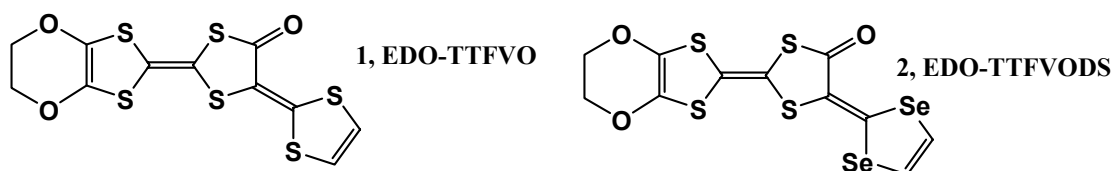


## Crystal Structures and Conducting/Magnetic Properties of Magnetic Molecular Conductors of EDO-TTFVODS

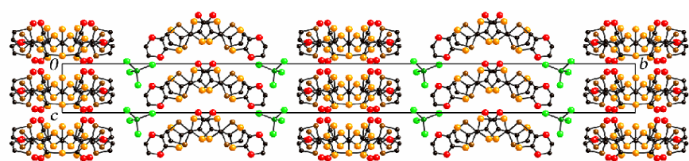
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Very recently, we observed both a metallic behavior down to 0.3 K and an antiferromagnetic ordering of Fe(III)  $d$  spins near 3 K in a 2:1 salt of EDO-TTFVO (**1**) with  $\text{FeCl}_4^-$  ion. The magnetoresistance results suggested a significant  $\pi$ - $d$  interaction. We now noticed a new donor molecule substituted by a 1,3-diselenole ring in place of a 1,3-dithiole ring in **1** (EDO-TTFVODS, **2**), since for the HOMO of **2** large AO coefficients appear at the two Se atoms in the 1,3-diselenole ring in addition to the central four S atoms. This paper reports the synthesis of **2**, and the crystal structures and conducting/magnetic properties of several salts of **2** with  $\text{FeCl}_4^-$  and  $\text{FeBr}_4^-$  ions.

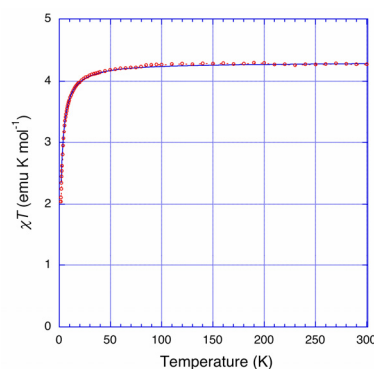


According to the previous method, **2** was synthesized and isolated as red crystals (mp: 193-194 °C) by recrystallization from  $\text{CS}_2/n$ -hexane. The molecular skeleton of **2** is almost planar, as evidenced by the small dihedral angles between the neighboring two rings. The redox potentials of **2** measured in benzonitrile at 25 °C were 0.61 and 0.91 V vs. Ag/AgCl and almost the same to those of **1** (0.60 and 0.89 V).

Electrochemical oxidation of **2** in the presence of  $\text{TBA}\cdot\text{FeCl}_4$  in chlorobenzene/ethanol (9:1, v/v) gave black needle-like crystals of  $\text{2}_2\cdot\text{FeCl}_4$ . In the crystal structure (Figure 1), three crystallographically-independent donor molecules are present. There are two different kinds of donor motif, and one motif is ordered and the other disordered. Both of them form a  $\beta$ -type packing. On the other hand, the  $\text{FeCl}_4^-$  ions intervene between the donor layers and are aligned in a uniform manner along the  $b$  axis. The  $\text{Cl}\cdots\text{Cl}$  (4.08 Å) distances between the neighboring  $\text{FeCl}_4^-$  ions are much longer than the van der Waals contact distance, and the  $\text{FeCl}_4^-$  ions also have almost no contact with the neighboring donor molecules. As expected from such a crystal structure, the SQUID measurement (Figure 2) showed that the Fe(III)  $d$  spins of  $\text{FeCl}_4^-$  ions are subject to very weak antiferromagnetic interaction ( $\theta = -1.5$  K).

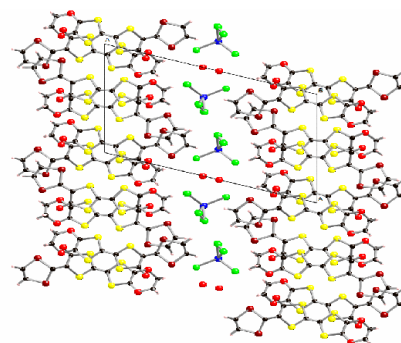


**Figure 1.** Crystal structure of  $\text{2}_2\cdot\text{FeCl}_4$



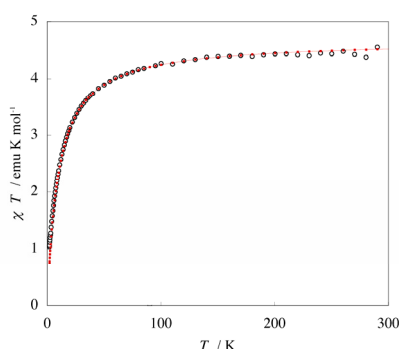
**Figure 2.** Temperature dependence of  $\chi T$  in the temperature range of 1.9–300 K. A solid line shows a Curie-Weiss fitting curve with Curie constant  $C = 4.42 \text{ emu K mol}^{-1}$  and Weiss temperature  $\theta = -1.5 \text{ K}$ .

By electrochemical oxidation of **2** in the presence of TBA•FeBr<sub>4</sub> in chlorobenzene/ethanol (9:1, v/v) were isolated two kinds of crystals. One was a black needle-like crystal and the other a black plate-like crystal. The crystal structure of the needle-like crystal is shown in Figure 3, and the composition of the salt is **2**<sub>2</sub>•(FeBr<sub>4</sub>)•(H<sub>2</sub>O). On the other hand, the plate-like crystal has a composition of **2**<sub>6</sub>•(FeBr<sub>4</sub>)<sub>2</sub>•(chlorobenzene). However, the donor motifs of the two salts are almost the same to each other. The donor molecule array of the two salts resembles a β''-type packing motif. In the **2**<sub>2</sub>•(FeBr<sub>4</sub>)•(H<sub>2</sub>O) salt, the FeBr<sub>4</sub><sup>-</sup> ions formed a two-dimensional rectangular arrangement with a short Br••Br contact (3.52 Å) along *b* axis. In addition, there were some short Br••Se contacts between the donor molecule and the FeBr<sub>4</sub><sup>-</sup> ion, suggesting a possibility of a strong π-*d* interaction by virtue of the bent molecular structure of **2**. MO calculations predict a large *d-d* interaction,  $J_{dd} = 2.77$  K and a moderate π-*d* interaction,  $J_{\pi d} = 3.69$  K. The magnetic measurement of the 2:1 salt is in progress. In the **2**<sub>6</sub>•(FeBr<sub>4</sub>)<sub>2</sub>•(chlorobenzene) the occupation ratio of the FeBr<sub>4</sub><sup>-</sup> ion and the chlorobenzene molecule is 0.66 : 0.34. The FeBr<sub>4</sub><sup>-</sup> ions formed a two-dimensional rectangular arrangement with a short Br••Br contact (3.40 Å) along *b* axis. In addition, there were some short Br••Se contacts between the donor molecule and the FeBr<sub>4</sub><sup>-</sup> ion. The SQUID measurement of the 3:1 salt (Figure 4) showed that the Fe(III) *d* spins are subject to strong antiferromagnetic interaction ( $\theta = -9.9$  K). However, an antiferromagnetic ordering of the Fe(III) *d* spins could not be recognized down to 1.9 K.

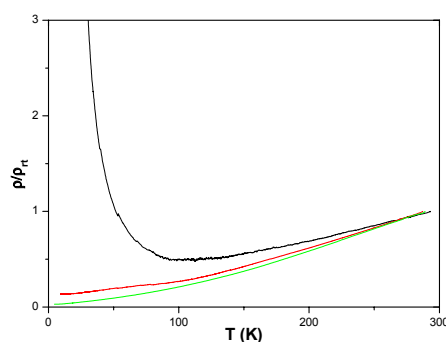


**Figure 3.** Crystal structure of **2**<sub>2</sub>•(FeBr<sub>4</sub>)•(H<sub>2</sub>O)

Electrical resistivities of **2**<sub>2</sub>•FeCl<sub>4</sub>, **2**<sub>2</sub>•(FeBr<sub>4</sub>)•(H<sub>2</sub>O) and **2**<sub>6</sub>•(FeBr<sub>4</sub>)<sub>2</sub>•(chlorobenzene) were measured down to 4.2 K (Figure 5), and their conductivities were 25, 25 and 10 S cm<sup>-1</sup> at room temperature, respectively. For the **2**<sub>2</sub>•FeCl<sub>4</sub> salt a metal-to-insulator transition occurred near 80 K. On the other hand, for the two FeBr<sub>4</sub> salts metallic behaviors were kept down to 4.2 K. This stabilization of metallic state is considered to originate from the achievement of a two-dimensional Fermi surface by the introduction of an ethylenedioxy group.



**Figure 4.** Temperature dependence of  $\chi T$  in the temperature range of 1.9–300 K. A solid line shows a Curie-Weiss fitting curve with  $C = 4.67$  emu K mol<sup>-1</sup> and  $\theta = -9.9$  K.



**Figure 5.** Temperature dependence of  $\rho/\rho_{300}$  down to 4.2 K for **2**<sub>2</sub>•FeCl<sub>4</sub> (black), **2**<sub>2</sub>•(FeBr<sub>4</sub>)•(H<sub>2</sub>O) (red) and **2**<sub>6</sub>•(FeBr<sub>4</sub>)<sub>2</sub>•(chlorobenzene) (green)