CHEMISTRY LETTERS, pp. 1799-1802, 1987.

New Radical Anion Complex, $[(CH_3)_4N][Ni(dmit)_2]_2$ with Metal-Semimetal Phase Transition

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The crystal structure determination was made on the multi-sulfur π-acceptor complex, $[(CH_3)_4N][Ni(dmit)_2]_2$, which is the first molecular metal composed of $Ni(dmit)_2$ (dmit=isotrithionedithiolate) molecules and the closed-shell cations. The metal-semimetal transition with large hysteresis was observed.

To date, five types of ambient-pressure organic superconductors have been known.[1,2] When the crystal structure of the first organic superconductor Bechgaard salt was reported, the 2D intermolecular Se..Se contacts were thought to be essential to distinguish it from the traditional one-dimensional(1D) molecular metals. From this point of view, the waved plane Fermi surface is the most important feature of Bechgaard salt. In contrast to the sulfur-containing π-donor complexes, there is almost no metallic π-acceptor complexes with fairly large transverse intermolecular interactions. In addition, the difficulties of obtaining metallic conductor composed of planar π-acceptors and closed-shell cations has been pointed out so far.[3] In fact, the only one metallic compound of π-acceptor molecule $Ni(dmit)_2$ hitherto known is $(TTF)[Ni(dmit)_2]_2$, which is composed of the open-shell π-acceptor and π-donor molecules.[4] However, we have obtained the first example of a molecular metal, $[(CH_3)_4N][Ni(dmit)_2]_2$ with closed-shell cations. In this paper, we will report the crystal and electronic structures and the electric conductivities of this system.

The black plates of $[(CH_3)_4N][Ni(dmit)_2]_2$ were obtained by the electrochemical method from the acetonitrile solution of $[(CH_3)_4N][Ni(dmit)_2]$ and $[(CH_3)_4N]ClO_4$. The constant current of 0.6 μA was applied. Crystal data are : $(C_4H_{12}N)[Ni(C_3S_5)_2]_2$, monoclinic, C2/c , a=13.856(4), b=6.498(2), c=36.053(11) Å, β= 93.83(3)°, V=3239(2) Å^3, Z=8. The final R value is 0.070 for 3867 independent reflections collected on a Rigaku automatic 4-circle diffractometer with $|F_o| > 3\sigma(|F_o|)$($2\theta < 60°$, Mo $K\alpha$).

The crystal structure of $[(CH_3)_4N][Ni(dmit)_2]_2$ is shown in Fig. 1. The

Ni(dmit)$_2$ molecules are almost planar. The average Ni-S distance is 2.158 Å and C=C distance is 1.393 Å. The Ni(dmit)$_2$ molecules are stacked along [110] forming apparent 1D fourfold structure. But the real repeating unit is two molecules, because of the C-centered lattice. Independent interplanar distances are 3.58 Å and 3.53 Å. The modes of the molecular overlaps are shown in Fig. 2. The tetramethylammonium cations are located on the twofold axis and therefore, they are in an ordered state. The independent C-N distances are 1.50(1) Å and 1.52(1) Å. The intermolecular short S···S contacts shorter than the sum of the van der Waals radii are found along the b direction. The shortest S···S distance is 3.49 Å. Similar close side-by-side arrangement of the molecules is commonly found in the crystals of molecular conductors based on the multi-sulfur π-molecules.$^{4,5)}$

The temperature dependence of the d.c. resistivity was examined along the three directions, which is shown in Fig. 3. The room-temperature conductivity was 60 S cm^{-1}. In the cooling cycle, a metallic behavior was observed down to 100 K and then the phase transition occured with large hysteresis. This behavior was observed for three crystals examined so far. Below the transition temperature, the resistivity was constant(1.4×10^{-2} Ω cm) along the direction of the highest conductivity (//2 in Fig. 3), suggesting that the system is in a semimetallic state. Along the direction 3, the resistivity behaved like narrow-gap semiconductor with activation energy 0.002 eV. The anisotropy of the resistivity is small in the crystal plane but the resistivity along the c direction is more than 10^3 times larger than that along the in-plane direction.

Unlike metallic $[(CH_3)_4N][Ni(dmit)_2]_2$, similar tetraethylammonium salt, $[(C_2H_5)_4N][Ni(dmit)_2]_2$ is a semiconductor (ρ(R.T.)≃30 Ω cm)$^{5)}$ and non-stoichiometric complex, $[(C_4H_9)_4N]_{0.29}[Ni(dmit)_2]$ is a 2D semiconductor (ρ(R.T.)≃0.2 Ω cm).$^{6)}$

It is well-known that Bechgaard salt with tetrahedral anion such as ReO_4^- and BF_4^- exhibits a metal-insulator transition accompanied by the order-disorder transition of the anions. However, the metal-semimetal transition of $[(CH_3)_4N][Ni(dmit)_2]_2$ has nothing to do with the orientational freedom of the cation because of its orderness in the metallic state.

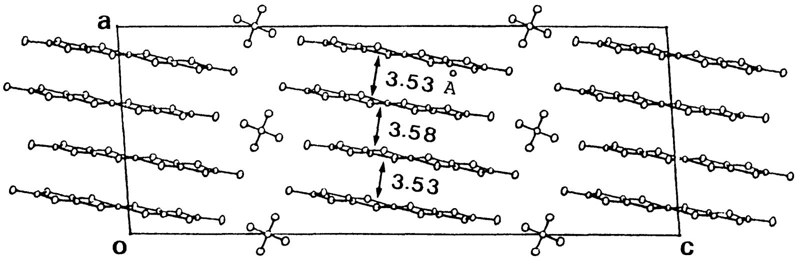


Fig. 1. Projection of the crystal structure along the b-axis.

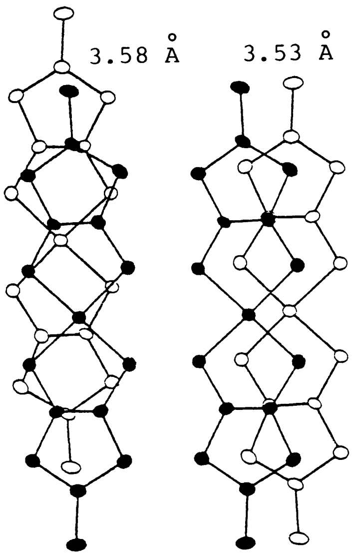


Fig. 2. Two modes of overlaps along [110].

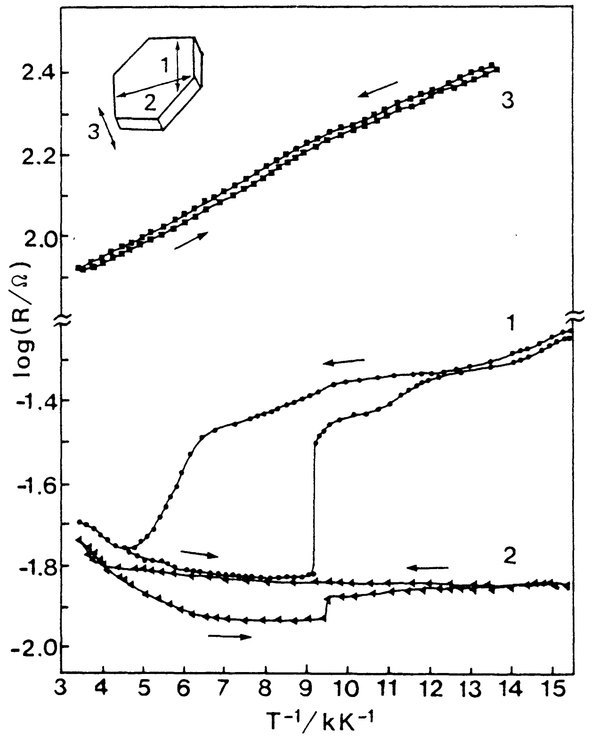
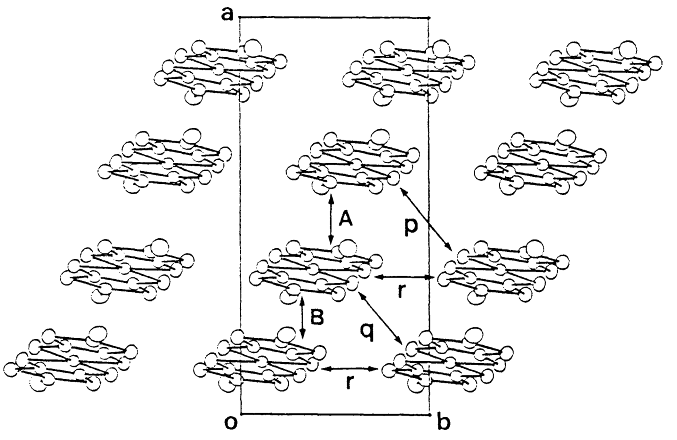


Fig. 3. Temperature dependence of the resistivity along the three directions. The directions 1 and 2 are in (001) and the direction 3 is parallel to [001].



A	10.21×10^{-3}	p	-3.053
B	-10.84	q	-0.5318
		r	0.3223

Fig. 4. Intermolecular overlap integrals(S) of LUMO of $Ni(dmit)_2$.

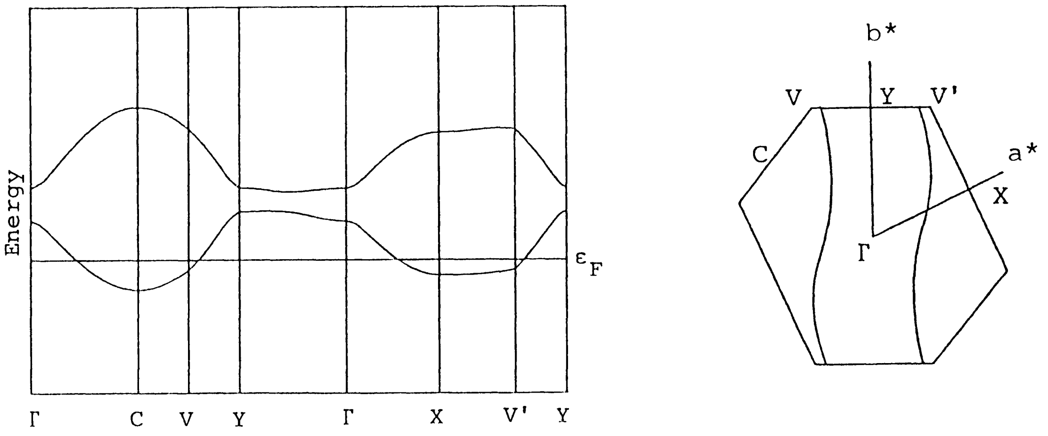


Fig. 5. Tight-binding band structure and Fermi surface of a metal layer of $Ni(dmit)_2$. Instead of the C-centered lattice (a_0,b_0,c_0), the primitive lattice (a,b,c) was adopted: $a=(a_0+b_0)/2$, $b=-b_0$, $c=-c_0$.

Since the conduction band is formed by the intermolecular overlapping of the lowest unoccupied molecular orbital(LUMO), intermolecular overlap integrals of LUMO(S) were calculated (Fig. 4). There are almost equal two independent interactions along the 1D column. Despite of the close side-by-side contact of $Ni(dmit)_2$ molecules, the transverse interactions are not so strong, which is characteristic of intermolecular interactions of $Ni(dmit)_2$.7) So that the system can be regarded as an approximately quarter-filled quasi-1D system. The tight binding band structure was calculated, using the simple approximation t=ES, where t is the transfer integral and E is the proportional constant. The periodically waved Fermi surface was obtained (Fig. 5).

$[(CH_3)_4N][Ni(dmit)_2]_2$ is composed of planar π-acceptor molecules and inorganic cations and corresponds to the reversed case of Bechgaard salt, which has organic π-donors and inorganic anions. The semimetallic state below 100 K seems to suggest that the electronic structure is not simply 1D. The crystal is composed of the metal layer with 1D fourfold stacks of $Ni(dmit)_2$ and cation sheets arranged alternately along [001]. Owing to the glide plane parallel to [001], the metal layers with the $Ni(dmit)_2$ stacks along [110] and those along [110] appear alternately along [001]. This structural feature is consistent with the small anisotropy of the resistivity in (001).

Recent high-pressure experiment shows that the metal-semimetal transition is suppressed at high pressure.8) But the resistivity increases gradually below 20 K, presumably due to some kind of localization effects.

In conclusion, we have found a new molecular metal $[(CH_3)_4N][Ni(dmit)_2]_2$ exhibiting a metal-semimetal transition with large hysteresis. What is the origin of the large hysteresis ? What is the origin of the semimetallic state ? These problems and the possibility of the superconductivity at high pressure9) are now being examined.

References

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9) After the submittion of this paper, we have observed the superconducting transition at 5 K(7 kbar).

(Received June 16, 1987)