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# A Conducting Crystal Based on A Single-Component Paramagnetic Molecule, $[Cu(dmdt)_2]$ (dmdt = Dimethyltetrathiafulvalenedithiolate)

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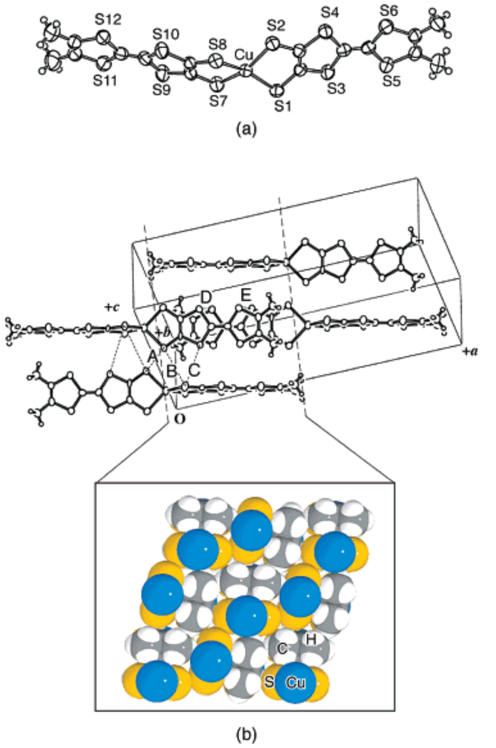
Until quite recently, it was believed that molecular conductors consist of more than two chemical species. Charge transfer between molecules comprising conduction bands and another chemical species has been considered indispensable to generate charge carriers. Since the middle 1990s, it has been reported that neutral transition-metal complexes with extended tetrathiafulvalene (TTF) dithiolate ligands can be conductive to some extent.[1−4] Most recently, we prepared the crystal of a neutral complex, $[Ni(tmdt)_2]^{0+}$ (tmdt = trimethylenetetrathiafulvalenedithiolate), and found that it had very high conductivity (400 S $cm^{-1}$ at room temperature) and metallic behavior down to 0.6 K.[5] The metallic properties are explained on the basis of a closely packed structure and a very small HOMO−LUMO gap.[5−7]

Single-component molecular metals should greatly extend the development of new types of molecular conductors. For example, while the first metallic molecule-based magnet has been reported recently,[8] it may be possible to create such metallic molecular magnets from single-component molecules containing paramagnetic ions such as $Cu^{2+}$ and $Co^{2+}$. Herein, we report the structural, electrical, and magnetic properties of crystals composed of a single-component copper complex with an extended TTF ligand, $[Cu(dmdt)_2]^{0+}$ **1** (dmdt = dimethyltetrathiafulvalenedithiolate), to contribute to clarify the possibility of single-component magnetic molecular conductors.

The syntheses of the extended TTF ligand, dmdt, and the corresponding copper complex were performed according to the literature methods under a strictly inert atmosphere using the Schlenk technique.[6] The copper source was $CuCl_2{\cdot}2H_2O$. The tiny, black platelike crystals of **1** were prepared by the electrochemical oxidation of $(Me_4N)^+{}_2[Cu(dmdt)_2]^{2-}$ using $(n\text{-}Bu_4N)PF_6$ as the electrolyte and tetrahydrofuran as solvent in an H-shaped cell. X-ray structure determinations were made on the crystals of **1** and $(n\text{-}Bu_4N)^+{}_2[Cu(dmdt)_2]^{2-}$ **2** obtained by cation exchange of tetramethylammonium salt.

Figure 1a shows the molecular structure of the dianion complex, $[Cu(dmdt)_2]^{2-}$ in **2**. The coordination geometry of copper is greatly distorted from planar and the molecular long axis is curved. The dihedral angle between the least-squares planes of two extended TTF ligands is 33.5°, which is smaller than that for the other copper complexes such as $[Cu(ptdt)_2]^{2-}$ (52.5°) and $[Cu(dmit)_2]^{2-}$ (57.3°) (ptdt = propylenedithiotetrathiafulvalenedithiolate: dmit = 4,5-dimercapto-1,3-dithiole-2-thionate).[3,9]

On the other hand, as shown in Figure 1b, the molecular structure of the neutral complex **1** is also nonplanar, while the dmdt ligand moiety is almost ideally planar and has a straight molecular long axis. The dihedral angle between the ligand planes is 80.29°. As shown in the lower part of Figure 1b, the neutral molecules take an unprecedented molecular arrangement. It is completely different from the molecular arrangement in $[Ni(tmdt)_2]^{0+}$ where, ideally, planar molecules are closely packed to form a three-dimensional metallic state.[5,6,10] One of the ligands of **1** overlaps, face-to-face, with the ligand of the adjacent molecule, and the opposite-side ligand overlaps with the ligand of the third molecule (see the Table of Contents graphic). Thus, the dmdt ligands take an arrangement similar to that of "κ-type organic superconductors" first found in 1987.[11] S⋯S short contacts exist between adjacent molecules, as shown in Figure 1b.



(a)

(b)

***Figure 1.*** (a) Molecular structure of dianion copper complex in **2**. (b) Molecular arrangement of **1**. The lower part of figure presents the arrangement of ligand moieties projected along the molecular long axis. The S⋯S contacts are shown as dotted lines. A: 3.45 Å, B: 3.69 Å, C: 3.73 Å, D: 3.70 Å, E: 3.66 Å.

The short S⋯S contacts exist not only in the layer with a κ-type ligand arrangement but also between the adjacent layers. These structural features suggest the possibility that three-dimensional electrical conduction pathways exist.

The resistivity measurements on the crystals of **1** showed fairly high conductivity though the quality of the crystals was poor (about 3 S $cm^{-1}$ at room temperature). Despite the semiconducting

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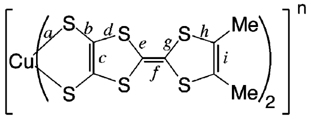
***Table 1.*** Average Bond Lengths (Å) of the Dianion ($n = 2-$) and Neutral ($n = 0+$) $[Cu(dmdt)_2]^{n\,a}$



| | $n = 2-$ | $n = 0+$ | $\Delta$ |
|---|---|---|---|
| *a* | 2.287(1) | 2.282(1) | −5 |
| *b* | 1.738(3) | 1.683(4) | −55 |
| *c* | 1.341(4) | 1.414(9) | 73 |
| *d* | 1.766(3) | 1.743(4) | −23 |
| *e* | 1.756(3) | 1.738(4) | −18 |
| *f* | 1.342(5) | 1.361(7) | 19 |
| *g* | 1.758(3) | 1.737(4) | −21 |
| *h* | 1.748(3) | 1.762(4) | 14 |
| *i* | 1.330(5) | 1.353 (9) | 23 |

[a] The standard deviations are in parentheses and $\Delta$ ($\times 10^{-3}$ Å) represents the differences of the bond lengths between neutral and dianion states.

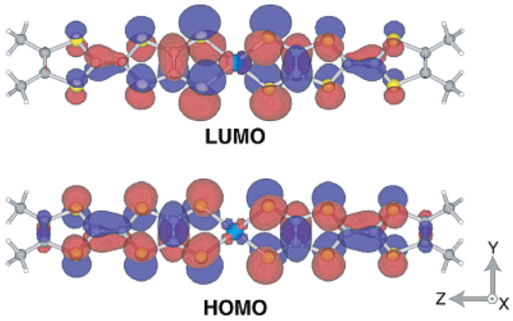


***Figure 2.*** Calculated HOMO and LUMO of **1**. The molecule has $D_2$ symmetry and the ligand plane of the left (right) part is rotated clockwise (anticlockwise) by 40.15° around the *z*-axis.

properties, the activation energy was very small (∼40 meV). On the other hand, the crystal of **2** was found to be an insulator.

The magnetic susceptibilities of crystals **1** and **2** were measured by SQUID. A Curie−Weiss behavior was observed for **2** ($\chi_{rt} = 1.33 \times 10^{-3}$ emu·mol$^{-1}$, $C = 0.40$ emu·K·mol$^{-1}$, $\theta = -0.2$ K), indicating the existence of an isolated $S = {}^1/_2$ spin on each molecule. The temperature dependence of the susceptibility of **1** was also completely fitted by a Curie−Weiss plot ($\chi_{rt} = 1.09 \times 10^{-3}$ emu·mol$^{-1}$, $C = 0.33$ emu·K·mol$^{-1}$, $\theta = -4.2$ K). The Curie constant suggests the existence of 84% of $S = {}^1/_2$ spin moments (estimated on the basis of a *g*-value (2.035) obtained by EPR experiments). This result is inconsistent with the reported ones about the similar copper complexes, in which the most of magnetic moments were lost by oxidation to the neutral state.[12]

It is well-known that the bond lengths of TTF-like $\pi$ donor molecules are changed systematically with alterations to the formal charge of the molecule. As shown in Table 1, the bond lengths of neutral molecule **1** ($[Cu(dmdt)_2]^n$, $n = 0+$) show a considerable difference from those of the dianion in **2** ($n = 2-$). Figure 2 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1**. The ab initio molecular orbitals were calculated by Gaussian 98 using the 6-311+G** basis set and unrestricted LANL2DZ functional with $D_2$ symmetry, and the dihedral angle was fixed at 80.29°.

The changes in the bond lengths between **1** and **2** reflect the symmetry of the LUMO. By the oxidation from (2−) to (0+), all the C═C bonds become longer, indicating that the LUMO has bonding character on each C═C bond. On the other hand, except for the bond *h* showing a very small positive change, S−C bonds tend to be shortened, suggesting antibonding character of the LUMO on C−S bonds. Very large changes in the bonds *b* and *c* suggest the large amplitude of the LUMO on the S and C atoms in the central five-membered ring. These features are in good agreement with the general features of the calculated molecular orbitals and also those of extended TTF ligand complexes such as $[Ni(ptdt)_2]^{0+}$ and $[Ni(tmdt)_2]^{0+}$.[6,7,10] In other words, the molecular orbital symmetry on the extended TTF ligands is similar to the HOMO of the TTF-like molecule, as was suggested previously.[5−7] The small change of Cu−S bond length and the large change in extended TTF ligands indicate that the oxidation of $[Cu(dmdt)_2]^{2-}$ takes place mainly in the ligand portion.

In conclusion, by using $Cu^{2+}$ and the dmdt ligand, a conducting crystal consisting of single-component molecules incorporating magnetic moments has been developed. The crystal structure shows an unprecedented, three-dimensional, close molecular packing structure. The comparison of bond lengths of $[Cu(dmdt)_2]^{0+}$ and $[Cu(dmdt)_2]^{2-}$ indicates that the LUMO of $[Cu(dmdt)_2]^{0+}$ has a molecular orbital symmetry on the extended TTF ligand similar to that of the HOMO of TTF-like $\pi$ donors.

**Supporting Information Available:** X-ray crystallographic files for **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data, in CIF format for **1** (CCDC-180569) and **2** (CCDC-180655), has been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html.

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