

A Novel BEDT-TTF-based Organic Conducting Salt with a Ferrocene-containing Dianion, α -(BEDT-TTF)₄(Fe(Cp-CONHCH₂SO₃)₂)·4H₂O

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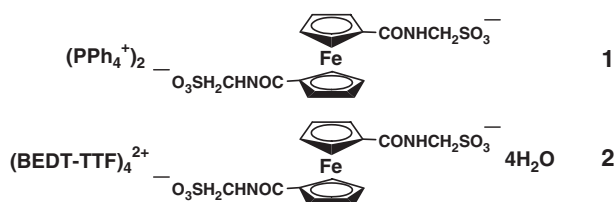
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We have prepared a new organic dianion containing the ferrocene derivative, Fe(C₅H₄-CONHCH₂SO₃⁻)₂, as a PPh₄ salt. Cyclic voltammetry indicates its oxidation potential is 0.14 V higher than that of BEDT-TTF. Electrocrystallization with BEDT-TTF gave the title compound. Its crystal structure and physical properties are reported.

In recent decades a growing topic in the field of materials science is the design and development of multifunctional materials. Many researchers have made efforts to create new materials that combine two or more properties in compounds that are liquid crystals,¹ molecular magnetic materials,² optically active molecules,³ and ionic,⁴ protonic,⁵ or electronic conductors.⁶ Indeed, multifunctional materials may display new phenomena where an interplay between properties plays a crucial role.

The ferrocene moiety is potentially useful owing to its versatile Fe(II)/Fe(III) redox chemistry and because the cationic form shows a variety of magnetic properties.⁷ Several kinds of materials have been reported with this moiety that have unusual electronic and/or magnetic properties. For example, a monoanionic tetraferrocenyl nickel dithiolene complex⁸ and several tetrathiafulvalene derivatives carrying the ferrocenyl group and/or their radical salts have been reported.⁸⁻¹⁰ However, the electrical conductivities of these salts are not so high, probably because the bulky ferrocenyl groups prevent close approach of the conjugated dithiolene rings. In fact the highest reported value is 7×10^{-3} S/cm.¹⁰

We have focussed on using a ferrocenyl containing anion as the nonconducting component of an organic conductor. Previously, we reported the preparation of anionic organic free radical derivatives and the first genuine organic magnetic conductor, α -(BEDT-TTF)₃(TEMPO-NHCOCH₂SO₃)₂·6H₂O (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene).¹¹ We have adapted the synthetic methods to obtain ferrocene-containing anions to be used in conductive salts of common electron donors such as tetramethyltetraselenafulvalene (TMTSF) and BEDT-TTF. In this paper, we report the preparations, structures and physical properties of the PPh₄ and BEDT-TTF salts of the novel dianionic ferrocene derivative Fe(Cp-CONHCH₂SO₃⁻)₂ (see figure below).



The acidic Fe(C₅H₄-CONHCH₂SO₃H)₂ was prepared by a condensation reaction between Fe(C₅H₄-COOH)₂ (1.8 mmol)

and H₂NCH₂SO₃H (4.4 mmol) in the presence of DCC (C₆H₁₁-N=C=N-C₆H₁₁, 4.4 mmol) and DMAP (4-(CH₃)₂N-C₅H₄N, 4.4 mmol). The reaction proceeded in 200 mL of dichloromethane at room temperature and with stirring over two days. Exchange of the counter cation with PPh₄Br yielded orange crystals of the PPh₄ salt (**1**, yield 35%), which were recrystallized from acetonitrile. X-ray diffraction data were collected on a Rigaku AFC-5R 4-circle diffractometer at room temperature.¹² The asymmetric unit contains one cation, half a dianion, and two water molecules. The Fe atom of the ferrocenyl moiety is located on a 2-folded axis. The distance between Fe and the Cp plane is 1.647(2) Å, which is similar to that of the unsubstituted ferrocene (1.654 Å).¹³

The redox properties of the dianion together with BEDT-TTF and ferrocene were determined by cyclic voltammetry, and the results are tabulated in Table 1. The E_1 value of **1** is about 0.14 V higher than that of BEDT-TTF, indicating BEDT-TTF is better electron donor than the dianion.

Needle-like single crystals of (BEDT-TTF)₄(Fe(Cp-CONHCH₂SO₃)₂)·4H₂O (**2**) were obtained by the controlled-current electrocrystallization method¹⁴ in *o*-dichlorobenzene (15 mL) with 10 mg of BEDT-TTF and 70 mg of **1**. Single-crystal X-ray diffraction data were collected with a Quantum CCD area detector on a Rigaku AFC-7R diffractometer, at room temperature.¹⁵ The crystal structure of the salt is shown in Figure 1a. Four BEDT-TTF molecules (**A**, **B**, **C**, and **D**), two halves of a dianion, and four water molecules are crystallographically independent. The overall structure contains alternating layers, along the *c* axis, of the donors and the dianions, with the water molecules in the anionic layers (Figure 1a). In the donor layers, there are two kinds of BEDT-TTF tetramers (**A-B-B'-A'** and **C-D-D'-C'**), each of which form stacks along the *b* axis and interact with each other in a side-by-side fashion along the *a* axis. Thus an α -type 2-D conducting sheet is formed (Figure 1b). The central C=C bond lengths of **A**, **B**, **C**, and **D** are 1.347(7), 1.372(6), 1.359(7), and 1.370(6) Å, respectively. The lengths of the C=C bond of the BEDT-TTF molecules on each end of the tetramers (**A** and **C**) are slightly shorter than those of inner ones (**B** and **D**), suggesting that molecules **A** and **C** have a smaller positive charge than **B** and **D**. Furthermore, as shown in

Table 1. Oxidation Potentials of (PPh₄)₂(Fe(Cp-CONHCH₂SO₃)₂)

Compound	E_1	E_2	ΔE
1	0.69		
Ferrocene	0.50		
BEDT-TTF	0.55	0.86	0.31

V vs saturated calomel electrode (SCE) in PhCN with 0.1 M Bu₄NClO₄, Pt electrode, at room temperature, under nitrogen, scan rate 50 mV s⁻¹.

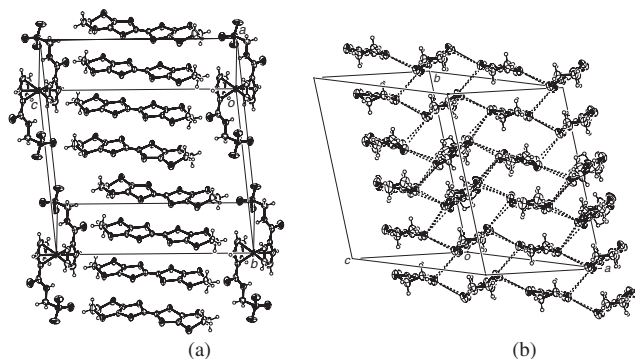


Figure 1. (a) Crystal structure of **2**. Water molecules are omitted for clarity. (b) Packing arrangement of BEDT-TTF. Dashed lines indicate S...S contacts shorter than the van der Waals distance (3.7 Å).

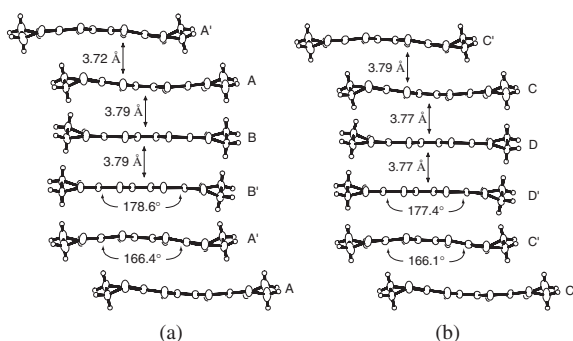


Figure 2. View of the BEDT-TTF tetramers of ABB'A' (a) and CDD'C' (b) along the outer C=C bonds including molecular plane-plane distances and intramolecular dihedral angles between planes made of four S atoms.

Figure 2, molecules **A** and **C** are not planar, as is the case for neutral BEDT-TTF. In contrast, **B** and **D** are almost planar, which is typical for cations. These results suggest that the system has charge disproportionation. The electrical resistivity, as measured down to 100 K, is semiconductive with $\rho_{RT} = 6.2 \Omega \cdot \text{cm}$ and $E_a = 0.11 \text{ eV}$.

In the anionic layer, the $-\text{SO}_3$ group and H_2O form a 1-D hydrogen-bond network along the a axis. The Fe-to-ring-center distances of 1.641(5) and 1.646(3) Å are not significantly different from those in the PPh_4 salt, and are about 0.06 Å shorter than in a ferrocene cation (1.7054(4) Å).¹⁶ This indicates that the ferrocenyl part is in the neutral state. The magnetic susceptibility of a polycrystalline sample from **2** to 300 K were measured using a Quantum Design MPMS-5S SQUID magnetometer. The magnetization is essentially constant versus temperature (5×10^{-4} emu/mol) with a small Curie tail ($<0.1\%$). The very small Curie term indicates that few of the ferrocene moieties are oxidized.

In conclusion we have made a novel BEDT-TTF-based radical ion salt that contains the ferrocene-derived dianion, $\text{Fe}(\text{Cp}-\text{CONHCH}_2\text{SO}_3^-)_2$. X-ray analysis indicates that the positive charge is unequally distributed over the BEDT-TTF molecules, and so the relatively high electrical conductivity of 0.16 S/cm is observed. This is about two orders of magnitude higher than the previously reported highest value.¹⁰ The oxidation potential of the dianion is higher than that of BEDT-TTF, which means the ferrocenyl moiety is in the neutral state even in **2**, thus the

salt is not significantly magnetic. Salts of BEDT-TTF with similar anions, but with a lower oxidation potential, are expected to show magnetic properties from the ferrocenyl moiety. Preparation of these salts is in progress.

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