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New organic charge transfer salts $(ET)_4(FeCl_4)_2$ and $(ET)FeCl_4$: preparation, structure, XP spectra and electrical properties

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New charge transfer salts $(ET)_4(FeCl_4)_2$ **1** and $(ET)FeCl_4$ **2** have been prepared by the diffusion method [ET = bis-(ethylenedithio)tetrathiafulvalene] and their crystal structures have been solved by X-ray analysis. The single crystals have a room temperature conductivity of 10 S cm^{-1}, metal-conducting behavior over the temperature range 250–300 K and 10^{-2} S cm^{-1}, semiconducting behavior over the temperature range 160–300 K, respectively. The XP spectrum of $(ET)_4(FeCl_4)_2$ **1** was also studied.

Recently incorporation of magnetic and electrical behavior into molecular materials has generated a lot of interest. For examples, Day prepared ET based FeX_4 and CuX_4 (X = Cl and Br) salts,[1] Ouahab and co-workers synthesized $(ET)_4(NEt_4)M(CN)_6\cdot 3H_2O$ ($M = Fe^{III}$, Co^{III})[2] and Kurmoo *et al.* have prepared $(ET)_4AFe(C_2O_4)_3\cdot PhCN$ (A = K, NH_4, H_2O).[3] We have also synthesized $(ET)_4K[Fe(CN)_5(NO)]_2$[4] and $(ET)_3Fe(CN)_5(NO)$. All these compounds exhibit interesting conducting and magnetic properties. It is very important to understand the interaction between conduction electrons and localized spins and the influence of the magnetic moments of the anions on the physical properties. This question leads chemists to rationalize designs of new types of molecular materials. As part of our series of studies of magnetic molecular materials, we have synthesized two new charge transfer salts $(ET)_4(FeCl_4)_2$ **1** and $(ET)FeCl_4$ **2**. In this contribution we report their preparation, crystal structures, and electrical properties. The XP spectra of $(ET)_4(FeCl_4)_2$ **1** are also discussed.

Experimental

ET was prepared by the literature method[5] and the compound $NMe_4FeCl_4\cdot 0.5H_2O$ **3** was prepared by treating a hot 3 M HCl solution of $Fe(ox)_3{}^{3-}$ with NMe_4Cl and the resulting precipitate was recrystallized from 3 M HCl. All products showed satisfactory elemental analyses. Crystallization by diffusion was carried in an H-shaped cell with an ET–CH_2Cl_2 solution in one compartment and $NMe_4FeCl_4\cdot 0.5H_2O$–CH_2Cl_2 solution in the other. After several days of diffusion, the solution turned green and black crystals adhered to the wall of the cell. The crystals have two phases, one long thin black needles and the other polyhedra.

Structure determination of the single crystals of these two compounds was carried out on a MAC SCIENCE DIP2000 diffractometer utilizing graphite monochromated Mo-Kα (λ = 0.710 73 Å) radiation from a rotating anode generator. Crystal and refinement data are listed in Table 1. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/57.

The temperature dependence of the relative resistivity of $(ET)_4(FeCl_4)_2$ **1** was carried out by the four-probe dc method. The current was flowed along the longest direction of the single crystals. Electrical contacts to the crystals were made with 25 μm gold wire and gold conductive paint. The crystals were held on CTI-Cryogenics cryodyne refrigerator and the temperature was controlled by DRC-91 CA Temperature Controller.

XP spectra were recorded on VG SCIENTIFIC Escalab 220i-XL photoelectron spectrometer using an Mg-Kα X-ray source. The compounds studied were $(ET)_4(FeCl_4)_2$ **1**, ET, $(ET)FeCl_4$ **2** and $NMe_4FeCl_4\cdot 0.5H_2O$ **3**. They were used in powder form and dusted on a double sided adhesive tape. The C 1s peak from contamination was used as the standard for charge correction (E_B for C 1s = 284.6 eV). Multi-scan data were collected and analyzed by an Eclipse Datasystem.

Results and Discussion

The structures of $(ET)_4(FeCl_4)_2$ **1** and $(ET)FeCl_4$ **2** are shown in Fig. 1(*a*) and Fig. 2(*a*), respectively, and selected bond lengths of the ET and $FeCl_4$ ions in **1** and **2** are listed in Table 2.

Four ET molecules and two $FeCl_4$ anions are contained in the asymmetric unit of **1**. The Fe—Cl bond lengths of the two anions 2.177(5)–2.208(5) and 2.174(5)–2.211(5) Å are similar to other $[FeCl_4]^-$ salts,[1,6,7] and imply that the formal charge of the anion is close to −1. The lengths of the central C=C double bond, the C—S bond near the molecular center, the other C—S bond, and the outer C=C bond within the ET molecule are related to the degree of charge transfer in ET. The central C=C bond lengths of the ET molecules are 1.344 [C(46)—C(59)], 1.334 [C(47)—C(53)], 1.348 [C(48)—C(51)] and 1.371 Å [C(60)—C(61)], respectively. The bond length differences signifies differences in the charge state of the ET molecules. Comparison with corresponding bond lengths in other ET salts with known levels of oxidation[8] indicates

Table 1 Crystal and refinement data of **1** and **2**

	1	**2**
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	6.651(2)	8.631(3)
b/Å	16.620(6)	10.731(5)
c/Å	31.940(1)	11.630(5)
α/°	89.64(8)	90.83(7)
β/°	85.62(7)	103.51(7)
v/°	81.88(7)	93.85(6)
V/Å^3	3484.68	1044.84
Z	2	2
D_c/g cm^{-3}	1.844	1.856
no. of reflections	7241	2518
R, R_w	0.0568, 0.0560	0.0514, 0.0503

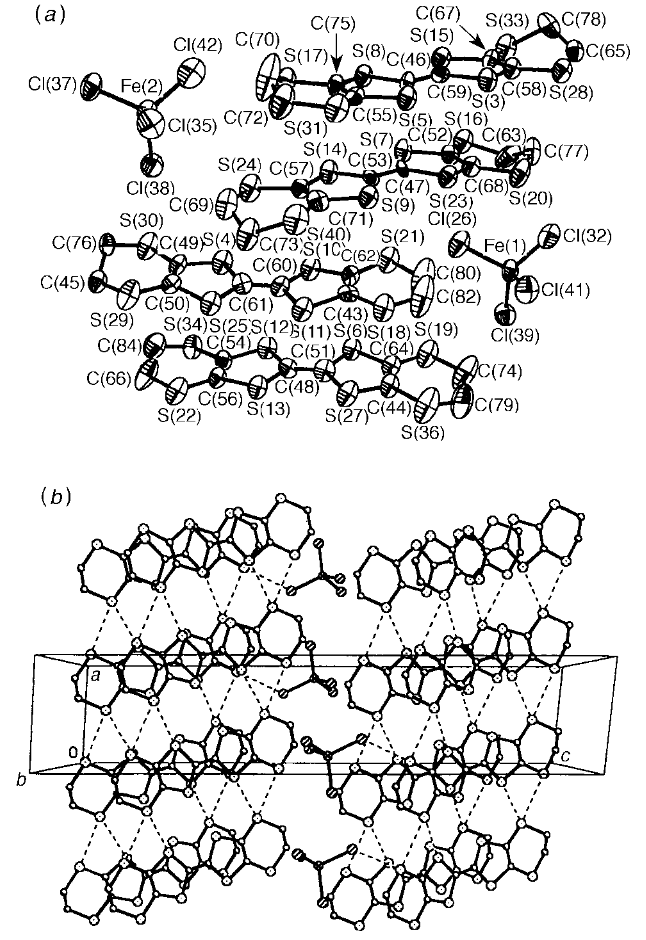

Fig. 1 (*a*) Atomic numbering of $(ET)_4(FeCl_4)_2$ **1**. (*b*) Projection diagram of $(ET)_4(FeCl_4)_2$ **1** along the *a* direction the side-by-side S···S intermolecular interactions.

charges of ET molecules in **1** of +1/2, +1/3, +1/3 and +2/3, respectively. In $(ET)_2FeCl_4$ prepared by Day by electrocrystallization the formal charges of two the ET molecules are both +1/2.[9] The structure of **1** consists of ET molecules separated by sheets of tetrahedral $[FeCl_4]$ anions [Fig. 1(*b*)] along the *c* direction. The anions are situated in the anion cavity formed by the ethylene groups of the ET molecules. Within the stacks the ET molecules are parallel with each other [Fig. 1(*b*)]. The intrastacking of ET molecules has only one mode with adjacent molecules stacking uniformly on top of each other along the long in-plane molecular axis with some displacement. However, there are two types of displacements, one is like the 'bond over ring' arrangement[10,11] but with the central C=C bond on the top of a six-membered ring, the other is where the central C=C crosses the five- and six-membered rings, while in $(ET)_2FeCl_4$ the intrastack packing mode alternates between the *a* and *c* modes.[9] The short S···S distances (<3.60 Å) between the ET stacks in **1** are observed in the *a* direction [S(6)···S(36) 3.418, S(8)···S(31) 3.521, S(10)···S(8) 3.528, S(14)···S(40) 3.494, S(16)···S(20) 3.572, S(16)···S(23) 3.469, S(18)···S(21) 3.508, S(19)···S(36) 3.494, S(29)···S(30) 3.462, S(25)···S(30) 3.358 Å]. Short S···Cl intermolecular interactions also exist between the ET stacks and the sheets of $FeCl_4$ [S(20)···Cl(32), 3.393, S(22)···Cl(37), 3.475 Å, both shorter than the sum of the van der Waals radii of S and Cl atoms of 3.65 Å].

One ET and one $FeCl_4$ anion exist in the asymmetric unit of **2**. The Fe—Cl bond lengths of the anion, 2.180(2)–2.186(2) Å confirm their identity as $[FeCl_4]$ as in **1**.[1,6,7] The bond length of the central C=C [C(1)—C(2)] in ET is 1.388(8) Å. According to corresponding bond lengths in other ET salts

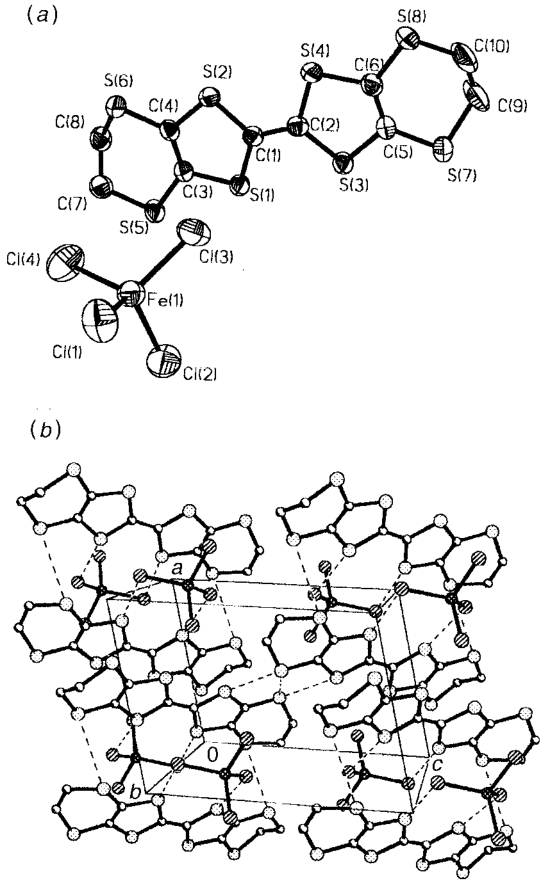

Fig. 2 (*a*) Atomic numbering of $(ET)FeCl_4$ **2**. (*b*) Projection diagram of $(ET)FeCl_4$ **2** along the *a* direction.

with established levels of oxidation,[8] the formal charge of this ET molecule is +1, *i.e.* ET is fully oxidized and will not show useful electrical properties. **2** is an analogue of $(ET)FeBr_4$,[9] and structural features of **2** are the same as $(ET)FeBr_4$, which lacks the stacks and planes of closely spaced ET molecules [Fig. 2(*b*)]. There are few short S···S intermolecular interactions between the ET molecules. Interactions between ET molecules *via* $FeCl_4$ anions are also impossible. The cell volume of $(ET)FeCl_4$ **2** is 1037.6(4) Å^3 with $Z=2$, while the volume of $(ET)FeBr_4$ is 1084.5 Å^3 with $Z=2$.[9] This means that the ET molecules in both compounds are separated to almost the same extent. These structural features are consistent with their insulating electrical behaviour.

The arrangement mode of the ET molecules in stacks can modify their interplanar separation which significantly affects the electronic properties. The difference of the stacking mode between $(ET)_4(FeCl_4)_2$ **1** and $(ET)_2FeCl_4$ should lead to different electronic properties. The room temperature conductivity of **1** is 10 S cm^{-1} and the temperature dependence of the relative resistivity of **1** is shown in Fig. 3. Compound **1** remains metallic from room temperature to 250 K and then undergoes a semiconducting transition with $E_a = 0.55$ eV. $(ET)_2FeCl_4$ shows semiconducting behavior from 160 to 300 K and its room temperature conductivity is 10^{-2} S cm^{-1} with $E_a = 0.21$ eV.[9] From the crystal structure data, $(ET)_4(FeCl_4)_2$ should show two dimensional conductivity along the *b* and *a* directions. However, because of the needle like crystal morphology we can not obtain any information on the anisotropy. $(ET)FeCl_4$ **2** is almost an insulator at room temperature with $\sigma = 10^{-4}$ S cm^{-1}.

The Fe, S and Cl spectra of $(ET)_4(FeCl_4)_2$ **1** are shown in Fig. 4(*a*), (*b*) and (*c*), respectively. The binding energies of Fe $2p_{3/2}$ in $NMe_4FeCl_4 \cdot 0.5H_2O$ **3** and $(ET)_4(FeCl_4)_2$ **1** are 711.1 and 710.6 eV respectively. From the change of binding energy

Table 2 Selected bond lengths (Å) of ET and $FeCl_4$ in $(ET)_4(FeCl_4)_2$ **1** and $(ET)FeCl_4$ **2**

1							
C(51)—C(48)	1.348(18)	S(6)—C(51)	1.746(13)	S(9)—C(53)	1.745(13)	S(7)—C(52)	1.748(13)
S(27)—C(51)	1.749(13)	S(12)—C(48)	1.746(13)	S(23)—C(68)	1.771(14)	S(9)—C(71)	1.749(14)
S(13)—C(48)	1.733(13)	S(6)—C(64)	1.757(14)	S(14)—C(57)	1.742(13)	C(52)—C(68)	1.330(19)
S(27)—C(44)	1.749(14)	S(12)—C(54)	1.754(13)	C(57)—C(71)	1.325(19)	C(46)—C(59)	1.344(17)
S(13)—C(56)	1.771(14)	C(44)—C(64)	1.324(19)	S(15)—C(59)	1.749(12)	S(3)—C(59)	1.755(13)
C(54)—C(56)	1.338(19)	C(60)—C(61)	1.371(17)	S(8)—C(46)	1.741(13)	S(5)—C46	1.757(13)
S(10)—C(60)	1.734(13)	S(11)—C(60)	1.760(13)	S(15)—C(67)	1.755(12)	S(3)—C(58)	1.756(13)
S(4)—C(61)	1.714(13)	S(25)—C(61)	1.745(13)	S(8)—C(75)	1.757(13)	S(5)—C(55)	1.773(12)
S(10)—C(62)	1.773(13)	S(11)—C(43)	1.776(13)	C(58)—C(67)	1.328(18)	C(55)—C(75)	1.333(19)
S(4)—C(49)	1.761(12)	S(25)—C(50)	1.757(13)	Fe(1)—C(126)	2.181(5)	Fe(1)—C(132)	2.177(5)
C(43)—C(62)	1.322(18)	C(49)—C(50)	1.345(18)	Fe(1)—C(141)	2.178(5)	Fe(1)—C(139)	2.208(5)
C(47)—C(53)	1.334(17)	S(7)—C(47)	1.750(14)	Fe(2)—C(135)	2.174(5)	Fe(2)—C(137)	2.189(5)
S(23)—C47	1.753(13)	C(14)—C(53)	1.728(13)	Fe(2)—C(142)	2.173(5)	Fe(2)—C(138)	2.211(5)
2							
S(1)—C(1)	1.721(6)	S(1)—C(3)	1.746(6)	S(8)—C(6)	1.744(6)	S(8)—C(10)	1.745(10)
S(2)—C(1)	1.718(6)	S(2)—C(4)	1.729(6)	C(1)—C(2)	1.388(8)	C(3)—C(4)	1.365(8)
S(3)—C(2)	1.714(6)	S(3)—C(5)	1.734(6)	C(5)—C(6)	1.352(8)	C(7)—C(8)	1.480(9)
S(4)—C(2)	1.720(6)	S(4)—C(6)	1.734(6)	C(9)—C(10)	1.278(12)	Fe(1)—Cl(1)	2.181(2)
S(5)—C(3)	1.731(6)	S(5)—C(7)	1.798(7)	Fe(1)—Cl(4)	2.180(2)	Fe(1)—Cl(3)	2.186(2)
S(6)—C(4)	1.740(6)	S(6)—C(8)	1.811(7)	Fe(1)—Cl(2)	2.181(2)		
S(7)—C(5)	1.742(6)	S(7)—C(9)	1.795(8)				

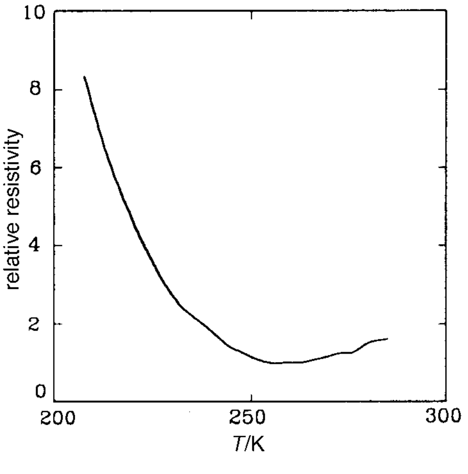

Fig. 3 Temperature dependence of the relative resistivity of $(ET)_4(FeCl_4)_2$ **1**

of Fe, the $FeCl_4$ anions may be reduced and the ET molecules oxidized after charge transfer. Although the formal charge of the anion is still -1 as stated previously, the binding energy of Fe in $(ET)_4(FeCl_4)_2$ **1** shows the actual oxidation state of Fe in the anions is in the range of 2–3, and close to $+3$ with Fe—Cl bond lengths similar to that of $[FeCl_4]$. Although there are two types of S atoms in the neutral ET molecule, they have the same binding energy (S $2p_{3/2} = 163.1$ eV). Two binding energies, however, are present in $(ET)_4(FeCl_4)_2$ **1** (S $2p_{3/2}$, 164.3, 165.6 eV). This suggests that charge transfer occurs in the tetrathiafulvalene and that the charge state difference between the two types of S atoms is increased. The binding energy of Cl $2p_{3/2}$ in $NMe_4FeCl_4 \cdot 0.5H_2O$ **3** is 198.6 eV whereas in $(ET)_4(FeCl_4)_2$ **1**, $E_B = 197.8$ and 199.4 eV. There should be two types of Cl atoms in $(ET)_4(FeCl_4)_2$ **1**. One binding energy should be smaller than that in $NMe_4FeCl_4 \cdot 0.5H_2O$ **3**. This may be the result of not only charge transfer between ET molecules and anions but also the intermolecular interactions *via* short Cl···S and Cl···H contacts as mentioned above. In the short Cl···S and Cl···H contacts, since Cl is more electronegative, its cloud may become denser and its binding energy will decrease.

Conclusion

We have synthesized $(ET)_4(FeCl_4)_2$ **1** and $(ET)FeCl_4$ **2** by a diffusion method and their single crystal structures have been

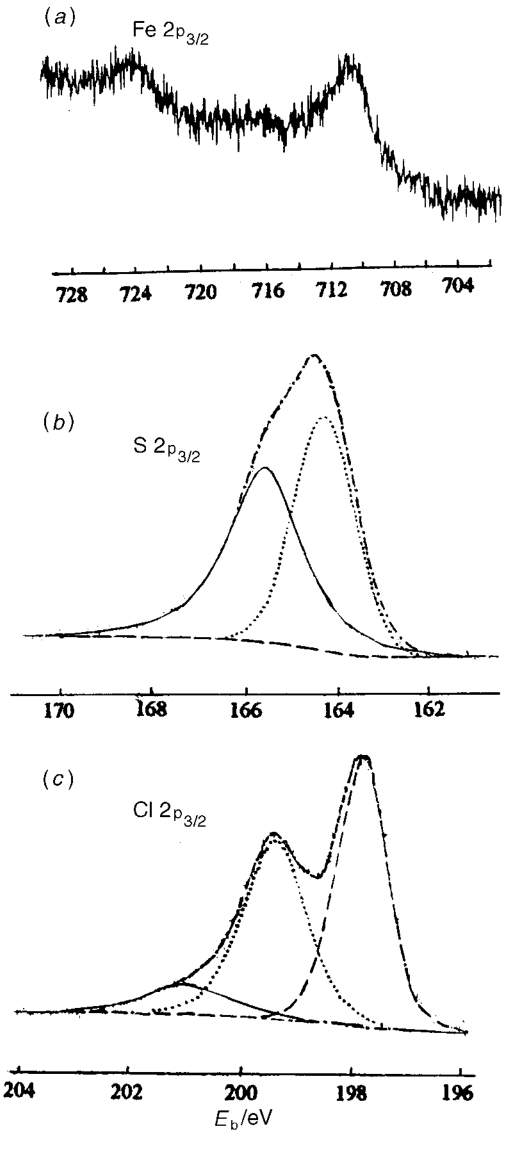

Fig. 4 XP spectra of $(ET)_4(FeCl_4)_2$ **1**: (*a*) Fe (*b*) S and (*c*) Cl

solved. Their electric properties and the XP spectra of $(ET)_4(FeCl_4)_2$ **1** have also been measured. Research work of other physical properties of these salts is in progress.

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