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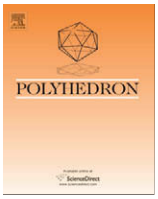

Synthesis and physical properties of a new single-component molecular conductor $[Au(dhdt)_2]$

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ABSTRACT

We have succeeded in synthesizing a new Au(III) complex coordinated by a dihydro-TTF-ditiolato ligand, $dhdt^{2-}$ (4,5-dihydrotetrathiafulvalene-4,5-dithiolato) as a tetrabutlylammoium or tetraphenylphosphonium salt. Crystal structural analysis of $(Ph_4P)[Au(dhdt)_2]$ revealed that the Au(III) ion adopts a square planar coordination and the mean Au–S bond length suggests the Au ions are in the trivalent Au(III) state. A neutral complex, $[Au(dhdt)_2]$, was obtained by the electrochemical oxidation of (n-Bu_4N) $[Au(dhdt)_2]$. Conducting behavior of $[Au(dhdt)_2]$ was semiconductive with conductivity at room temperature of 8.3 $S cm^{-1}$ and activation energy of 23 meV. Magnetic susceptibility of $[Au(dhdt)_2]$ was well explained by the sum of the Curie and temperature independent components.

1. Introduction

Most of electrical conducting molecular materials have generally been composed of charge transfer complexes, or radical salts based on organic donors or acceptors; more than two constituent molecules were required for the molecular conductors. Although considerable efforts have been devoted to preparation of single-component molecular conductors, the conductivity was not more than the semiconductor [1]. In 2001, however, Kobayashi and coworkers succeeded in developing the first single-component molecular metal, $[Ni(tmdt)_2]$ ($tmdt^{2-}$ = trimethylenetetrathiafulvalenedithiolato), which retained the metallic state down to 0.6 K [2]. The metallic state of this Ni complex originates in a small HOMO–LUMO energy gap leading to crossing the valence and conduction bands and then the formation of semi-metallic Fermi surface [3]. From this point of view, metal complexes with extended π-electron system are one of the promising molecules for the single-component metals.

On the other hand, we are currently investigating to develop organic π-donors, which can destabilize the metallic states and enhance the electron correlation in the molecular conductors in order to realize superconducting transition. We prepared organic donors with the reduced π-electron systems compared with the conventional TTF donors, leading to the enhancement of the on-site Coulomb repulsion, and succeeded in developing several pressure-induced superconductors from such a π-reduced donor [4]. Reduction of the π-electron system of the single-component conducting metal complexes with extended TTF ligands is interesting. We have already reported the Ni complex with a TTF-type ligand which has the reduced π-electron system compared with those of TTF-dithiolato ligands, $[Ni(dhdt)_2]$, and it showed semiconducting behavior [5]. We disclose here the synthesis and physical properties of a new Au complex with π-reduced TTF-ditholato type ligands.

2. Experimental

2.1. Materials

All solvents and chemicals were reagent-grade, purchased commercially, and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under a nitrogen atmosphere prior to use, and methanol, diethyl ether and acetonitrile were distilled from CaH_2. Tetrabutylammonium hexafluorophosphate, which was used for electrochemical measurements, was recrystallized from ethanol (EtOH) before use.

2.2. Syntheses of (n-Bu_4N)$[Au^{III}(dhdt)_2]$ and $(Ph_4P)[Au^{III}(dhdt)_2]$

Synthesis of (n-Bu_4N)$[Au^{III}(dhdt)_2]$ was performed according to the method for the Ni complex reported previously as shown in Scheme 1. To a THF solution of the cyanoethyl-protected dihydrotetrathiafulvalenedithiolate **1** (30 mg, 0.08 mmol) was added a methanol solution of tetrabutylammonium hydroxide at −78 °C and the mixture was allowed to warmed to room temperature. To the mixture was added dropwise a methanol solution of hydrogen tetrachloroaurate(III) tetrahydrate (16 mg, 0.039 mmol) at −78 °C. After the reaction mixture was allowed to warm to room temperature, the resulting precipitate was filtered off. Addition of

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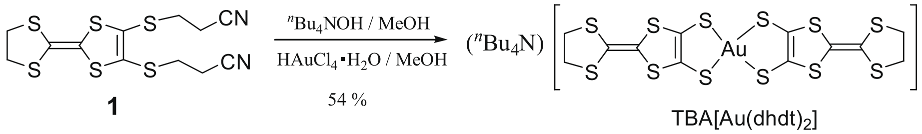

Scheme 1.

diethyl ether to the filtrate afforded (n-Bu$_4$N)[Au^{III}(dhdt)$_2$] as brown powder in 54% yield.

Tetraphenylphosphonium salt, (Ph$_4$P)[Au^{III}(dhdt)$_2$], was obtained by slow diffusion of THF–methanol solution of tetraphenylphosphonium bromide to THF–methanol solution of (n-Bu$_4$N)[Au^{III}(dhdt)$_2$] to give black needle crystals suitable for X-ray structural analysis.

2.3. Preparation of neutral complex [Au(dhdt)$_2$]

Neutral complex, [Au(dhdt)$_2$], was prepared by electrochemical oxidation of (n-Bu$_4$N)[Au^{III}(dhdt)$_2$] at a constant current of 0.2–0.5 μA in benzonitrile or benzonitrile with 5–20% methanol or ethanol containing n-Bu$_4$NBr as a supporting electrolyte at 25 °C. All the solvents were purified before use. Concentration of (n-Bu$_4$N)[Au^{III}(dhdt)$_2$] and n-Bu$_4$NBr were 0.3–3.0 and 25 mM, respectively. For all the reaction condition, only powder samples were obtained. *Anal.* Calc. for [Au(dhdt)$_2$] ($C_{12}H_8AuS_{12}$): C, 19.64; H, 1.10. Found: C, 19.77; H, 1.22%.

2.4. X-ray crystallography

Diffraction data were collected at 293 K on a Bruker SMART APEX diffractometer fitted with a CCD type area detector, and a full sphere of data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data frames were integrated using SAINT and merged to give a unique data set for structure determination. Total reflections collected were 18 646 of which independent reflections were 5686 ($R_{\text{int}} = 0.0531$). The structure was solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELEX 5.1 package (Bruker Analytical X-ray Systems). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those the parent atoms.

Crystal data for (Ph$_4$P)$_2$[Au^{III}(dhdt)$_2$]$_2$: $C_{72}H_{56}Au_2P_2S_{24}$, F.W. = 2146.48; black needle, monoclinic, space group $P2_1/c$, $a = 8.304(1)$, $b = 22.249(3)$, $c = 21.571(3)$ Å, $\beta = 95.738(2)°$, $V = 3965.5(8)$ Å^3, $Z = 2$, $R = 0.0521$, $Rw = 0.1339$.

2.5. Electrical conductivity and magnetic susceptibility

Temperature dependence of resistivity was measured on a compressed pellet of a powder sample of [Au(dhdt)$_2$] by the four-probe dc method using gold wire contacted to the pellet by carbon paste. Magnetic susceptibility was measured for a powder sample in the temperature range of 2–300 K using a superconducting quantum interference device magnetometer with 20 000 Oe field application. The diamagnetic contribution of [Au(dhdt)$_2$] was calculated to be -305.46×10^{-6} emu mol^{-1} using Pascal's law. Magnetization data were collected as a function of the applied field up to 5 T at 1.8 K.

3. Results and discussion

3.1. Electrochemical property of Au complex

The redox potentials of (Ph$_4$P)[Au^{III}(dhdt)$_2$] were investigated by cyclic voltammetry at 25 °C in acetonitrile containing n-Bu$_4$NPF$_6$ as a supporting electrolyte at a scan rate of 50 mV s^{-1}, using glassy-carbon working and platinum counter electrodes and a saturated calomel electrode (SCE) as the reference electrode. The redox potentials of Au complex were summarized in Table 1 together with those of Ni complex, (Ph$_4$P)[Ni^{III}(dhdt)$_2$]. While the irreversible step corresponding to the oxidation from monovalent [Au(dhdt)$_2$]$^-$ to neutral Au complex was observed at −0.06 V, the reduction step from [Au(dhdt)$_2$]$^-$ to divalent [Au(dhdt)$_2$]$^{2-}$ at −0.85 V. Compared with the corresponding potentials of the Ni complex, oxidation to the neutral complexes occurs at almost same potentials, but the reduction potential to the divalent species of the Au complex is more negative than that of the Ni complex.

3.2. Crystal structure of (Ph$_4$P)[Au^{III}(dhdt)$_2$]

X-ray structural analysis for (Ph$_4$P)[Au^{III}(dhdt)$_2$] revealed that the complex crystallized in the monoclinic space group $P2_1/c$ consisting of two [Au^{III}(dhdt)$_2$]$^-$ anions and one tetraphenylphosphonium cation. The Au(III) ions are located on the center of inversion, so that the stoichiometry of tetraphenylphosphonium cation and [Au^{III}(dhdt)$_2$]$^-$ anion is 1: 1. Fig. 1a shows the molecular structure of the [Au^{III}(dhdt)$_2$]$^-$ anion. The Au(III) ions of both the crystallographically independent [Au^{III}(dhdt)$_2$]$^-$ anions adopt a square planar coordination surrounded by four sulfur atoms from dhdt^{2-} ligands. The Au–S bond lengths are 2.288(3)–2.308(3) Å, which are comparable to the mean Au–S bond length (2.296 Å) observed in [Au^{III}(tmdt)$_2$] [6], suggesting the Au ions in [Au(dhdt)$_2$]$^-$ anions are trivalent Au(III). The [Au(dhdt)$_2$]$^-$ anions are arranged in a windmill manner [7] in the *bc* plane and they stacked along the *a*-axis as shown in Fig. 1b. The cations are located in the hollow surrounded by four [Au(dhdt)$_2$]$^-$ anions. There is no sulfur–sulfur contacts shorter than the sum of van der Waals radii between the [Au(dhdt)$_2$]$^-$ anions.

3.3. Electrical conductivity and magnetic susceptibility of [Au(dhdt)$_2$]

Fig. 2 shows the temperature dependence of resistivity of the neutral complex [Au(dhdt)$_2$] measured on a compress pellet. The electrical conductivity at room temperature was $\sigma_{\text{rt}} = 8.3$ S cm^{-1}, which is higher than that of the corresponding Ni complex, [Ni(dhdt)$_2$], measured for a single crystal ($\sigma_{\text{rt}} = 0.084$ S cm^{-1}) [5]. As seen in Fig. 1, the conducting behavior was the activation-type, and the activation energy was calculated to be $E_a = 23$ meV from the Arrhenius plot, $\rho(T) = A\exp(\Delta E/k_BT)$, where A is a temperature-independent constant, k_B, the Boltzmann constant, and ΔE, the activation energy. The activation energy of the Au complex is smaller than that of the Ni complex ($E_a = 40$ meV).

Since the Au(III) ion has d^8 electronic configuration, the neutral Au dithiolato complex has one unpaired electron. Thus magnetic

Table 1
Redox potentials of (Ph$_4$P)[M^{III}(dhdt)$_2$] (M = Au and Ni) in acetonitrile (V vs. SCE, 25 °C).

Compound	E_1	E_2
(Ph$_4$P)[Au^{III}(dhdt)$_2$]	−0.06	−0.85
(Ph$_4$P)[Ni^{III}(dhdt)$_2$]	−0.12	−0.52

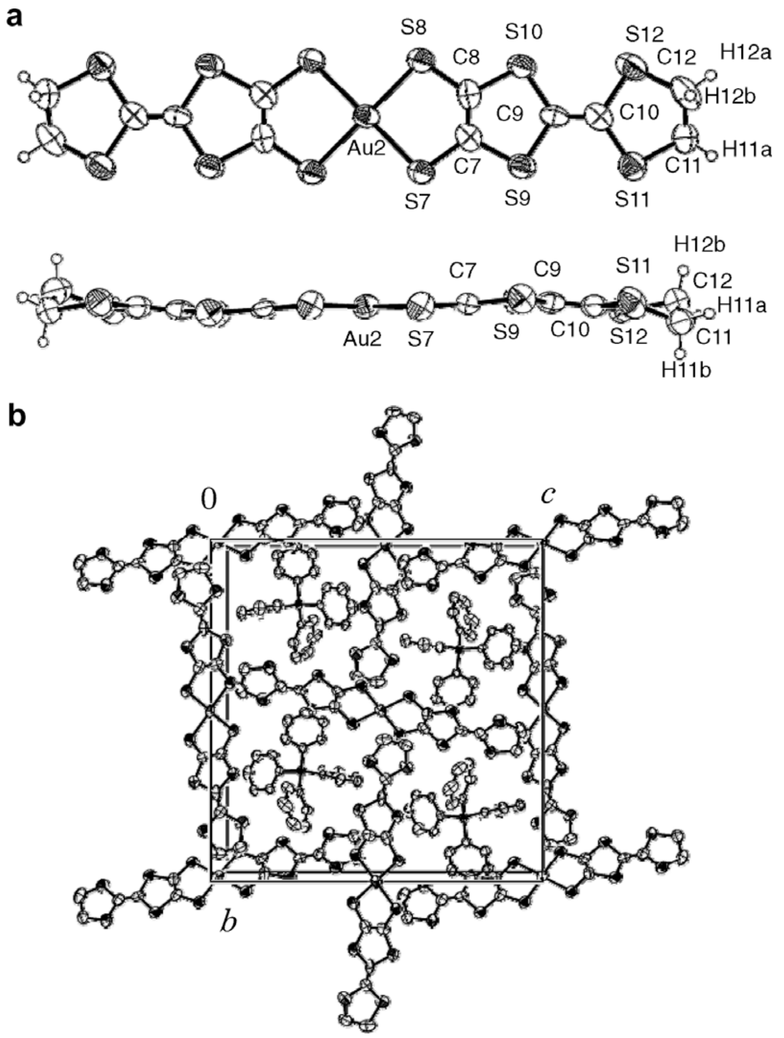

Fig. 1. Crystal structure of $(Ph_4P)[Au(dhdt)_2]$. (a) Molecular structure of $[Au(dhdt)_2]^-$ anion. (b) Crystal structure viewed along *a*-axis.

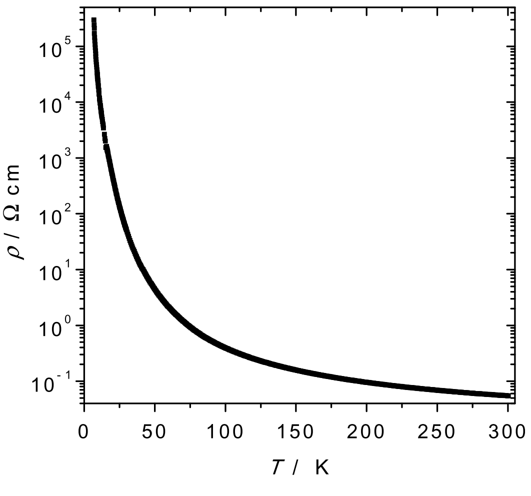

Fig. 2. Temperature dependence of resistivity of $[Au(dhdt)_2]$.

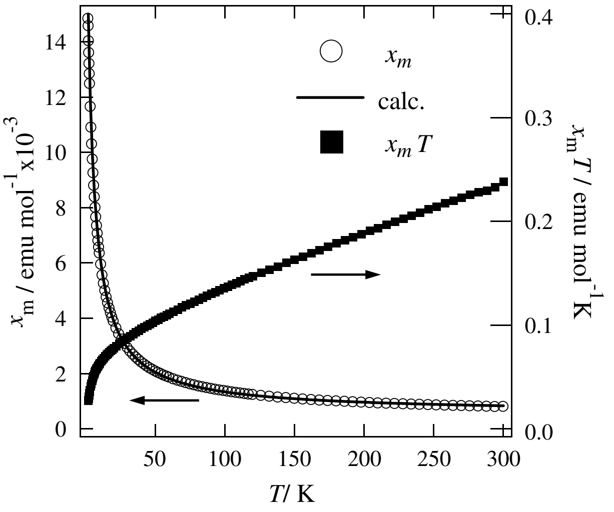

Fig. 3. Temperature dependence of magnetic susceptibility and $\chi_m T$ of $[Au(dhdt)_2]$. The solid line is a fit by the sum of the Curie–Weiss law and temperature independent component.

properties of the neutral Au complex should be very attractive [6]. In order to investigate magnetism of the neutral complex $[Au(dhdt)_2]$, temperature dependence of the magnetic susceptibility was measured by using a SQUID magnetometer at 20000 Oe from 300 to 2 K (Fig. 3). The susceptibility at 300 K was 7.94×10^{-4} emu mol^{-1}. The $\chi_m T$ value was 0.238 emu mol^{-1} K at 300 K, which is smaller than the expected value of 0.375 emu mol^{-1} K for $S = 1/2$, and decreased gradually with

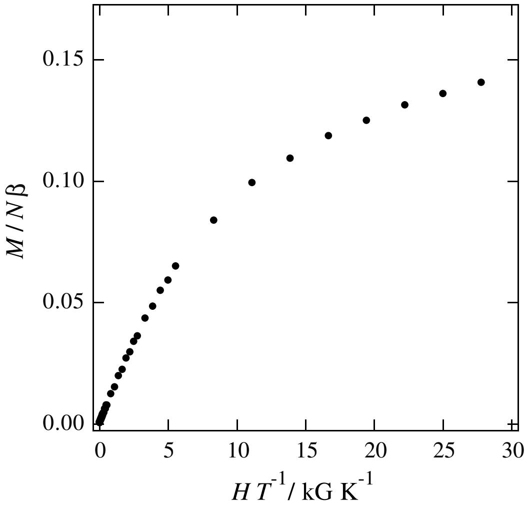

Fig. 4. Magnetization (M) vs. magnetic field strength (H/T) plot for [Au(dhdt)$_2$].

decrease of temperature, and then sudden drop was observed at 20 K. The magnetic susceptibility was well reproduced by the sum of the Curie–Weiss law and the temperature independent component attributable to the conduction π-electron over the whole temperature range as shown by the solid line in Fig. 3. The least-squares fit is found for the Curie constant $C = 7.98 \times 10^{-2}$ emu mol^{-1} K, Weiss temperature $\theta = -3.46$ K, and $\chi_\pi = 5.75 \times 10^{-4}$ emu mol^{-1}, respectively. The value of Curie term is about 20% of the $S = 1/2$ paramagnetic system, which is fairly large for impurity. Fig. 4 shows the magnetic field dependence of magnetization measured at 1.8 K up to 5 T with a SQUID magnetometer. The $M/N\beta$ values increased with increasing magnetic filed strength, and did not show saturation up to 5 T. Although the saturation was not complete, the magnetization under the applied field of 5 T was *ca.* 0.15 $N\beta$ which is much smaller than the value for $S = 1/2$ and comparable to the result obtained by the magnetic susceptibility measurement.

4. Conclusion

A gold dithiolato complex coordinated by the dihydro-TTF ligand of which π-electron system is reduced compared with those of TTF-dithiolato metal complexes was newly synthesized and isolated as tetra-*n*-butylammoium salt of [Au(dhdt)]$^-$ monoanion. Crystal structure of tetraphenylphosphonium salt, (Ph$_4$P)[Au(dhdt)], was revealed by X-ray crystallography. The Au(III) ions in the [Au(dhdt)]$^-$ anions have a square planar coordination and the mean Au–S bond length suggests the Au ions are in the trivalent Au(III) state. A neutral complex [Au(dhdt)$_2$] was obtained by the electrochemical oxidation of (n-Bu$_4$N)[Au(dhdt)$_2$] to give a dark brown powder sample. Conducting behavior of the neutral [Au(dhdt)$_2$] complex was semiconductive with room temperature conductivity of $\sigma_{rt} = 8.3$ S cm^{-1} and activation energy of $E_a = 23$ meV, indicating higher conductivity than those of the neutral Ni complex [Ni(dhdt)$_2$] ($\sigma_{rt} = 0.084$ S cm^{-1}, $E_a = 40$ meV). Magnetic susceptibility of [Au(dhdt)$_2$] was well explained by the sum of the Curie component and the constant value attributable to the conduction π-electron. The Curie term is about 20% of the $S = 1/2$ paramagnetic system. Details on the electronic and magnetic structure of this complex is continuously investigated as well as preparation of a single crystal of the neutral [Au(dhdt)$_2$] complex for X-ray structural analysis and further investigation on the physical properties.

5. Supplementary data

CCDC 702730 contains the supplementary crystallographic data for (Ph$_4$P)$_2$[Au^{III}(dhdt)$_2$]$_2$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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