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Structural and electrical properties of (BEDT-TTF)$_2$X(diiodoacetylene) (X = Cl, Br): the novel self-assembly of neutral Lewis-acidic molecules and halide anions in a molecular metal

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A neutral Lewis-acidic molecule, diiodoacetylene, forms one-dimensional chains with halide anions (Cl^- and Br^-) and affects the donor (BEDT-TTF) arrangement in the cation radical salts, which exhibit metallic resistivity behaviour down to 1.6 K.

In the field of molecular conductors, three-component systems such as (BEDT-TTF)$_2$[M(CF$_3$)$_4$](trihaloethane) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; M = Cu, Ag, Au][1] have attracted much attention because the third (neutral) component (trihaloethane in this example) affects the crystal structure and thus tunes its physical properties. In many cases, however, the third component comes from the solvent used for the crystal growth and is incorporated incidentally. The solvent molecules tend to be packed loosely and are often disordered. In order to produce a well-organized architecture for the three-component system, a more rational method for the introduction of neutral molecules into the molecular conductors is required.

Electron-deficient neutral molecules with halogen atoms can form complexes with Lewis bases such as halide anions. Recently, Ghassemzadeh *et al.* revealed that diiodoacetylene (DIA) and halide anions generate two-dimensional networks by this type of acid–base interaction.[2] This self-assembly should be applicable to the formation of new architectures for molecular conductors. We report here the novel self-assembly of this iodine-substituted neutral molecule and halide anion in the crystals of metallic cation-radical salts.

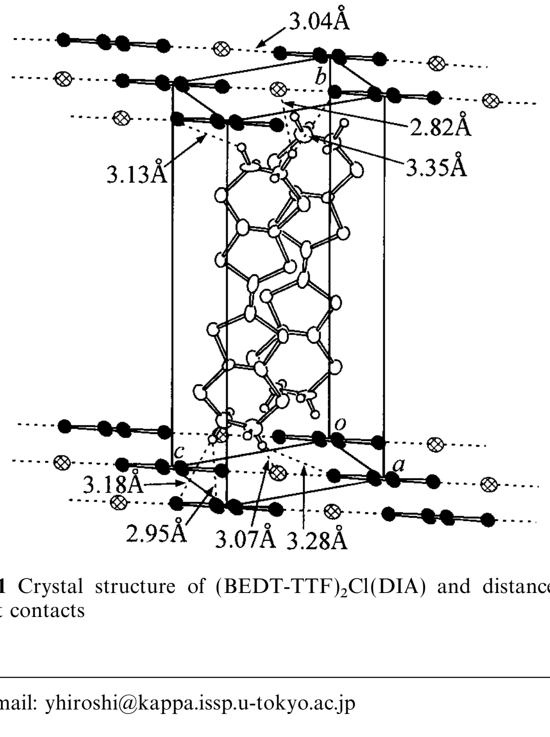

Fig. 1 Crystal structure of (BEDT-TTF)$_2$Cl(DIA) and distances of short contacts

Dark brown plates of (BEDT-TTF)$_2$X(DIA) (X = Cl, Br) were obtained by galvanostatic oxidation of a solution containing BEDT-TTF (*ca.* 8 mg), DIA (*ca.* 90 mg) and tetraphenylphosphonium chloride (*ca.* 30 mg: X = Cl) or tetra(*n*-butyl)ammonium bromide (*ca.* 30 mg: X = Br) in chlorobenzene (20 ml) under argon atmosphere at 45 °C. A standard H-shaped cell and platinum electrodes (1 mm diameter) were used. A constant current (1.0 μA) was applied for 7 days. X-Ray structure analyses were performed on these cation-radical salts.‡ The crystal structure of (BEDT-TTF)$_2$Cl(DIA) (Cl salt) is shown in Fig. 1. The Br salt is isomorphous with the Cl salt. The two donor molecules in the unit cell are interrelated by an inversion centre, and both Cl^- and DIA are on inversion centres. There is no positional disorder in the terminal ethylenedithio fragments of the donor molecule. The donor arrangement resembles the β″-type, but is not the same.[3]

The most striking feature of this crystal is the one-dimensional (1D) chains constructed from DIA molecules and halide anions, with the DIA molecules and Cl^- anions alternating along the chains. The interatomic Cl···I distance [3.041(1) Å] is noticeably shorter than the sum [3.65 or 3.82 Å] of the anion radius of Cl^- (1.67 Å)[4] and the van der Waals radius of iodine [1.98 (Bondi)[5] or 2.15 Å (Pauling)[6]]. This characteristically short distance should originate from a strong acid–base interaction. In the Br salt, a similar characteristic structure and interatomic distances are also observed [I···Br: 3.154(1); $r(Br^-)+r(I) = 3.80$ (Bondi) or 3.97 Å (Pauling)].

The donor molecules fit into the channels formed by the 1D chains of DIA and Cl^- along the '*a*–*c*' direction (Fig. 2). The C—C bonds of the terminal ethylene groups of BEDT-TTF

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‡ X-Ray diffraction data were collected on a MAC Science automatic four-circle diffractometer (MXC18) with graphite-monochromated Mo-Kα radiation up to $2\theta = 55°$. The intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares methods using reflections with $I \geqslant 3\sigma(I)$. Analytical absorption correction was carried out. Anisotropic thermal parameters were used for non-hydrogen atoms. All calculations were performed with use of 'teXsan' crystallographic software package of Molecular Structure Co.

Crystal data for (BEDT-TTF)$_2$Cl(DIA): $C_{22}S_{16}H_{16}I_2Cl$, $M_W = 1082.59$, triclinic, space group $P\bar{1}$, $a = 7.642(3)$, $b = 17.477(6)$, $c = 6.728(3)$ Å, $\alpha = 99.49(3)$, $\beta = 104.90(3)$, $\gamma = 83.20(3)°$, $V = 853.8(6)$ Å^3, $Z = 1$, $D_c = 2.105$ g cm^{-3}, $R = 0.095$, $R_w = 0.093$, 4257 reflection measured, of which 3438 used [$I > 3\sigma(I)$].

Crystal data for (BEDT-TTF)$_2$Br(DIA): $C_{22}S_{16}H_{16}I_2Br$, $M_W = 1127.04$, triclinic, space group $P\bar{1}$, $a = 7.743(1)$, $b = 17.651(2)$, $c = 6.739(9)$ Å, $\alpha = 99.82(1)$, $\beta = 106.90(1)$, $\gamma = 82.39(1)°$, $V = 864.9(2)$ Å^3, $Z = 1$, $D_c = 2.164$ g cm^{-3}, $R = 0.079$, $R_w = 0.078$, 3966 reflection measured, of which 2935 used [$I > 3\sigma(I)$].

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 1145/69.

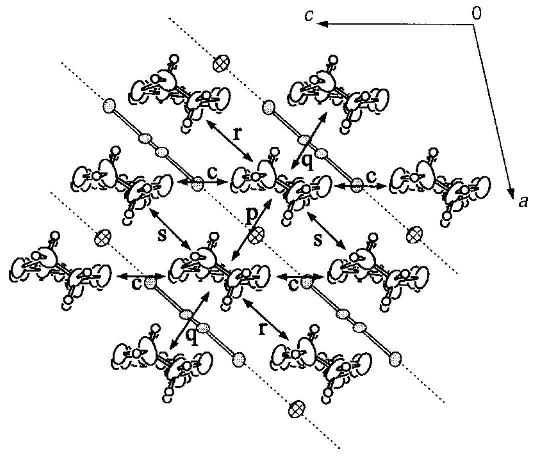

Fig. 2 Crystal packing viewed along the *b* axis. Overlap integrals ($S/10^{-3}$) are as followings: $S(c)=2.45$, $S(p)=-1.56$, $S(q)=-1.45$, $S(r)=-8.85$, $S(s)=-8.94$ for the Cl salt; $S(c)=2.18$, $S(p)=-2.17$, $S(q)=-1.89$, $S(r)=-8.50$, $S(s)=-8.59$ for the Br salt.

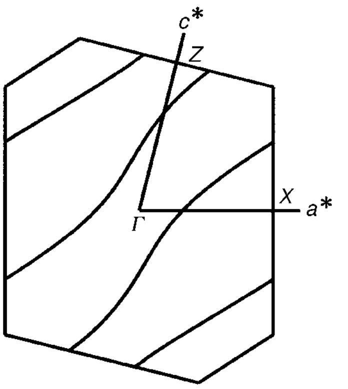

Fig. 3 Fermi surface of $(BEDT\text{-}TTF)_2Cl(DIA)$

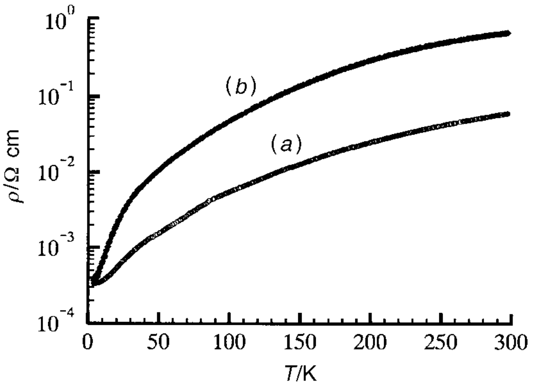

Fig. 4 Temperature dependence of resistivity along the *c* axis (the most grown axis) for $(BEDT\text{-}TTF)_2X(DIA)$; (*a*) X=Cl and (*b*) X=Br

are almost parallel to the 1D chain. Several distances between hydrogen atoms and iodine atoms or chloride anion are short enough to be regarded as van der Waals contacts (Fig. 1). These short contacts stabilize the crystal structure thermodynamically.[7] This stabilization effect seems to align BEDT-TTF molecules parallel to the 1D chain. It should be noted that in β-$(BEDT\text{-}TTF)_2X$ salts (X^- = linear triatomic anion) the weak C—H···X contacts arrange the X^- anion almost perpendicular to the donor plane.[8]

Overlap integrals of the HOMOs of the donor molecules are shown in Fig. 2. Two strong interactions (r and s) are observed along the direction parallel to the 1D chain. An interaction in this direction is also strong in the β″-type salts. In the β″-type salts, however, donor molecules along this direction repeat by a unit translation *c*. The Fermi surface calculated by the tight-binding method is rather one-dimensional (Fig. 3). On the other hand, the Fermi surface of the β″-type consists of one- and two-dimensional components.

Fig. 4 shows the temperature dependence of the d.c. resistivities (ρ) of the single crystals measured by a standard four-probe method. Both Br and Cl salts remain metallic down to 1.6 K. The ρ (room temp.)/ρ(4.2 K) ratio is fairly large for the Br salt (*ca.* 1500).

It should be noted that conventional BEDT-TTF salts with halide anions (Cl, Br) frequently crystallize from unrelated electrolytes or solvents (*e.g.* $CoCl_4^-$, CH_2Cl_2) and contain water molecules.[8] The structural properties of all of these salts are different from those of our system, and these salts exhibit a metal–insulator transition at low temperatures.

In summary, we have prepared molecular metals with a novel polymeric configuration based on halide anions and *neutral* Lewis-acidic molecules. Among polymeric anion layers, this type of self-assembly possesses an advantage over conventional ones such as $Cu^+[N(CN)_2^-]Br^-$,[9] because there is no need to adjust the charge in designing the polymeric framework. In addition, the physical and chemical properties of the neutral molecule (for example, electronic polarization of soft iodine atoms in DIA), which can be tuned by the choice of functional groups and molecular shape, should open new possibilities for molecular conductors.

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