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Short communication

Structures and properties of new ferrocene-based paramagnetic anion octamethylferrocenedisulfonate and its TTF salt

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ABSTRACT

The structure and properties of a new ferrocene-based disulfonate anion, octamethylferrocenedisulfonate ($Fe(C_5(CH_3)_4(SO_3))_2$), obtained as tetraphenylphosphonium (PPh_4) salts, are described. Recrystallisation gave two types of salts, yellow crystals and green powder. The former composition was found to be $(PPh_4)_2[Fe(C_5(CH_3)_4(SO_3))_2]$, where $Fe(C_5(CH_3)_4(SO_3))_2$ is dianionic. The green powder was determined to be $(PPh_4)[Fe(C_5(CH_3)_4(SO_3))_2]\cdot 0.4H_2O$, in which the iron complex is monoanionic despite it having two anionic sulfo groups. The ferrocenyl part has a charge of +1 and temperature-dependent magnetic susceptibility indicates that the green salt is paramagnetic. Metathesis of either PPh_4 salts with $(TTF)_3(BF_4)_2$ (TTF = tetrathiafulvalene) gave the same compound, $(TTF)[Fe(C_5(CH_3)_4(SO_3))_2]\cdot 3.5H_2O$, in which the anion is paramagnetic. This is the first TTF-type salt that contains a non-diamagnetic ferrocenyl-based counter-ion. The structure and properties of the TTF salt are reported.

1. Introduction

Over the last quarter of a century, multifunctional molecule-based materials have attracted considerable interest [1–3]. In this regard one of the most widely used functional materials is ferrocene (Fc). It is potentially useful because of its versatile Fe(II)/Fe(III) redox chemistry. In its neutral Fe(II) form Fc is diamagnetic, whereas its cationic form has a magnetic moment, which can become the source of a variety of magnetic properties. The cationic form of the ferrocenyl moiety has already been widely used as a magnetic source. One of the most well-known examples is the charge-transfer salt of decamethylferrocene, $Fe(C_5(CH_3)_5)_2$, with TCNE (tetracyanoethylene), which has a ferromagnetic transition at $T_C = 4.8$ K [4]. Furthermore, many research groups in the field of organic conductors have tried to introduce similar functions into organic charge transfer salts [5–8].

For the past decade, we have prepared several ferrocenyl-containing anions for use as counter-ions in donor-anion type organic conductors. So far we reported four TTF and four BEDT-TTF salts (TTF = tetrathiafulvalene; BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) [9–14]. For example, the dianion $Fe(C_5H_4\text{-}CONHCH_2SO_3^-)_2$ (**1** in scheme 1) provides two BEDT-TTF salts [9–11], one of which shows metallic behaviour down to 70 K with a room temperature conductivity of 40 S/cm [11]. This is the highest reported conductivity for any ferrocenyl-containing organic conductor. However, the ferrocenyl parts of all these salts are neutral and therefore diamagnetic. We speculated [13,14] that this was because the oxidation potential of the ferrocenyl part is lower than TTF or BEDT-TTF so that the Fc unit should be oxidized before the organic donors. Recently we reported a new anion, $Fe(C_5H_4\text{-}CH(CH_3)NHCOCH_2SO_3^-)_2$ (**2** in scheme 1), and its TTF salt [13]. The oxidation potential of **2** is lower than that of TTF. However, even though the ferrocenyl unit is more easily oxidized than TTF, it remained neutral in the TTF salt. This is probably because each TTF is strongly dimerised and each dimer has a higher oxidation potential than a TTF monomer. What is required is a ferrocenyl-based anion with a much lower oxidation potential than the corresponding donor. Generally the introduction of methyl groups on ferrocene will lower the oxidation potential by approximately 0.05 V per methyl group [15]. Here we reported the structures and properties of tetraphenylphosphonium and TTF salts of octamethylferrocenedisulfonate, $Fe(C_5(CH_3)_4SO_3^-)_2$, (**3** in scheme 1).

2. Results and discussion

2.1. Tetraphenylphosphonium salts of octamethylferrocenedisulfonate

Reaction of octamethylferrocene with chlorosulfonic acid yielded the acidic octamethylferrocenedisulfonate (**3**). Neutralisation, followed by exchange of the counter-cation with tetraphenylphosphonium bromide (PPh_4Br) gave a yellow crystalline solid (**4**), the photograph

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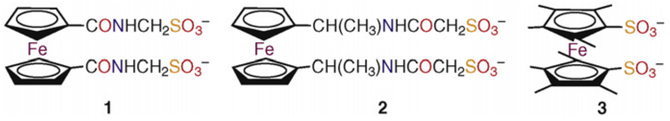

Scheme 1. Molecular structures of ferrocene-based anions.

of which is shown in Fig. 1a. Exchange of the cation, without the neutralisation step, provided green powder (**5**), the photograph of which is shown in Fig. 1b. X-ray analyses of **4** and **5** indicated that these two compounds have different compositions.

Single crystal X-ray data of a yellow crystal of **4** were collected at room temperature [16]. Views of the molecular structure are shown in Fig. 2. The asymmetric unit has two PPh_4 cations and two halves of the anion **3**, which lie about the centre of symmetry.

The ratio of PPh_4 and **3** is 2:1, indicating that **3** is dianionic. The dianion has two anionic sulfo groups so that the ferrocenyl moiety is neutral. We have previously reported [13,14] the Fe···Cp (Cp = cyclopentadienyl ring) distances of neutral (~1.65 Å in $(PPh_4^+)Fc\text{-}SO_3^- \cdot H_2O$) and cationic ferrocenyl parts (~1.70 Å in $Fc^+\text{-}SO_3^-$) are significantly different [14]. The distances shown in Fig. 2 (Fe···Cp = 1.661 and 1.662 Å) are consistent with a neutral and diamagnetic ferrocenyl moiety. The oxidation potential of **4** was determined by cyclic voltammetry. The E_1 value of −0.08 V versus SCE in PhCN is 0.46 V lower than that of TTF. Therefore **4** is a stronger donor than TTF.

The salt **5** was normally obtained as green powder, in which we found only a few crystals. Single crystal X-ray data collection was performed at room temperature. The structure was solved as (PPh_4)**3**$\cdot 0.4H_2O$ [17]. The molecular and crystal structures are shown in Fig. 3. One PPh_4 cation, one molecule of **3** and a partially occupied water molecule are crystallographically independent. The ratio of PPh_4

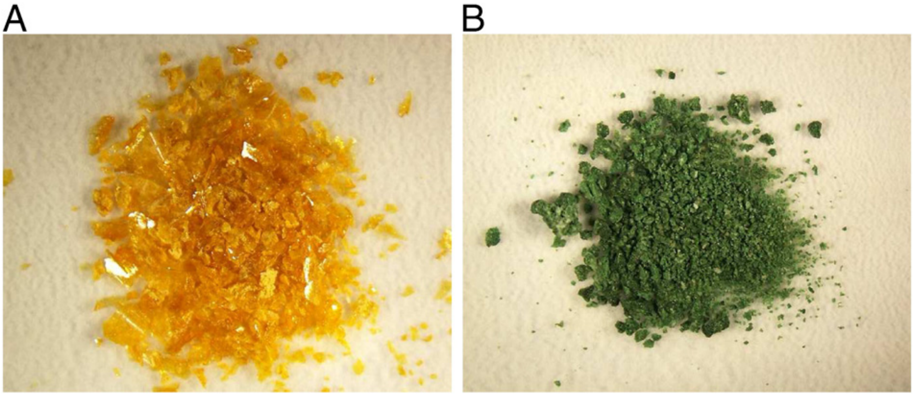

Fig. 1. Photographs of the yellow crystalline solid (a) and green powder (b).

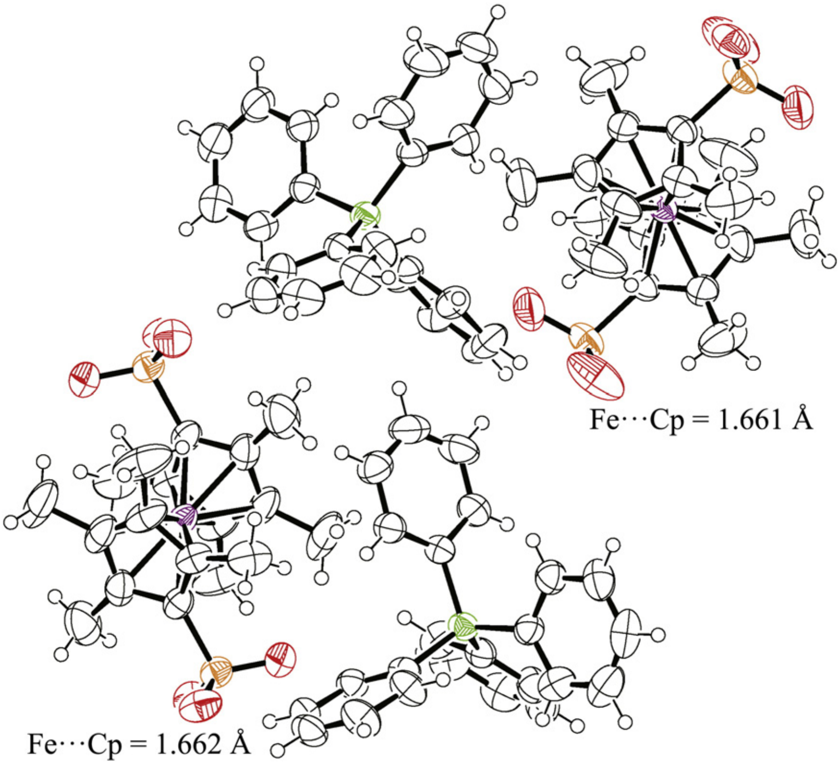

Fig. 2. Molecular structures of $(PPh_4)_2$**3** (**4**).