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Notes

Molecular Charge-Transfer Salt of BEDT−TTF [Bis(ethylenedithio)tetrathiafulvalene] with the Oxalate-Bridged Dimeric Anion $[Fe_2(C_2O_4)_5]^{4-}$

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Introduction

Of the numerous BEDT−TTF charge-transfer salts containing metal trisoxalate anions, the majority have the formula (BEDT−TTF)$_4$[A·M(C_2O_4)$_3$]·S where A is either K^+, NH_4^+, or H_3O^+, M is a trivalent metal, and S is a solvent molecule,[1−4] with structures consisting of alternating layers containing $[M(C_2O_4)_3]^{3-}$, A and S, and BEDT−TTF cations. In the inorganic layer, S sits in the approximately hexagonal-shaped cavity formed by the uncoordinated O atoms of the metal trisoxalate anions and A. This family of compounds exhibits a range of electronic ground states[2,5] including the first organic superconductor with paramagnetic anions.[1] These ground states are a function of the donor packing motif, the S···S close contacts in the donor layer, and the conformation of the donor molecule, which has been correlated to the packing requirements of the anion layer. In contrast, a "checker board" structure is observed in the compound (BEDT−TTF)$_2$[Ge(C_2O_4)$_3$]·C_6H_5CN[6] in which changing the anion charge to −2 eliminates the need for the A group and gives rise to a new structure type. This consists of discrete face-to-face dimers of BEDT−TTF interspersed with $[Ge(C_2O_4)_3]^{2-}$ in the *a* and *c* directions and by $[Ge(C_2O_4)_3]^{2-}$ and benzonitrile molecules in the *b* direction. The salt is a semiconductor between 300 and 120 K with a low activation energy of 0.127 eV. In our efforts to synthesize more compounds of this type we have made the first BEDT−TTF charge-transfer salt containing an iron oxalate bridged dimer. The anion charge of −4 is incompatible with a layered structure and induces a different packing motif similar to that observed in (BEDT−TTF)$_2$[Ge(C_2O_4)$_3$]·C_6H_5CN.

Experimental Section

Synthesis and Purification of Starting Materials. $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ (Aldrich) was recrystallized twice from water. BEDT−TTF (Aldrich) was recrystallized from chloroform, and 18-crown-6 ether (Aldrich) was dried over CH_3CN. CH_2Cl_2 was shaken with portions of concentrated sulfuric acid until the acid layer remained colorless, then washed with water, dried with magnesium sulfate, and distilled over P_2O_5.[7] CH_3CN was dried with Linde 4 Å molecular sieves, then stirred with calcium hydride until there was no further evolution of hydrogen to remove traces of acetic acid and fractionally distilled at high reflux over calcium hydride immediately prior to use.[7]

Electrocrystallization. Standard electrochemical synthesis of BEDT−TTF charge-transfer salts involves the oxidation of BEDT−TTF in the presence of a solution of the anion. $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ (100 mg) was dissolved in a 1:1 (v:v) mixture of CH_2Cl_2 and CH_3CN (50 mL total volume) with the aid of 18-crown-6 ether (200 mg). BEDT−TTF (10 mg) was placed in the anode compartment of an H-shaped cell, and the remainder was filled with the solution of the anion. A constant current of 1 μA was passed across the cell. Small, dark, flat needles of (BEDT−TTF)$_4$[Fe$_2$(C_2O_4)$_5$] (5 mg) suitable for X-ray diffraction were harvested from the platinum anode after 3 weeks.

Physical Measurements. The magnetic susceptibility of a polycrystalline sample was measured using a Quantum Design MPSM7 superconducting quantum interference device (SQUID) magnetometer under an applied magnetic field of 1 T. The diamagnetism was estimated as -883×10^{-6} emu mol^{-1} from Pascal's constants. Two probe DC transport measurements were made using an Oxford Instruments Maglab System 2000. Gold wires (0.0025 mm diameter) were attached to the crystal using Pt paint (Degussa), and the attached wires were connected to an eight-pin integrated circuit plug with Ag paint (RS components). The resistance of the contacts was assumed to be negligible, since the crystal had a high intrinsic resistance. Single-crystal X-ray diffraction data were collected at 150(2) K using an Enraf Nonius Kappa CCD area detector with Mo Kα radiation and an Oxford Cryosystem N_2 open flow cryostat. The structure was solved by direct methods and refined anisotropically on F^2 using SHELX97. All hydrogen atoms were placed in idealized positions and refined using a riding model.

Results and Discussion

Crystal Structure. The structure of (BEDT−TTF)$_4$[Fe$_2$(C_2O_4)$_5$] consists of discrete units of $[Fe_2(C_2O_4)_5]^{4-}$ interspersed with four BEDT−TTF molecules in a "checker board" arrangement. Table 1 shows the crystallographic data, and Figure 1

Table 1. Crystallographic Data for (BEDT−TTF)$_4$[Fe$_2$(C_2O_4)$_5$] at 150(2) K

chemical formula	$C_{25}H_{16}FeO_{10}S_{16}$
a, Å	16.8068(3)
b, Å	10.9556(2)
c, Å	19.4109(3)
β, deg	102.1593(9)
V, Å^3	3493.92(10)
Z	4
fw	1045.19
space group	$P2_1/n$ (No. 14)
temp, K	150(2)
λ (Mo Kα), Å	0.710 73
ρ_{calc}, g cm^{-3}	1.987
μ, cm^{-1}	14.45
$R(F_o)^a$	0.0336
$R_w(F_o^2)^b$	0.0805

^{a} $R = \sum(F_o - F_c)/\sum F_o$. ^{b} $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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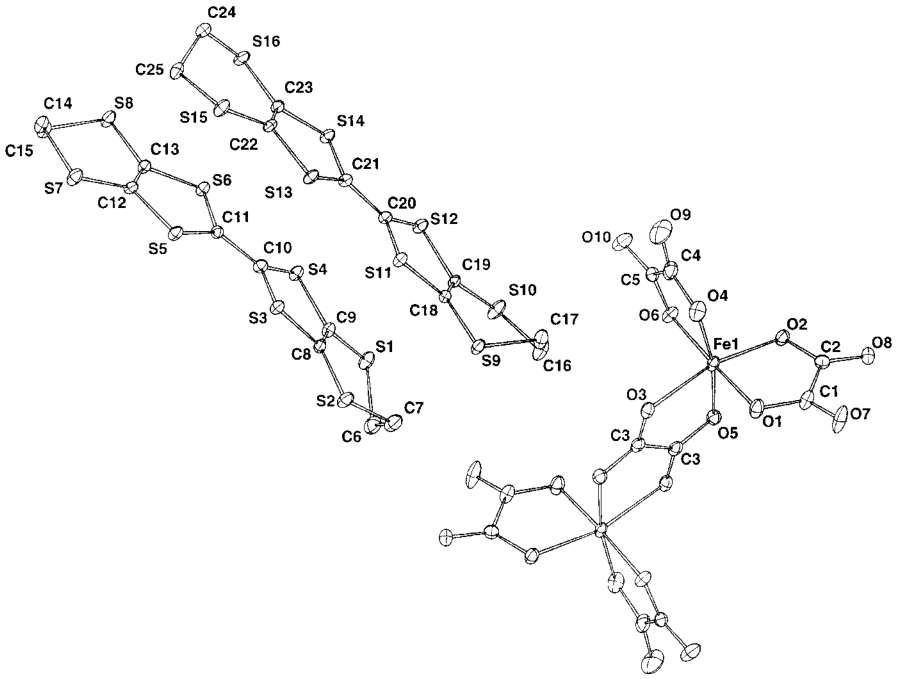

Figure 1. ORTEP diagram of $(\mathrm{BEDT{-}TTF})_4[\mathrm{Fe}_2(\mathrm{C}_2\mathrm{O}_4)_5]$ at 150(2) K showing 50% thermal elipsoids and the atom numbering scheme.

Table 2. Selected Bond Lengths (Å) in the BEDT−TTF Molecules Used To Calculate Their Charge and Selected Bond Lengths (Å) in the $[\mathrm{Fe}_2(\mathrm{C}_2\mathrm{O}_4)_5]^{4-}$ Unit

BEDT−TTF 1		BEDT−TTF 2		selected bond lengths in$[\mathrm{Fe}_2(\mathrm{C}_2\mathrm{O}_4)_5]^{4-}$ unit	
S3−C10	1.724(3)	S11−C20	1.723(3)	Fe1−O2	1.9659(19)
S3−C8	1.748(3)	S11−C18	1.729(3)	Fe1−O4	1.971(2)
S4−C10	1.720(3)	S12−C20	1.729(3)	Fe1−O1	1.9720(19)
S4−C9	1.748(3)	S12−C19	1.746(3)	Fe1−O6	1.9747(18)
S5−C11	1.714(3)	S13−C21	1.732(3)	Fe1−O3	2.0827(19)
S5−C12	1.737(3)	S13−C22	1.737(3)	Fe1−O5	2.1024(19)
S6−C11	1.709(3)	S14−C21	1.717(3)	O3−C3	1.260(3)
S6−C13	1.736(3)	S14−C23	1.748(3)	O6−C5	1.294(3)
C10−C11	1.403(4)	C21−C20	1.388(4)	O1−C1	1.296(3)
				O4−C4	1.305(4)

shows a standard ORTEP diagram of the structure with 50% thermal elipsoids. The unit cell contains two crystallographically independent BEDT−TTF molecules. Figure 2 shows the structure projected on the *ac* plane. The charge on a BEDT−TTF molecule can be estimated with an accuracy close to 10% using the empirically determined relationship between C−C and C−S bond lengths in the central TTF portion of the molecule.[8] By this method, the two BEDT−TTF molecules have calculated charges of +1.2 and +1.0. Table 2 shows the bond lengths used in the charge calculation. One BEDT−TTF molecule has the "boat" conformation at both ends, and the other has a "twisted-boat" conformation. The "boat" conformation is defined here as one having both of the terminal ethylene carbon atoms on the same side of the central TTF plane, and the "twisted" conformation is when one of the terminal ethylene carbons is above and the other below the plane. The BEDT−TTF molecules occur as face to face dimers overlapping in the bond over ring mode. There are three short S⋯S contacts between the two crystallographically independent BEDT−TTF molecules (S3⋯S11, 3.48 Å; S4⋯S12, 3.50 Å; S6⋯S14, 3.58 Å) and one short S⋯S contact between parallel BEDT−TTF molecules in neighboring dimers (S9⋯S15, 3.25 Å). The $[\mathrm{Fe}_2(\mathrm{C}_2\mathrm{O}_4)_5]^{4-}$ unit has D_{2h} molecular symmetry, and the Fe−Fe distance is 5.472 Å, which can be compared with metal−metal distances in other bimetallic compounds with bridging oxalate ligands.[9−13]

Physical Measurements. Two-probe transport measurements were performed from 300 to 138 K, recording the resistance as a function of temperature. A plot of $\ln R$ versus $1000/T$ gives a straight line from which a linear fit gives an activation energy of 1.2 eV and a room-temperature conductivity of 0.002 Ω^{-1} cm^{-1}, indicating that the compound is a semiconductor.

The magnetic susceptibilities of a polycrystalline sample was measured as a function of temperature in the temperature range 2−300 K and an applied field of 1 T. The magnetic susceptibility of the $[\mathrm{Fe}_2(\mathrm{C}_2\mathrm{O}_4)_5]^{4-}$ unit, χ^{D}, is the susceptibility derived from the expression of an isotropic exchange interaction between two iron(III) centers separated by a distance greater than 5 Å.[14] This interaction is described by the Hamiltonian $H = -JS_1 \cdot S_2$

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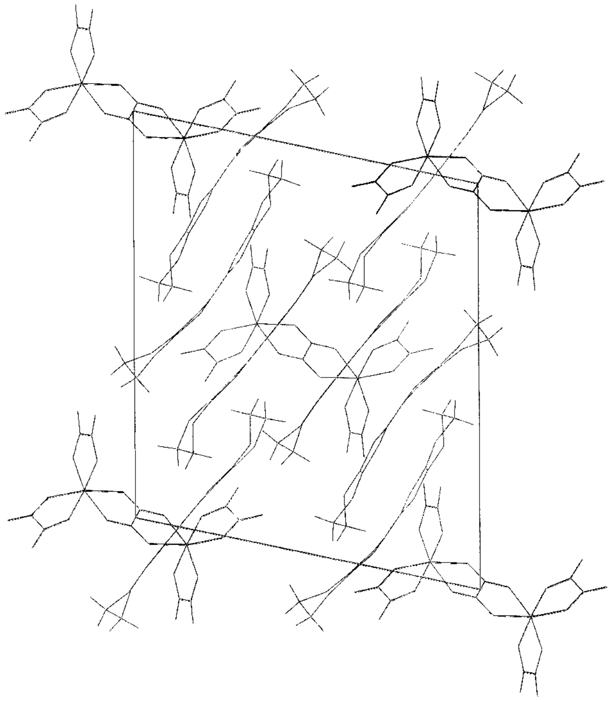

Figure 2. Packing diagram of (BEDT−TTF)$_4$[Fe$_2$(C$_2$O$_4$)$_5$] viewed along the *b* axis.

where $S_1 = S_2 = {}^5/_2$.

$$\chi^{D} = \frac{2N\beta^2 g^2}{kT}\,\frac{x + 5x^3 + 14x^6 + 30x^{10} + 55x^{15}}{1 + 3x + 5x^3 + 7x^6 + 9x^{10} + 11x^{15}}$$

where

$$x = \exp\left(\frac{J}{kT}\right)$$

The susceptibility χ_M shows characteristic behavior of an antiferromagnetic interaction between the two high-spin Fe^{3+} ions in the dimer with a small amount *p* of paramagnetic impurity[15] with susceptibility χ^I.

$$\chi_M = \chi^D(1 - p) + \chi^I p$$

It is assumed that the BEDT−TTF molecules do not contribute to the susceptibility, since the BEDT−TTF molecules, each with one unpaired electron, are dimerized and hence have no net spin. The paramagnetic impurity is therefore judged to be monomeric Fe^{3+} with a susceptibility obeying the Curie law. Figure 3 shows that the $\chi_M T$ vs T plot in a magnetic field of 1 T decreases gradually from a value of about 8 emu K mol^{-1} at room temperature to about 1 emu K mol^{-1} at 2 K, clearly indicating antiferromagnetic interaction between the Fe(III) centers.

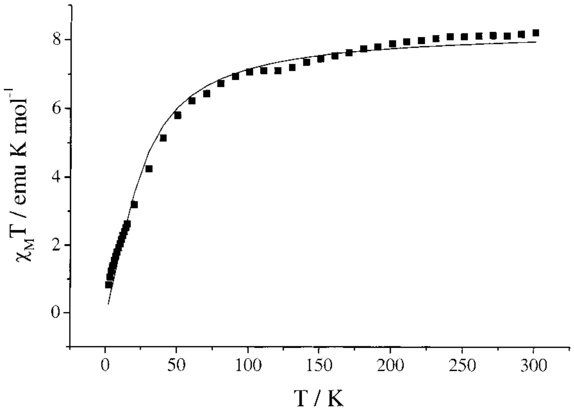

Figure 3. $\chi_M T$ vs T in magnetic field of 1 T. The solid line represents the best fit using the Heisenberg isotropic exchange model for a linear dimer Fe^{III}−Fe^{III}.

The best fit (overlaid line in Figure 3) is found with $g = 1.99$, $J = -3.44$ cm^{-1}, $p = 0.044$. The exchange interaction in this compound ($J = -3.44$ cm^{-1}) is in good agreement with those reported for other oxalate-bridged Fe(III) dimers of −3.61 for [Fe$_2$(acac)$_4$(C$_2$O$_4$)]·0.5H$_2$O and −3.84 for [NEt$_4$]$_4$[Fe$_2$(NCS)$_8$(C$_2$O$_4$)].[15] More particularly, it can be favorably compared to two very recent materials of a similar nature, −3.57 for [TTF]$_5$[Fe$_2$(C$_2$O$_4$)$_5$]·2PhMe·2H$_2$O and −3.69 for [TMTTF]$_4$[Fe$_2$(C$_2$O$_4$)$_5$]·PhCN·4H$_2$O.[13]

Conclusion

We have synthesized a new BEDT−TTF charge-transfer salt containing the novel anion [Fe$_2$(C$_2$O$_4$)$_5$]$^{4-}$. The bridging oxalate ligand provides an exchange pathway between the two Fe$^{(III)}$ centers, which results in an antiferromagnetic interaction between pairs of Fe atoms. The exchange coupling *J* is slightly lower than the one observed in the neutral complex [Fe$_2$(acac)$_4$(C$_2$O$_4$)]·0.5H$_2$O[14] with the same Fe^{III}−Fe^{III} bridge and may be due to the combined influence of the BEDT−TTF molecules and the large −4 charge. The apparent small anomaly in the experimental data of Figure 3 at ca. 125 K is not reproduced by the simulation used. However, the equations have been proven to be valid for this structure type in the published material outlined above. A possible origin of the anomaly is a structural phase transition below the temperature at which the reported structure was made. Further experiments will be carried out to determine the extent of magnetic interactions between the inorganic and organic components of the compound and to identify the possible structural change.

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Supporting Information Available: Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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