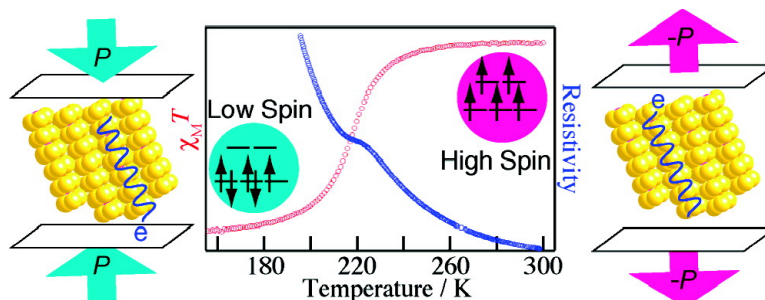


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## Evidence of the Chemical Uniaxial Strain Effect on Electrical Conductivity in the Spin-Crossover Conducting Molecular System: $[\text{Fe}^{\text{III}}(\text{qnal})_2][\text{Pd}(\text{dmit})_2]_5 \cdot \text{Acetone}$

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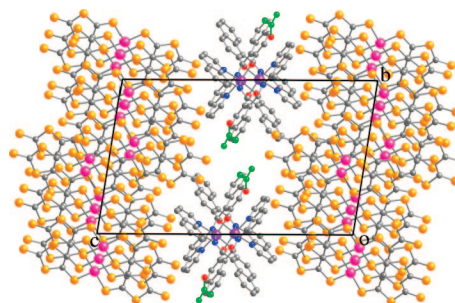
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Electronic properties in a molecular solid strongly depend upon their crystal structures because they consist of relatively weaker intermolecular interactions than a usual inorganic solid. Therefore, applying hydrostatic pressure is one of the most powerful tools to control the electronic properties of a molecular solid. Accordingly, there have been a great number of reports<sup>1</sup> about the pressure effects on molecular conductors, molecular magnets, and molecular di- and ferroelectrics.

Modification of the molecular structure by substitution of smaller or larger substituents also realizes a similar pressure effect on a molecular solid, which is known as chemical pressure effect. Deuterium substitution for the methyl groups of  $\text{DMeDCNQI}_2\text{Cu}$  ( $\text{DMeDCNQI} = 2,5\text{-dimethylidicyanoquinodiiimine}$ ) is one of the most remarkable examples of a chemical pressure effect because the conducting properties not only change from metallic to insulating states but also exhibit a reentrant transition between metallic and insulating states.<sup>2</sup>

Recently, the possibility of controlling electrical properties of molecular solids has been extensively explored by introducing a spin-crossover (SCO) ion into various potential conducting units<sup>3</sup> such as  $\text{TCNQ}^{3a}$  and  $\text{Ni}(\text{dmit})_2^{3c}$  ( $\text{TCNQ} = 7,7,8,8\text{-tetracyanoquinodimethane}$ ,  $\text{dmit} = 4,5\text{-dithiolato-1,3-dithiole-2-thione}$ ). Since the SCO phenomena are associated with a large structural change in the coordination environment of SCO ions, a spin transition can be considered to induce a type of chemical pressure effect. We have focused on strong intermolecular interactions such as interchalcogen atom<sup>3b</sup> and  $\pi\text{-}\pi^{3d,f}$  interactions for realization of a cooperative spin transition. In examining these interactions, we have discovered the first SCO conductor,  $[\text{Fe}(\text{qsal})_2][\text{Ni}(\text{dmit})_2]_3 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  [ $\text{qsalH} = N\text{-}(8\text{-quinolyl})\text{-salicylaldimine}$ ],<sup>3f</sup> which realizes the bistability of the conducting states coupled with a cooperative spin transition with a hysteresis loop. Unfortunately, we were not able to determine the crystal structure of the low-temperature phase, and thus the mechanism of the bistability of the electrical conducting states is still unclear. In the course of further studies on the related molecular systems, we found a novel SCO molecular conductor,  $[\text{Fe}(\text{qnal})_2][\text{Pd}(\text{dmit})_2]_5 \cdot \text{acetone}$  [ $\text{qnalH} = N\text{-}(8\text{-quinolyl})\text{-2-hydroxy-1-naphthaldimine}$ ], where an almost complete spin transition between the low-spin (LS) and high-spin (HS) states is coupled with not only an electrical conducting modulation but also a uniaxial crystal lattice deformation. The comparison of the low-temperature and high-temperature crystal structures revealed that the anisotropic strong intermolecular  $\pi\text{-}\pi$  interaction between the SCO cations as well as the chemical pressure effect of an SCO cation plays an important role in the electrical conducting modulation.



**Figure 1.** Crystal structure of  $[\text{Fe}(\text{qnal})_2][\text{Pd}(\text{dmit})_2]_5 \cdot \text{acetone}$  along the  $a$  axis. The acetone molecules are green, and the hydrogen atoms are omitted for clarity.

The starting material,  $[\text{Fe}(\text{qnal})_2][\text{Pd}(\text{dmit})_2] \cdot \text{acetone}$ , was prepared by metathesis of  $[\text{Fe}(\text{qnal})_2]\text{Cl}^4$  and  $\text{TBA}[\text{Pd}(\text{dmit})_2]_5$ .<sup>5</sup> The conducting complex,  $[\text{Fe}(\text{qnal})_2][\text{Pd}(\text{dmit})_2]_5 \cdot \text{acetone}$ , was obtained as very tiny black needles by oxidation through the application of a constant voltage of 1.5 V between two platinum electrodes fitted with an H-type glass cell.

Single-crystal structural analysis was performed by using a Rigaku CMF007 Mercury CCD system. The crystal structure of  $[\text{Fe}(\text{qnal})_2][\text{Pd}(\text{dmit})_2]_5 \cdot \text{acetone}$  at 293 K is shown in Figure 1. One  $\text{Fe}(\text{qnal})_2$  molecule and five  $\text{Pd}(\text{dmit})_2$  molecules are crystallographically independent in an unsymmetrical unit (Figures S1–S3). According to the Pd–Pd distances in the dimer<sup>6</sup> (Table S3) and the magnetic data described in the following, two kinds of dimers,  $[\text{Pd}(\text{dmit})_2]_2^0$  ( $\text{D}^0$ ) and  $[\text{Pd}(\text{dmit})_2]_2^-$  ( $\text{D}^-$ ), and one neutral monomer,  $[\text{Pd}(\text{dmit})_2]^0$  ( $\text{M}^0$ ), of the  $\text{Pd}(\text{dmit})_2$  molecules are stacked in a  $\text{D}^0\text{-M}^0\text{-D}^-$ – $\text{D}^-$ – $\text{M}^0\text{-D}^0$  manner, giving a one-dimensional column along the  $a$ - $b$  direction. A two-dimensional conducting layer of the  $\text{Pd}(\text{dmit})_2$  molecules is constructed by the much weaker intercolumn overlaps on the basis of the extended Hückel calculation (Table S4). The  $\text{Fe}(\text{qnal})_2$  cation is built up by the coordination of two tridentate  $\pi$  ligands to the central iron atom in an almost perpendicular manner. Each  $\pi$  ligand in the  $\text{Fe}(\text{qnal})_2$  cation overlaps that in the neighboring cations, forming one-dimensional cation chains along the  $a$  axis. The one-dimensional chains of the cations are divided by the number of acetone molecules.

The temperature dependence of the  $\chi_M T$  product is shown in Figure 2a and Figure S4. The  $\chi_M T$  value of  $4.70 \text{ emu K mol}^{-1}$  at 300 K suggests that the  $\text{Fe}(\text{III})$  ion is in the high-spin (HS) state and one spin on five  $\text{Pd}(\text{dmit})_2$  molecules survives. On lowering the temperature, the  $\chi_M T$  value gradually decreased at around 220 K and a plateau appeared below 150 K. The  $\chi_M T$  value on this plateau is  $1.02 \text{ emu K mol}^{-1}$ , which indicates the 93%  $\text{Fe}(\text{III})$  ion is in the low-spin (LS) state and one spin on five  $\text{Pd}(\text{dmit})_2$

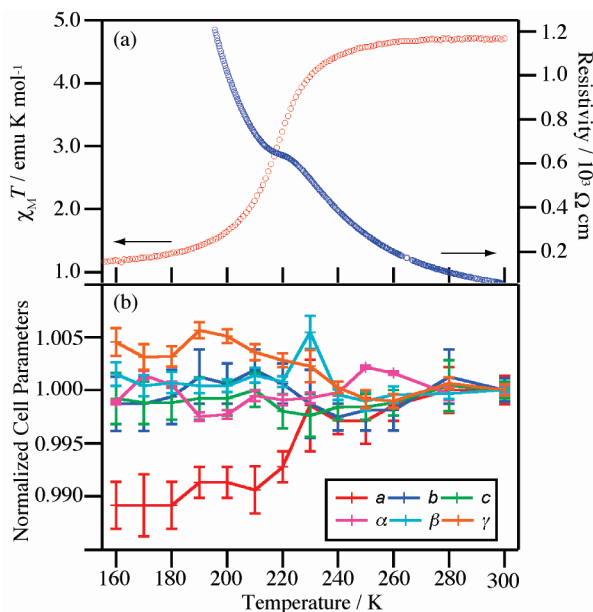
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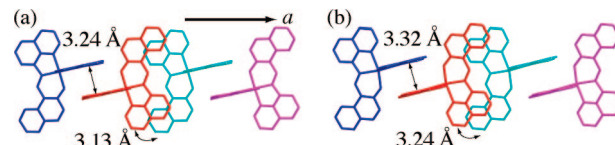
**Figure 2.** Temperature dependences of (a)  $\chi_M T$  and resistivity, and (b) the cell parameters normalized for 300 K.

molecules still survives. The gradual decrease in the  $\chi_M T$  value between 5 and 50 K suggests that the spins on the Pd(dmit)<sub>2</sub> layer are antiferromagnetically coupled. On heating, the  $\chi_M T$  value exactly traces the cooling process curve, resulting in no hysteresis loop associated with a spin conversion. The Mössbauer spectra of the <sup>57</sup>Fe-enriched sample at 9, 100, and 293 K are in good agreement with the above-described spin states, respectively.<sup>7</sup> In addition, on illuminating with a YAG laser (532 nm), this complex exhibited the light-induced excited spin state trapping (LIESST) effect at 5 K (Figure S5).

The temperature dependence of resistivity is also shown in Figure 2a. This complex is a semiconductor with  $1.6 \times 10^{-2} \text{ S cm}^{-1}$  at room temperature. Interestingly, the anomaly of resistivity was observed at around 220 K, in the same temperature range as the spin transition. The activation energies below and above the temperature of the anomaly were 0.37 and 0.24 eV, respectively.

The temperature dependence of the cell parameters normalized for 300 K are shown in Figure 2b. It should be noted that only the *a* axis, which runs exactly along the one-dimensional direction of the Fe(III) SCO cation molecules, is shortened at around 220 K, which is exactly in the same temperature range as the spin transition and the anomaly of resistivity. This cooperative shrinking of the *a* axis indicates that the structural modulation would be the origin of the anomalies of the conducting and magnetic properties.

Fortunately, the determination of the crystal structure at 105 K was successful. The crystal system and space group did not change between before and after the spin transition (Table S1). In the Pd(dmit)<sub>2</sub> layers, the distances between Pd atoms were slightly shortened on lowering the temperature (Table S3), but no significant change that could have driven both the *a* axis shrinking and the change in the charges of the Pd(dmit)<sub>2</sub> molecules was observed. On the other hand, a remarkable structural change in the coordination bond lengths ( $\Delta_{\text{Fe-O}}$ : 0.03–0.04 Å,  $\Delta_{\text{Fe-N}}$ : 0.15–0.18 Å; Table S2) and angles around the Fe(III) atom was observed, suggesting that the cation contraction induces the



**Figure 3.** 1D arrays of Fe(qnal)<sub>2</sub> cations along the *a* axis at (a) 105 and (b) 293 K. The values are the mean distances between neighboring  $\pi$  ligands. A van der Waals distance is 3.6–3.7 Å in a similar molecular system.

isotropic chemical pressure effect on the conducting layer. Furthermore, since the mean distances between  $\pi$  ligands of the neighboring cation molecules indicate the retention of strong  $\pi$ – $\pi$  interactions after the spin conversion from the HS to LS states (Figure 3), the connection of the contracted SCO cations parallel to the *a* axis results in the anisotropic shrinking of the *a* axis (0.2 Å). This clearly indicates that strong  $\pi$ – $\pi$  interactions as well as the contraction of an SCO cation play a key role in the coupling between electrical conducting modulation and spin transition.

In conclusion, [Fe(qnal)<sub>2</sub>][Pd(dmit)<sub>2</sub>]<sub>5</sub>·acetone is a novel SCO conductor coupled with a uniaxial lattice deformation. Recently, a uniaxial strain method has led to the creation of new electronic phases for molecular solids.<sup>8</sup> The present cooperative SCO phenomenon is considered to induce a chemical uniaxial strain effect on the conducting layer. Such a cooperativity based on supramolecular interactions is crucial for controlling or switching the electronic properties of a molecular solid by external stimuli.

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**Supporting Information Available:** Crystal analyses, magnetic data, and the LIESST effect. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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