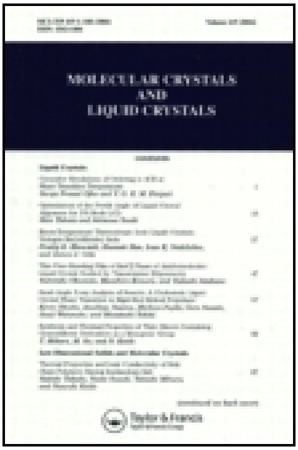

Molecular Crystals and Liquid Crystals

Molecular metals and superconductors based on transition metal complexes with dmit or extended-ttf ligands

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MOLECULAR METALS AND SUPERCONDUCTORS BASED ON TRANSITION METAL COMPLEXES WITH DMIT OR EXTENDED-TTF LIGANDS

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The crystal structure of a high-pressure superconductor $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ *at 10 kbar was determined by diamond-anvil cell to clarify the origin of unique P-T phase diagram of this system. The doubling of lattice spacing along the* $Pd(dmit)_2$ *stack was observed. The novel neutral nickel complex with the extended TTF dithiolato ligand, trimethylenedithiotetrathiafulvalenedithiolate*[$tmdt^{2-} = (S_6C_9H_6)^{2-}$], *have been synthesized. The single crystal of* [$Ni(tmdt)_2$] *was metallic down to 0.6 K. The crystal structure and electronic band structure calculation showed* [$Ni(tmdt)_2$] *is the first single-component molecular metal with three-dimensional Fermi surfaces.*

Keywords: dmit; extended TTF ligand; superconductor; single-component molecular metal

INTRODUCTION

The discovery of the first organic superconductor, $(TMTSF)_2PF_6$(TMTSF = tetramethyltetraselenafulvalene) has opened the new era of organic conductors [1]. Its crystal structure gave a greate hint to establish the molecular design to develop the organic conductor without one-dimensional metal instability. That is, it noticed us the important role of intermolecular chalcogen…chalcogen contacts in the formation of metal bands. Similar intermolecular contacts were also found in the molecular conductors based on transition metal complexes. Unlike partially oxidized

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platinum complexes with one-dimensional Pt-Pt metal bond, the metallic properties and the crystal structure of $(H_3O)_{0.33}$ $Li_{0.8}[Pt(mnt)_2]_2 \cdot 1.67H_2O$ and the first superconductor based on transition metal complex molecules $(TTF)[Ni(dmit)_2]_2$ indicated the importance of π- orbitals of S atoms and $S\cdots S$ networks in the formation of conduction paths (mnt = 1,2-dicyano-1,2-ethylenedithiolate; dmit = 1,3-dithiol-2-thione-4,5-dithiolate) [2,3]. We found that the structure-chemical concept of molecular design can be expressed in terms of extended Hückel tight-binding band picture and examined various molecular metals based on the multi-sulfur (chalcogen) π-donor and π-acceptor molecules such as TMTSF, BEDT-TTF(= bis (ethylenedithio)tetrathiafulvalene) and $M(dmit)_2$ (M = Ni, Pd, . . .) to develop the two-dimensional molecules. In the course of these studies, we have observed superconducting transitions in many systems such as θ- and κ-$(BEDT\text{-}TTF)_2I_3$, $(DMET\text{-}TSF)_2AuI_2$, $[(CH_3)_4N][M(dmit)_2]_2$ (M=Ni, Pd), $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$, $(EDT\text{-}TTF)[Ni(dmit)_2]$ since 1986[4–8]. When we found the first κ-type organic superconductor κ-$(BEDT\text{-}TTF)_2I_3$, we considered that our initial goal to design an ideally two-dimensional organic metal was accomplished [9]. Besides these superconductors, we have recently found many organic superconductors based on BETS (= bis(ethylenedithio)tetraselenafulvalene), λ- and κ-$(BETS)_2MX_4$ (M=Fe, Ga, X=Cl, Br) including the antiferromagnetic organic superconductors, κ-$(BETS)_2FeX_4$ and the system showing an unprecedented superconductor-to-insulator transition, λ-$(BETS)_2Fe_x\ Ga_{1-x}Br_yCl_{4-y}$[10].

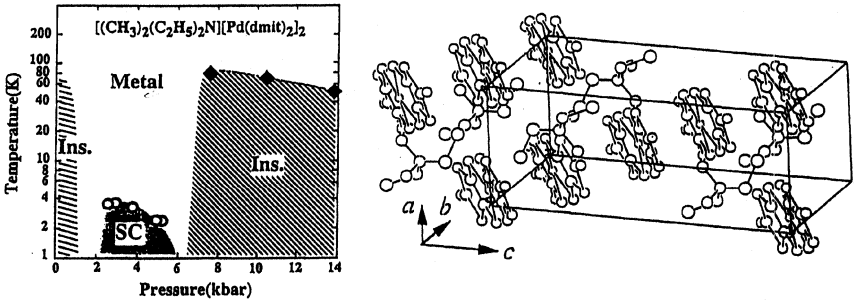
MOLECULAR DESIGN BASED ON SIMPLE TIGHT-BINDING BAND PICTURE

One of the conclusions derived from the molecular design based on extended Hückel tight-binding band picture is the excellence of the TTF-donors in the design of two-dimensional metal band. In TTF-donor, the highest occupied molecular orbital (HOMO) constructing conduction band has the same sign on all the sulfur (or selenium) atoms, which means that each intermolecular $S\cdots S$ contact contributes additively to enhance the intermolecular interaction between the neighbouring molecules. While the lowest unoccupied molecular orbital (LUMO) is mainly responsible for the formation of conduction band in $Ni(dmit)_2$ conductors. Owing to the nodal plane of LUMO on the central Ni atom, the intermolecular transverse interaction through S atoms becomes diminished even when there are many intermolecular close $S\cdots S$ contacts [11]. However, in the case of $Pd(dmit)_2$ superconductors having strongly dimerized columns, HOMO becomes most important due to the level inversion caused by the intradimer HOMO-HOMO and LUMO-LUMO interactions. Since the symmetry of HOMO of M(dmit)$_2$ is same to that of HOMO of TTF-donor, the electronic structure tends to resemble to those of organic metals based on TTF-donors. It gave a very important hint for us to design new types of molecular conductors based on the multi-sulfur π molecules with TTF-like skeletons.

PHASE DIAGRAM AND HIGH-PRESSURE STRUCTURE OF MOLECULAR SUPERCONDUCTOR, $[(CH_3)_2(C_2H_5)_2N][Pd(DMIT)_2]_2$

Here we present our recent study on a Pd(dmit)$_2$ superconductor. As mentioned above, we have found that $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ has a superconducting phase at 2–6 kbar [8,12]. Unlike usual molecular superconductors, the system undergoes a metal-insulator (MI) transition above the pressure where the superconducting phase is suppressed. Thus, the superconducting phase is sandwiched between low- and high-pressure insulating phases (see Figure 1a). Since this unusual phase diagram will be hardly explained on the basis of usual pressure dependence of the electronic structure, we proposed the possibility of pressure-induced level re-exchange between HOMO and LUMO of Pd(dmit)$_2$ [12]. At low pressure, HOMO forms a conduction band with two-dimensional nature. But if the Pd(dmit)$_2$ arrangement tends to be uniform along the stack with increasing pressure, LUMO will become to form one-dimensional metal band due to the nordal plane of LUMO on the central Pd atom. And this one-dimensionality might cause the insulating instability at high pressure.

We have examined the crystal structure of $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ up to 10 kbar by using specially designed very flat diamond anvil. The diffraction patterns showed the doubling of the lattice constant



(a) (b)

FIGURE 1 (a) A phase diagram of $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ and (b) crystal structure of $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ at 10 kbar.

along the stacking direction of $Pd(dmit)_2$ molecules above 8 kbar. The crystal structure determined at 10 kbar is shown in Figure 1b[13]. The calculated intermolecular overlap integrals LUMO and HOMO indicated strong dimeric nature of the $Pd(dmit)_2$ column: e.g., LUMO$\cdots$LUMO overlap integral between intra- and interdimer molecules are $47(45)\times10^{-3}$ and $1(4)\times10^{-3}$, respectively (the values in parentheses are those at ambient-pressure). Therefore, the HOMO-LUMO re-inversion model was ruled out. As mentioned above, the doubling of lattice spacing along the $Pd(dmit)_2$ stack was observed at the pressure (>8 kbar) approximately equal to the critical pressure where the pressure-induced MI transition begins to appear. This structural transition is coupled with the order-disorder transition of ammonium cations (in the low-pressure phase, the ammonium cations are on the inversion centers). By doubling of the periodicity, it becomes very easy for the system to transform into insulating CDW(=charge density wave) state because of the 2 : 1 stoichiometry and fourfold stacks of $Pd(dmit)_2$. Thus, it is highly possible that the order-disorder transition of cation induces the MI transition at low temperature.

DEVELOPMENT OF MOLECULAR METAL BASED ON SINGLE COMPONENT MOLECULES

The design of molecular metal composed of single component molecules was a very difficult problem in the field of molecular conductors. In contrast to the typical inorganic metals such as sodium and copper composed of single elements, all the molecular metals ever developed were consisted of more than two components. It has been long believed that the formation of electronic band structure and the charge transfer between the molecules (A) constructing the band and other chemical species (B) are two essential requirements to obtain metallic state. In some cases, both molecules A and B form conduction bands where the electron and hole carriers are generated by the charge transfer between A and B. This was the reason why more than two components were needed to construct molecular metals. The difficulty of the design of single-component molecular metal is of course related to the fact that the molecule has usually even number of electrons and the highest occupied molecular orbital is doubly occupied.

We have recently obtained the guiding principle of molecular design of neutral metal composed of single component molecule based on the metal complexes with extended-TTF dithiolato ligands: [14] The energy separation between HOMO and LUMO should be small enough to make the HOMO and LUMO bands overlap each other by two-dimensional or three-dimensional intermolecular interactions and to form partially filled bands.

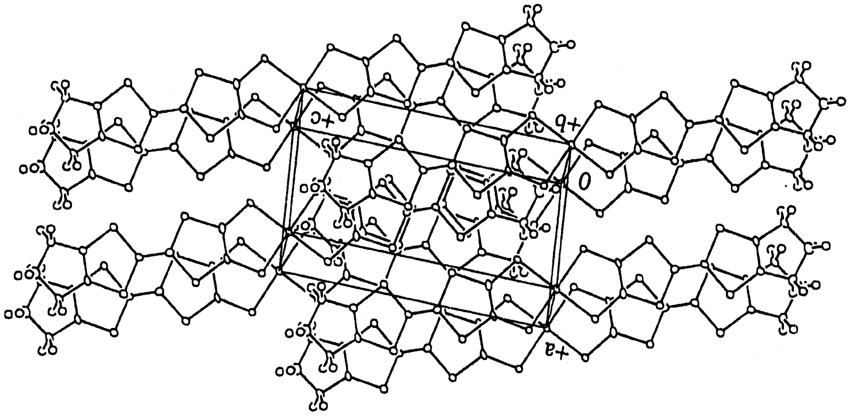


FIGURE 2 Crystal structure of [Ni(tmdt)$_2$].

According to these guiding principle, we have prepared the first metallic crystal composed of single component molecules [Ni(tmdt)$_2$] (tmdt = tri methylenetetrathiafulvalenedithiolate) [15].

The syntheses of tmdt ligand moiety with cyanoethylene group were performed according to the literature methods [16,17]. The oxidation of metal complexes was performed by electrochemical method and black plate crystals were obtained. The composition was determined by EPMA (electron probe microanalysis) and elemental analysis.

As shown in Figure 2, [Ni(tmdt)$_2$] molecules crystallize into very simple and compact structure with triclinic symmetry. Lattice constants are: $a = 6.376(3)\text{Å}$, $b = 7.359(1)$, $c = 12.012(7)$, $\alpha = 90.384(7)^\circ$, $\beta = 96.688(4)$, $\gamma = 103.587(4)$, triclinic $P\bar{1}$. The unit cell contains only one [Ni(tmdt)$_2$] molecule and half of the molecule is crystallographically independent. The molecule is ideally planar even at terminal trimethylene groups. It is very impressive that the neutral molecules form a closely packed structure. There are many short S$\cdots$S contacts between the molecules neighboring in the *ac* plane and also along [111] direction. The interplanar distance between the molecules on (0, 0, 0) and (a, b, c) is 3.346 Å and those on (0, 0, 0) and (a, 0, c) is 3.677 Å. These structural features suggest that the system has three-dimensional intermolecular interactions.

The single-crystal resistivity measurement was made down to 0.6 K using four-probe method. The room-temperature conductivity was 400 S cm^{-1} and the system retained metallic state down to 0.6 K (Figure 3) [15]. That is, neutral [Ni(tmdt)$_2$] crystal is the first single-component molecular metal. The resistivity measurement on a compacted powder sample also showed very high conductivity at room temperature (200 S cm^{-1}) and exhibited a

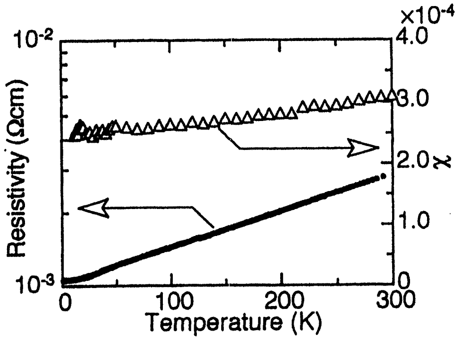


FIGURE 3 Resistivity and susceptibility measurements of Ni(tmdt)$_2$.

metallic behavior down to 70 K. Below 70 K, the resistivity was slightly increased but the value at 4 K was less than the room-temperature value. These facts suggest the small anisotropy of the resistivity, which is consistent with three-dimensional nature of the system. The susceptibility was measured on polycrystalline samples by SQUID magnetometer down to 2 K, which showed approximately temperature independent paramagnetic susceptibility consistent with Pauli paramagnetism of the system (Figure 3).

We have reported the *ab initio* MO calculation on the analogous molecule [Ni(ptdt)$_2$] with extended-TTF ligand ptdt (= propylenedithiotetrathiafulvalenedithiolate), which shows HOMO and LUMO are π-like molecular orbitals with b_{2g} and b_{1u} symmetries, (Figure 4a) respectively with HOMO-LUMO energy separation (ΔE) being very small (0.1 eV). We

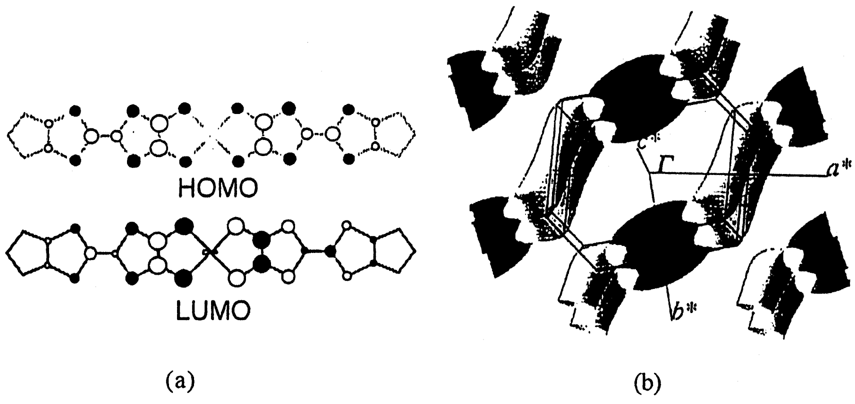


FIGURE 4 (a) HOMO and LUMO of [Ni(tmdt)$_2$] and (b) Three-dimensional Fermi surface of [Ni(tmdt)$_2$].

performed tight-binding band calculation of [Ni(tmdt)$_2$] crystal based on HOMO and LUMO orbitals. The intermolecular overlap integrals show that the system has a three-dimensional π band. As suggested previously, [14] three-dimensional intermolecular interaction is considered to produce the sufficiently large Fermi surfaces even when HOMO and LUMO form the "crossing bands". Considering the difficulty in the precise estimation of ΔE, the band calculations were performed with varying ΔE, which revealed that the system has the three-dimensional Fermi surfaces for $\Delta E < 0.6$ eV. The calculated Fermi furface is shown in Figure 4b. The electron and hole Fermi surfaces are arranged alternately in the plane approximately parallel to the $a^* - b^*$ and c^* axes.

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[13] The lattice constants at 10 kbar are: $a = 6.054(3)$ Å, $b = 14.521(5)$, $c = 18.226(6)$, $\alpha = 93.89(3)^\circ$, $\beta = 96.89(3)^\circ$, $\gamma = 94.02(4)$, where the relation between high pressure phase and low-pressure phase (a_0, b_0, c_0) are, $a = c_0, b = 2a_0 + c_0$ and $c = b_0$.

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