR (CDCl_3): δ = 4.92 s (4H), 4.50 m (8H). – IR (KBr): ν = 3104, 2973, 2911, 1713, 1111 cm^{-1} . – $\text{C}_{16}\text{H}_{16}\text{FeO}_4$: calcd. C 56.03, H 4.03; found C 58.13, H 4.21. – MALDI-TOF MS: m/z = 300 (M^+).

2: Yield 65 %. M.p. 132–133 °C. – ^1H NMR (CDCl_3): δ = 4.77 s (4H), 4.47 s (4H), 4.35 s (4H), 1.99 s (4H). – IR (KBr): ν = 1706, 1153, 2932 cm^{-1} . – $\text{C}_{16}\text{H}_{16}\text{FeO}_4$: calcd. C 58.35, H 4.29; found C 58.56, H 4.41. – MALDI-TOF MS: m/z = 328 (M^+).

Crystal structure determinations

X-ray diffraction data were collected on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation (λ = 0.71073 Å) at r.t. The structure was solved by Direct Methods and refined by full-matrix least-squares methods on F^2 with the program SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 619281 and 619280 (for **1** and **2**). Copies of this information may be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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