Supramolecular Ni(dmit)$_2$ salts with halopyridinium cations - development of multifunctional molecular conductors with the use of competing supramolecular interactions

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Halopyridinium cations with multiple halogen and hydrogen bonding donor sites have been used as the counter ions for the Ni(dmit)$_2$ anion. Because of the competing supramolecular interactions, such as halogen and hydrogen bondings, some of the Ni(dmit)$_2$ salts showed complicated structures with multiple functionality that originates from the intriguing molecular arrangements. In these multifunctional salts, Ni(dmit)$_2$ molecules play two roles, conducting and magnetic, depending on the molecular arrangement in the layers that they belong to. The physical properties of these salts have been examined by conductivity measurements, with or without hydrostatic/uniaxial pressure, as well as magnetic susceptibility and band calculations. By analysing the low temperature conductivity, it can be concluded that the itinerant electrons in the conducting layer have magnetic coupling with the localized spins in the magnetic layers to result in a Kondo singlet formation.

Introduction

Multifunctional materials are of wide and intense interest in material science because interference among different physical properties sometimes provides a source of fast, low-dissipation and/or high-density electronic devices that cannot be achieved without them. In particular, the interaction between the charge and spin of an electron is one of the most important issues in spintronics, heavy fermions and high-$T_c$ superconductors. Though the quest for inorganic multifunctional materials is preceding that of organic materials, the organic counterparts are also under considerable investigation in this regard. The number and variety of organic multifunctional materials are, however, still limited and expansion is needed to enrich the technology and science of organic devices in the next era. Since the properties of organic materials are severely dependent on the molecular arrangements inside them, we have been studying a supramolecular strategy to control the conduction and magnetic properties of molecular conductors by introducing halogen interactions. In this paper, we report some supramolecular Ni(dmit)$_2$ radical anion salts with bi-functionality based on the molecular arrangement. Many halogen and hydrogen bonds are found in the crystal structures and the competition and cooperation among these supramolecular interactions play an important role in constructing the unique and complex crystal structures. Such a special structure resulted in a coexistence of conducting and magnetic activities in the crystal, in which one kind of molecule plays two contrasting roles. The nature of the thioketone–halogen/hydrogen interactions will be also discussed.

Results and discussion

Electrochemical oxidation of $(n$Bu$_4$N)[Ni(dmit)$_2$] in the presence of the cations listed in Scheme 1 afforded five Ni(dmit)$_2$ anion-radical salts with supramolecular networks: (Me-3,5-DBP)[Ni(dmit)$_2$]$_2$ (1), (Me-3,5-DIP)[Ni(dmit)$_2$]$_3$ (2), α-(Me-3,5-DIP)[Ni(dmit)$_2$]$_2$ (3) β-(Me-3,5-DIP)[Ni(dmit)$_2$]$_2$ (4) and (Me-3,5-BIP)[Ni(dmit)$_2$]$_2$ (5). Because of the high directionality of halogen bonding and hydrogen bonding, the crystal structure
is restricted to exhibit asymmetry to some extent. This asymmetry is relaxed in crystals 1 and 2 by the introduction of disorder, while highly complex structures that accommodate this asymmetry are realized in crystals 3 and 5. From these results, we anticipate that supramolecular frustration introduced by multiple halogen and hydrogen bonding interactions can be a tool to induce unconventional complications. Because such structures resulted in alternate formations can be a tool to induce unconventional complications. Because such structures resulted in alternate stacking of conducting and magnetic 2D (2D = two-dimensional) layers in 3 and 5, this seems a good strategy for the construction of bi-functional materials to bring in such competing supramolecular interactions, although rational design is not possible as yet.

**Crystal structures and band calculations**

(Me-3,5-DBP)[Ni(dmit)2]2 (1). The crystal structure of 1 is shown in Fig. 1 and 2. Two Ni(dmit)2 anions (A/B) and one cation are crystallographically independent, both of which form 2D layers that stack alternately to one another. The Ni(dmit)2 anions form conventional columnar structures where the anions stack along the a−b direction with their molecular planes parallel to each other. A repeating unit contains four molecules (A, A’, B’ and B), two pairs of which are interrelated by an inversion center (A-A’ and B-B’). The interplanar distances are 3.57 (A-B), 3.68 (A-A) and 3.51 Å(B-B). The cation (Me-3,5-DBP)+ is orientationally disordered and possesses two possible positions (Sites A and B) with an occupancy ratio of 60:40. The Br atom of the terminal thioketone groups of the dmit ligand form halogen bonding Br⋯S interactions, whose lengths are 3.08 and 3.24 Å (Site A) and 3.51 and 3.40 Å (Site B), respectively. In addition to these halogen bonding interactions, there seem to be hydrogen bondings, although the positions of the hydrogen atoms are not refined and determined by calculations. For example, the hydrogen atom of the pyridine ring (at the 2 position) interacts with the thioketone group to form H⋯S interactions with lengths of 3.82 (Site A) and 3.16 Å (Site B), respectively. These are much shorter than the sum of the van der Waals radii of 3.65 Å (for Br⋯S, Br: 1.85 Å, S: 1.80 Å) or 3.00 Å (for H⋯S, H: 1.20 Å), respectively, which builds up the supramolecular network through these strong interactions. In each site, through these interactions, one cation molecule bridges two Ni(dmit)2 layers with supramolecular interactions and a 1D supramolecular chain along the b + c direction is formed (Fig. 1). The yellow ellipses mark the molecules that do not participate in the infinite supramolecular chain but interact with the cation to form a branch. The coexistence of sites A and B seems to be a result of competition between the hydrogen and halogen interactions, where a strong halogen bond (3.08/3.24 Å) and a weak hydrogen bond (2.82 Å) are formed in site A while a weak halogen bond (3.40/3.51 Å) and a strong hydrogen bond (2.78 Å) are formed in site B. Although this kind of competition exists, the whole crystal structure is still a product of the cooperation of these two interactions. The calculated overlap integral for p3 is much larger than p1 and p2 (Fig. 3). This suggests strong dimerization of the Ni(dmit)2 anions, which reflects the short interplanar distance of p3. Every intercolumnar interaction (s1–s3, r1 and r2) is rather small because of the symmetry of the LUMO of the Ni(dmit)2 molecule. Since the weaker intracolumnar and the intercolumnar interactions are comparable, this system should have a 2D character with a narrow dispersion. The tight-binding band calculations imply a large separation between the highest and lowest sub-bands associated with the strong dimerization. Every sub-band has a narrow width due to the weak inter-
dimer and intermolecular interactions. With a band filling of \(1/4\), this system would be a band insulator with a band gap \(E_g\) of \(\sim 100\) meV. Indeed, the temperature dependence of this crystal shows an activation-type behavior with a 55 meV activation energy, as will be discussed later.

**\((\text{Me-3,5-DIP})[\text{Ni(dmit)}_2]_3\) (2).** The crystal structure of 2 is shown in Fig. 4. One and a half of the \(\text{Ni(dmit)}_2\) anions (A and B) and a half of the cation \(\text{Me-3,5-DIP}\) are crystallographically independent. The \(\text{Ni(dmit)}_2\) anion A is located on the inversion center. The cation is located on the two-fold rotation axis and occupies two possible positions (Sites A and B) due to the orientational disorder. The occupancy ratio of Sites A and B is 50 : 50. Their positions, however, cannot be exactly determined because these sites are very close to one another. The unit cell contains two crystallographically equivalent layers of \(\text{Ni(dmit)}_2\) anions. In each layer, the \(\text{Ni(dmit)}_2\) anions form two columns, which are interrelated to one another by the glide plane. The \(\text{Ni(dmit)}_2\) molecules are arranged in a herringbone manner. The interplanar distances are 3.48 (A–B) and 3.68 Å (B–B). The cation and \(\text{Ni(dmit)}_2\) anions form supramolecular I–S and H–S interactions, whose lengths are 3.28, 3.52 Å (I–S; Sites A and B, respectively) and 2.91 Å (H–S), respectively. These are shorter than the sum of van der Waals radii (3.78 Å for I–S, 1.98 Å, S: 1.80 Å) and a supramolecular network is formed with these interactions. The supramolecular patterns based on the cations at Sites A and B, however, are different from one another. Infinite 1D chains run along the \(a + 2c\) direction and are associated with the cation in Site A (Fig. 4 upper panel). On the other hand, the cations in Site B form 1D zig-zag chains (Fig. 4 lower panel).

Calculated overlap integrals suggest that the \(\text{Ni(dmit)}_2\) anions exhibit weak trimerization in the column. Every intercolumnar interaction (\(r_1–r_3\) and \(s_1–s_3\)) is considerably weaker than intracolumnar interactions (Fig. 5). This column, therefore, should have a q1D (=quasi-one dimensional) character with weak degeneracy. The tight-binding calculation affords energy bands. Six branches are divided into three groups (Fig. 5) due to the following three aspects: 1) there are no interlayer interactions between the two crystallographically equivalent \(\text{Ni(dmit)}_2\) anion layers in the unit cell and thus, the sub-bands associated with Layers I and II are degenerate to each other, 2) two equivalent 3-fold columns within the anion layer afford three groups and 3) small intercolumnar interactions weakly break the degeneracy within each subgroup. This band structure indicates a q1D metallic character. However, since the lower sub-band group is effectively half-filled and the band width is narrow, this system would be a Mott insulator.

**\(\text{a-(Me-3,5-DIP})[\text{Ni(dmit)}_2]_2\) (3).** This crystal can be selectively yielded by electrochemical crystallization with current switching. The crystal structure of 3 is shown in Fig. 6. Two \(\text{Ni(dmit)}_2\) anions (A and B) and one cation are crystallographically independent. The crystal comprises four stacked repeating \(\text{Ni(dmit)}_2\) anion layers, two of which are crystallographically independent (Layers I and II). The internal structures of Layers I and II are considerably different from one another. These layers are repeated alternately along the \(c\)-axis. The terminal thiketone groups of the \(\text{Ni(dmit)}_2\) anion in both layers are associated with the iodine and hydrogen atoms of the cations through supramolecular interactions. The I–S lengths are 3.28 and 3.49 Å and the S–H lengths are 2.80 and 2.86 Å, respectively. These are rather shorter than the sum of van der Waals radii (3.78 Å for I–S, 1: 1.98 Å, S: 1.80 Å) and a supramolecular network is formed with these interactions. The supramolecular patterns based on the cations at Sites A and B, however, are different from one another. Infinite 1D chains run along the \(a + 2c\) direction and are associated with the cation in Site A (Fig. 4 upper panel). On the other hand, the cations in Site B form 1D zig-zag chains (Fig. 4 lower panel).

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**Fig. 4** Supramolecular network of 2 for Site A (upper panel) and B (lower panel). Supramolecular I–S and H–S interactions are indicated by dotted lines.

**Fig. 5** End-on projection of the \(\text{Ni(dmit)}_2\) layer, band dispersion and Fermi surface for 2. Overlap integrals among the LUMOs \((\times 10^{-3})\) are as follows: \(b_1 = -6.63, b_2 = -3.76, s_1 = -0.84, s_2 = 0.64, s_3 = 0.079, r_1 = -0.053, r_2 = 0.66, r_3 = 0.82\). \(E_F\) denotes the Fermi energy.

**Fig. 6** Crystal structure of 3 (side view). Supramolecular I–S and H–S interactions are indicated by dotted lines.
the other interdimer interactions in Layer I (p2, s1–s2, and b1). The interplanar distances are 3.45 Å within the dimer and 3.82 Å between the dimers. The Raman spectra indicate that the formal charge of the Ni(dmit)₂ anions in Layers I and II are the same. The tight-binding band calculation suggests a large separation ($\gamma \approx 400$ meV) between the upper and lower sub-bands, each of which has an extremely narrow bandwidth, $W$, of $\sim 20$ meV [Fig. 9]. HOMO–LUMO band inversion does not occur in every layer because the HOMO–LUMO energy difference is 0.6–0.8 eV. Meanwhile, one molecule overlaps with only one molecule in Mode II. The band calculation affords a two-dimensional Fermi surface with an elliptical cross-section (Fig. 11), suggesting that Layer II exhibits 2D metallic conduction. Since the Ni(dmit)₂ anion in Layer II has a charge of $-0.5$, the 2D Fermi surface has 50% of the area of the first Brillouin zone. This calculation is consistent with a result from quantum (Schubnikov–de Haas) oscillation where a Fermi surface of 51% of the first Brillouin zone is observed. It is notable that the band filling for both Layer I and II is the same despite the Fermi level and should be different (due to the different band structure). Such a situation can be explained by a strong on-site Coulomb repulsion in Layer I that excludes an addition of excess electrons from Layer II, which is reminiscent of the relationship between the s- and d-electrons in Kondo insulators.

$[\text{Me-3,5-DIP}\{\text{Ni(dmit)}_2\}]_{2}$ (4). This compound was obtained in the same batch as crystals 2 and 3. The crystal structure is shown in Fig. 12 and 13. Two Ni(dmit)₂ anions and one cation displays paramagnetism based on a localized spin on the dimer unit $[\text{Ni(dmit)}_2]_{2}^-$. On the other hand, in Layer II, the Ni(dmit)₂ anions form a non-columnar structure that includes two overlapping modes (Modes I and II), as shown in Fig. 10. In Mode I, one molecule overlaps with two molecules, which is called the “spanning-overlap”. Meanwhile, one molecule overlaps with only one molecule in Mode II. The band calculation affords a two-dimensional Fermi surface with an elliptical cross-section (Fig. 11), suggesting that Layer II exhibits 2D metallic conduction. Since the Ni(dmit)₂ anion in Layer II has a charge of $-0.5$, the 2D Fermi surface has 50% of the area of the first Brillouin zone. This calculation is consistent with a result from quantum (Schubnikov–de Haas) oscillation where a Fermi surface of 51% of the first Brillouin zone is observed. It is notable that the band filling for both Layer I and II is the same despite the Fermi level and should be different (due to the different band structure). Such a situation can be explained by a strong on-site Coulomb repulsion in Layer I that excludes an addition of excess electrons from Layer II, which is reminiscent of the relationship between the s- and d-electrons in Kondo insulators.
are crystallographically independent. The molecular arrangement of Ni(dmit)$_2$ is a columnar structure similar to that in 1 but the supramolecular interactions between the cations and Ni(dmit)$_2$ anions are different. The lengths of the supramolecular I···S interactions are 3.27 and 3.31 Å (I···S). In addition, the 2-position H atom of the pyridine ring and the thioketone are associated to form supramolecular H···S interactions, whose lengths are 2.97 Å. With these interactions, one cation molecule bridges two Ni(dmit)$_2$ columns within a Ni(dmit)$_2$ layer and a supramolecular 2D network is constructed in the bc plane (Fig. 13). The calculated overlap integrals $p_1$ and $p_2$ are significantly stronger than $p_3$ (Fig. 14). This suggests a tetramerization, which is supported by the interplanar distances between the Ni(dmit)$_2$ anions of 3.56, 3.53 and 3.61 Å (corresponding to $p_1$, $p_2$ and $p_3$, respectively). The tight-binding calculation affords the band structure, where the band structure of the tetramer splits into four sub-bands. Since $p_2$ is larger than $p_1$, the highest and lowest sub-bands are widely separated and the other two sub-bands are associated to form supramolecular H···S interactions, which is due to the enhancement of the a-axis direction. The tight-binding band calculations for Layer I still afford two widely separated sub-bands. However, the lower sub-band has a wider band width, $W$, of 50 meV than that of 3, which is due to the enhancement of the interdimer interactions. The effective on-site Coulomb repulsion in the dimer, $U_{eff}$, is still greater than $W$ ($U_{eff} > W$) for the half-filled lower sub-band (Fig. 9, right panel) and Layer I would be in a Mott insulating state. On the other hand, every overlap integral is almost comparable to those of 3 in Layer II. The calculated Fermi surface, therefore, implies that Layer II exhibits 2D metallic character (Fig. 15).

**Overview of the crystal structures.** A metal dithiolate complex M(dmit)$_2$ (M = Ni, Pd, Pt, etc.) can form conducting anion radical salts with various cation species. Since side-by-side interactions between Ni(dmit)$_2$ anions tend to be cancelled out due to the $b_{3g}$ symmetry of the LUMO, many of their conduction properties have 1D character. [Me$_3$N][Ni(dmit)$_2$]$_3$, for example, has a columnar structure which is conventional among the Ni(dmit)$_2$ anion radical salts. This system has two pairs of q1D Fermi surfaces that originate from the “solid crossing columnar structure”: two crystallographically equivalent q1D columns are aligned in a cross direction to each other. On the other hand, in $\alpha$-...
Synthons affect the arrangement of Ni(dmit)$_2$ in the crystal. Here, we overview the ways in which the supramolecular cations in Site A form 1D 2-leg chains with the Ni(dmit)$_2$ anions. The shortest distance of 2.78 Å and 3.08 and 3.22 Å (for Br…S and I…S, respectively), which are 15% shorter than the sum of the van der Waals radii. Furthermore, the H atoms of the pyridine rings (2 and 5 positions) form supramolecular H–S interactions with the Ni(dmit)$_2$ anions. The shortest distance of 2.78 Å is ca. 7% shorter than the sum of van der Waals radii. The C–X…S, H–S, and Br…S interactions are comparable to or weaker than the H–S interactions, whereas the I–S interaction is stronger than the H–S interactions. This competition between the halogen and hydrogen bondings results in the difference in the stacking motifs. In addition to these examples, the coexistence of columnar and spanning-overlap structures found in crystals 3 and 5 is quite rare in Ni(dmit)$_2$ salts. Because the lengths of the C–I and C–H covalent bonds in Me-3,5-DIP are quite different, the Ni(dmit)$_2$ molecules need to twist their principle axes from the normal stacking positions to satisfy all the halogen and hydrogen bonding interactions. Taking only short interactions into account, the $\varphi$ values are in the range of 100–150° (for Br–S) and 105–125° (for I–S), while the $\theta$ values have no specific angular limitation (Table 3).

Generally, the distances of halogen bonding interactions are mainly given by electrostatic effects. For an ideal sp$^2$ molecule, the cations in Site B form 1D chains with branches of the Ni(dmit)$_2$ anions. Compounds 3 and 5 have closely linked supramolecular grids comprised of the cations and Ni(dmit)$_2$ anions to construct the 2D network. Compound 4 has a 2D supramolecular mesh. Three kinds of arrangements of the Ni(dmit)$_2$ anions, columnar, herringbone and spanning-overlap structures, have been observed in the present five compounds 1–5. These arrangements are also found in the conventional conducting Ni(dmit)$_2$ anion radical salts but many differences are observed in these cases. For example, compounds 1 and 4 have similar 4-fold columnar structures of the Ni(dmit)$_2$ anions. However, the Ni(dmit)$_2$ anions in 1 are dimerized within the column, whereas those in 4 are tetramerized. This seems to be due to the difference between the supramolecular Br–S and I–S interactions. In 1, the H atoms of the cations interact with one kind of thioketone group to form significantly short supramolecular H–S interactions. On the other hand, one of the two Br atoms of the cations interacts with two kinds of thioketone groups (Sites A and B) due to the disorder. This orientational disorder of the cation seems to originate from the weakness of the Br–S halogen bonding. In 4, on the other hand, short supramolecular I–S interactions are formed and the H–S interactions are relatively longer than those in 1. This could mean a difference in priority of these interactions: the Br–S interactions are comparable to or weaker than the H–S interactions, whereas the I–S interaction is stronger than the H–S interactions. This competition between the halogen and hydrogen bondings results in the difference in the details of the stacking motifs. In addition to these examples, the coexistence of columnar and spanning-overlap structures found in crystals 3 and 5 is quite rare in Ni(dmit)$_2$ salts. Because the lengths of the C–I and C–H covalent bonds in Me-3,5-DIP are quite different, the Ni(dmit)$_2$ molecules need to twist their principle axes from the normal stacking positions in order to satisfy all the halogen and hydrogen bonding geometries. This competition and cooperation among the multiple interactions are the origin of such a unique structure.

The distances and angles of the X–S and H–S interactions between the cations and Ni(dmit)$_2$ anions are summarized in Table 2. The shortest distances of the supramolecular X–S interactions are 3.08 and 3.22 Å (for $r_{Br-S}$ and $r_{I-S}$, respectively), which are ca. 15% shorter than the sum of the van der Waals radii. Furthermore, the H atoms of the pyridine rings (2 and 5 positions) form supramolecular H–S interactions with the Ni(dmit)$_2$ anions. The shortest distance of 2.78 Å is ca. 7% shorter than the sum of van der Waals radii. The C–X–S angles are almost restricted to ca. 155°–170°, except for the interactions with long distances. This is because the coordination angles in the C–X–S interaction are governed by the geometry of the σ-hole of the X atom, which is projected in the opposite direction to the C–X bond. On the other hand, Fig. 17 depicts a schematic of the sp$^2$ orbitals of the C=S bond. The $\varphi$ and $\theta$ represent the directions of the interactions. Taking only the short interactions into account, the $\varphi$ values are in the range of 100–150° (for Br–S) and 105–125° (for I–S), while the $\theta$ values have no specific angular limitation (Table 3).

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For the numbering of the atoms, see Fig. 17.

### Orbital

The $\varphi$ and $\theta$ values should be 120° (or 240°) and 90°, respectively. Most of the $\varphi$ values are situated within a narrow range around 120°, while the $\theta$ values are distributed in a wide range. These correspond to previously reported data for halogen bonding with ketones. It seems that both lone pairs of the ketonic sulfur and the $\pi$ electrons of the C=S bond are participating in the halogen bonding.

### Physical properties

The coexistence of conduction and magnetic electrons leads to numerous intriguing phenomena. In the field of inorganic systems, for example, some metal oxides can exhibit a steep decrease in the electrical resistivity when a magnetic field is applied. This is called the giant magnetoresistive (GMR) effect. Moreover, competition between the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interactions and the Kondo singlet state leads to the enhancement of the effective mass, called the heavy fermion state. Molecular conductors have provided a wide variety of materials that exhibit a coexistence of metallic conduction and magnetic properties. In most molecular conductors without localized 3d moments have been scarcely reported and the sole example is the $\pi$-Per$_2$M(mnt)$_2$ series (Per = perylene; mnt = maleonitrile-dithiolate; M = Ni, Pd, Pt, Fe, Cu, Au and Co). This system exhibits one-dimensional metallic behavior and magnetism with antiferromagnetic (AF) interactions, which are derived from the molecular $\pi$-electrons of Per$^{2+}$ and M(mnt)$_2^-$, respectively.

### Conductivity

The electrical resistivities of 1, 2, and 4 are shown in Fig. 18. The room-temperature resistivities, $\rho_{RT}$, of 1 and 4 are 3.2 and 0.60 $\Omega$ cm, respectively and increase monotonically with decreasing temperature. This supports that they are band insulators, as anticipated from the tight-binding band calculation. Compound 2 also shows semiconductive behavior with a $\rho_{RT}$ of 0.16 $\Omega$ cm, which indicates that 2 is a Mott insulator, as is also expected from the band calculation.

The anisotropic temperature dependence of the electrical resistivities for 3 and 5 are depicted in Fig. 19. As anticipated from the band calculations, compound 3 exhibits 2D metallic behavior in the $ab$-plane. The resistivity along the $b$-axis

### Table 2

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For the numbering of the atoms, see Fig. 17.
decreases monotonically with decreasing temperature. The resistivity along the $a$-axis also shows essentially metallic behavior down to 4.2 K, although it has a broad minimum and a broad maximum around 155 K and 72 K, respectively. In contrast, for the interlayer direction (along the $c$-axis), the resistivity increases with decreasing temperature. A broad maximum and a broad minimum are observed at about 65 and 20 K, respectively. In addition, an anomaly appears at about 185 K. At 4.2 K, the resistivity along this direction is larger than along the $a$- and $b$-axis directions by more than four orders of magnitude. These features clearly indicate that the metallic layer (Layer II) and the thick insulating layer (Layer I; $\sim 19$ Å) alternate. Compound 5 shows 2D metallic behavior in the $ab$-plane similar to that of 3. The resistivity along the $b$-axis decreases monotonically, whereas along the $a$-axis, it decreases with a broad minimum ($\sim 145$ K) and maximum ($\sim 52$ K). Below 10 K, an increase in the resistivity is observed along both directions. On the other hand, the resistivity along the $c$-axis increases with a broad maximum ($\sim 50$ K) and a broad minimum ($\sim 10$ K) with decreasing temperature. All the temperatures where these resistivity anomalies appear for 5 are lower than those for 3. This appears to be due to the “chemical pressure” effect, which is consistent with the resistivity measurement under hydrostatic pressure. At 4.2 K, the resistivity anisotropy between the parallel and perpendicular directions to the $c$-axis is more than three orders of magnitude, suggesting strong 2D character for this system.

The absolute values for the in-plane resistivity ($\|a$ and $\|b$), however, are larger than those of 3, although both compounds have essentially the same Fermi surface. This would be due to the cation disorder in 5.

The first differential curves of the electrical resistivities for 3 are shown in Fig. 20. All the inflection points in the three directions appear at the same temperatures in each axis direction, around 46, 102 and 175 K. This means that the resistivity for each axis has the same tendency towards temperature dependence and the electronic states are coupled to one another.

In order to further investigate the transport properties where itinerant electrons and localized spins are associated, the electrical resistivity was measured under hydrostatic pressure or uniaxial strain. Fig. 21 shows the electrical resistivity ($\rho||a$, $\rho||b$ and $\rho||c$) for 3 under hydrostatic pressure. For the $a$- and $b$-axis directions, an application of pressure lowers the temperatures where the broad maximum and minimum appear (Fig. 21). These effects correspond to the chemical pressure effect in 5. At 15 kbar, this system exhibits normal 2D metallic behavior in the temperature region of about 80–300 K. On the other hand, for the $c$-axis direction, the broad maximum is diminished and the resistivity increases with an increase of the applied pressure. Although there are differences in the high temperature region, there is a common feature at low temperature. In each case, the resistivity increases with decreasing temperature and can be fit with $-\log T$. This type of temperature dependence is typical for the Kondo effect, which means that the itinerant and localized electrons form a singlet bound state to exhibit a heavier effective mass. These behaviors are enhanced by the application of pressure (Fig. 21). This suggests that the interactions between localized (Layer I) and conduction (Layer II) electrons are increased by the pressure and result in an enhancement of the Kondo temperature.

Fig. 22 shows the electrical resistivity ($\rho||a$ and $\rho||b$) for 3 under uniaxial strain along the interlayer direction ($P||c$). In a low pressure region, each resistivity for the $a$- and $b$-axes exhibits normal metallic behavior without any observed anomalies under hydrostatic pressure. With further application of the strain, on the other hand, the resistivity increases with decreasing temperature and starts to obey $-\log T$ dependence in the low temperature region.

In the px-d system, the difference in energy levels between the itinerant electron (the HOMO of the donor molecule) and the localized electron (d orbitals) is about 1 eV, while in the present system, the conduction and magnetic electrons should have almost the same energy levels because both are electrons.
from the same molecular orbitals. Moreover, for π-electrons, localized and itinerant states are convertible to each other. These situations can provide a strong interaction between conduction and magnetic electrons, potentially leading to a new hybrid phenomena associated with conduction and magnetism. Indeed, the physical measurements, such as Schubnikov–de Haas oscillation and NMR, as well as the present results suggest interplay of the conduction and magnetic electrons.

**Magnetism.** For 3 and 5, magnetic susceptibility ($\chi$) is plotted against temperature in Fig. 23. Both of them show paramagnetic behavior at high temperature, which 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 a linear combination of the Currie–Weiss term ($\chi_{CW} = C/(T - \theta)$; $C = 0.375$ emu K mol$^{-1}$ (fixed)) and a constant, $\chi_{const}$, for the Pauli paramagnetic contribution from the conduction electrons in Layer II, $\chi_{total} = (\chi_{CW} + \chi_{const})/2$. For 3, the Weiss temperature, $\theta$, is estimated to be $-5.3$ K, indicating that the spins interact antiferromagnetically with each other. An estimated $\chi_{const}$ of $7.2 \times 10^{-4}$ emu mol$^{-1}$ is close to that of conventional Pauli paramagnetic molecular metals (ca. $5 \times 10^{-4}$ emu mol$^{-1}$). The $\chi-T$ curve has a broad maximum at 20 K, which is due to short-range ordering of antiferromagnetic spins, and anomalies at 6 and 10 K (Fig. 23, inset of the left panel). However, no anisotropy of $\chi$ can be observed. The $^{13}$C NMR measurements indicate that no magnetic transition occurs at these temperatures.

On the other hand, $\theta$ and $\chi_{const}$ for 5 are estimated to be $-10.7$ K and $7.5 \times 10^{-4}$ emu mol$^{-1}$, respectively. The increase of $\theta$ is due to the enhancement of the interdimer interactions. Although the antiferromagnetic interactions are enhanced, $\chi$ steeply increases below 10 K (Fig. 23, right panel). The $M-H$ curve indicates free spin like behavior below this temperature (Fig. 24), but the absolute value of $M$ is much smaller than that of an ideal free spin of 1/2 (saturated at $-5.5 \times 10^{3}$ emu mol$^{-1}$). Although the cation disorder appears to prevent the antiferromagnetic ordering and lead to the generation of partially free spins, the mechanism remains an open question.

**X-ray diffraction at low temperature.** X-ray diffraction patterns for 3 in a low temperature region are shown in Fig. 25. On decreasing the temperature, superlattice spots with quasi-four-fold periodicity gradually appear from 170 K. As marked by the red circles, they correspond to the $a^* + b^*$ and $a^* - b^*$ directions. A further decrease of the temperature leads to modulation of the period (from four-fold to three-fold, as...
shown in Fig. 25). Quasi-three-fold superlattice spots appear below 110 K. Compound 5, on the other hand, provides a different diffraction pattern. On decreasing the temperature, quasi-four-fold superlattice spots along the \(a^* + b^*\) and \(a^* - b^*\) directions gradually appear from about 235 K and they remain down to 6 K. The three-fold spots do not appear. Since the half-width at half maximum (HWHM) of these superlattice spots are much wider than those of normal spots, they are not Bragg spots but diffuse spots. This indicates that the first-order structural phase transition does not occur. This is also supported by the fact that the resistivity and magnetic susceptibility do not exhibit hysteresis in the corresponding temperature region. Although these structure modulations may provide small perturbations to the system, the electrical structure seems not to be affected by these small structural fluctuations because the section area of the Fermi surface, determined by quantum oscillation methods, matches well with the calculated value of 50%.

**Conclusions**

Preparation, crystal structure analysis and physical property measurements have been done to understand the role of halogen and hydrogen bonding in forming the unique structures that resulted in a coexistence of conducting and magnetic properties. It is known that many organic–inorganic hybrid materials form halogen bond.\(^\text{24}\) In crystals 3 and 5, however, almost all types of chemical bonds are used to construct the crystal structure: covalent, metal-coordination, ionic, van der Waals, metallic, hydrogen, chalcogen and halogen bonds are included in these crystals.

The most interesting point in these materials is the interplay between their conduction and magnetic properties. Since one kind of molecule, Ni(dmit)\(_2\), constitutes two kinds of layers with completely different properties, coexistence as well as interplay between the itinerant and localized electrons are realized in a single molecular crystal. Such an interplay has resulted in the formation of a Kondo singlet state, the research of which is attracting recent attention.

**Experimental**

**Synthesis**

All syntheses were performed under Ar. THF was freshly distilled and other solvents were used without further purification. \((\text{nBu}_4\text{N})[\text{Ni(dmit)}_2]\) was synthesized according to the literature method.\(^\text{25}\)

**3,5-Diiodopyridine.** A mixture of 3,5-dibromopyridine (5.0 g, 21.1 mmol), KI (114.7 g, 691 mmol) and CuI (10.5 g, 55.1 mmol) was placed in a three-necked flask (1 L). DMF (450 mL) was added and the flask was heated at 180 °C. After 1 week, the flask was allowed to cool to room temperature and the reaction mixture was poured onto ice-water. The precipitate was collected on a G4 glass filter by filtration and dissolved in CH\(_2\)Cl\(_2\)–pyridine (5 : 1). A saturated Na–EDTA solution was added to remove any Cu ions from the organic layer and the mixture was stirred overnight. The organic layer was separated and dried over MgSO\(_4\). After filtration, the residue was purified with column chromatography on silica gel with CH\(_2\)Cl\(_2\). The same procedure was repeated three times until two bromine atoms were completely replaced by iodine atoms. Final purification yielded 3,5-diiodopyridine (5.42 g, 77.6%) as a white powder. MS (EI): 331.

**5-Bromo-3-iodopyridine.** A THF solution of \(\text{iPrMgCl}\) (5.1 mL, 10.2 mmol) was added dropwise to a solution of 3,5-dibromopyridine (2.01 g, 8.55 mmol) dissolved in THF (20 mL) in a three-necked flask (300 mL) at 0 °C. After stirring for 15 min whilst maintaining the temperature, I\(_2\) (2.54 mg, 10.2 mmol) dissolved in THF (15 mL) was added slowly. The reaction mixture was then allowed to warm to room temperature and stirred continuously for 1 h. A 10% NH\(_4\)Cl solution was poured onto the reaction mixture and the precipitate was extracted with Et\(_2\)O. The organic layer was washed with a 10% Na\(_2\)SO\(_4\) solution and brine and dried over Na\(_2\)SO\(_4\). After removing the solvent, the residue was purified with column chromatography on silica gel with CH\(_2\)Cl\(_2\)–n-hexane (1 : 1). 5-Bromo-3-iodopyridine (2.43 g, 67.5%) was afforded as a white powder. MS (EI): 283, 285.

**5-Bromo-3-iodopyridine.** A mixture of 3,5-diiodopyridine (2.20 g, 14.9 mmol) and Me\(_3\)OBF\(_4\) (2.15 g, 6.20 mmol) was placed in a three-necked flask (100 mL). Toluene (100 mL) was added and the solution was heated at 100 °C. After 7 hours, EtOH (20 mL) was added at room temperature and the mixture was filtered.
thorough a G4 glass filter. The precipitate was washed with benzene and dissolved in MeCN. After removal of MeCN under reduced pressure, the residue was recrystallized from EtOH–CH3CN–n-hexane to yield [Me-3,5-DIP]BF4 (0.92 g, 34.3%) as colorless crystals. MS (ESI+): 346.

(Me-3,5-DBP)BF4. An MeCN solution of 3,5-dibromopyridine was dropped onto a Me3OBF4 in MeCN in a three-necked flask and was stirred at room temperature. The solvent was then removed to a small volume in vacuo and then excess Et2O was added. The precipitate was recrystallized from MeCN–Et2O to yield (Me-3,5-DBP)BF4 as colorless crystals (93.9% yield). (Me-3,5-BIP)BF4, was obtained by the same method.

Crystal structure

Crystal data were collected at room temperature using an automatic CCD diffractometer (RIGAKU/MSC Mercury) for 1, 2 and 4 or an imaging plate detector (RIGAKU/R-AXIS) for 3 and 5 with graphite-monochromated Mo–Kα (λ = 0.7107 Å) radiation. The crystal structures were solved by the direct method and refined by the full-matrix least-squares procedure. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at geometrically calculated positions. For all the salts, calculations were performed using the teXsan crystallographic software package from Molecular Structure Co. Application of the numerical absorption correction based on the azimuthal scans of several reflections to compounds 1–4 yielded transmission factors of 0.5862–0.9453, 0.5685–0.8541, 0.432–0.896, and 0.316–0.452, respectively. An empirical absorption correction based on the azimuthal scans of several reflections of compound 5 yielded transmission factors of 0.337–0.647. The crystallographic data for 1–5 are summarized in Table 4 (CCDC 910061–910062, 915357, 645114, and 910623).

Band calculation

Overlap integrals (S) between the LUMOs of adjacent Ni(dmit)2 molecules were calculated on the basis of the obtained crystal structures using the extended Hückel MO method and semiempirical parameters for Slater-type atomic orbitals. Double-ζ orbitals were used for Ni. Band structures were obtained by tight-binding band calculations using the transfer integrals (t) with an approximation of t = tS, where c is a constant corresponding to the order of the energy level of the HOMO (~ −10 eV).

Conductivity measurements

Measurements of the temperature dependence of the electrical resistivity under ambient pressure were carried out by a standard four-probe dc method. Gold leads (15 μm diameter) were attached to the sample with carbon paste. For the resistivity measurement under hydrostatic pressure, the sample was put in a Teflon capsule filled with a pressure medium (DN-oil 7373) and then the capsule was set in a clamp type pressure cell made of BeCu. For the resistivity measurement under uniaxial strain, the sample was immersed in an epoxy liquid (stycast 1266/A). Then the epoxy containing the sample was molded into a cylinder and placed in the cylinder of a clamp-type pressure cell. The relation between the pressure applied on the epoxy and strain was checked with a strain gauge. For the resistivity measurement for 3, a conventional four-probe dc method was performed. The current was applied along the a-, b- and c-axis directions for

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1. R = Σ||Fo|| − |Fo||Σ||Fo||. 2. Ru = [Σw(|Fo| − |Fo|)²/ΣwFo²]¹/².
the measurements under hydrostatic pressure and along the a- and b-axis directions for the measurements under uniaxial strain.

Magnetic measurements

The temperature-dependent magnetic susceptibility of the polycrystalline samples was measured using a SQUID magnetometer (Quantum Design MPMS XL) over a temperature range of 2.0–300 K under an applied magnetic field of 1 T. The diamagnetic contributions of the cations and Ni(dmit)₂ anions were subtracted with Pascal’s Law.

Low temperature X-ray

Crystal data for 3 and 5 were collected using an imaging plate detector (RIGAKU/R-AXIS) with graphite-monochromated Mo-Kα (λ = 0.71070 Å) radiation. The temperature was controlled with a temperature controller (Lake Shore/Model 331) in a temperature range of 6–300 K.

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Notes and references


