Single-component Molecular Conductor $[Zn(tmdt)_2]$ and Related Zn Complexes

Kimiko Yamamoto, Emiko Fujiwara, Akiko Kobayashi,* Yuichi Fujishiro,† Eiji Nishibori,† Makoto Sakata,†
Masaki Takata,†† Hisashi Tanaka,††† Yoshinori Okano,†††† and Hayao Kobayashi††††
Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113-0033
†*Department of Applied Physics, Nagoya University, Nagoya 464-8603*
††*Japan Synchrotron Radiation Research Institute/SPring-8, Sayo-gun, Hyogo 679-5198*
†††*Nanotechnology Research Institute, AIST, Tsukuba, Ibaraki 305-8568*
††††*Institute for Molecular Science and CREST, JST, Okazaki 444-8585*

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Single-component molecular conductors based on zinc complexes with filled 3d shells and extended-TTF ligands, $[ZnL_2]$ (L = tmdt, dmdt, and dt) were prepared. The crystal structure of semiconducting $[Zn(tmdt)_2]$ (ρ (rt) $\approx 50\,\Omega\,cm$) was determined by the synchrotron radiation X-ray powder diffraction experiments. The molecule has a tetrahedral geometry and two ligand planes are almost perpendicular to each other.

Recently, a considerable interest has been attracted to the conducting systems consisting of single-component molecules.[1,2] We have recently reported the observation of de Haas–van Alphen oscillation of the first single-component molecular metal, $[Ni(tmdt)_2]$ (tmdt = trimethylenetetrathiafulvalenedithiolate),[3] which rigorously proved $[Ni(tmdt)_2]$ to be a three-dimensional metal as expected. However, there seems to remain some question on the role of d orbitals of the central transition metal atom. Is the role of d orbital of the central transition atom is essential to make the system conducting? Since the zinc atom has the filled 3d shell, the role of the d orbitals will be less important. The ligand π orbitals will be responsible for the band formation. Herein, we report the crystal structure, electrical and magnetic properties of Zn complexes with extended-TTF (= tetrathiafulvalene) dithiolate ligands, $[ZnL_2]$ (L = tmdt (**1**), dmdt (**2**), and dt (**3**); dmdt = dimethyltetrathiafulvalenedithiolate and dt = tetrathiafulvalenedithiolate).

All the syntheses were carried out under argon atmosphere.[4,5] $(Me_4N)_2[ZnL_2]$ (L = tmdt, dmdt, and dt) were obtained as air-unstable orange powder by hydrolysis of three ligands with cyanoethyl group using 25 wt % Me_4NOH/methanol in dry tetrahydrofuran, followed by the reaction of $ZnCl_2$/dry methanol solution at −78 °C to the room temperature. Electrochemical oxidation of $(Me_4N)_2[ZnL_2]$ (L = tmdt, dmdt, and dt) was performed in the presence of $^{n}Bu_4N{\cdot}PF_6$ in dry acetonitrile under a constant current of 0.1 µA. The air-stable black microcrystals were obtained after 2 weeks.[6] The electron probe microanalysis (EPMA) measurements on **1** and **2** showed that the ratio of S and Zn atoms of these compounds is almost 12:1.

The synchrotron radiation X-ray powder diffraction experiments were carried out on **1** by use of the imaging plate detectors and the large Debye–Sherrer Camera at the SPring-8 BL02B2.[7] The wavelength of incident X-ray was 1 Å and the exposure time of measurement was 120 min. An X-ray pattern was obtained in 0.01° steps in 2θ from 3.50° to 72.00°. The crystal structure was determined by Rietveld/MEM method, which revealed that both the molecular geometry and packing resemble those of $[Cu(dmdt)_2]$ (Figure 1).[8] The geometry around Zn atom is tetrahedral and the Zn–S distances are both 2.326(2) Å and the S–Zn–S angle is 94.21(7)°. The ligands are planar and two ligand planes are almost perpendicular to each other (the dihedral angle of two planes = 89.63° (cf. 80.29° in $[Cu(dmdt)_2]$). As shown in Figure 1b, one of the tmdt ligands overlaps, face-to-face, with the ligand of the neighboring molecule, and the opposite side ligand overlaps with the ligand of the third molecule. The interplanar distance between the ligand planes is 3.438 Å, which is fairly shorter than 3.496 Å in $[Cu(dmdt)_2]$. The tmdt ligands take an arrangement similar to the "κ-type arrangement" of organic superconductors and the adjacent "ligand planes" with κ-type arrangement are connected by Zn atoms. In addition, there exist many intermolecular short S···S contacts (<3.7 Å) (see Figure 1b). Thus $[Zn(tmdt)_2]$ (**1**) is considered to have 3D conduction paths.

The magnetic susceptibility of **1** was measured using a SQUID magnetometer at a field of 1 Tesla over the temperature range of 2–300 K. The diamagnetic contribution of magnetic susceptibility (-2.92×10^{-4} emu·mol^{-1}) was deduced from the susceptibility measurements of $tmdt(CH_2CH_2CN)_2$ and Pascal's constants. The magnetic susceptibility of **1** gave almost temperature-independent paramagnetism ($\chi_p = 1.3 \times 10^{-4}$

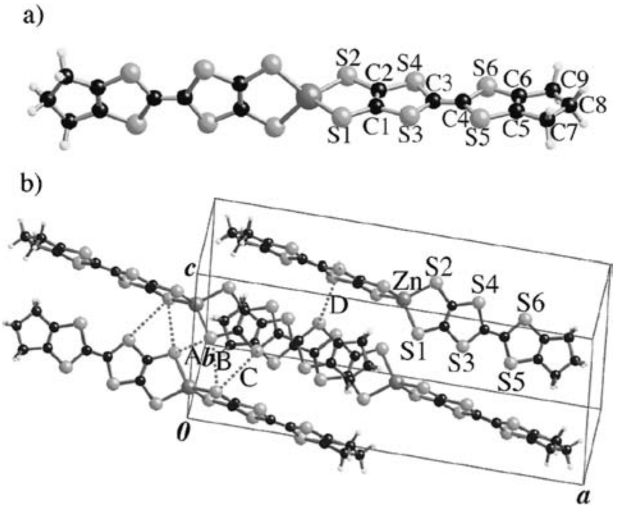

Figure 1. a) Molecular structure of $[Zn(tmdt)_2]$ (**1**). b) Crystal structure of **1**. Short S···S contacts A, B, C, and D were shown with dotted lines. A: 3.542 Å, B: 3.656 Å, C: 3.567 Å, D: 3.659 Å.

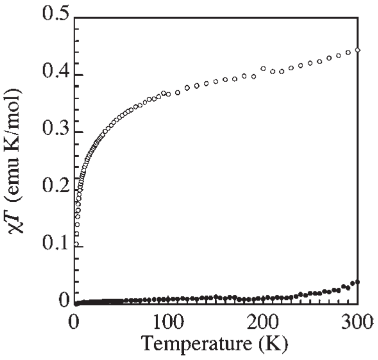

Figure 2. χT vs T plot of the susceptibilities of [Zn(tmdt)$_2$] (●) and [Cu(dmdt)$_2$] (○) (based on the data reported in ref 7). The low-temperature impurity Curie terms were subtracted.

emu·mol^{-1}) at $T > 230$ K, below which the system seems to be almost nonmagnetic (Figure 2). The complexes **2** and **3** showed almost the linear decrease of χT values down to ca. 100 K and gave the similar tendency of magnetic behavior to that of **1**.

[Cu(dmdt)$_2$] has been reported to be a paramagnetic semiconductor (ρ (rt) $= 0.3\,\Omega$ cm, $E_a = 40$ meV).[8] The magnetic susceptibilities suggested that the localized 84% Cu^{2+} 1/2 spin and π-conduction electrons coexist (Figure 2). In addition, similar to the cases of Zn complexes, there exists a T-linear term in the χT vs T plot of [Cu(dmdt)$_2$] ($\chi_p = 3.8 \times 10^{-4}$ emu·mol^{-1}, $T > 100$ K), though the origin of temperatue-independent paramagnetism is not clear at present.

The electrical resistivities of the compressed pellet samples of **1**–**3** were measured by usual four-probe method, which showed these systems are semiconductors. But as for compressed powder sample, **1** showed fairly small resistivities (ρ (rt) $= 50\,\Omega$·cm (**1**), 2×10^2 (**2**) and 2×10^3 (**3**); $E_a = 0.15$ eV (**1**), 0.16 (**2**), and 0.11 (**3**)).

The extended-Hückel type tight-binding band structure calculation of **1** was carried out.[9] Figure 3a shows HOMO and LUMO of **1**. Those of [Cu(dmdt)$_2$] are also shown for comparison.[9] As expected, there is almost no contribution from the d orbital. Consequently, HOMO and LUMO of Zn complex are almost degenerate. It might be possible that Zn complex has a triplet ground state but unfortunately ESR studies on the molecule could not be made because of the very small solubility of the complex. As mentioned above, owing to "κ-type ligand arrangement", there are fairly compact intermolecular S···S contacts, which produces 3D conduction paths. The calculated density of states (DOS) of **1** gave the band gap of about 0.1 eV (Figure 3b). These results show that even the complexes without the contribution of 3d orbitals can form a 3D conduction band.

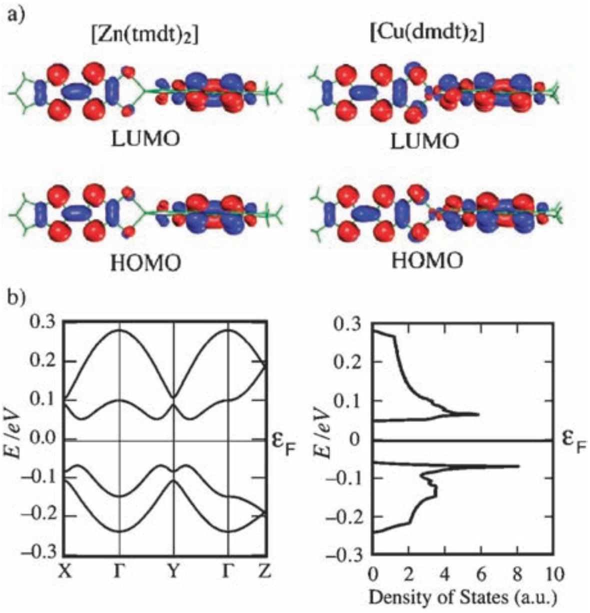

Figure 3. a) The HOMOs and the LUMOs of [Zn(tmdt)$_2$] and [Cu(dmdt)$_2$]. b) Band energy dispersion curves and density of state of **1**.

In conclusion, we have prepared new zinc complexes with extended-TTF dithiolate ligands, **1**, **2**, and **3**. These complexes are semiconducting and paramagnetic at high temperatures. The crystal structure analysis of **1** revealed that extended-TTF ligands form κ-type arrangement similar to the case of [Cu(dmdt)$_2$].

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References and Notes

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6 The elemental analysis of **1** is: Found: C, 32.12; H, 2.17; N, 0.00%. Calcd for $C_{18}H_{12}S_{12}Zn$: C, 31.36; H, 1.78; N, 0.00%.
7 X-ray crystallographic data of [Zn(tmdt)$_2$]: $C_{18}H_{12}ZnS_{12}$, $M_r = 678.51$, monoclinic, space group $C2/c$, $a = 25.3284(2)$, $b = 8.06737(5)$, $c = 11.35959(9)$ Å, $\beta = 92.7107(8)°$, $V = 2318.54(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.94$ g cm^{-3}. 1978 observed [$I > 3.00\sigma(I)$]. The final R_{wp} and R_I are 2.1% and 5.8%, respectively.
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9 The atomic orbital parameters of Zn reported by E. Clementi and C. Roetti were used (*At. Data Nucl. Data Tables*, **4**, 177 (1974)).