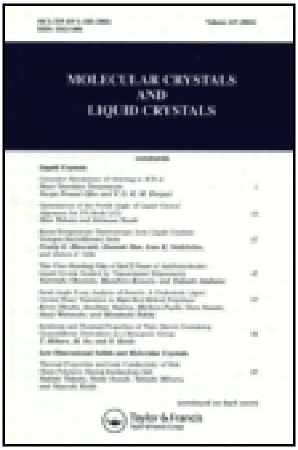

Molecular Crystals and Liquid Crystals

Single-Component Molecular Conductors

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Single-Component Molecular Conductors

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The novel nickel complex with the extended-TTF dithiolate ligand [Ni(tmdt)$_2$](tmdt = trimethylenedithiotetrathiafulvalenedithiolate) is the first single-component molecular crystal with metallic state down to very low temperature. Recently, a direct evidence for the presence of three-dimensional electron and hole Fermi surfaces was obtained by detecting de Haars-van Alphen (dHvA) oscillations of this system. An isostructural highly conducting [Au(tmdt)$_2$] system ($\sigma(RT) \approx 50$ S cm^{-1} (compaction pellet sample)) undergoes an antiferromagnetic transition around 110 K without loss of its high conductivity ($\sigma(110K) > 20$ S cm^{-1}). [Au(tmdt)$_2$] is the first molecular conductor exhibiting the coexistence of π conduction electrons and magnetic order above 100 K.

Keywords: de Haas-van Alphen effect; extended-TTF ligand; magnetic molecular conductor; single-component molecular metal

INTRODUCTION

Around 1950, D. D Eley discovered the semiconducting properties of metal-free phthalocyanine and copper phthalocyanine, well fitted in the formula $\rho = \rho_o \exp E/RT$ [1] and H. Akamatu and H. Inokuchi

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pointed out that violanthrone, iso-violanthrone and are semiconductors with resistivities of 10^9–10^{15} ohm cm, whose electrical conductivities were thought to be derived from π-electrons of carbon atoms of the network planes [2]. In 1954, H. Akmatu, H. Inokuchi, Y. Matsunaga reported that perylene-bromine complex was relatively stable and had very good conductivity of 1–10^{-3} S cm^{-1} [3]. Since these studies, the realization of molecular metal based on single-component molecules had been a long-standing target in the field of chemistry of molecular conducting systems.

In contrast to the typical inorganic metals such as sodium and copper composed of single elements, molecular metals developed until recently were consisted of more than two components (A, B). It had 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 necessary for the development of molecular metal.

However, we have recently succeeded to prepare a single-component molecular metal with stable metallic state down to very low temperatures. In this report, we present briefly the guiding principle of the design of single-component molecular metal and the physical properties of the first single-component molecular metal [Ni(tmdt)$_2$] [4–6] and the isostructural magnetic conductor [Au(tmdt)$_2$] [7].

GUIDING PRINCIPLE OF DESIGN OF SINGLE-COMPONENT MOLECULAR METAL

As indicated above, if the electron transfer between the electronic band derived from HOMO (the highest occupied molecular orbital) and that from LUMO (the lowest unoccupied molecular orbital) can be realized, the conduction electrons will be generated even in the crystal composed of single kind of molecules. Such situation will occur when the bottom of LUMO band is energetically lower than the top of the HOMO band. Considering that the band width of usual organic conductor is about 0.5 eV ($\approx 4000\,\mathrm{cm}^{-1}$), the anomalous molecule with electronic excitation energy (or HOMO-LUMO gap) in the infrared energy region must be developed in order to realize the "electron transfer" between HOMO and LUMO bands.

We adopted the transition metal complex molecule with extended π ligands having TTF skeleton to obtain the molecule with very small

HOMO-LUMO gap and the ability to form conduction bands. If the interaction between the ligands and the central transition metal atom can be neglected, an energy level pair with a small energy separation (ΔE) will appear due to the weak interaction between the left and the right TTF-like ligands through the small $\pi \ldots \pi$ overlap of sulfur atoms ($S_{\pi\pi}$) separated by the central metal atom ($\Delta E \approx 2kS_{\pi\pi}$). The resultant wave functions of these two states can be roughly written as ϕ_{H} and ϕ_{L} which represent HOMO and LUMO, respectively: $\phi_{\mathrm{H}} = \phi_1 + \phi_2$ and $\phi_{\mathrm{L}} = \phi_1 - \phi_2$ where ϕ_1 and ϕ_2 represent the left half and the right half of the ligand wave function. *Ab initio* MO calculations performed on [Ni(ptdt)$_2$] (ptdt = propylenedithiotetrathiafulvalenedithiolate) molecule to confirm the validity of this simple idea suggested very small HOMO-LUMO gap of this molecule as expected [8].

In the molecular conductors based on dithiolene complexes, the sign of intermolecular overlap intergal (S) (or transfer integral ($t = kS$; $k \approx 10\,\mathrm{eV}$)) of HOMO-HOMO interaction (S_{HH}) tends to be different from that of LUMO-LUMO interaction (S_{LL}) due to the difference of the symmetries between HOMO and LUMO. That is, HOMO and LUMO tend to form “crossing bands”, where HOMO-LUMO interaction will destroy Fermi surfaces. One way to protect Fermi surface is the enhancement of transverse interactions, which is almost the same condition required to stabilize the metallic state of molecular conductor against one-dimensional metal instability. This is the reason why the dithiolene complexes with extended TTF-ligands were adopted (the molecule with a TTF-like skeleton has a great advantage in enhancing transverse intermolecular interactions).

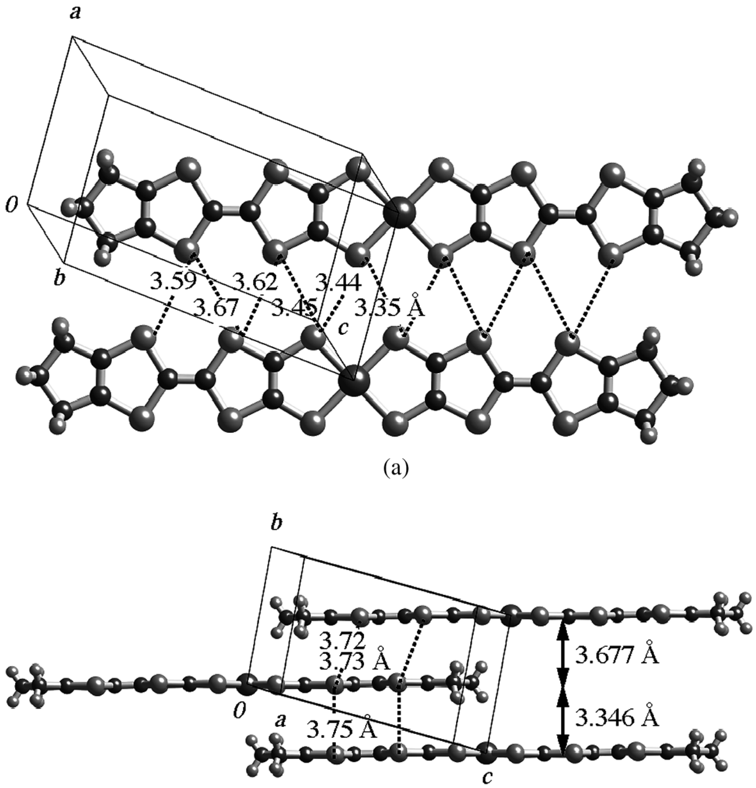
Thus, the following guiding principles to develop single-component molecular metals were derived: (1) The HOMO-LUMO energy gap of the constituent molecule must be anomalously small. (2) In the systems with crossing bands, large HOMO-HOMO and LUMO-LUMO transverse interactions are necessary to stabilize the metallic state. The dithiolene complex molecules with extended-TTF ligands are the suitable molecules to satisfy these requirements.

THE FIRST SINGLE-COMPONENT MOLECULAR METAL

According to the above guiding principle, we have prepared the crystal of [Ni(tmdt)$_2$] (tmdt^{2-} = trimethylenetetrathiafulvalenedithiolate) [4–6]. The synthesis of tmdt ligand moiety with cyanoethylene group was performed according to the literature methods [9]. The oxidation of metal complex, [Bu$_4$N]$_2$[Ni(tmdt)$_2$] was made by electrochemical method. Small black plate crystals of [Ni(tmdt)$_2$] were grown on platinum electrode.

As shown in Figure 1, [Ni(tmdt)$_2$] molecules crystallize into very simple and compact structure with triclinic symmetry. Lattice constants are: $a = 6.376(3)$ Å, $b = 7.359(1)$, $c = 12.012(7)$, $\alpha = 90.384(7)°$, $\beta = 96.688(4)$, $\gamma = 103.587(4)$, triclinic $P1$. The unit cell contains only one [Ni(tmdt)$_2$] molecule and half of the molecule is crystallographically independent. The molecule is ideally planar and the neutral molecules form a closely packed structure. There are many short S…S contacts between the molecules neighboring in the *ac* plane and also along [111] direction. These structural features suggest that [Ni(tmdt)$_2$] has three-dimensional (3D) intermolecular interactions.

The single-crystal resistivity measurement was made using four-probe method. The room-temperature conductivity was 400 S cm^{-1}



(a)

(b)

FIGURE 1 (a) Crystal structure of [Ni(tmdt)$_2$] viewed along the perpendicular axis of the molecular plane and S…S short contacts. (b) Side view of the molecular stacking and interplanar distances with S…S short contacts.

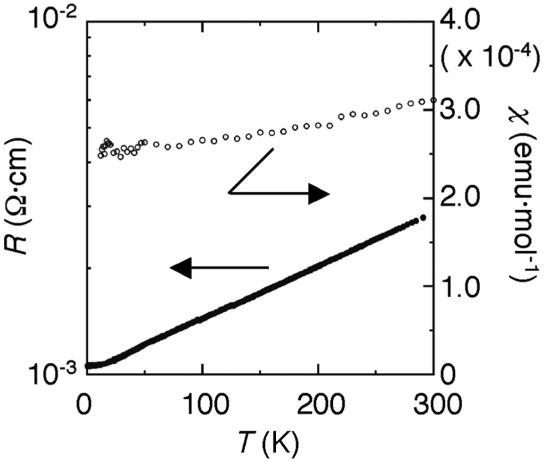
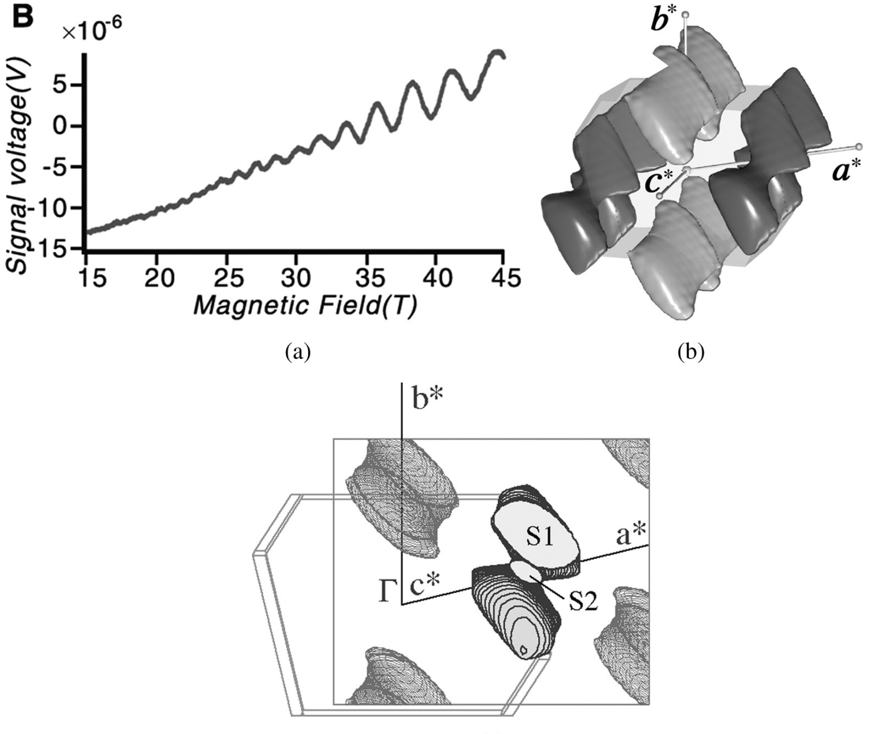


FIGURE 2 Temperature dependence of resistivities of single crystal (approximately along the a-axis) of [Ni(tmdt)$_2$] (solid line) and magnetic susceptibility χ of [Ni(tmdt)$_2$] crystals. The susceptibility was measured on a polycrystalline sample with a SQUID magnetometer within the temperature range of 2–300 K.

and the crystal retained metallic state down to 0.6 K (Fig. 2). The susceptibility was measured on polycrystalline samples by SQUID magnetometer down to 2 K, which showed approximately temperature independent paramagnetic susceptibility suggesting Pauli paramagnetism of the system (Fig. 2).

The direct experimental evidence for the Fermi surfaces was obtained by detecting the quantum oscillations in magnetization, the de Haas-van Alphen (dHvA) effect [10]. Torque magnetometry measurements of tiny single crystal of [Ni(tmdt)$_2$] using a sensitive microcantilever at low temperature in high magnetic field revealed the presence of electron and hole Fermi surfaces (Fig. 3). In order to compare the experimental results with electronic band structure calculations, the local density approximation (LDA) calculations based on the *ab initio* plane-wave norm-conserved pseudopotential method with Troullier-Martins potential were performed [11]. The HOMO and LUMO band widths were estimated to be 0.707 and 0.577 eV, respectively, and the two bands had an overlap of 0.195 eV, which is consistent with the results of the calculations by C. Rovira *et al.* [12] The electron and hole Fermi surfaces obtained by the dHvA experiments correspond well with the calculated 3D Fermi surfaces which unambiguously proved the existence of the metallic crystal consisting of single-component molecules.



(a) (b)

(c)

FIGURE 3 (a) Representative angular dependent dHvA oscillations. Measurements were carried out at temperatures down to 0.5 K in *dc* magnetic fields up to 45 T using the hybrid magnet at the National High Magnetic Field Laboratory at Florida State University. (b) Hole and electron Fermi surfaces and the first Brillouin zone of [Ni(tmit)$_2$]. (c) The extremal hole orbits (S1 and S2) for the field applied parallel to c^*.

NOVEL GOLD COMPLEX, [Au(tmdt)$_2$] WITH ANTIFERROMAGNETIC TRANSITION TEMPERATURE ABOVE 100 K

By replacing a central transition metal and/or ligands of [Ni(tmd)t]$_2$], various new single-component molecular conductors can be obtained. Some of them are metals and others are semiconductors, which are shown in Table 1. Among them, [Au(tmdt)$_2$] is one of very interesting systems [7]. Unlike a neutral bis(dithiolato)nickel complex, a neutral bis(dithiolato)gold complex has an odd number of total electrons. Since the crystals of [Au(tmdt)$_2$] were very small, the crystal structure of [Au(tmdt)$_2$] was determined by the synchrotron radiation X-ray

TABLE 1 Electrochemical Oxidation of Metal Complexes

Anionic complex	Electrolyte	Condition	Product	ρ (300 K)
$(Me_4N)_2[Ni(dmdt)_2]$	$(^nBu_4N)PF_6$ (50 mg)	MeCN (0.2 µA, 14 days)	$[Ni(dmdt)_2]$	300–400 $S\,cm^{-1}$ Metallic down to 230 K
$(Me_4N)_2[Pd(dmdt)_2]$	$(Me_4N)Cl$ (50 mg)	MeCN (0.4 µA, 10 days)	$[Pd(dmdt)_2]$	150 $S\,cm^{-1}$ Semiconductor
$(Me_4N)_2[Ni(tmdt)_2]$	$(^nBu_4N)ClO_4$ (50 mg)	MeCN (0.2 µA, 14 days)	$[Ni(tmdt)_2]$	400 $S\,cm^{-1}$ Metallic down to 0.6 K
$(Me_4N)_2[Cu(dmdt)_2]$	$(^nBu_4N)PF_6$ (50 mg)	THF (0.4 µA, 10 days)	$[Cu(dmdt)_2]$	3.0 $S\,cm^{-1}$ Semiconductor, $E_a = 40$ meV
$(^nBu_4N)[Au(tmdt)_2]$	$(^nBu_4N)ClO_4$ (80 mg)	THF (0.2 µA, 21 days)	$[Au(tmdt)_2]$	15 $S\,cm^{-1}$ $E_a = 20$ meV (300 K-50 K)
$(Me_4N)[Au(dmdt)_2]$	$(^nBu_4N)ClO_4$ (80 mg)	CH_2Cl_2 (0.2 µA, 21 days)	$[Au(dmdt)_2]$	12 $S\,cm^{-1}$ $E_a = 9$ meV (300 K-50 K)
$(Me_4N)_2[Co(dt)_2]$	$(^nBu_4N)ClO_4$ (80 mg)	PhCN (0.5 µA, 14–21 days)	$[Co(dt)_2]_2$	19 $S\,cm^{-1}$ (Metal)
$(Me_4N)_2[Ni(eodt)_2]$	$(^nBu_4N)ClO_4$ (80 mg)	PhCN (0.5 µA, 21–28 days)	$[Ni(eodt)_2]$	8 $S\,cm^{-1}$ Metallic down to 120 K
$(Me_4N)_2[Ni(chdt)_2]$	$(^nBu_4N)PF_6$ (80 mg)	PhCN (1.0 V, 40°C, 21–28 days)	$[Ni(chdt)_2]$	2 $S\,cm^{-1}$ Semiconductor, $E_a = 38$ meV
$(Me_4N)_2[Ni(hfdt)_2]$	$(^nBu_4N)PF_6$ (80 mg)	PhCl (1.0 µA, 14 days)	$[Ni(hfdt)_2]$	1.4×10^{-4} $S\,cm^{-1}$ Semiconductor, $E_a = 22$ meV
$(Me_4N)[Ni(ptdt)_2]$	$BaCS_3$ (95 mg)	20% Et_2O-MeCN (0.1 µA, 63 days)	$[Ni(ptdt)_2]$	7 $S\,cm^{-1}$ Semiconductor, $E_a = 30$ meV
$(Me_4N)_2[Ni(tmdt)_2]$ $(^nBu_4N)[Au(tmdt)_2]$	$(^nBu_4N)PF_6$ (250 mg)	MeCN (0.3 µA, 28 days)	$[Ni_{0.75}Au_{0.25}(tmdt)_2]$	180 $S\,cm^{-1}$ Metallic down to 0.5 K
$(Me_4N)_2[Ni(tmstfdt)_2]$	$(^nBu_4N)ClO_4$ (80 mg)	THF (0.3 µA, 21 days)	$[Ni(tmstfdt)_2]$	100 $S\,cm^{-1}$ Metallic down to 100 K

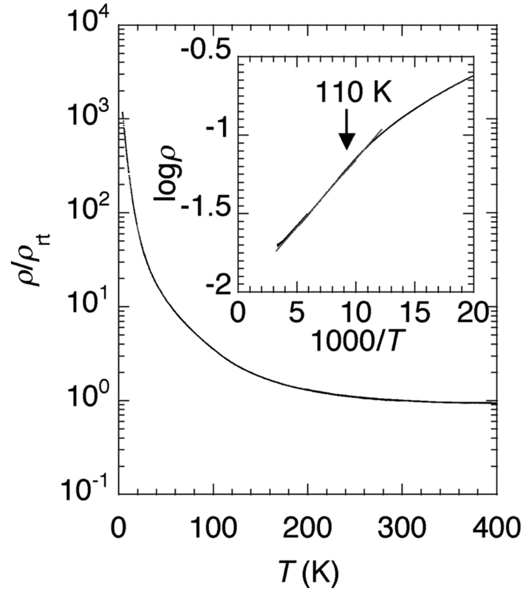


FIGURE 4 Resistivity of compressed pellet sample of [Au(tmdt)$_2$]. Inset shows the anomaly of the resistivity around 110 K.

powder diffraction experiments. The crystal structure of [Au(tmdt)$_2$] was found to be isostructural to that of [Ni(tmdt)$_2$]. Resistivity measurements were made by the four-probe method from room temperature down to 4 K on a compaction pellet sample, which gave large room-temperature conductivity of 50 S cm^{-1} and small activation energy of 16 meV (Fig. 4). The ESR spin susceptibility of polycrystalline sample of [Au(tmdt)$_2$] were measured at the temperature range of 3.4–300 K. The χ_s values was almost constant within the temperature range of 200–300 K, then increased gradually down to 130 K and decreased abruptly at 110 K, while the line width decreased almost linearly down to 120 K where an onset of rapid increase of line width was observed (Fig. 5). Recent ^{1}H NMR measurement showed the antiferromagnetic phase transition around 110 K [13]. Considering the high conductivity of the compaction powder sample ($>$20 S cm^{-1}) at 110 K, it is highly possible that [Au(tmdt)$_2$] takes an antiferromagnetic metal state below 110 K. The first principle band structure calculation suggested the disappearance of a part of the Fermi surfaces of [Au(tmdt)$_2$] around phase transition temperature. To our best knowledge, [Au(tmdt)$_2$] is the first molecular conductor exhibiting magnetic phase transition above 100 K without loss of its high conductivity.

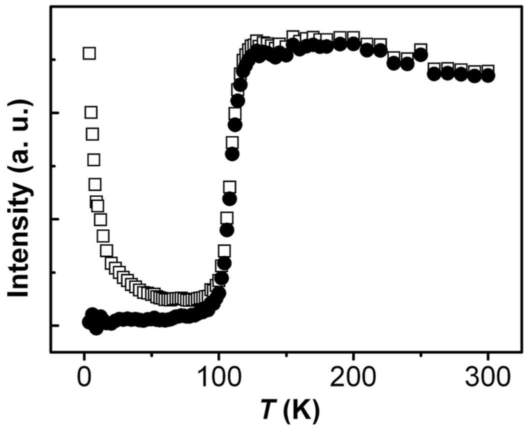


FIGURE 5 Spin Susceptibility of [Au(tmdt)$_2$]. The white squares show the original data and black circles show the values subtracted impurities.

It may be noteworthy that the antiferromagnetic transition temperature of [Au(tmdt)$_2$] is comparable to that of Mn, a representative inorganic antiferromagnetic metal consisting of metallic single-component elements ($T_N \approx 100\,K$).

CONCLUSION

The design and development of single-component molecular metal had been one of the long-standing problems in the field of chemistry of molecular conductors. [Ni(tmdt)$_2$] has solved this problem. The molecular crystal and metallic crystal had been considered to be the antipodal systems to each other. But [Ni(tmdt)$_2$] completely removed the boundary between them. Since the single-component molecular metal has been already realized, it might be not so difficult to realize "single-component molecular superconductor". Single-component molecular conductors will provide various possibilities for future development of molecular conducting systems.

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