THE FIRST MOLECULAR SUPERCONDUCTOR BASED ON THE \( \pi \)-ACCEPTOR MOLECULE AND THE CLOSED SHELL CATION, \([(\text{CH}_3)_4\text{N}][\text{Ni(dmit)}]_2\)

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ABSTRACT
Molecular designing analyses and electrical properties of \([(\text{CH}_3)_4\text{N}][\text{Ni(dmit)}]_2\) and \(\alpha\)– and \(\beta\)-\([(\text{CH}_3)_4\text{N}][\text{Pd(dmit)}]_2\) are presented. In \([(\text{CH}_3)_4\text{N}][\text{Ni(dmit)}]_2\), the resistivity jump at around 100 K and the sharp rise of resistivity below 20 K were observed. In the sample where the low temperature anomaly was suppressed by high pressure, we have observed a superconducting transition: 3.0 K at 3.2 kbar and 5.0 K at 7 kbar. The 100 K anomaly is accompanied by large hysteresis. Non-linear conducting behavior was observed in this temperature region.

INTRODUCTION
The partially oxidized 1,2-dithiolene complexes have the conduction band derived from the ligand-centered \(\pi\)-system (predominantly sulfur orbitals), while partially occupied Pt-\(d_z^2\) electron energy band causes the high conductivity of the inorganic one-dimensional (1D) metals based on the tetracyanoplatinate or the bis(oxalato)platinum. The 1,2-dithiolene metal complexes based on the multi-sulfur ligand, 4,5-dimercapto-1,3-dithiole-2-thione(dmit) form conductive anion radical salts with various counter cations, and have provided new molecular superconductors, TTF[\text{Ni(dmit)}]_2[1] and \([(\text{CH}_3)_4\text{N}][\text{Ni(dmit)}]_2\]_2[2,3].

\(\text{M(dmit)}_2\) (M=Ni, Pd, Pt) is a nearly planar molecule. At first sight, the side-by-side arrangement of \(\text{M(dmit)}_2\) molecules similar to those found in BEDT-TTF complexes may be expected to make the \(\text{M(dmit)}_2\) complexes form multi-dimensional molecular metals. Recent discovery of stable metal state of (TTF)[\text{Ni(dmit)}]_2 and its three-dimensional (3D) intermolecular close S...S networks seemed to be an extremely good example. However, our molecular designing analysis based on the
extended Hückel band examination shows that the transverse interaction is not so strong enough to make the system multi-dimensional[4]. We consider the system to be essentially 1D and the origin of the stable metallic state of (TTF)[Ni(dmit)2]2 is not in the multi-dimensionality of the band structure but in the "multi-Fermi surfaces" nature. Similar to other planar \( \pi \)-acceptor molecules, M(dmit)2 molecules tend to stack face-to-face to form columns, which are connected by many intercolumnar S...S contacts. For the formation of the 2D metal state, the intermolecular side-by-side interaction must be large. The amplitude of the LUMO of M(dmit)2, which forms the electron conduction band, is very small on the "outer sulfur atom" in the five-membered heteroring compared with that on "the inner sulfur". Moreover owing to \( b_{2g} \) symmetry of LUMO, the intermolecular transverse overlap integrals are almost cancelled (Fig. 1). According to the map of intermolecular overlap integral(S) of LUMO of Ni(dmit)2 calculated as a function of configuration parameter[4], the side-by-side overlaps are less than 2x10^{-3}. These facts leads to the conclusion that the 2D metals can be hardly found in the M(dmit)2 complexes as long as the complex has a usual columnar structure.

There are many conductors based on the multi-sulfur \( \pi \)-molecules with weakly dimeric stacks, such as (TMTTF)2X (X=ClO4,PF6,...)[5] and [(CH3)4N][Ni(dmit)2]. Judging from the anisotropy of the overlap integrals, these materials have similar band structures. It may be of special interest that in these compounds only [(CH3)4N][Ni(dmit)2]2 maintains the high conductivity down to low temperatures.

Our simple extended Hückel band structure analyses, which assume that the fundamental feature of the band structure is determined from the HOMO of donor molecules and/or LUMO of acceptor molecules, lead to the following results: (1) When the band calculation gives a 2D closed Fermi surface, the system has a large possibility to retain a metallic state down to low temperatures, inspite of the relatively small S and the small room-temperature conductivity. (2) When the molecules are stacked face-to-face, it is almost impossible to realize a stable metallic state. To our knowledge, there are two exceptional cases in the metal-dmit complexes. They are (TTF)[Ni(dmit)2]2 and [(CH3)4N][Ni(dmit)2]2. In this report, molecular designing analysis and electrical properties of [(CH3)4N][Ni(dmit)2]2 and its Pd analogues will be presented.

RESULTS AND DISCUSSIONS

[(CH3)4N][Ni(dmit)2]2. Black plates of [(CH3)4N][Ni(dmit)2]2 were obtained by the electrochemical method from the acetonitrile solution of [(CH3)4N][Ni(dmit)2] and [(CH3)4N]ClO4. Crystal data are: monoclinic, C2/c, a=13.85, b=6.498, c=36.05 Å, \( \beta=93.8^\circ \). Planar Ni(dmit)2 molecules exhibit the face-to-face stack (Fig. 2).
There are two Ni(dmit)$_2$ columns parallel to [110] and [1$ar{1}$0], respectively. The close side-by-side arrangement of the Ni(dmit)$_2$ molecules are observed along the b axis. The tetrahedral tetramethylammonium cations are located on the two-fold axis and therefore they are in an ordered state. The room-temperature conductivity in the bc plane was 60 S cm$^{-1}$. The anisotropy of the electrical conduction parallel and perpendicular to the crystal (ab) plane is about 10$^3$. An anomalous resistivity jump at around 100 K and a rise of resistivity below 20 K were observed (Fig. 3). The resistivity behavior was sample dependent and sometimes strongly dependent on the measurement cycles. The rise of the resistivity below 20 K was observed generally but the resistivity anomaly around 100 K was sample dependent. In order to examine the possibility of some structure changes around 100 K, the X-ray oscillation photographs at 92 K were examined preliminary but no indication of structure change (or diffuse reflections) was observed. The 100 K anomaly is accompanied by large hysteresis. It is very interesting that the hysteresis loop depends on the temperature cycle (Fig. 4). Non-linear conducting behavior was also observed in this temperature region (Fig. 5). The resistivity was measured by applying a pulse current of 5 $\mu$s in order to avoid the heating effect. The critical current $I_c$ above which the resistivity decreases, increases with increasing temperature. This means that the critical voltage $V_c$ decreases with lowering temperature. The resistivity raise at low temperature region was observed for every sample. A preliminary ESR measurements gave no evidence of the phase transition. The line width becomes sharp with decreasing temperature. We think that this resistivity raise comes from the localization of electron due to the random potential, not a phase transition. The resistivity in this region is expressed as $\rho \propto \exp(\Delta E/kT)$ where $\Delta E$ is around 10 K. Although it is well-known that the superconductivity of the molecular systems is easily destroyed by the introduction of the random potential and the large sample dependence of the resistivity seems to indicate that there are fairly large lattice defects. We considered that [(CH$_3$)$_4$N][Ni(dmit)$_2$]$_2$ is a possible candidate of a new superconductor because this system exhibits no metal-insulator transition except for a small jump around 100 K. It might be possible that the pressure can suppress the electron localization effect. Since the samples become very fragile in the high-pressure cell and sensitive to the heat cycles, it seems to be not so easy to see a pure pressure effect. However, qualitative feature of the pressure effect was common to several samples examined. The pressure effect reduces both the 100 K and low temperature anomalous resistivity raises, but the extent to which the anomalies are suppressed was found to depend on samples. In the sample shown in Fig. 6, the increase of $\rho$ below 20 K is well suppressed at 8 kbar but no superconductivity observed down to 1.5 K. On the other hand, in the case shown in Fig. 7,
Fig. 1. Schematic drawing of LCAO of LUMO of Ni(dmit)$_2$.

Fig. 2. Crystal structure of [(CH$_3$)$_4$N][Ni(dmit)$_2$]$_2$.

Fig. 3. Temperature dependence of the resistivity from three different crystals.  
a) the current is along the crystal c-axis  
b,c) the current is in the ab plane.

Fig. 4. The resistivity anomaly around 100 K accompanied by large hysteresis.

Fig. 5. Non-linear conducting behavior around 100 K.
Fig. 6. Effect of the pressure on the temperature dependence of the resistivity.

Fig. 7. a) Low temperature resistivity which exhibits the superconducting transition under high pressure. The inset shows the change of the resistivity of temperature cycles. b) Magnetic field dependence of the resistivity under 3.2 kbar. The inset shows critical magnetic field as a function of temperature.

Fig. 8. Band energy and multi-Fermi surface.
the resistivity increase at low temperature can be suppressed completely. Although the resistivity increase tends to reappear by repeating the measurements, we have observed a sudden decrease of $\rho$ indicating a possible onset of superconductivity. We can draw a picture of the appearance of the superconducting state as follows. We suppose that the random potential in this sample is weak compared with other samples. In the ambient pressure, however, it is still so strong that electrons have localized wave functions which give rise to the exponentially increasing resistivity at low temperatures. When a high pressure is applied, on the other hand, the increase in the transfer probability of electrons between neighboring molecules makes the electron localization weak and in this rather pure sample it is sufficient to destroy the localization and to allow the superconducting state to appear. The onset temperature of the superconductivity transition is determined to be 3.0 K for 3.2 kbar and 5.0 K for 7 kbar. Such a positive pressure effect of $T_c (dT_c/dP>0)$, unusual in the molecular superconductors, is also observed in TTF[Ni(dmit)$_2$].

A calculation of the intermolecular overlap integrals of LUMO of Ni(dmit)$_2$, from which the conduction band is formed, suggests quasi-1D electronic structure (Fig. 8). Besides the band width, the band structure of one metal layer resembles to that of the well-known Bechgaard salt, we have examined many molecular conductors with similar weakly dimeric stacks of multi-sulfur $\pi$ molecules. All the systems are weakly metallic or semiconductive around room temperature. Except $[(\text{CH}_3)_4\text{N}][\text{Ni(dmit)}_2]_2$, however, all of them become insulator at low temperatures. What makes the $[(\text{CH}_3)_4\text{N}][\text{Ni(dmit)}_2]_2$ exceptional? The crystal is composed of the metal layer with 1D 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]. The cation sheet is sandwiched by two Ni(dmit)$_2$ sheets with different stacking directions. This means that the Brillouin zone contains two pairs of plane-like Fermi surfaces which cannot be nested by a single modulation wave vector. It may be possible that the "mismatch of the two lattice distortion waves" needed to vanish the two pairs of the plane-like Fermi surfaces will oppose the development of CDWs. The absence of the one-dimensional instability would be explained by the "multi-Fermi surface" nature of this system.

$[(\text{CH}_3)_4\text{N}][\text{Pd(dmit)}_2]_2$. We have obtained two different types of Pd analogues of $[(\text{CH}_3)_4\text{N}][\text{Pd(dmit)}_2]_2$, a triclinic form($\alpha$) and a monoclinic form($\beta$). Crystal data are: $\alpha$-form, triclinic, $P\overline{1}$, $a=35.48$, $b=7.807$, $c=6.320$ Å, $\alpha=112.10$, $\beta=94.21$, $\gamma=92.70^\circ$, $Z=2$; $\beta$-form, monoclinic, $C2/c$, $a=38.95$, $b=6.494$, $c=13.835$ Å, $\beta=99.630$, $Z=4$. The black plate-type crystals of $\alpha-[(\text{CH}_3)_4\text{N}][\text{Pd(dmit)}_2]_2$ were obtained by electrochemical oxidation of $[(\text{CH}_3)_4\text{N}][\text{Pd(dmit)}_2]_2$ in acetonitrile. The constant
current 0.6 \mu \text{A} was applied for 6 weeks and \[(\text{CH}_3)_4\text{N}]\text{ClO}_4\] was used as supporting electrolyte. The crystal structure of \(\alpha\)-[(\text{CH}_3)_4\text{N})[\text{Pd}(\text{dmit})_2]_2 is shown in Fig 9. There are crystallographically two independent molecules of Pd(dmit)_2 (A and B), which form uniform stacks along [010] and [011]. The cations lie between the two independent molecular columns. As shown in Fig. 9, two Pd(dmit)_2 molecules form a M...M dimer with interplanar distances 3.32 and 3.28 \AA. The Pd...Pd distances are 3.17 (A column) and 3.13 \AA (B column). The intermolecular contacts of S atoms within a dimer are short (3.28 \AA). The average displacement of the Pd atom from the plane of four ligand sulfur atoms is 0.09 \AA and the dmit ligands are bent towards the outside due to ligand-ligand repulsion. Hoffmann et al. have pointed out that metal-dithiolene complexes of Pt and Pd are tend to form the metal-metal dimer compared to Ni complexes, based on their theoretical calculation of potential energy of M...M and M...S dimerization of \([\text{M}(\text{S}_2\text{C}_2\text{H}_2)_2]\) (M=Pt, Ni) and a ligand-ligand repulsion [7]. In tetramethylammonium salts, the average Pd-S distances is 2.294 \AA, while Ni-S distance 2.158 \AA (formal oxidation state of Ni and Pd is 3.5+). The S-Pd-S angle is almost 90° and the four ligand sulfur atoms form a good geometry of square with both sides 3.24 \AA long. In the case of Ni salt, the sides of the square are 2.97 and 3.13 \AA and the S-Ni-S angle in the five-membered chelate ring is 93°. The \(\beta\)-form are prepared by diffusion method. The crystal structure resembles [(\text{CH}_3)_4\text{N})[\text{Ni}(\text{dmit})_2]_2, although Pd(dmit)_2 form a M...M dimer structure. \text{Cs}[\text{Pd}(\text{dmit})_2]_2, which has been recently prepared by Underhill, is isomorphous to \(\beta\)-form. The Cs salt show weakly metallic behavior down to about 60 K. The room temperature conductivity of \(\alpha\)-form is 50 S cm\(^{-1}\) and the resistivity slightly increases with the temperature decreases. The activation energy is 0.004 eV. Recently high pressure conductivity experiment of \(\alpha\)-form made by Murata [8], revealed that the weakly metallic behavior appears above 6kbar and the metal-insulator transition becomes sharp. It may be of interest that above 6 kbar increasing pressure increases the M-I transition temperature. The \(\beta\)-form shows semiconducting behavior. The R.T. conductivity is 50 S cm\(^{-1}\). The band energy calculations of these Pd(dmit)_2 salts suggest extremely narrow half-filled bands appear owing to their strong dimer structures. The dimeric arrangement of Pd(dmit)_2 suggests that Pd(dmit)_2 is not suitable for retaining stable metallic state.

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Fig. 9. a) Crystal structure of $\alpha$-[(CH$_3$)$_4$N][Pd(dmit)$_2$]$_2$ projected along the c-axis. b) dimer structures and modes of overlaps of Pd(dmit)$_2$ molecules.

REFERENCES

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