Two Electrically Different Molecular Conductors Based on Unsymmetrical Au(III)-Dithiolene Complexes with Similar Crystal Structures

Kazuya Kubo\textsuperscript{a}, Akiko Nakao\textsuperscript{a}, Yasuyuki Ishii\textsuperscript{a}, Masafumi Tamura\textsuperscript{a}, Reizo Kato\textsuperscript{a}, and Gen-etsu Matsubayashi\textsuperscript{b}

\textsuperscript{a}RIKEN, JST-CREST, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan; e-mail: kkubo@riken.jp; \textsuperscript{b}Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan; e-mail: matsu@ch.wani.osaka-u.ac.jp

The cation radical salt based on unsymmetrical metal-dithiolene complexes $[\text{Au(ppy)}(\text{C}_8\text{H}_4\text{S}_8)^2][\text{PF}_6]$ (1) is a semiconductor with small activation energy under ambient pressure, and shows metallic behavior under high pressure. On the other hand, $[\text{Au(ppy)}(\text{C}_8\text{H}_4\text{S}_8\text{O}_2)^2][\text{BF}_4]$ (2) is an insulator in spite of the structural similarity. Effective conduction pathways through the $S\cdots S$ contacts were found in the crystal structure of 1. However, the crystal of 2 contains no such conduction pathways. Comparison of the energy band structures of 1 and 2 suggests that even a subtle difference in cation arrangements makes a remarkable difference between the electrical properties of 1 and 2.

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1. INTRODUCTION

We have reported the preparations and the crystal structures of mixed-ligand metal-dithiolene complexes of $[\text{M(N-N)(S-S)}]$ type (M = Pd\textsuperscript{2+}, Pt\textsuperscript{2+}; N-N = diimine ligand; S-S = dmit\textsuperscript{2-}, C\textsubscript{8}H\textsubscript{4}S\textsubscript{8}\textsuperscript{2-}) which contain HOMO on the dithiolene ligand and LUMO on the diimine ligand\textsuperscript{1,2}. These unsymmetrical metal-dithiolene complexes are capable of providing novel molecular conductors based on the unconventional electronic structures of the molecules. However, little is known about such type of metal-dithiolene complexes for molecular conductors\textsuperscript{3}, because of the difficulties in their preparation. The cation radical salts which contain $[\text{M(N-N)(S-S)}]$ type complexes exhibited an insulating or semiconducting behavior\textsuperscript{2}. In order to improve the conducting ability, we have prepared unsymmetrical

\begin{center}
\begin{figure}
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\includegraphics[width=0.8\textwidth]{Scheme_1.png}
\caption{Scheme 1}
\end{figure}
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\[ \text{[Au(ppy)(S-S)]} \quad (\text{ppy}^- = \text{C-2'-dehydro-2-phenylpyridine}; \text{S-S}^{2-} = \text{C}_8\text{H}_4\text{S}_8^{2-}; \text{C}_8\text{H}_4\text{S}_2\text{O}_2^{2-}) \text{ type complexes} \text{ (Scheme 1)}\]. The dithiolene ligands, \( \text{C}_8\text{H}_4\text{S}_8^{2-} \) and \( \text{C}_8\text{H}_4\text{S}_2\text{O}_2^{2-} \), include moieties of the organic donor ET or BO, respectively\(^5\), which have provided many metals and superconductors. Various cation radical salts of them have been obtained. Among them, a cation radical salt, \[ \text{[Au(ppy)(C}_8\text{H}_4\text{S}_8)]_2[\text{PF}_6] \] (1) is a semiconductor at ambient pressure and easily turns to be metallic by pressure. However, \[ \text{[Au(ppy)(C}_8\text{H}_4\text{S}_2\text{O}_2)]_2[\text{PF}_6] \] (2) is a tough insulator. In this paper, this difference is discussed on the basis of crystal structures, energy band calculations and magnetic susceptibility.

2. RESULTS AND DISCUSSION

Crystal structures of 1 and 2 were reported previously\(^3\). Schematic end-on projection of the cation arrangement in the crystal of 1 is shown in Scheme 2. There are two crystallographically independent cation radicals, A and B, in 1. The columnar structure is formed by the two-fold head-to-head stacking of the cation radicals. The crystal of 2 also contains the stacking pattern similar to that of 1. Subtle differences of cation arrangements exist between 1 and 2. In 1, there are many \( \text{S}^\cdots\text{S} \) contacts (3.339-3.616 Å) shorter than the sum of van der Waals radii (< 3.7 Å) within and between the columns. On the other hand, non-bonded \( \text{S}^\cdots\text{S} \) contacts (3.686 Å) are observed only between the columns in 2. The distances between the molecular planes are 3.49 and 3.51 Å in the column of 1. The corresponding distances in 2 (3.56 and 3.61 Å) are longer than those of 1. Formation of hydrogen bonds (O\cdots H distance: 2.62-2.70 Å) is observed between the cation radicals within the column in 2\(^6\). The molecules are slid along the molecular long axes by the hydrogen bonds, resulting in reductions of the number of the \( \text{S}^\cdots\text{S} \) contacts and the face-to-face overlapping. There are no hydrogen bonds in the crystal of 1.

The energy band structures of 1 and 2 have been calculated by the tight-binding method based on the crystal structural data (Fig. 1). The results

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**Scheme 2**

Table 1 Calculated overlap integrals between HOMOs (S) (×10^3)

<table>
<thead>
<tr>
<th>S</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>-7.9</td>
<td>-0.9</td>
</tr>
<tr>
<td>a2</td>
<td>-8.6</td>
<td>-4.6</td>
</tr>
<tr>
<td>b1</td>
<td>1.2</td>
<td>-0.2</td>
</tr>
<tr>
<td>b2</td>
<td>-1.9</td>
<td>-0.4</td>
</tr>
<tr>
<td>b3</td>
<td>1.0</td>
<td>-1.5</td>
</tr>
<tr>
<td>b4</td>
<td>-1.2</td>
<td>-0.2</td>
</tr>
<tr>
<td>p1</td>
<td>1.1</td>
<td>-0.7</td>
</tr>
<tr>
<td>p2</td>
<td>-0.8</td>
<td>-0.2</td>
</tr>
</tbody>
</table>
of the calculations show that the difference in the cation arrangements provides remarkable distinctions. Dimerization in 2 is remarkable, i.e. the face-to-face interaction a1 is much weaker than a2 (Table 1). This explains the larger gap between the second and third band. The difference between a1 and a2 in 2 comes from the slipping molecular overlap caused by the hydrogen bonds. The hydrogen bonds sometimes contribute to make effective conduction pathways in the molecular Conductors. In the case of 2, however, the hydrogen bonds prohibit effective interactions between the cations. The upper two bands are separated from each other as a result of the two-fold intercolumn interactions in 2 (Fig. 1(b)). The band structure of 1 shows different features (Fig. 1(a)). In 1, the face-to-face interactions (a1 and a2) are larger than the side-by-side interactions (b1-b4 and p1-p2), indicating that this system has a quasi one-dimensional character. The second and third bands are much less separated than in 2, in accordance with the weak dimerization within the column. Each of the two conduction bands slightly separated by the two-fold arrangement of the columns along the b axis is not half-filled. These band calculations suggest that 1 can be a metal but 2 is a band insulator.

Fig. 1 Calculated band structures of (a) 1 and (b) 2. Γ-X and Γ-Y lines denote the \( a^* \) and \( b^* \) axes, respectively, and L, M, N are the corners on the boundary of the first Brillouin zone.

Temperature dependence of electrical resistivities of 1 and 2 was measured from 300 K to 4 K by the standard four-probe DC method. The salt 2 is an insulator (\( \rho_{\text{L},\text{T}} = 1 \times 10^5 \) Ω cm) at ambient pressure as indicated by the band calculation. The salt 1 exhibits a semiconducting behavior with small activation energy (\( \rho_{\text{L},\text{T}} = 2.6 \) Ω cm, \( E_a = 0.03 \) eV) under ambient pressure. A metallic behavior is observed from 300 K to 100 K under 0.8 GPa, and it is retained down to 20 K under 2.0 GPa. The temperature dependence of magnetic susceptibility of 1 was measured from 300 K to 4 K.
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at 5 T. The spin susceptibility of 1 gradually decreased down from 300 K to 50 K. Below 50 K, the susceptibility exhibits a rapid decrease accompanied by anisotropic temperature dependence, which is an indication of an antiferromagnetic ordering. A one-dimensional Heisenberg model is applicable to the data above 100 K. These results indicate that 1 is a paramagnetic insulator at ambient pressure with a localized $S = 1/2$ spin on each repeating unit (A and B), in spite of the expected metallic band structure. This discrepancy suggests significant role of the strong correlation.

3. CONCLUSIONS

Examination of the crystal and band structures of the present compounds has revealed that the intracolumn hydrogen bonding between the donor molecules prevents the conduction pathways, as shown by the entirely insulating behavior of 2. Metallic conductivity was observed in 1 at high pressures (>0.8 GPa). Contrary to the calculated band structure, 1 is found to be a paramagnetic insulator at ambient pressure with the localized $S = 1/2$ spin on the formula unit.

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REFERENCES