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 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 FeCl\(_4^-\) and FeBr\(_4^-\) ions.

According to the previous method, 2 was synthesized and isolated as red crystals (mp: 193-194 °C) by recrystallization from 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 TBA•FeCl\(_4\) in chlorobenzene/ethanol (9:1, v/v) gave black needle-like crystals of 2•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 FeCl\(_4^-\) ions intervene between the donor layers and are aligned in a uniform manner along the \( b \) axis. The Cl•••Cl (4.08 Å) distances between the neighboring FeCl\(_4^-\) ions are much longer than the van der Waals contact distance, and the 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 FeCl\(_4^-\) ions are subject to very weak antiferromagnetic interaction (\( \theta = -1.5 \) K).

**Figure 1.** Crystal structure of 2•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 \( C = 4.42 \) emu K mol\(^{-1}\) and Weiss temperature \( \theta = -1.5 \) K.
By electrochemical oxidation of 2 in the presence of TBA•FeBr₄ 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•(FeBr₄)•(H₂O). On the other hand, the plate-like crystal has a composition of 2•(FeBr₄)₂•(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•(FeBr₄)•(H₂O) salt, the FeBr₄⁻ 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 FeBr₄⁻ 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, Jₕd = 2.77 K and a moderate π-d interaction, Jπd = 3.69 K. The magnetic measurement of the 2:1 salt is in progress. In the 2•(FeBr₄)₂•(chlorobenzene) the occupation ratio of the FeBr₄⁻ ion and the chlorobenzene molecule is 0.66 : 0.34. The FeBr₄⁻ 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 FeBr₄⁻ ion. The SQUID measurement of the 3:1 salt (Figure 4) showed that the Fe(III) d spins are subject to strong antiferromagnetic interaction (θ = -9.9 K). However, an antiferromagnetic ordering of the Fe(III) d spins could not be recognized down to 1.9 K.

Electrical resistivities of 2•FeCl₄, 2•(FeBr₄)•(H₂O) and 2•(FeBr₄)₂•(chlorobenzene) were measured down to 4.2 K (Figure 5), and their conductivities were 25, 25 and 10 S cm⁻¹ at room temperature, respectively. For the 2•FeCl₄ salt a metal-to-insulator transition occurred near 80 K. On the other hand, for the two FeBr₄ 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.