Syntheses, Structures and Physical Properties of Palladium Complexes with an Extended-TTF Dithiolate Ligand, Bis(di-*n*-propylthiotetrathiafulvalenedithiolato)palladate

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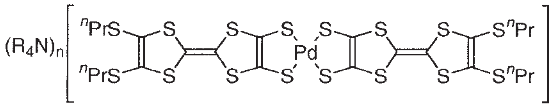
New palladium complexes with an extended-TTF ligand, (^{n}Bu$_4$N)[Pd(C3-tdt)$_2$] and [Pd(C3-tdt)$_2$] were prepared and their crystal structures were determined. The magnetic susceptibility of (^{n}Bu$_4$N)[Pd(C3-tdt)$_2$] gave good agreement with the Bonner-Fisher model ($J = -16$ K), suggesting anions form approximately a one-dimensional antiferromagnetic chain. Neutral [Pd(C3-tdt)$_2$] was a semiconductor with a room temperature conductivity of ca. 10^{-2} S·cm^{-1}.

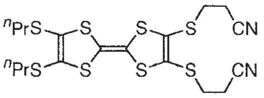
For the past few decades, the investigation of bis(dithiolato)-metal complexes had been a long subject in the field of molecular conductors due to their interesting electrical and magnetic properties. For example, a series of [M(dmit)$_2$]^n (dmit^{2-} = 4, 5-dimercapto-1,3-dithiole-2-thione, M=Ni, Pd, Pt, Au etc., n = 2−, 1−, 0) was well known to provide a number of conducting radical anion salts including various superconductors.[1] Recently, the dithiolene complexes have attracted an increasing interest because they display fairly high conductivities even in the neutral state.[2]

We reported a metallic crystal composed of a single-component molecule, [Ni(tmdt)$_2$] (tmdt^{2-}=trimethylenetetrathiafulvalenedithiolate), which retains a metallic state down to 0.6 K.[3,4] Single-component molecular metals with extended-TTF (=tetrathiafulvalene) dithiolate ligands should greatly extend the development of new types of molecular conductors. However, there are few crystal structures so far determined, since it is difficult to grow large single crystals because of their poor solubility for common organic solvents.[5] Most recently, we obtained good single crystals of palladium complexes with a new extended-TTF dithiolate ligand containing two *n*-propylthio groups, (C3-tdt)$^{2-}$ (=di-*n*-propylthiotetrathiafulvalenedithiolate), which was expected to have good solubility to organic solvents. Herein, we report the crystal structures, electrical and magnetic properties of palladium complexes with a new ligand (C3-tdt)$^{2-}$, (^{n}Bu$_4$N)[Pd(C3-tdt)$_2$] (**1**) and [Pd(C3-tdt)$_2$] (**2**).



(R$_4$N)$_n$[Pd(C3-tdt)$_2$]

R = ^{n}Bu, n = 1···**1**
n = 0···**2**
R = Me, n = 2···**6**



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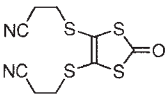

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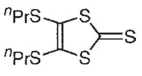

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All the syntheses were carried out under argon atmosphere. The compound **3** was synthesized by the cross-coupling reaction of **4** and **5** in dry trimethylphosphite at 110 °C.[6,7] The complex **6** was obtained by hydrolysis of the compound **3** using 10% Me$_4$NOH/methanol in dry tetrahydrofuran, followed by the reaction of PdCl$_2$(C$_6$H$_5$CN)$_2$/dry methanol solution at −78 °C–room temperature. Electrochemical oxidation of **6** was performed in the presence of ^{n}Bu$_4$N·ClO$_4$ in dry acetonitrile under a constant current of 0.1 μA. The relatively air-stable dark red plate-like crystals of **1** and black plate-like crystals of **2** were obtained after 10 days. The electron probe microanalysis (EPMA) measurements on **1** and **2** showed that the ratio of sulfur and palladium atoms of these compounds is almost 16 : 1.

The electrochemical properties of **6** were investigated by the cyclic voltammetry technique at 20 °C and scan rate of 200 mV·s^{-1}. The cyclic voltammogram measured in dimethylformamide showed three pairs of reversible redox waves. The first, second and third potentials are −0.92, −0.30 and +0.47 V vs. Ag/AgCl, respectively.

The crystal structures of **1** and **2** were examined. The crystal structure of **1** is shown in Figure 1.[8] Not only the terminal *n*-propylthio group but the TTF part of the monoanionic complex is curved from the central PdS$_8$C$_4$ plane. The geometry around the Pd atom is square-planar and the average Pd-S distance is 2.290(1) Å and the average S-Pd-S angle is 89.41(4)°. As shown in Figure 1(a), the anions form a zig-zag chain structure along the *a* axis and some short S···S contacts (< 3.7 Å) exist between neighboring molecules (see Figure 1(b)). But there is no close S···S contact shorter than 3.7 Å along the *b* axis because of the existence of bulky tetra-*n*-butylammonium cations. These structural features suggest that **1** has one-dimensional intermolecular interaction along the transverse direction of the anions.

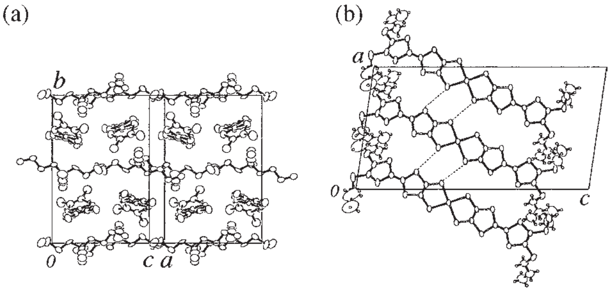

Figure 1. Crystal structure of **1** (a) viewed along the molecular long axis and (b) projected onto the *ac*-plane. The four *n*-propylthio groups and hydrogen atoms in (a) and the tetra-*n*-butylammmonium molecules in (b) are omitted for

The magnetic susceptibility of **1** was measured using a SQUID magnetometer at a field of 1 Tesla over the temperature range of 300–2 K. The temperature dependence of the susceptibility is shown in Figure 2. The diamagnetic contribution of magnetic susceptibility (6.80×10^{-4} emu·mol^{-1}) was subtracted using Pascal's law in Figure 2. The Curie constant, $C =$ 0.373 emu·K·mol^{-1} was approximately equal to 0.375 emu·K·mol^{-1} expected for the $s = 1/2$ localized spin system with $g = 2.0$. The magnetic susceptibility of **1** is well consistent with the Bonner-Fisher behavior with $J = -16$ K, indicating the existence of the spin-1/2 antiferromagnetic Heisenberg chain.[9] This corresponds to the suggestion from the crystal structure of **1**. The electron spin resonance measurement of **1** was carried out in the temperature range of 300–3 K. The temperature dependence of the g-values and the peak-to-peak linewidths, ΔH_{pp}, showed a small anomaly around 120 K. The low-temperature structural studies indicated the change of the cell parameters around 120 K, suggesting the magnetic anomaly around 120 K to be related to some structural change.

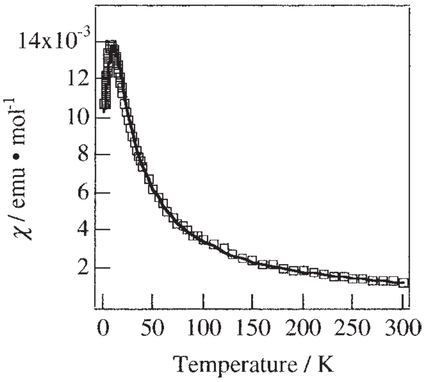

Figure 2. The temperature dependence of magnetic susceptibility of **1**. The line is the simulated curve calculated using the equation of the Bonner-Fisher model ($J = -16$ K).[10]

The crystal structure of the neutral complex **2** is shown in Figure 3.[10] The molecular structure is almost planer except for four n-propylthio groups and more planer than that in **1**, which is in contrast to the case of BEDT-TTF (=bis(ethylenedithio)tetrathiafulvalene)-like molecule where the molecular plane becomes more concaved in the neutral state. The complex **2** shows the average Pd-S distance of 2.295(1) Å and the average S-Pd-S angle of 90.83(6)°. The complexes **2** are stacked along the a direction with slip distance of 9.37 Å. Some short S···S contacts are observed along the stacking and the transverse directions (see Figure 3). However, **2** has no S···S contact along the molecular long axis because **2** has large steric hindrance through large n-propylthio groups. Thus **2** has two-dimensional intermolecular S···S interactions.

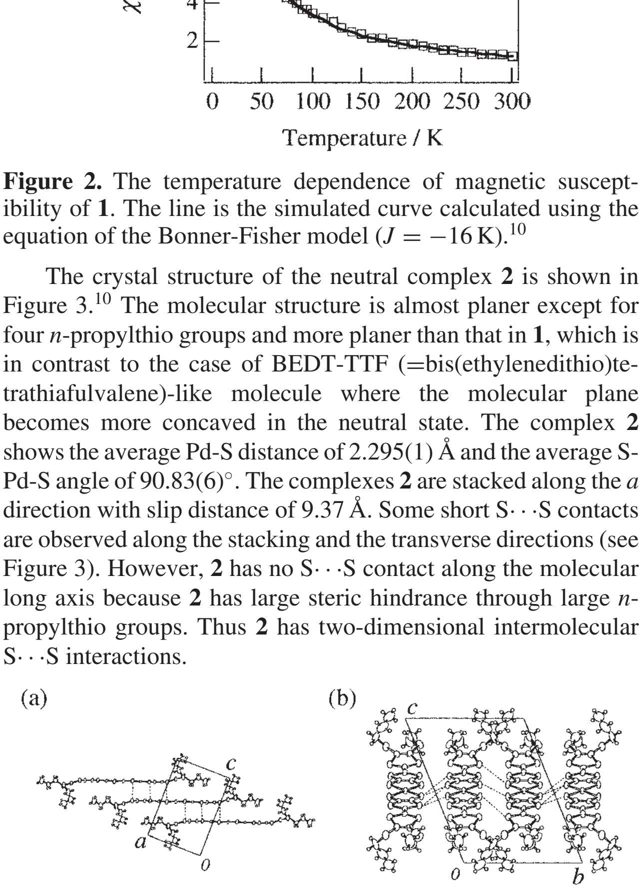

Figure 3. Crystal structure of **2** projected onto (a) the ac-plane and (b) the bc-plane.

The electrical resistivity of the single crystal of the neutral complex **2** was measured by a usual four-probe method from room temperature to the liquid nitrogen temperature. The complex **2** exhibited semiconducting behavior. The room temperature conductivity was ca. 10^{-2} S·cm^{-1}. But the activation energy was very small; 0.034 eV at 300–120 K and 0.011 eV at 120–80 K. The small energy gap is consistent with the small HOMO-LUMO gap calculated in the analogous semiconducting complex of $Ni(C_{10}H_{10}S_8)_2$.[11]

In conclusion, we have prepared new palladium complexes with an extended-TTF dithiolate ligand, **1** and **2**. The magnetic susceptibility of the monoanionic complex **1** was fitted by the Bonner-Fisher model ($J = -16$ K). The crystal of the neutral complex **2** shows the two-dimensional intermolecular short S···S contacts and the semiconducting behavior with the very small activation energy.

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8 X-Ray crystallographic data of $(^{n}Bu_4N)[Pd(C3\text{-}tdt)_2]$: $C_{40}H_{64}NPdS_{16}$, $M = 1178.31$, crystal dimension $0.25 \times 0.10 \times 0.01$ mm^3, monoclinic, space group $P2_1/a$, $a = 13.329(4)$, $b = 16.699(5)$, $c = 25.076(7)$ Å, $\beta = 81.786°$, $V = 5524(2)$ Å^3, $Z = 4$, $D_{calc} = 1.417$ g cm^{-3}. 21491 unique reflections and 5195 observed [$I > 3.00\sigma(I)$]. The final R (R_w) and *GOF* values are 0.059 (0.063) and 1.39, respectively.

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10 X-Ray crystallographic data of $[Pd(C3\text{-}tdt)_2]$: $C_{24}H_{28}PdS_{16}$, M = 935.85, crystal dimension $0.30 \times 0.20 \times 0.02$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.007(7)$, $b = 12.019(9)$, $c = 15.92(1)$ Å, $\alpha = 112.14(1)$, $\beta = 89.665(6)$, $\gamma = 90.02(1)°$ $V = 1773(2)$ Å^3, $Z = 2$, $D_{calc} = 1.752$ g cm^{-3}. 7990 unique reflections and 3637 observed [$I > 5.00\sigma(I)$]. The final R (R_w) and *GOF* values are 0.056 (0.069) and 2.20, respectively.

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