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Crystal and Electronic Structures of a New Two-dimensional Molecular Metal, α-$Et_2Me_2N[Ni(dmit)_2]_2$

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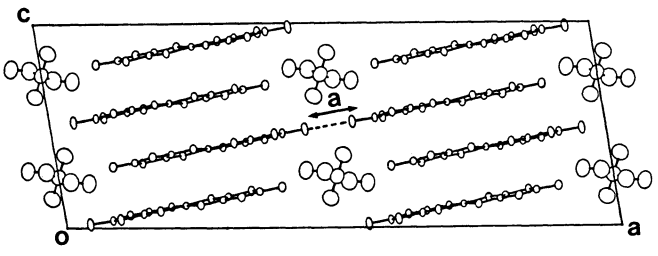
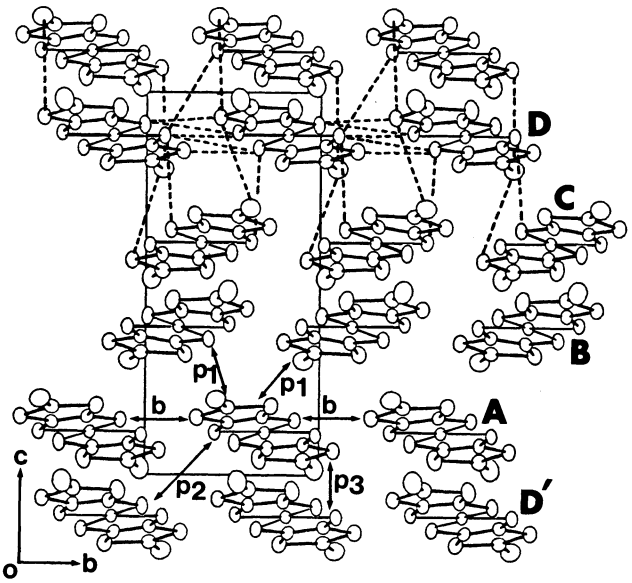
The anion radical salt α-$Et_2Me_2N[Ni(dmit)_2]_2$ retains metallic behavior down to 1.5 K. Planar $Ni(dmit)_2$ units lying side-by-side along the b axis stack along the c axis in such a way that one molecule overlaps with two molecules. Such a "spanning overlap" mode has provided two-dimensional electronic structure.

The typical one-dimensional metal is characterized by "a pair of planar Fermi surfaces", which can be easily nested by a single modulation wave vector at low temperature. The "nesting" of the Fermi surfaces turns the system into an insulator. The desire to overcome such an instability of the one-dimensional metal has motivated the development of systems with the multi-dimensional intermolecular interaction. The organic superconductors based on the π-donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) with a large number of sulfur atoms on the periphery of the molecule have non-columnar structures and non-planar Fermi surfaces.[1] On the other hand, the sulfur-rich 1,2-dithiolene complex $Ni(dmit)_2$ (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) has provided two new kinds of molecular superconductors, $TTF[Ni(dmit)_2]_2$[2] and $Me_4N[Ni(dmit)_2]_2$.[3] These systems have the column structure and planar Fermi surfaces. There are, however, so many Fermi surfaces that no single modulation wave vector can nest all of them. Our proposal is that such a "multi Fermi surfaces" mode is the second strategy for avoiding metal-insulator transition encountered in the one-dimensional system.[4] In the course of survey of $Ni(dmit)_2$ compounds, we have found a new two-dimensional molecular metal, $Et_2Me_2N[Ni(dmit)_2]_2$. This compound is the first typically two-dimensional system derived from the π-acceptor molecule and has indicated a new type of multi-dimensional molecular packing arrangement.

Electrochemical oxidation of $Et_2Me_2N[Ni(dmit)_2]$ in acetonitrile-acetone (1:1) with a constant current of 2.0 μA gave black hexagonal plates (α type) and black elongated plates (β type). $Et_2Me_2NClO_4$ was used as supporting electrolyte. Crystal data of the α phase are; Monoclinic, space group C2/c, a=38.95(2), b=6.494(2), c=13.835(9) Å, β=99.63(5)°, V=3450.4 $Å^3$, Z=4.[5] Intensities were measured on a Rigaku automated four-circle diffractometer with Mo-Kα radiation.

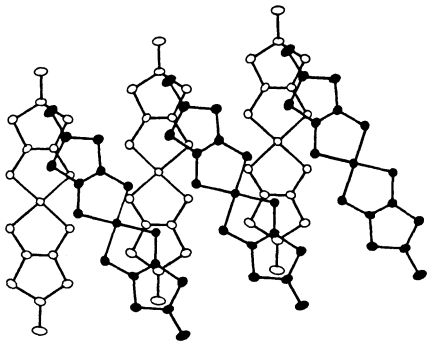


(a)

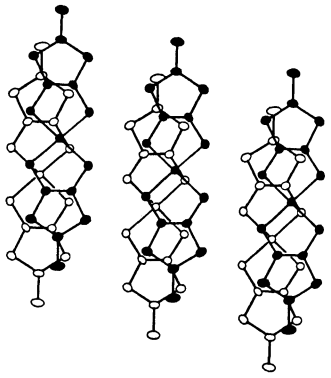


(b)

Fig. 1. Crystal structure of α-Et_2Me_2N-$[Ni(dmit)_2]_2$. Short S•••S distances (<3.70 Å) are indicated by dotted lines.

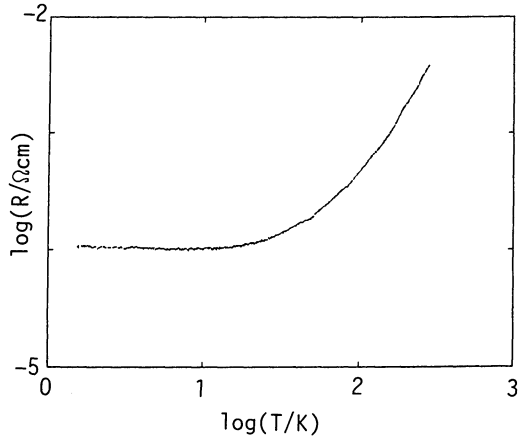


Mode I



Mode II

Fig. 2. Mode of intermolecular overlapping.



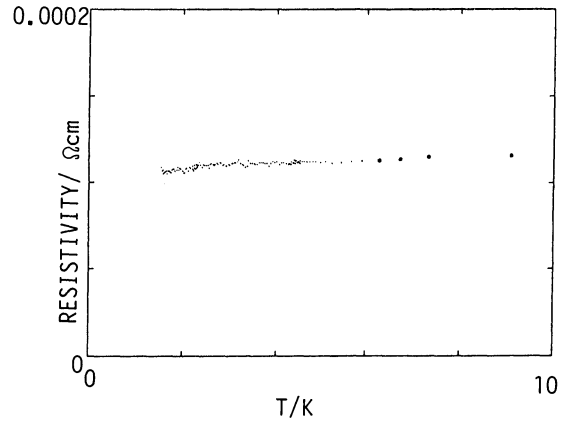


Fig. 3. Temperature dependence of the electrical resistivity along the direction parallel to (100).

Table 1. Intermolecular overlap integrals ($\times 10^3$) of the LUMO's of the $Ni(dmit)_2$ molecule (See Fig. 1).

a	0.670	p1	-7.24
b	0.645	p2	-2.48
		p3	-9.98

Independent 2616 reflections ($2\theta \leq 60°$, $|F_o| \geq 3\sigma(|F_o|)$) were used for calculations. The structure was solved by the direct method and refined by the block-diagonal least-squares method to the conventonal R value of 0.070 .

The crystal structure is shown in Fig. 1. The unit cell contains one crystallographically independent $Ni(dmit)_2$ molecule. Along the b axis, the planar $Ni(dmit)_2$ molecules are arranged in the side-by-side fashion, and short intermolecular S•••S distances (3.424-3.605 Å) are observed in this direction. In Fig. 1b, the repeating unit in the c axis direction consists of four $Ni(dmit)_2$ molecules, A(x,y,z), B(1/2-x,1/2+y, 1/2-z), C(x,2-y,1/2+z), and D (1/2-x,3/2-y,1-z). There are two types of overlapping modes, I(A•••B, C•••D) and II(B•••C, A•••D'), as shown in Fig. 2. In the mode I, the dihedral angle between the molecular planes is 171°, and one molecule overlaps with two molecules. We call this new type of overlapping mode "spanning overlap" one. In the mode II, the molecular planes are parallel to each other, and the interplanar distance is 3.52 Å. In addition to the S•••S network parallel to the bc plane (Fig. 1b), very short intermolecular S•••S contact (3.352 Å) is observed between terminal thionyl S atoms (Fig. 1a). Large thermal parameters of cation atoms indicate that Et_2Me_2N cations are in a disordered state.

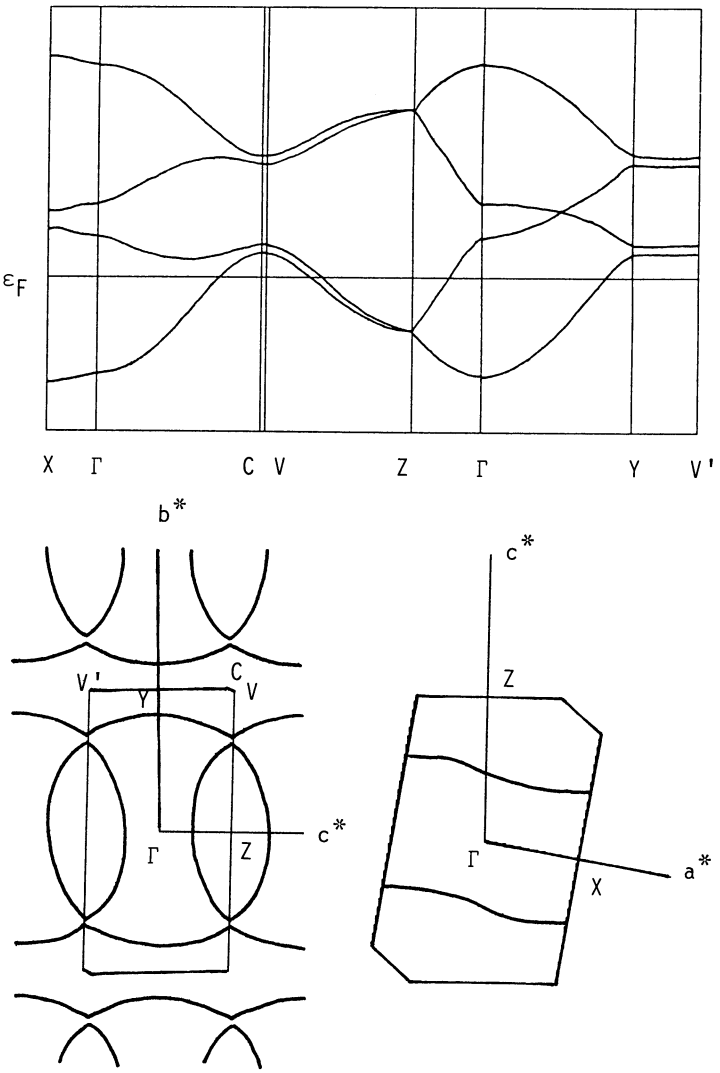


Fig. 4. Tight-binding band structure and Fermi surface of α-$Et_2Me_2N[Ni(dmit)_2]_2$.

The electrical conductivity in the bc plane was isotropic and 20-100 S cm^{-1} at room temperature. A metallic behavior was observed down to 1.5 K with no metal-insulator transition (Fig. 3). It shoud be noted that the conductivity along the a axis direction was fairly high (1 S cm^{-1} at room temperature). The pressure dependence of the resistivity was measured up to 5 kbar. Although the

pressure reduced the resistivity, the superconducting transition was not observed down to 1.5 K.

Table 1 shows intermolecular overlap integrals (S) of the LUMO's (lowest unoccupied molecular orbital) which form the conduction band.[6] For the calculation of the band structure, the primitive cell was adopted. The primitive vectors $\mathbf{a}_p$, $\mathbf{b}_p$, and $\mathbf{c}_p$ are given by the vectors (a+b)/2, -b, and -c, respectively. The lattice constants of this primitive unit cell are a_p=19.745, b_p=6.494, c_p=13.835 Å, α_p=90, β_p=80.50, γ_p=99.47°. The approximation that the transfer integral (t) is proportional to the overlap integral (t=-ES, where E is a constant of the order of the energy of the LUMO) was used. The result of the calculation has indicated a strongly two-dimensional character with a small but definite dispersion along the third direction, which is the first case in the dmit system (Fig. 4).

The $Ni(dmit)_2$ molecule with a large number of sulfur atoms on the periphery of the molecule was expected to exhibit the strong transverse interaction of the conduction molecular orbital as is the case in the BEDT-TTF system. Calculations of intermolecular overlap integrals of the LUMO's for series of the dmit complexes, however, have shown that the b_{2g} symmetry of the LUMO reduces the transverse overlap.[4] This is not favorable for the formation of the two-dimensional electronic structure. The "spanning overlap" mode has opened a route to the two-dimensional system based on the dmit complex. The "long" π-conjugated system extended as far as the terminal thionyl S atoms makes the dmit complex suitable for the "spanning overlap" mode.

In conclusion, we have found the first typically two-dimensional metal derived from the π-acceptor molecule, α-$Et_2Me_2N[Ni(dmit)_2]_2$. The face-to-face overlap arrangement is favored by the planar π-molecule and tends to bring one-dimensional character. However, the new type of the two-dimensional molecular packing arrangement based on the face-to-face overlap, found in α-$Et_2Me_2N[Ni(dmit)_2]_2$, has given a hint to the design of new multi-dimensional molecular metals and superconductors.

References

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4) A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, and H. Kobayashi, Solid State Commun., 62, 57 (1987).
5) Crystal data of β-$Et_2Me_2N[Ni(dmit)_2]_2$ are; Monoclinic, space group $P2_1/m$, a=6.015(5), b=36.28(3), c=8.082(6) Å, β=104.05(5)°, V=1710.8 $Å^3$. Detailed crystal structure and physical properties will be reported elsewhere.
6) The LUMO was obtained by means of the extended Hückel method.

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