Highly Conducting Crystals Based on Single-Component Gold Complexes with Extended-TTF Dithiolate Ligands

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Recently, a considerable interest has been focused on the conducting systems consisting of a single-component molecule.[1−6] We have prepared the crystal of a neutral transition metal complex with extended-TTF (tetrathiafulvalene) ligands, [Ni(tmdt)$_2$]$^{0+}$ (tmdt = trimethylenetetrathiafulvalenedithiolate) exhibiting metallic behavior down to 0.6 K.[7,8] Very recently, the conducting crystal consisting of single-component molecules incorporating magnetic moments, [Cu(dmdt)$_2$]$^{0+}$ (dmdt = dimethyltetrathiafulvalenedithiolate) was developed, which suggests the possibility of the development of single-component magnetic molecular conductors.[9] Similar to the copper complex with tetrahedral coordination geometry around the central copper atom, the gold complex has an odd number of total electrons. However, unlike the copper complex, the bis(dithiolato)gold complex is planar. In terms of valence electrons, the neutral bis(dithiolato)gold complex is isoelectronic to the planar bis(dithiolato)nickel monoanion complex with one unpaired electron per molecule, which makes the electromagnetic properties of the neutral gold complex very attractive. It has been thought that these unpaired electrons or holes in the bis(dithiolato)gold complexes have a possibility to form a metallic band. Almeida et al. suggested the metallic state of the crystal of neutral gold dithiolene complex, [Au(α-tpdt)$_2$]$^{0+}$ (α-tpdt = 2,3-thiophenedithiolate).[10] Bjørnholm et al. showed that the crystal of [Au(bdt)$_2$]$^{0+}$ (bdt = benzene-1,2-dithiolate) consisting of nearly uniform stacks of neutral molecular radicals is a semiconductor with one charge carrier per molecule and exhibits a weak dimerization of the stack at low temperature.[11] Schultz et al. found that in the insulating crystal of [Au(dddt)$_2$]$^{0+}$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), the molecules form dimers as in the case of neutral ET [bis(ethylenedithio)-TTF] molecules.[12]

Herein, we report the structural, electrical and magnetic properties of the crystals composed of single-component gold complexes with extended-TTF ligands, [Au(dmdt)$_2$]$^{0+}$ (**1**) and [Au(tmdt)$_2$]$^{0+}$ (**2**).

1; R = -CH$_3$, **2**; 2R = -(CH$_2$)$_3$-
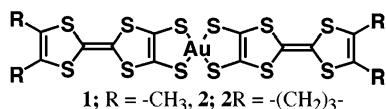
The syntheses of the corresponding gold complexes **1** and **2** were performed according to the literature methods.[13,14] Crystals of **1** and **2** were obtained electrochemically, and composition was determined by electron probe X-ray microanalysis and elemental analysis.[15]

Resistivity measurements were made by the four-probe method from room temperature down to 0.6 K on a compaction pellet sample of microcrystals of **1**, which gave a fairly large room-temperature conductivity of 12 S cm^{-1} and a very small activation energy
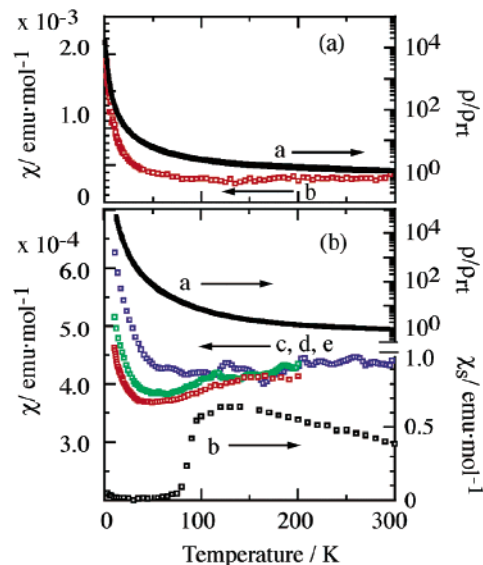
Figure 1. (a) Resistivities and susceptibilities of **1**: a (black), resistivity of compaction pellet (ρ_{rt} = 0.083 Ω cm); b (red), magnetic susceptibility measured at 30 kOe. (b) Resistivities and susceptibilities of **2**: a, resistivity of compaction pellet (ρ_{rt} = 0.067 Ω cm); b, spin susceptibility χ_s by ESR; c−e, magnetic susceptibilities by SQUID at 30 (blue, <300 K), 10 (red, <200 K), and 3 (green, <200 K) kOe.

of 9 meV (50−300 K) (Figure 1). The magnetic susceptibilities of **1** (4.3 mg) were measured by a SQUID magnetometer at 30 kOe in the temperature range from 300 to 1.9 K. The data were corrected for the diamagnetic contribution (χ^{dia} = −3.25 × 10^{-4} emu mol^{-1}). Magnetic susceptibility was 3.4 × 10^{-4} emu mol^{-1} at room temperature and showed Pauli-like paramagnetism at least above 50 K (Figure 1), which is consistent with the results of ESR measurements. Despite the weakly semiconducting behavior of the compaction sample, these data indicate that **1** is essentially metallic at least above 50 K.

The compaction sample of **2** also showed a large room-temperature conductivity of 15 S cm^{-1} and a small activation energy of 20 meV (50−300 K). The XPS and NEXAFS measurements suggested the valence of the neutral gold complex **2** to be almost Au^{3+}, and the existence of density of states at Fermi level indicated the system to be a metal.[16] ESR spectra of polycrystalline samples of **2** were measured in the temperature range of 3.5−300 K. Spin susceptibility, peak-to-peak line width, and g-value at room temperature were: χ_s = 3.8 × 10^{-4} emu mol^{-1}, ΔH_{pp} = 250 G, and g = 2.005. The χ_s values increased gradually down to 130 K and decreased abruptly at 100 K (Figure 1), while the line width decreased almost linearly with decreasing temperature down to 100 K where an onset of rapid increase of line width was observed (ΔH_{pp}= 40 G at 100
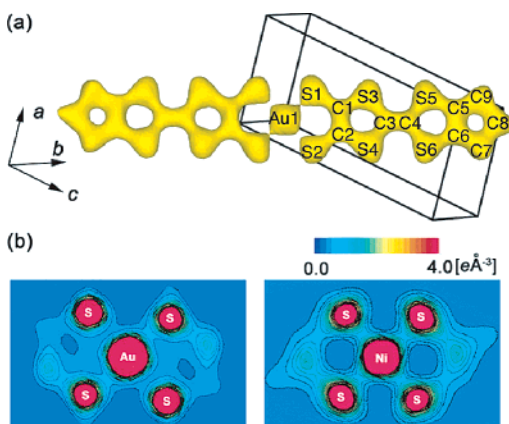
Figure 2. (a) Unit lattice and MEM electron density of **2** ($AuS_{12}C_{18}H_{12}$) as equicontour surface of 1.0 e Å^{-3}. The unit cell contains only one molecule, and the central Au atom is on the lattice point. (b) Comparison of electron densities of **2** and [Ni(tmdt)$_2$] around the central metal atoms, showing relatively small bonding electron density on Au−S bonds.

K). These facts indicate that **2** undergoes a magnetic transition around 100 K with keeping its high conducting state. The magnetic susceptibility of polycrystalline sample of **2** (2.9−5.3 mg) were measured by the SQUID magnetometer under the magnetic fields of 30, 10, 5, and 3 kOe. Figure 1 shows the magnetic susceptibilities at 30, 10, and 3 kOe. For the magnetic field above 30 kOe, the susceptibilities were roughly constant above 50 K, below which the magnetic impurities seemed to dominate the susceptibility behavior. Unlike the gradual increase of χ_s, the magnetic susceptibilities were approximately constant down to 100 K even at 3 kOe, indicating the temperature dependence of χ_s to be possibly affected by the skin effect of microwave. Around 100 K the susceptibility decrease indicating magnetic transition was observed, which is consistent with the ESR behavior. To our knowledge, there has been no molecular conductor exhibiting (antiferro)magnetic transition at the temperature as high as 100 K without loss of its high conductivity. However, no anomaly above 30 kOe and the susceptibility decrease around 100 K below 10 kOe seem to suggest the possibility that the 100 K-transition is an antiferromagnetic transition with the critical magnetic field of spin flipping transition between 10 and 30 kOe.

Since the crystals were very small, the synchrotron radiation X-ray powder experiments were performed to obtain the structural information of **1** and **2**. The imaging plate detectors and the Large Debye−Scherrer camera at the facility SPring-8 BL02B2 were used. The wavelength of incident X-rays was 1 Å. The exposure time was 200 min. Although the sufficient diffraction patterns could not be obtained on **1**, an ideal X-ray powder pattern of **2** was obtained in 0.02° steps in 2θ from 3.0° to 60.0°, which showed the crystal structure of **2** to be isostructural to that of the single-component molecular metal [Ni(tmdt)$_2$]$^{0+}$. The lattice constants of **2** were determined as: $a = 6.4129(1)$ Å, $b = 7.5514(2)$ Å, $c = 12.1543(3)$ Å, $\alpha = 90.473(3)°$, $\beta = 96.698(2)°$, $\gamma = 103.008(3)°$, $V = 569.21(2)$ Å^3. The structure was analyzed by the MEM/Rietveld method, a self-consistent iterative analysis of a combination of the maximum entropy method (MEM) and Rietveld analysis.[17] The structure of **2** was successfully visualized as electron densities by using synchrotron radiation powder diffraction, by which all the atoms were located. The final R factors for 3751 points (2θ range for analysis is 2.5−40.0°) were $R_{wp} = 2.8\%$ and $R_I = 7.3\%$. Figure 2 shows the unit lattice and MEM electron density of **2** as equicontour surface of 1.0 eÅ^{-3}. Molecule **2** is almost planar. The gold atom has a square planar coordination with average Au−S distance of 2.296-(2) Å and S−Au−S angle of 89.9(1)°. These values well correspond to those of neutral bis(dithiolato)gold complex [Au(dddt)$_2$]$^{0+}$ (Au−S

2.304(5) Å, S−Au−S 89.15(2)°).[12] Intermolecular S···S contacts less than the sum of the van der Waals radii (3.43 to 3.64 Å) are a little longer than those found in [Ni(tmdt)$_2$]$^{0+}$. The average interplanar distance between molecules on (0,0,0) and (1,1,1) is 3.543 Å, and the average of those between (0,0,0,) and (1,0,1) is 3.667 Å.

In conclusion, the crystal structure of **2** was determined by using synchrotron radiation powder X-ray diffraction data. Resistivity and susceptivility measurements on the powder sample of **2** showed that it undergoes a magnetic transition around 100 K without loss of its high conductivity. The powder sample of **1** also exhibited high conductivity with Pauli-like susceptibility down to at least 50 K.

Supporting Information Available: Tables of bond lengths and angles, intermolecular short S···S contacts, and atomic coordinates for **2** (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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(14) The dmdt ligand was dissolved in THF and MeOH solution of 10 wt % Me$_4$NOH was added to the solution at −78 °C. A pink precipitate was obtained after cooling to −78 °C again. The MeOH solution of HAuCl$_4$·4H$_2$O was added to the system. The blue-violet gold complexes were obtained as (Me$_4$N)[Au(dmdt)$_2$]. By a similar procedure, (^{n}Bu$_4$N)[Au(tmdt)$_2$] was prepared. The complexes were oxidized electrochemically using (^{n}Bu$_4$N)ClO$_4$ and dichloromethane or THF. After applying 0.4 μA current for 3 weeks, the microcrystals of **1** and **2** were obtained, which were stable in air and insoluble in conventional organic solvents.

(15) The elemental analysis of the neutral gold complex of **1** is C$_{16}$H$_{12}$S$_{12}$Au: found (calcd) C, 25.18 (24.45); H, 1.93 (1.54); N, 0.00 (0.00). The ratio of Au:S = 1:12.72 for **1** and 1:12.49 for **2** was determined by electron probe X-ray microanalysis.

(16) The B.E. of Au4f$_{5/2}$ and Au4f$_{7/2}$ of **2** are 90.3 and 86.7 eV and those of (^{n}Bu$_4$N)[Au(tmdt)$_2$] are 90.5 and 86.7 eV, respectively. (Kondo, H. and Ohta ,T. private communication.)

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JA0292243