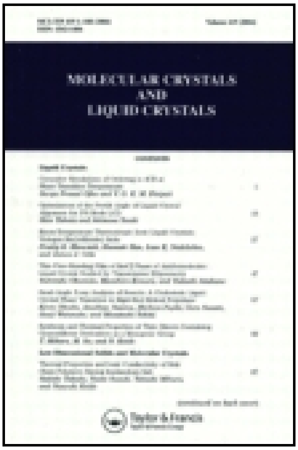

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New Molecular Conductors Containing Magnetic Tetrahedral Anion, $(DIETS)_2FeX_4$ and $(DIETS)FeX_4$: [DIETS = Diiodo-Ethylenedithiodithiadiselenafulvalene, X = Cl, Br]

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NEW MOLECULAR CONDUCTORS CONTAINING MAGNETIC TETRAHEDRAL ANION, $(DIETS)_2FeX_4$ AND $(DIETS)FeX_4$: [DIETS = DIIODO-ETHYLENEDITHIODITHIADISELENAFULVALENE, X = Cl, Br]

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Abstract In the crystals of new molecular conductors constructed by the Iodine-bonded π-donor DIETS (diiodo-ethylenedithiodithiadiselenafulvalene) and magnetic anions FeX_4^- [X = Cl, Br] with tetrahedral symmetry, the unique –I···X– cation···anion interactions provide a variety of crystal structures.

INTRODUCTION

One of the current interest in the research for the molecular based conducting material is how to control their molecular arrangements that are closely connected to their physical properties. To control molecular arrangements in donor-based molecular conductors, it is necessary to consider not only donor···donor interactions but also donor···anion interactions. From this viewpoint, we have proposed introducing the *strong* and *directional* –I···X– (X = CN, Br or S) type cation···anion interactions into molecular conductors.[1-3] A model of such intermolecular interactions is the *strong* and *directional* intermolecular –I···NC– interaction which constructs the one-dimensional chain structure in the crystal of *p*-iodobenzonitrile.[4,5] We have already shown some examples of the well-controlled crystal structures using linear[1] or square planer anions[3] containing cyano groups, halogeno anions[1] or transition metal complexes.[2] In contrast to these linear or planar counter anions, the tetrahedral anion would be promising other new modes of the molecular arrangements. In fact, in the crystal engineerings in the crystals of the neutral molecules,[6] tetrahedral components are useful parts to construct three-dimensional intermolecular contacts.[7] On the other hand, the molecular conductor that has both itinerant π-electrons and localized magnetic moments is one of the current interest.[8] Thus, when the central atom of the tetrahedral anion has localized magnetic moments, donor···anion contacts would bring about not only specific molecular arrangements but also an interaction pathway between the itinerant π-electrons and the localized spins. In this paper, we report four new molecular conductors, $(DIETS)_2FeX_4$ and $(DIETS)FeX_4$ [DIETS=diiodo-ethylenedithiodithiadiselenafulvalene, X = Cl, Br], and their conducting properties that are closely related to their molecular arrangements.

RESULTS AND DISCUSSION

New cation radical salts are obtained by galvanostatic oxidation (0.4-0.6 μA) of a solution containing DIETS[3] (*ca.* 8 mg) and Bu_4NFeX_4 [X = Cl or Br] (*ca.* 15-20 mg) with Pt electrodes in chlorobenzene (20 ml) under argon atmosphere at 20 °C.

In the case of X = Cl, two types of crystals, fine needles and blocks, were obtained. The electrical resistivity of the needle-shaped crystal is metallic down to 4.2 K (Figure1) and the block-shaped crystal is semiconductive (ρ_{rt} ~4×10^3 Ωcm, Ea ~0.2 eV). X-ray diffraction studies[9] have revealed that the donor-anion ratio for the needle is 2:1 and that for the block is 1:1 respectively (Table I). In the crystal of the 2:1 salt, the DIETS molecules exhibit alternating stack along the crystallographic *a* axis. Figure 2 shows the

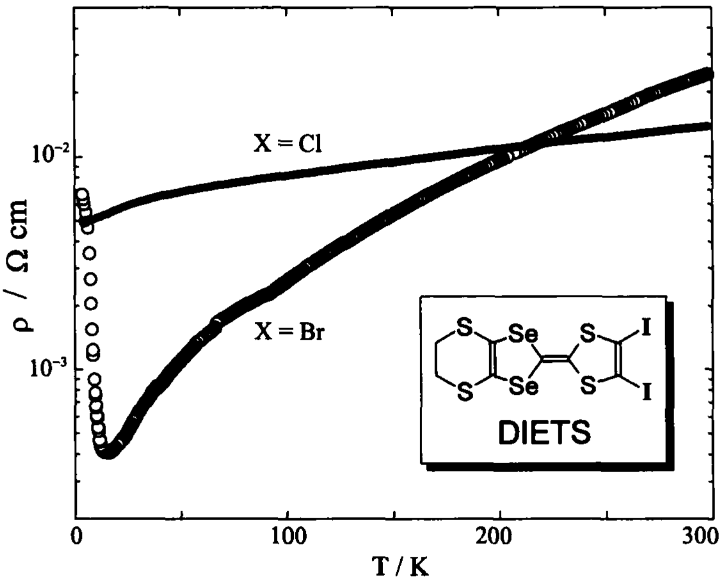

FIGURE 1 Temperature dependence of the resistivity for $(DIETS)_2FeX_4$ [X = Cl, Br].

TABLE I Crystal data of (DIETS)$_2$FeX$_4$ and (DIETS)FeX$_4$ [X = Cl, Br].

	(DIETS)$_2$FeCl$_4$	(DIETS)FeCl$_4$	(DIETS)$_2$FeBr$_4$	(DIETS)FeBr$_4$
Shape	needle	block	rod	block
Crystal system	triclinc	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	Ibam	$P\bar{1}$
a / Å	8.034(8)	8.908(3)	7.310(1)	8.879(2)
b / Å	14.48(1)	10.683(3)	36.238(4)	10.937(2)
c / Å	17.69(2)	11.103(5)	13.673(2)	11.427(2)
α / degree	104.4(1)	92.99(5)		90.69(1)
β / degree	100.8(1)	99.48(3)		100.64(1)
γ / degree	102.3(1)	93.25(4)		92.62(1)
V / Å^3	1883(3)	1038.4(7)	3622.1(7)	1089.3(6)
Z	2	2	4	2
No. of observed reflections	2167 ($I \geq 3\sigma(I)$)	3525 ($I \geq 3\sigma(I)$)	2091 ($I \geq 3\sigma(I)$)	3030 ($I \geq 4\sigma(I)$)
No. of Unique	2174	3545	2102	3216
R, R$_W$	0.064, 0.073	0.065, 0.076	0.039, 0.045	0.079, 0.094

three-dimensional donor···anion network in (DIETS)$_2$FeCl$_4$. There exist four kinds of short I···Cl distances d1-d4 (3.28(2) Å-3.62(1) Å) among the DIETS molecules and FeCl$_4$ anions. These distances are more than 3-12% shorter than the sum of the van der Waals radii (3.73 Å: *Bondi*, 3.95Å: *Pauling*) and this characteristic shortening indicates an existence of the strong intermolecular –I···Cl– interactions between donor molecules and counter anions. Similar strong intermolecular –I···Cl– interactions also exist in the crystal of the 1:1 salt (Figure 3) which is isostructural with (ET)FeBr$_4$ [ET = bis(ethylenedithio)tetrathiafulvalene].[10]

In the case of X = Br, two types of crystals, rods and blocks, were obtained as the case of X = Cl. In most experiments, we obtained only the block-shaped crystals. A few number of rods were occasionally mixed. The electrical resistivity of the rod-shaped crystal is metallic down to ~15 K (Figure 1) and then shows sharp metal-semiconductor transition. The block-shaped crystal is semiconductive from room temperature (ρ_{rt}~4× 10^3 Ωcm, Ea ~0.2 eV). X-ray diffraction studies have revealed that the donor-anion ratio for the rod is 2:1 and that for the block is 1:1 (Table I). The metallic 2:1 salt crystallizes

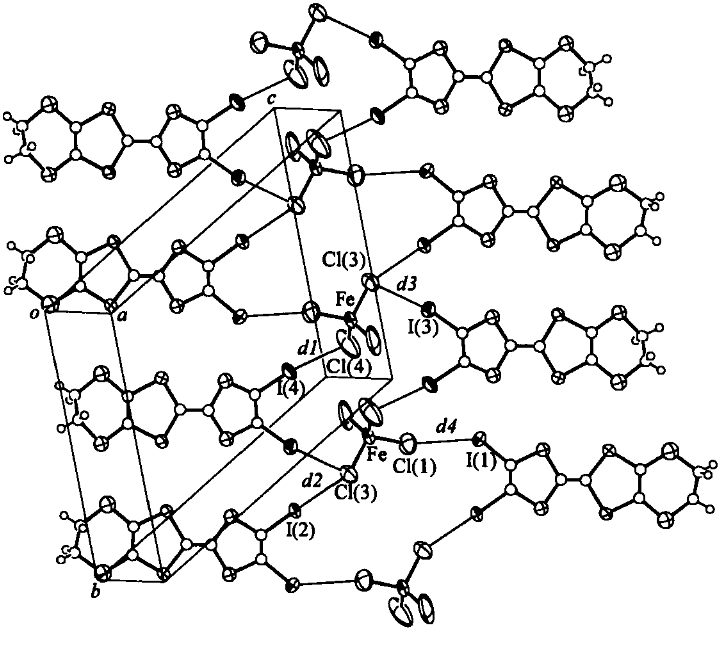

FIGURE 2 Three-dimensional donor···anion network in $(DIETS)_2FeCl_4$; *d1* = 3.28(2) Å, *d2* = 3.45(1) Å, *d3* = 3.52(1) Å, *d4* = 3.62(1) Å.

in the space group Ibam. The DIETS molecules are stacked alternatively along the *a* axis. Four donor molecules are connected by one anion through the intermolecular –I···Br– interaction (Figure 4). This interaction constructs a infinite chain along the crystallographic *c* axis. The short –I···Br– distance between the donor molecule and the counter anion is 3.629(1) and is 5-10% shorter than the sum of the van der Waals radii

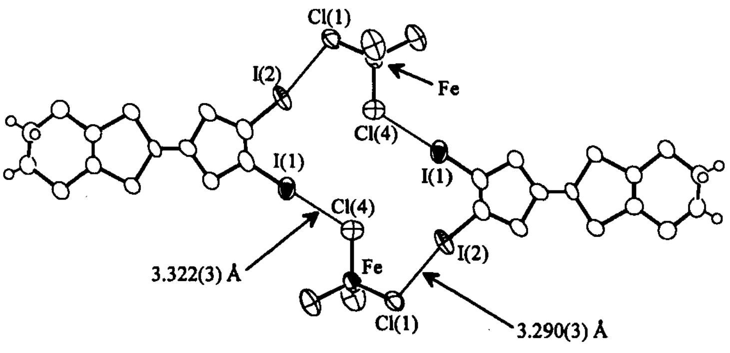

FIGURE 3 Ring-like structure of $(DIETS)FeCl_4$.

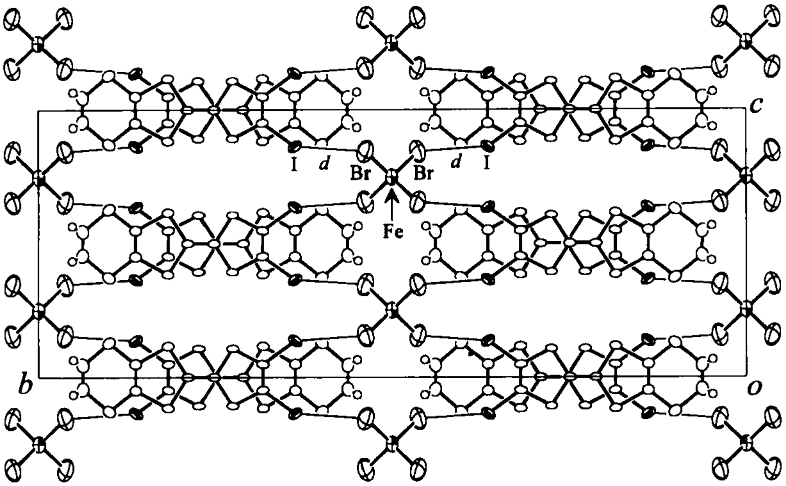

FIGURE 4 Packing diagram of $(DIETS)_2FeBr_4$. The short intermolecular I···Br distance $d = 3.629(1)$ Å.

(3.83 Å: *Bondi*; 4.05 Å: *Pauling*). Crystal structure of $(DIETS)FeBr_4$ is isostructural with that of $(DIETS)FeCl_4$ and there also exist two kinds of short –I···Br– contacts between the donor molecule and the counter anion.

In all four salts, a ring-like repetition unit composed of two donor molecules and two counter anions is formed by the strong intermolecular –I···X– interactions (for example, see Figure 3). In the 1:1 salt, the ring-like unit is isolated from each other. On the other hand, in the 2:1 salts, the ring-like units are fused along the side-by-side direction of the donor molecules to make infinite chains. These varieties of the packing pattern have not been seen in the crystals containing linear or planar counter anions.

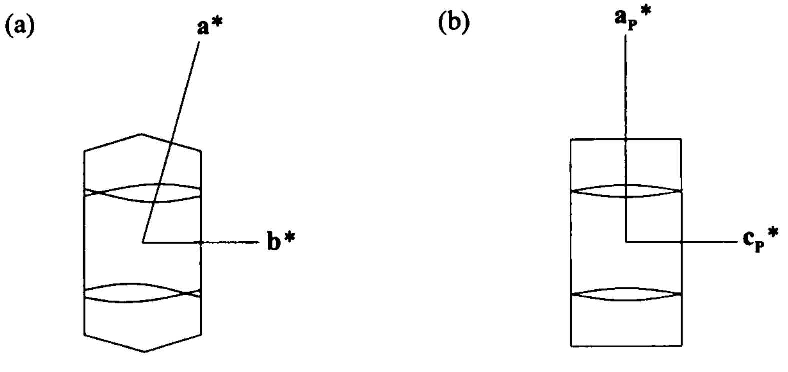

FIGURE 5 Calculated Fermi surfaces: (a) $(DIETS)_2FeCl_4$; (b) $(DIETS)_2FeBr_4$: body-centered cell is reduced to the primitive one as $a_P = a$, $b_P = (a+b+c)/2$, $c_P = c$.

In the two metallic 2:1 FeX_4 salts, intermolecular overlap integrals of HOMO's in DIETS indicate weak inter-column interactions (~1/40–1/6 of the intra-column interactions). Simple tight-binding band calculations indicate that there exist two pairs of quasi one-dimensional opened Fermi surfaces both for the $FeCl_4$ salt and for the $FeBr_4$ salt (Figure 5). At present, low yield of the 2:1 salts has hindered the study of the magnetic properties. Possibility of the interaction between the itinerant π-electrons on the donor molecules and the localized spins on the Fe atoms in the counter anions through the characteristic –I···X– short contacts in the 2:1 salts is under investigations.

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REFERENCES

1. T. Imakubo, H. Sawa and R. Kato, Synth. Met., 73, 117 (1995).
2. T. Imakubo, H. Sawa and R. Kato, J. Chem. Soc., Chem. Commun., 1097 (1995).
3. T. Imakubo, H. Sawa and R. Kato, J. Chem. Soc., Chem. Commun., 1667 (1995).
4. E. O. Schlemper and D. Britton, Acta. Crystallogr., 18, 419 (1965).
5. G. R. Desiraju and R. L. Harlow, J. Am. Chem. Soc., 111, 6757 (1989).
6. G. R. Desiraju, Crystal Engineering: The Design of Organic Solids (Elsevier, Amsterdam, 1989).
7. For example, B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, Nature, 369, 727 (1995) and references cited therein.
8. M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse and P. Guionneau, J. Am. Chem. Soc., 117, 12209 (1995) and references cited therein.
9. X-ray diffraction data were collected on a MAC Science automatic four-circle diffractometer for $(DIETS)_2FeBr_4$, or MAC Science DIP 320S imaging-plate system for other three salts with monochromated Mo K_α (λ = 0.71069 Å) radiation up to 2θ = 60°. The intensities were corrected for Lorentz and polarization effects. The analytical absorption correction was carried out for $(DIETS)_2FeBr_4$. The structures were solved by the direct method and refined with full-matrix least-squares method. Anisotropic thermal parameters were used for non-hydrogen atoms except for $(DIETS)_2FeCl_4$. All calculations were performed with use of a 'teXsan' program package of MSC.
10. T. Mallah, C. Hollis, S. Bott, M. Kurmoo, P. Day, M. Allan and R. H. Friend, J. Chem. Soc., Dalton Trans., 859 (1990).