IV-E Control of Intermolecular Interactions with Chemical and Physical Methods

The electronic state of the molecular conductor is quite sensitive to molecular arrangement and orientation that are governed by the inter-molecular interaction. Design of the inter-molecular interaction is indispensable in the rational development of molecular conductors to still higher forms. An introduction of supramolecular chemistry is a possible solution to this problem. This means that we change our viewpoint from the molecule to the *supramolecular synthon*. Tellurium has a strong tendency to form secondary bonds in crystalline compounds. We have used the tellurium-based secondary bond as a supramolecular synthon in anion radical salts.

On the other hand, the electronic state of molecular conductors can be quite sensitive to the pressure application if they are situated near the phase boundary and are soft enough to allow appreciable changes of molecular arrangement and orientation. The application of hydrostatic pressure has played significant roles in changing electronic states of low-dimensional molecular conductors. Furthermore, recent development of the uniaxial stress and strain methods have enabled selective or anisotropic regulation of the intermolecular interaction and provided a powerful means to search for novel electronic states. We have examined the uniaxial strain effect in the two-dimensional strongly correlated system based on the metal dithiolene complex.

IV-E-1 Unique Structural and Physical Properties of Ni(dmit)$_2$ Anion Radical Salts Characterized by Short Te···S Contacts, where dmit = 1,3-dithiole-2-thione-4,5-dithiolate

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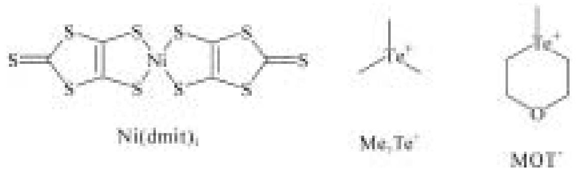
Five new Ni(dmit)$_2$ anion radical salts, [Me$_3$Te][Ni(dmit)$_2$]$_2$ **1**, [Me$_3$Te][Ni(dmit)$_2$]$_3$·acetone **2**, α-[MOT][Ni(dmit)$_2$]$_2$ **3**, β-[MOT] [Ni(dmit)$_2$]$_2$ **4** and γ-[MOT][Ni(dmit)$_2$]$_2$ **5** (MOT = 1-oxa-4-methyl-4-telluracyclohexane), have been prepared by the galvanostatic electrolysis (Scheme). X-ray crystal structure analyses show that all the salts are characterized by short Te···S contacts (3.41 ~ 3.85 Å) between the anions and cations. Each salt shows unique molecular packing of the Ni(dmit)$_2$ units. Electronic structures deeply depend on these unique molecular arrangements. Among them, **1** and **3** show metallic behavior (down to 60 and 160 K, respectively) and the resistivity of **4** is almost independent from the room temperature and increases moderately below 40 K.

This work has revealed that the Te(IV)-based cations have an ability to induce novel arrangements of the Ni(dmit)$_2$ units through the intermolecular Te···S contacts. Our results would open a way to the feasible control of the arrangement of the Ni(dmit)$_2$ anion radical by tuning cations with various shapes.



Scheme 1. Molecular structures of Ni(dmit)$_2$, Me$_3$Te$^+$, and MOT$^+$.

IV-E-2 Uniaxial Strain Effect in the Two-Dimensional Strongly Correlated System, β'-(CH$_3$)$_4$As[Pd(dmit)$_2$]$_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate)

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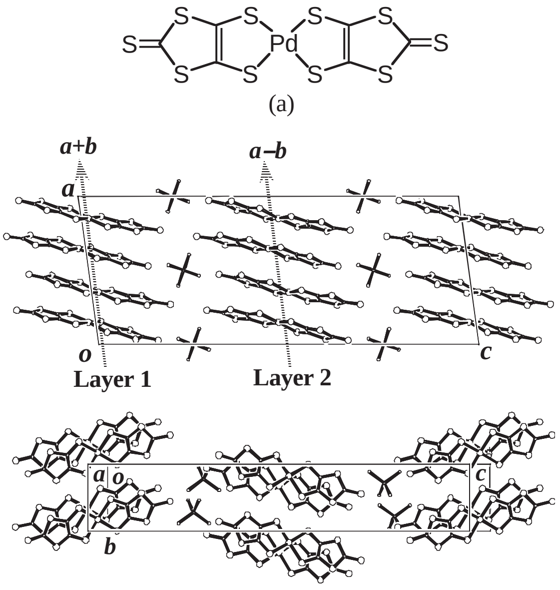
The molecular conductor β'-(CH$_3$)$_4$As[Pd(dmit)$_2$]$_2$ is a two-dimensional strongly correlated system based on the dimer structure (Figure 1). At low temperature, this system is a Mott insulator under ambient and hydrostatic pressure conditions. The electrical resistivities of this system have been measured under uniaxial strain along all three crystallographic axes. When the strain is applied parallel to the ***b*** axis within the ***a***-***b*** conducting layer, the non-metallic behavior is readily suppressed and superconductivity appears at 4 K under 7 kbar (Figure 2). On the other hand, small strain around 2 kbar along both the ***a***- and ***c***-axis directions effectively enhances the non-metallic behavior. With further increase of the strain, the non-metallic behavior is suppressed, but cannot be removed even at 15 kbar. These unusual results suggest the crucial role of intra- and inter-dimer interactions that affect the band width and the effective on-site Coulomb interaction.



(a)

(b)

Figure 1. (a) Molecular structure of Pd(dmit)$_2$. (b) Crystal structure of β’-(CH$_3$)$_4$As[Pd(dmit)$_2$]$_2$.

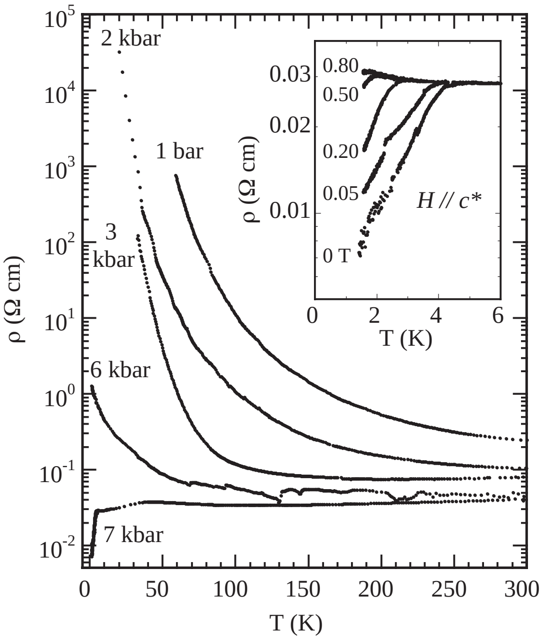


Figure 2. Temperature-dependence of the resistivity (ρ) under the uniaxial strain along the ***b*** axis. The inset shows the resistivity under the magnetic field parallel to the ***c****** direction at 7 kbar.