Coexistence of conducting and magnetic electrons based on molecular $\pi$-electrons in the supramolecular conductor (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$

Yosuke Kosaka,†,‡,§ Hiroshi M. Yamamoto,†,‡,§ Akiko Nakao,† Masafumi Tamura,†,‡,§ and Reizo Kato*†,‡,§

Department of Chemistry, Faculty of Science, Saitama University, Saitama, Saitama 338-8570, Japan, RIKEN, JST-CREST, Wako, Saitama 351-0198, Japan, and High-Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan

Received December 8, 2006; E-mail: reizo@riken.jp

Coexistence of conducting electrons and localized spins leads to numerous intriguing phenomena. Multicomponent molecular crystals would be superior candidates for materials with such a state. Several compounds, the paramagnetic superconductor $\beta$-(ET)$_2$-(H$_2$O)Fe(C$_5$O$_2$)$_3$C$_6$H$_5$CN$^2$ (ET = bis(ethylenedithio)tetrathiafulvalene), the ferromagnetic metal (ET)$_2$[MnCr(C$_2$O$_4$)$_3$], the antiferromagnetic superconductors $\kappa$-(BETS)$_2$FeX$_4$ (BETS = bis(ethylenedithio)tetrathiafulvalene; X = Br, Cl), and the magnetic-field-induced superconductor $\lambda$-(BETS)$_2$FeCl$_4$ have been reported as typical examples exhibiting “bi-functional”. These cation radical salts contain $d$-block metals in their counter anions, known as the “$\pi$-$d$ system”. However, systems without localized $d$ moments have been scarcely reported. The sole example is the radical salt$(\text{3,5-DIP})_2\text{Ni}(\text{dmit})_2$ containing $d$-block metals in their counter anions.

The metal complex Ni(dmit)$_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) has been widely used in conducting or magnetic materials, 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. However, despite their potentially applicable interactions, which make the molecular architecture designable, no further investigations have been reported. Our first approach to introduce supramolecular 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 $\pi$-electrons of Ni(dmit)$_2$ anions.

Single crystals of (Me-3,5-DIP)[Ni(dmit)$_2$]$_2$ were grown by galvanostatic electrolysis (0.5 $\mu$A; 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. 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 $\pi$-$\pi$ 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 $p_1$ is approximately 2 orders of magnitude larger than all other interdimer interactions ($p_2$, $s_1$, and $b_1$). 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 ($\sim 20$ meV). The effective on-site Coulomb repulsion in the dimer $U_{\text{eff}}$ is expressed by the equation in terms of the intradimer transfer integral $t_{\text{intradimer}}$ and intermolecular Coulomb repulsion $V^\text{W}$ and is obviously greater than $W$ ($U_{\text{eff}} \gg W$) for the half-filled lower sub-band. Layer I, therefore, should be
in a Mott insulating state which displays paramagnetism based on a localized spin on the dimer unit \([\text{Ni(dmit)}_2]^{2-}\).

On the other hand, in Layer II, \(\text{Ni(dmit)}_2\) anions form a non-collinear 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 \(p_5\) in Figure 1b). Meanwhile, one molecule overlaps with only one molecule in Mode II. This packing motif is almost the same as that in \((\text{Et}_2\text{Me}-3,5\text{DIP})\)[\(\text{Ni(dmit)}_2\)]. The solid line represents the Curie-Weiss model with an additional constant term \(x_{\text{const}}\) of \(7.2 \times 10^{-4}\) emu mol\(^{-1}\) (see text). The Curie constant \(C\) is fixed at 0.375 emu K mol\(^{-1}\), and the Weiss temperature \(\theta\) 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.

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 \(\text{Ni(dmit)}_2\) 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- and II- modes. This packing motif is almost the same as that in \((\text{Et}_2\text{Me}-3,5\text{DIP})\)[\(\text{Ni(dmit)}_2\)]. The solid line represents the Currie-Weiss model with a Weiss term (\(\alpha/(T - \theta)\); \(\theta = 0.375\) emu K mol\(^{-1}\)) and a constant \(x_{\text{const}}\) of \(7.2 \times 10^{-4}\) emu mol\(^{-1}\) for the Pauli paramagnetic contribution from the conducting electrons in Layer II. The Weiss temperature \(\theta\) is estimated to be \(-5.3\) K, indicating that the spins interact antiferromagnetically with each other. The \(x_{\text{const}}\) value is close to that of conventional Pauli paramagnetic molecular metals \((\sim 5 \times 10^{-4}\) 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 \(^{13}\text{C}\)-NMR measurements are in progress.

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

Acknowledgment. This work was partially supported by a Grant-In-Aid for Scientific Research (No. 16GS0219) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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.

References

(9) Crystal data for (Me-3,5-DIP)[\(\text{Ni(dmit)}_2\]): \(C_5H_8N_2\text{NiS}_4\text{S}_4\), \(M_0 = 1248.66, T = 297\) K, monoclinic, space group \(C2/c\), \(a = 14.35(7)\) Å, \(b = 6.47(3)\) Å, \(c = 76.54(3)\) Å, \(\beta = 92.99(4)^\circ\), \(V = 7096.2(6)\) Å\(^3\), \(Z = 8\), \(w_p = 2.34\) g cm\(^{-3}\), \(F(000) = 48240, R = 0.064, R_p = 0.19, GOF = 1.05\).

JA0687825