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Coexistence of Conducting and Magnetic Electrons Based on Molecular π-Electrons in the Supramolecular Conductor (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$

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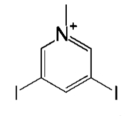
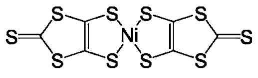
Coexistence of conducting electrons and localized spins leads to numerous intriguing phenomena.[1] Multicomponent molecular crystals would be superior candidates for materials with such a state. Several compounds, the paramagnetic superconductor β''-(ET)$_4$-(H$_2$O)Fe(C$_2$O$_4$)$_3$·C$_6$H$_5$CN[2] (ET = bis(ethylenedithio)tetrathiafulvalene), the ferromagnetic metal (ET)$_3$[MnCr(C$_2$O$_4$)$_3$],[3] the antiferromagnetic superconductors κ-(BETS)$_2$FeX$_4$ (BETS = bis(ethylenedithio)tetraselenafulvalene; X = Br, Cl),[4] and the magnetic-field-induced superconductor λ-(BETS)$_2$FeCl$_4$,[5] have been reported as typical examples exhibiting "bi-functionality". These cation radical salts contain d-block metals in their counter anions, known as the "π-d system". However, systems without localized 3d moments have been scarcely reported. The sole example is the α-Per$_2$M(mnt)$_2$ series (Per = perylene; mnt = maleonitriledithiolate; M = Ni, Pd, Pt, Fe, Cu, Au, and Co), exhibiting one-dimensional metallic behavior and paramagnetism with antiferromagnetic (AF) interactions, which are derived from molecular π-electrons of Per$_2{}^+$ and M(mnt)$_2{}^-$, respectively.[6] These compounds undergo a metal−insulator transition (T_c = 8.2−73 K), becoming insulators in the low-temperature region.

The metal complex Ni(dmit)$_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) has been widely used in conducting or magnetic materials,[7] whose molecular arrangement can be sensitively affected by strong and directional non-covalent interactions. The supramolecular Te···S associations between the Te-containing closed-shell cations and the terminal thioketone groups of Ni(dmit)$_2$ lead to rather unique molecular packing in anion radical salts.[8] However, despite their potentially applicable interactions, which make the molecular architecture designable, no further investigations have been reported. Our first approach to introduce supramolecular halogen (I···S) interactions into the Ni(dmit)$_2$ salt has yielded a new magnetic molecular conductor without localized d moments. Here, we report the anion radical salt (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$ (Me-3,5-DIP = *N*-methyl-3,5-diiodopyridinium). The two kinds of layers of Ni(dmit)$_2$ anions contained in this material exhibit two-dimensional metallic conduction and paramagnetism with AF interactions down to 4.2 K, respectively. These contrastive properties are derived solely from the molecular π-electrons of Ni(dmit)$_2$ anions.



(Me-3,5-DIP)$^+$



Ni(dmit)$_2$

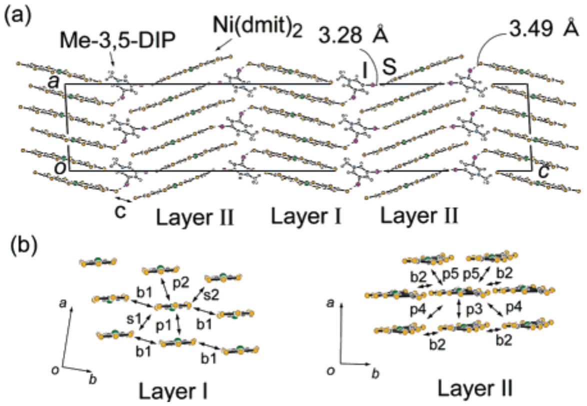


Figure 1. Crystal structure of (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$: (a) side view and (b) end-on projection of Ni(dmit)$_2$ anions. Supramolecular I···S interactions are indicated by dotted lines. Overlap integrals (*S*) among LUMOs ($\times10^{-3}$) are as follows: (Layer I) p1 = 23.35, p2 = −0.38, b1 = 0.41, s1 = −0.66, s2 = 0.67; (Layer II) p3 = −13.30, p4 = −0.50, p5 = −8.80, b2 = 0.68, (interlayer) c = 0.30.

Single crystals of (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$ were grown by galvanostatic electrolysis (0.5 μA; current switching 80:20/s) of (nBu$_4$N)[Ni(dmit)$_2$] (6.5 mg) in the presence of (Me-3,5- DIP)BF$_4$ (22.4 mg) in acetone/acetonitrile (1:1, v/v; 20 mL) at 30 °C under Ar (see Supporting Information).

X-ray structural analysis was performed.[9] The unit cell contains four Ni(dmit)$_2$ anion layers (Layers I and II; Figure 1), two of which are crystallographically independent and considerably different from each other. These layers are repeated alternately along the *c*-axis. The terminal thioketone groups of the Ni(dmit)$_2$ anion in both layers are associated with the cations through two kinds of short I···S supramolecular interactions, whose lengths are 3.28 and 3.49 Å, respectively. The shorter one (3.28 Å) is approximately 15% shorter than the sum (3.78 Å) of the van der Waals radius of iodine (1.98 Å) and sulfur atom (1.80 Å). In Layer I, Ni(dmit)$_2$ anions are stacked along the *a*−*b* direction. Calculated overlap integrals among LUMOs suggest strong dimerization of the Ni(dmit)$_2$ units (Figure 1b). The intradimer interaction p1 is approximately 2 orders of magnitude larger than all other interdimer interactions (p2, s1−2, and b1). The interplaner distances are 3.45 Å within the dimer and 3.82 Å between the dimers. The tight-binding band calculation (see Supporting Information) suggests a large separation (∼400 meV) between the upper and lower sub-bands, each of which has extremely narrow bandwidth W (∼20 meV). The effective on-site Coulomb repulsion in the dimer U_{eff} is expressed by the equation in terms of the intradimer transfer integral $|t_{\text{dimer}}|$ and intermolecular Coulomb repulsion V[10] and is obviously greater than W ($U_{\text{eff}} \gg W$) for the half-filled lower sub-band. Layer I, therefore, should be

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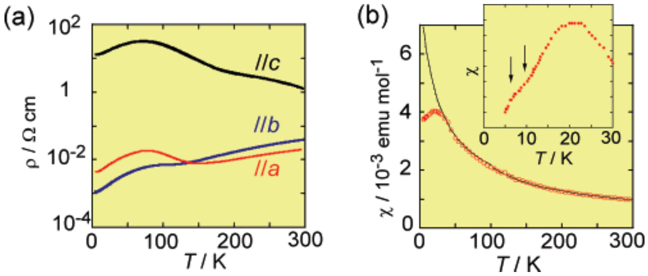

Figure 2. (a) Anisotropic temperature dependence of electrical resistivity for (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$ and (b) magnetic susceptibility for (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$. The solid line represents the Currie−Weiss model with an additional constant term $\chi_{\text{Const.}}$ of 7.2×10^{-4} emu mol^{-1} (see text). The Curie constant C is fixed at 0.375 emu K mol^{-1}, and the Weiss temperature θ is estimated to be −5.3 K. The data below 40 K is expanded in the inset, where the arrows mark anomalies at 6 and 10 K.

in a Mott insulating state which displays paramagnetism based on a localized spin on the dimer unit [Ni(dmit)$_2$]$_2{}^-$.

On the other hand, in Layer II, Ni(dmit)$_2$ anions form a non-columnar structure that includes two overlapping modes (Modes I and II). In Mode I, one molecule overlaps with two molecules, which is the “spanning-overlap” (corresponding to p5 in Figure 1b). Meanwhile, one molecule overlaps with only one molecule in Mode II. This packing motif is almost the same as that in α-(Et$_2$-Me$_2$N)[Ni(dmit)$_2$]$_2$,[11] except for the minor difference (see Supporting Information). The band calculation affords a two-dimensional Fermi surface with elliptical cross-section (see Supporting Information), suggesting that Layer II exhibits two-dimensional metallic conduction.

The considerable difference in molecular arrangement between Layers I and II stem from the “non-equivalence” between the two sides of the cation layer: every methyl group of the cation is projected toward Ni(dmit)$_2$ anions in Layer I, while the opposite side faces those in Layer II. A similar feature has been described in ref 12. In the present system, the supramolecular I···S interactions fix the cation orientations with their strong associations, strongly leading to two kinds of layers of Ni(dmit)$_2$ anions. This could provide us with clues as to how to design a multifunctional molecular system.

The anisotropic temperature dependence of electrical resistivities (ρ) was measured on a plate-like single crystal (0.6 mm × 0.3 mm × 0.008 mm) by the four-probe method in the temperature range of 4.2−300 K (Figure 2a). As anticipated from band calculations, a two-dimensional metallic behavior is observed in the *ab*-plane. The resistivity along the *b*-axis decreases monotonically with decreasing temperature. The resistivity along the *a*-axis also shows an essentially metallic behavior down to 4.2 K, although it has a broad minimum and maximum around 155 and 72 K, respectively. In contrast, for the interlayer direction (along the *c*-axis), the resistivity increases with decreasing temperature down to about 65 K and is more than 3 orders of magnitude larger than those along the *a*- and *b*-axis directions at 4.2 K. These features clearly indicate that the metallic layers (Layer II) and the thick insulating layers (Layer I; ∼19 Å) are sandwiched by each other. The magnetic susceptibility (χ), measured for a polycrystalline sample under 2.5 T by a SQUID magnetometer, is plotted against temperature in Figure 2b. The diamagnetic contribution was subtracted. The paramagnetic behavior presumably arises from the Ni(dmit)$_2$ anions because the cation (Me-3,5-DIP)$^+$ is diamagnetic (closed shell). The $\chi - T$ curve in the temperature range of 100−300 K can be fitted by the superposition of the Currie−Weiss term ($\chi = C/(T - q)$; $C = 0.375$ emu K mol^{-1} (fixed)) and a constant $\chi_{\text{Const.}}$ of 7.2×10^{-4} emu mol^{-1} for the Pauli paramagnetic contribution from the conducting electrons in Layer II, $\chi_{\text{total}} = (\chi_{\text{AF}} + \chi_{\text{Const.}})/2$ (Figure 2b). The Weiss temperature θ is estimated to be −5.3 K, indicating that the spins interact antiferromagnetically with each other. The $\chi_{\text{Const.}}$ value is close to that of conventional Pauli paramagnetic molecular metals (∼5×10^{-4} emu mol^{-1}). The $\chi - T$ curve has notable anomalies at 6 and 10 K (Figure 2b, inset), indicating some magnetic transitions. Further studies including ^{13}C-NMR measurements are in progress.

In summary, our development of the *supramolecular* Ni(dmit)$_2$ anion radical salts provides a new magnetic molecular conductor that has two kinds of layers of Ni(dmit)$_2$ anions. Two-dimensional metallic conduction and paramagnetism with AF interactions both stem from molecular π-electrons of Ni(dmit)$_2$ contained separately in each layer: “one” kind of molecule playing “two” contrastive roles. This is the first system where conducting and magnetic π-electrons coexist down to 4.2 K. Studies of the cooperative properties of the two types of electrons are underway.

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Supporting Information Available: Overlapping mode (Layer II), band calculations (Layers I and II), and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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