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Structural and Magnetic Properties of a Novel Ferrocenyl–Diiodine Charge Transfer Complex

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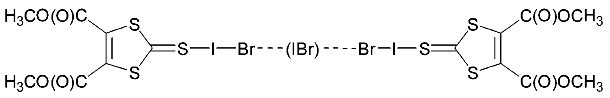
The reaction of 4-ferrocenyl-1,3-dithiole-2-thione with diiodine affords an unprecedented "double" charge-transfer complex; the highly ordered ferrocenium units are held by a supramolecular polyiodide chain, and the material shows evidence of the formation of zigzag magnetic chains below 2 K.

It has long been postulated that "charge-transfer" complexes formed between neutral chalocogen donors and halogens might be useful components in molecular electronics.[1−3] However, the majority of these complexes do not display any cooperative electronic properties since they do not form open-shell species or structures that facilitate close intermolecular π interactions.

Recent studies have demonstrated that charge-transfer interactions between nitrogen[4] or sulfur[5] donors and dihalogens can be used for the formation of ordered supramolecular assemblies. For example, we have reported the structure of a 1,3-dithiole-2-thione−IBr complex **1** that self-assembles into a highly ordered three-dimensional network.[5] In **1** each thiocarbonyl donor and IBr acceptor, together with an occluded "free" IBr molecule, is linked through an extensive array of S···I, I···I, I···Br, and hydrogen-bonded close contacts. Since the sulfur heterocycle in **1** is not a good electron donor (the diester groups draw electron density away from the heterocycle), it is not surprising that the dithiole ring was not oxidized by the free IBr. Nevertheless, enforcing a secondary formal charge-transfer process by adapting the donor ability would be an extremely attractive prospect and, if the result is an open-shell species with a high degree of dimensionality, then the criteria for a conducting or magnetic material may be satisfied. With this aim in mind, we have investigated the reaction of ferrocenyl derivative **2**[6] with I_2 and IBr. Our choice of electron donor was based on the excellent stability of the oxidized ferrocenium species and the propensity of ferrocene-based charge-transfer materials to exhibit high levels of magnetism.[7]



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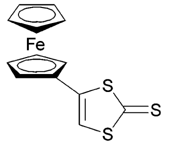

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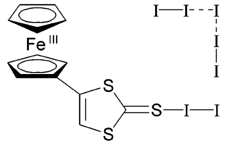

Treatment of **2** with I_2 in refluxing toluene yields, upon cooling overnight in a refrigerator, blue/black crystals of composition $\mathbf{2}\cdot(I_2)_{3.5}$ (**3**).[15] This unusual stoichiometry suggested that the iron in **3** had been oxidized from Fe^{2+} to Fe^{3+}, and this was confirmed by magnetic measurements (vide infra) and Mössbauer spectroscopy ($\delta = 0.44$ mm s^{-1}, $\Delta E_Q = 0.23$ mm s^{-1}, at 293 K), which falls in the expected range for Fe^{3+}.[8] This is a most remarkable result since treatment of phosphorus donors or sulfur donors bearing ferrocene groups with diiodine usually results in the forma-

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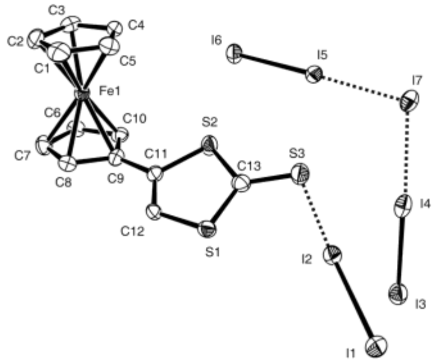

Figure 1. X-ray crystal structure of compound **3** with H atoms omitted.

tion of molecular charge-transfer adducts *without* simultaneous oxidation of the ferrocenyl groups.[9] Treatment of **2** with IBr gave the same stoichiometry (by elemental analysis) for the resulting product, which was obtained as a microcrystalline material.[15]

The X-ray crystal structure of **3**[16] (Figure 1) revealed that the compound had simultaneously undergone two different "charge-transfer" processes: (i) the sulfur of the 1,3-dithiole-2-thione heterocycle forms a molecular charge-transfer adduct with a molecule of I_2, the thiocarbonyl sulfur interacting with the I_2 in the established manner,[1,2] with S···I and I−I bond lengths of 2.705(2) and 2.857(11) Å, respectively; (ii) the ferrocenyl groups have been oxidized to ferrocenium, with the charge counterbalanced by an I_5^- anion. The Fe−Cp mean distance in **3** is elongated compared to **2** (**2**, Fe−Cp$_{\mathrm{unsub}}$ = 2.034 Å, Fe−Cp$_{\mathrm{sub}}$ = 2.039 Å; **3**, Fe−Cp$_{\mathrm{unsub}}$ = 2.086 Å, Fe−Cp$_{\mathrm{sub}}$ = 2.092 Å).[10] The only significant difference between the 1,3-dithiole-2-thione rings in **2** and **3** is the thiocarbonyl bond, which is longer in **3** due to the transfer of electron density to the I_2 molecule. The I_5^- anion adopts a V-shaped geometry with an angle of 96.88(3)° [I(5)−I(7)−I(4)], comprising two I_2 molecules coordinating to an I^-; the bond lengths of the I_2 molecules are 2.818(10) Å [I(6)−I(5)] and 2.799(17) Å [I(4)−I(3)], whereas the coordinating distances are 3.054(10) Å [I(5)−I(7)] and 3.160(2) Å [I(4)−I(7)].

The ferrocenium donor fragment and the polyiodide anion are linked through a series of I···I contacts into an elaborate supramolecular structure. Close intermolecular distances are observed between I(1) and I(1) [3.677(1) Å], I(1) and I(3) [3.704(2) Å], and I(4) and I(6) [3.895(2) Å], which are all shorter than the sum of the van der Waals radii for two iodine atoms (3.96 Å). Molecules I(3)−I(4) and I(5)−I(6) experience different intermolecular close contacts. In the absence of secondary interactions, the pentaiodide species normally adopts C_{2v} symmetry;[11] therefore, it is this difference in the supramolecular chemistry of the I_5^- unit that is responsible for the asymmetric arrangement. The entire network of contacts results in a polymeric structure, consisting of eight-membered iodine macrocycles, linked by four iodine atoms, to form a "chain of beads" type arrangement (Figure 2). The polyiodide chain is also interacting with the heterocycles via hydrogen bonding [C(12)−H(12)···I(6) = 3.041(2) Å; C(12)−H(12)···I(5) = 3.177(2) Å; sum of the van der Waals radii for iodine and hydrogen = 3.18 Å], which holds the dithiole rings almost perpendicular to the polymer chain.

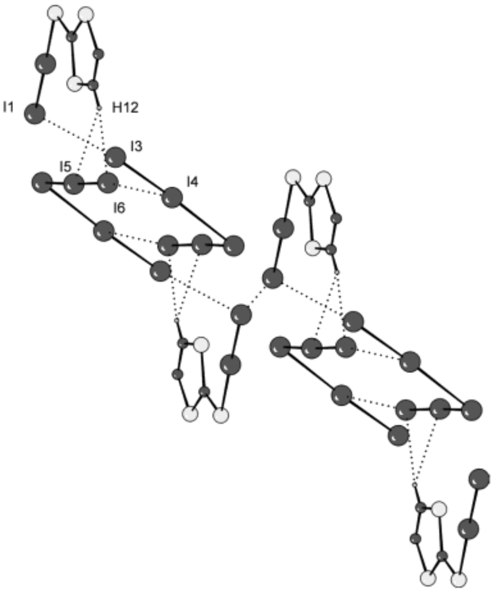

Figure 2. Polyiodide structure of **3**; ferrocenium units omitted for clarity.

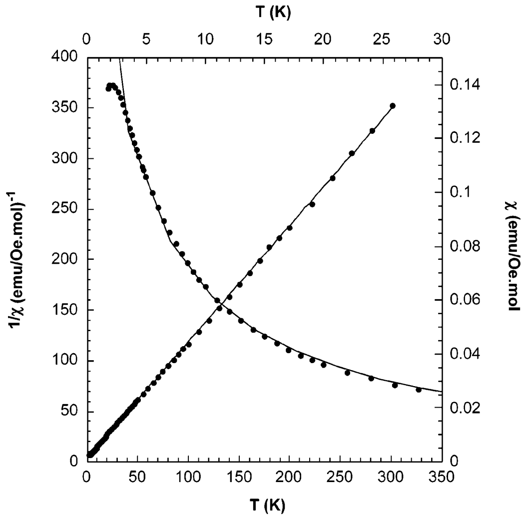

Figure 3. 1/χ versus temperature (T) and paramagnetic susceptibility (χ) versus T. Solid lines are the Curie−Weiss fit to the experimental values.

Magnetic susceptibility measurements were made on a Quantum Design MPMS magnetometer over a temperature range of 1.8−300 K at 10 kOe. Diamagnetic corrections were made for the sample holder and sample (Pascal's constants). Isothermal magnetization measurements as a function of applied field were carried out between 1 and 50 kOe at 1.8, 2, 2.5, 3.0, and 300 K. The experimental data were corrected for diamagnetic contributions (Pascal's constants) and for the presence of a small quantity (ca. 24 μg) of metallic Ni impurity. The effective room temperature magnetic moment

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(10) The X-ray crystal structure and data for **2** and the temperature dependence of magnetic susceptibility of **3** over the range 1.8−300 K can be found in the Supporting Information.

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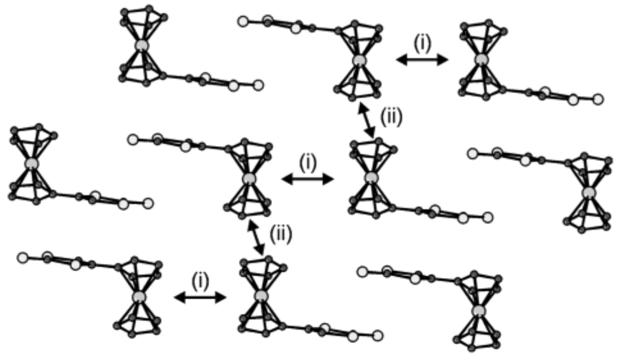

Figure 4. Slipped stack pattern of ferrocenium units viewed along the *b*-axis (I atoms omitted); Fe···Fe distances are (i) 7.905 Å and (ii) 6.785 Å.

of **3** is 2.61 μ_B, which is within the experimental range of values found for ferrrocenium derivatives.[12] This degree of deviation from the spin-only value of 1.73 μ_B is indicative of the $^2E_{2g}$ as the ground state for the ferrocenium ion and shows that symmetry distortions due to the differences between the two five-member rings are not very large. The susceptibility follows Curie−Weiss behavior (Figure 3), with $C = 0.8709$ emu K Oe^{-1} mol^{-1} and $\theta = -3.57$ K. For $S = {}^1/_2$ characteristic of ferrocenium radical ions the calculated g value for **3** is 3.04, similar to those of similar compounds.[13] Below 2.5 K the susceptibility deviates from the Curie−Weiss behavior, reaching a maximum at 2.1 K before decreasing. This is indicative of antiferromagnetic interactions which become dominant in this temperature range. No magnetic ordering is observed above 1.8 K, the minimum of the experimental temperature range.

A close look to the crystal structure shows a slipped stack structure along the *b*-axis with two different significant interactions between the ferrocenium species (Figure 4). Thus, the structural pattern can be regarded as zigzag chains where Fe···Fe distances alternate between 6.785 and 7.905 Å. Using the extrapolations from finite chains made by Bonner et al.[14] one can estimate $J_1 = -1.7$ K and $\alpha = |J_2|/|J_1| = 0.8$.

The results obtained for **3** provide further evidence that thio- or selenocarbonyl dihalogen adducts may form the basis of novel molecular materials for magnetic and conductive applications.

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Supporting Information Available: Crystallographic files for the structures of **2** and **3**. X-ray crystal structure of **2**. Temperature dependence of the magnetic susceptibility of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Elemental anal. Calcd for **3**, $C_{13}H_{10}FeI_7S_3$: C, 12.94; H, 0.84; S, 7.97. Found: C, 13.20; H, 0.77; S, 7.56. Calcd for **2**$(IBr)_{3.5}$, $C_{13}H_{10}Fe(IBr)_{3.5}S_3$: C, 14.98; H, 0.97; S, 9.23. Found: C, 15.16; H, 0.76; S, 9.20.

(16) $C_{13}H_{10}S_3I_7Fe$, $M_r = 1206.54$, triclinic, $a = 9.607(2)$ Å, $b = 9.838(2)$ Å, $c = 14.600(3)$ Å, $\alpha = 94.50(3)°$, $\beta = 100.14(3)°$, $\gamma = 112.38(3)°$, $V = 1239.9(4)$ Å^3, space group $P1$, $Z = 2$, crystal size 0.17 × 0.13 × 0.02, $D_c = 3.232$ g cm^{-3}, $F(000) = 1066$, μ(Mo Kα) = 9.574 mm^{-1}, $T = 150$ K, 18434 data merged to 5610 unique ($R_{int} = 0.0681$), final R, Rw indices [$F^2 > 2\sigma(F^2)$] 0.0448, 0.0982.