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New Molecular Conductors, α- and β-(EDT-TTF)[Ni(dmit)$_2$] Metal with Anomalous Resistivity Maximum vs. Semiconductor with Mixed Stacks

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Two donor-acceptor type molecular conductors, α- and β-(EDT-TTF)[Ni(dmit)$_2$] (EDT-TTF = ethylenedithiotetrathiafulvalene, dmit = 4,5-dimercapto-1,3-dithiole-2-thione) have been electrochemically obtained. The α-form has a segregated column structure and is a metal with an anomalous resistivity maximum around 14 K. The curve-fitting analysis of the polarized reflectance spectra shows a small anisotropy of the oscillator strength in the ab plane. The β-form is a semiconductor with a mixed-stacking structure.

The metal-dmit (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) complexes form various highly-conducting molecular systems with closed shell monocations or with organic cation radicals. Some of them have exhibited superconductivity.$^{1,2)}$ The organic donor EDT-TTF (ethylenedithiotetrathiafulvalene) is a hybrid between TTF and BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) molecules, and its homolog, MDT-TTF (methylenedithiotetrathiafulvalene), has provided the superconducting salt.$^{3)}$ In this paper we report that the coupling of Ni(dmit)$_2$ and EDT-TTF has given two conducting 1:1 salts. The one remains metallic down to 4.2 K, and the other is a semiconductor. They have been characterized by X-ray diffraction, conductivity measurements, reflectance spectroscopy, and tight-binding band calculations.

Single crystals of α- and β-(EDT-TTF)[Ni(dmit)$_2$] were electrochemically obtained. The galvanostatic (1 μA) anodic oxidation of EDT-TTF (10 mg) and (n-Bu)$_4$N[Ni(dmit)$_2$] (100 mg) in acetonitrile (20 ml) was performed under N_2 using the Pt wire electrodes. Crystal data are : The α form (black large plates), space group P$\bar{1}$, a= 6.658(3), b=7.626(8), c=27.385(3) Å, α=93.23(3), β=91.43(3), γ=119.29(3)°, V=1208.6 Å^3, Z=2. The β form (black elongated plates), space group P2$_1$/c, a= 27.685(7), b=7.845(2), c=11.508(3) Å, β=101.33(2)°, V=2450.7 Å^3, Z=4. Intensity data were collected on a Rigaku automatic four-circle diffractometer with monochromated Mo-Kα radiation. The structures were solved by the direct method and refined by the block-diagonal least-squares method using reflections with $|F_o|>3\sigma(|F_o|)$. The final R values are 0.096 for the α form and 0.082 for the β form.

Crystal structure of the α form is shown in Fig. 1. The Ni atoms are located at (0,0,0) and (0,1/2,0), and the planar Ni(dmit)$_2$ molecules form a uniform column along the b axis with the interplanar distance of 3.52 Å. Many short inter-stack S•••S distances (3.496-3.618 Å) are observed. The asymmetric EDT-TTF molecules stack alternately along the [110] direction. The interplanar distances are 3.62 and 3.61 Å. The mode of molecular overlapping is the usual "double bond over ring" type. Short interchain S•••S distances are observed between the molecules aligned along the [$\bar{1}$10] direction. The most interesting feature is that the stacking direction of the EDT-TTF molecules ([110]) is different from that of the Ni(dmit)$_2$ molecules ([010]), which is the first case in the 1:1 donor-acceptor system. The Ni(dmit)$_2$ column and the EDT-TTF column are repeated alternately along the c axis.

The room temperature conductivity of the α form is about 10^2 S cm^{-1}. Upon cooling, the electrical resistivity exhibits a monotonous decrease down to 20 K. At 20 K, the resistivity begins to increase and has a peak around 14 K. It then decreases again to lower temperature, as a metal (Fig. 2).

Figure 3 shows the reflectance spectra of the α form within the ab plane for the light polarized parallel and perpendicular to the b axis. The shape of broad dispersions appearing in both polarizations are well reproduced by the following Drude formula.

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_c - \omega_p^2/(\omega^2 + i\omega\gamma)$$

$$R(\omega) = \frac{(\varepsilon_1^2+\varepsilon_2^2)^{1/2} - \sqrt{2}[\varepsilon_1+(\varepsilon_1^2+\varepsilon_2^2)^{1/2}]^{1/2} + 1}{(\varepsilon_1^2+\varepsilon_2^2)^{1/2} + \sqrt{2}[\varepsilon_1+(\varepsilon_1^2+\varepsilon_2^2)^{1/2}]^{1/2} + 1}$$

As the results of the least-squares fitting by use of the above formula, the parameters are determined to be ε_c=2.77, ω_p=8.6×10^3 cm^{-1}, γ=2.6×10^3 cm^{-1}, for the polarization parallel to the b axis, and ε_c=4.18, ω_p=5.6×10^3 cm^{-1}, γ=3.0×10^3 cm^{-1}, for the polarization perpendicular to the b axis. The ratio of oscillator strength for both polarizations [$\omega_p(//b)^2/\omega_p(\perp b)^2$] is 2.4, suggesting a small anisotropy of the electronic structure in the ab plane.

The simple 1:1 donor(D)-acceptor(A) type metal with the one-dimensional (1D) segregated column structure has a strong tendency toward the Peierls insulating state. One possible way to suppress the Peierls instability is to increase an interchain interaction, especially between the like chains (D•••D or A•••A).[4] The intermolecular interaction of the conduction orbitals (HOMO of EDT-TTF and LUMO of Ni(dmit)$_2$) in the α form, however, is rather one-dimensional. Therefore, as the first approximation, the tight-binding band structure, calculated on the basis of extended Hückel approximation, is constructed by two quasi 1D metallic bands, each of which is associated with Ni(dmit)$_2$ and EDT-TTF respectively. Since the degree of charge transfer from EDT-TTF to Ni(dmit)$_2$ (ρ) is not clear, we tentatively assume that ρ is 1/2. The formal charge of -1/2 (+1/2) is commonly observed in the anion (cation) radical salts of Ni(dmit)$_2$ (EDT-TTF). The calculated Fermi surface consists of two pairs of "warped" planes (Fig. 1d), when the interchain coupling between the unlike chains (c1, c2, c3) is negligibly small. Due to the alternation of two types of columns with different stacking

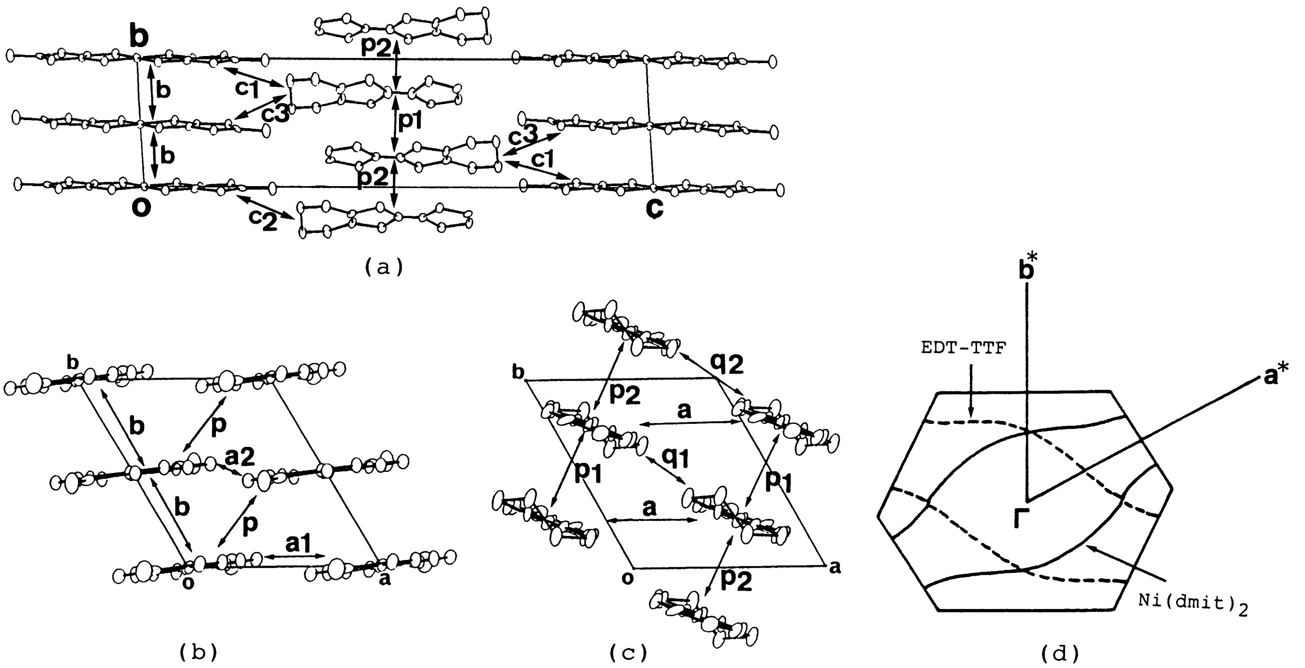

Fig. 1. (a) Crystal structure of α-(EDT-TTF)[Ni(dmit)$_2$]. (b), (c) Molecular arrangements of Ni(dmit)$_2$ and EDT-TTF molecules. Overlap integrals (× 10^3) of the conduction orbitals are: b;-10.8, a1;0.35, a2;-0.20, p;-2.24, p1;16.48, p2;13.0, q1;0.25, q2;-0.17, a;-2.28, c1;0.13, c2;-0.28, c3;-0.36. (d) Calculated Fermi surface.

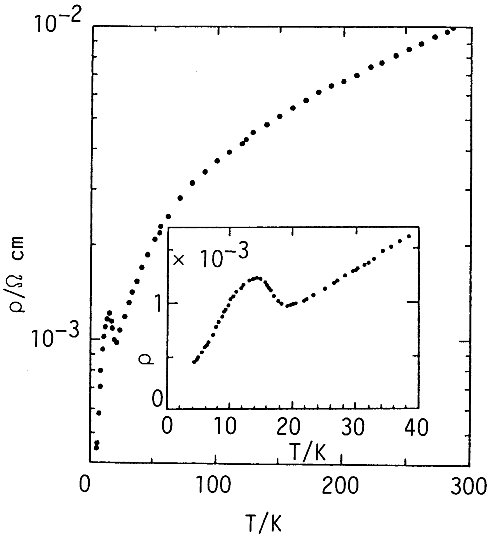

Fig. 2. Electrical resistivity of α-(EDT-TTF)[Ni(dmit)$_2$] parallel to (001).

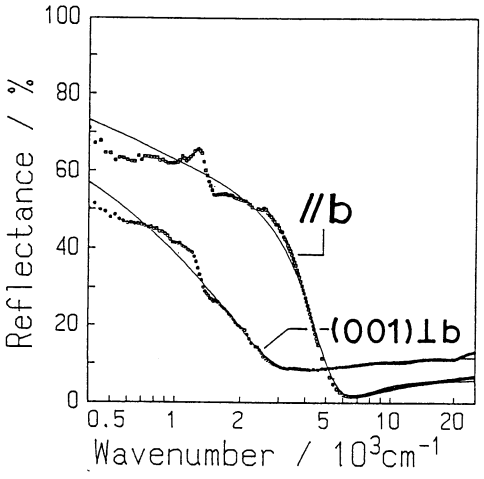

Fig. 3. Reflectance spectra of α-(EDT-TTF)[Ni(dmit)$_2$].

directions, the orientation of each plane is different to each other and the planes are not completely nested by a single modulation wave vector. It may be possible that this structural feature contributes to the stabilization of the metallic state in the α form. This characteristic feature is very similar to that of the high-pressure superconductor $(CH_3)_4N[Ni(dmit)_2]_2$.[2)] One possible origin of the anomalous resistivity maximum is a partial nesting of the Fermi surface.

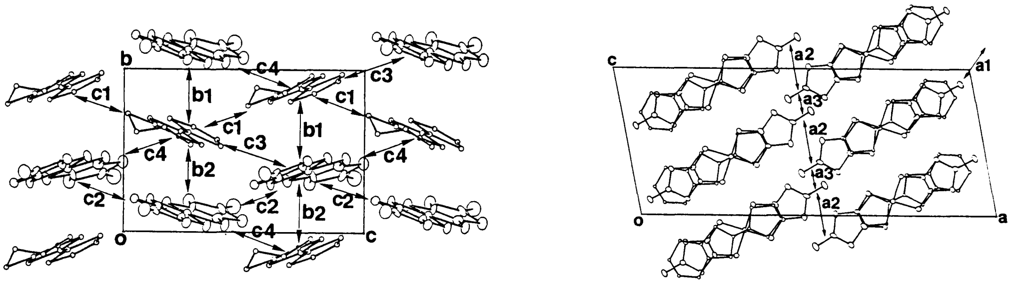

Fig. 4. Crystal structure of β-(EDT-TTF)[Ni(dmit)$_2$]. Overlap integrals (× 10^3) of the conduction orbitals are: b1;2.03, b2;1.63, c1;1.36, c2;0.85, c3;0.57, c4;-0.77, a1;0.72, a2;-0.40, a3;0.35.

As shown in Fig. 4, the β form has a mixed-stacking structure. A noticeable structural feature is that there exist short intermolecular S•••S distances (3.426-3.686 Å) based on the terminal thionyl S atoms between the Ni(dmit)$_2$ molecules aligned along the a axis. In the simple band picture, the usual mixed-stacking system is an insulator. We have pointed out that it is possible to transmute the mixed-stacking system into a metal by an introduction of the strong transverse intermolecular interaction between the like molecules.[5] In the β form, however, the interaction between the like molecules (c1 and c2) is not enough to form the metallic band. The calculated band structure is semiconductive for any ρ value, which is consistent with the resistivity measurement ($\rho_{R.T.}=10^2$ Ω cm).

In conclusion, two conducting 1:1 salts have been obtained by the coupling of Ni(dmit)$_2$ and EDT-TTF. The α form is particularly interesting because the "solid crossing" arrangement of the unlike chains has made it possible to construct a non-1D electronic structure based on the 1D column. This has renewed a perspective of the 1:1 donor-acceptor type compounds.

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