Structures of a Single-component Palladium Complex with Extended TTF-type Dithiolate Ligands, Bis(tetrathiafulvalenedithiolato)palladium Determined by Powder X-ray Diffraction

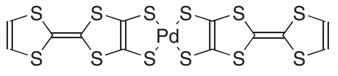
Wakako Suzuki, Emiko Fujiwara, Akiko Kobayashi,* Yuichi Fujishiro,†† Eiji Nishibori,†† Masaki Takata,††
Makoto Sakata,†† Yoshinori Okano,††† and Hayao Kobayashi†††
Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033
††*Department of Applied Physics, Nagoya University, Chikusa-ku, Nagoya 464-8603*
†††*Institute for Molecular Science and CREST, JST, Myodaiji, Okazaki 444-8585*

(Received September 11, 2003; CL-030850)

A new palladium complex with extended-TTF (TTF = tetrathiafulvalene) dithiolate ligands, [Pd(dt)$_2$] (dt = tetrathiafulvalenedithiolate) was prepared and its crystal structure was determined by synchrotron radiation X-ray powder experiments. [Pd(dt)$_2$] is a semiconductor with a room temperature conductivity of 0.3 S cm^{-1}.

Single component molecular metals have received attention as a new material in the field of molecular conductors.[1,2] Recently, an extended-TTF (TTF = tetrathiafulvalene) dithiolato nickel complex, [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate), which keeps a metallic state down to 0.6 K ($\sigma_{rt} = 400$ S cm^{-1}), was reported[2] and the tight-binding electronic band structure calculation of [Ni(tmdt)$_2$] revealed that this neutral complex is a three dimensional metal.

Square-planar complexes such as nickel and palladium complexes can form large intermolecular interactions in crystals. Moreover, the size of the terminal substituent of the extended-TTF ligand greatly influences the intermolecular interaction. These observations caused us to expect that a square-planar metal complex with extended-TTF dithiolate ligands and small substituents would have strong intermolecular interactions and a high conductivity. Thus, we synthesized a new single-component palladium complex consisting of extended-TTF dithiolate ligands without a substituent, [Pd(dt)$_2$] (dt = tetrathiafulvalenedithiolate).



[Pd(dt)$_2$]

Crystal structure information is essential for understanding the physical properties. However, few crystal structures of single-component extended-TTF dithiolato metal complexes have been reported because of the difficulties in obtaining sufficiently large single crystals. Therefore, we determined the crystal structure of [Pd(dt)$_2$] by synchrotron X-ray powder diffraction measurements. To the best of our knowledge, there are few metal complexes whose crystal structures were determined by a powder diffraction method, although some crystal structures of organic compounds have been solved using X-ray powder diffraction data. Herein, we report the crystal structure and electrical properties of a new palladium complex, [Pd(dt)$_2$].

All the syntheses were carried out under an argon atmosphere. (Me$_4$N)$_2$[Pd(dt)$_2$] was obtained as air-unstable brown microcrystals by hydrolysis of 4,5-bis(2′-cyanoethylsulfanyl)TTF using 25 wt % Me$_4$NOH/methanol (MeOH) solution in dry tetrahydrofuran (THF), followed by the reaction of PdCl$_2$-(C$_6$H$_5$CN)$_2$/dry MeOH solution at −78 °C to room temperature.[3] Electrochemical oxidation of (Me$_4$N)$_2$[Pd(dt)$_2$] was performed in the presence of ^{n}Bu$_4$N·ClO$_4$ in dry THF under a constant current of 0.2 μA at room temperature. Air-stable black needle-like microcrystals of [Pd(dt)$_2$] were grown on the electrode within 10 days.[4]

The synchrotron radiation X-ray powder diffraction experiment of this complex was carried out by means of the imaging plate detectors and the Large Debye–Scherrer camera at the facility SPring-8 BL02B2. The wavelength of the incident X-ray was 1.00112(2) Å and the exposure time was 200 min. An ideal X-ray powder pattern of [Pd(dt)$_2$] was obtained in 0.01° steps in 2θ from 0.01° to 75.00°.

The structure was analyzed by the genetic algorithm (GA) and the Rietveld methods. Details of these analyses will be described elsewhere.[5] The structure of [Pd(dt)$_2$] was successfully determined using the synchrotron radiation powder diffraction data. This is a unique example of structural determination of the powder sample with an unknown structure by the synchrotron radiation X-ray powder diffraction experiments. The final R factors for the 3601 points (2θ range for analysis was 4.0–40.0°) were $R_{wp} = 3.9$ and $R_I = 7.1\%$, respectively. Figure 1 shows the crystal structures of [Pd(dt)$_2$]. The palladium atom has a square planar coordination geometry and the twelve sulfur atoms on the ligands are coplanar. The palladium atom and the two C=C bonds (C(3)–C(5) and C(4)–C(6)) on the TTF frame are located on the mirror plane and the half of [Pd(dt)$_2$] molecule is crystallographically independent (see Figure 1a). The average Pd–S bond distance and the S–Pd–S angle are 2.288(2) Å and

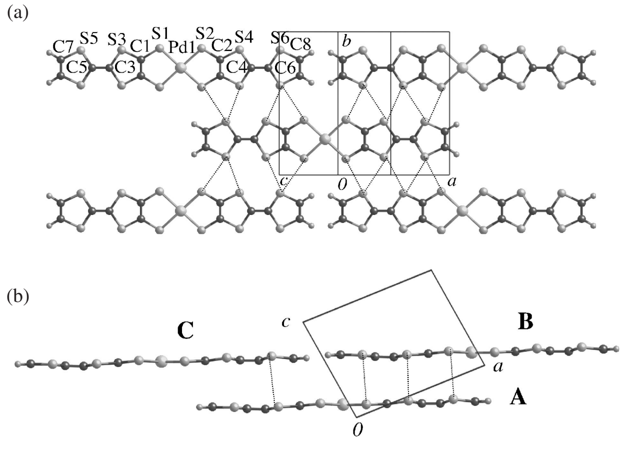


Figure 1. The crystal structure of [Pd(dt)$_2$]. (a) The arrangement of [Pd(dt)$_2$] viewed perpendicular to the molecular plane. (b) Bridged structure of [Pd(dt)$_2$] viewed along the *b* axis.

86.5°, respectively. As shown in Figures 1a and 1b, one [Pd(dt)$_2$] molecule is adjacent to four molecules in the transverse direction and overlaps with the upper two molecules. The molecules are stacked along the [1 0 0] and [1 0 $\bar{1}$] directions with slip distances of 10.05 and 13.38 Å, respectively. The interplanar distances are 3.39 Å between molecules **A** and **B**, and 3.64 Å between the molecules **A** and **C**. The Pd$\cdots$Pd distances are 13.532 Å for **A** and **B**, and 10.046 Å for **A** and **C**. There are many intermolecular S$\cdots$S contacts (the dotted lines in Figure 1) less than the sum of van der Waals radii (3.7 Å) along the transverse direction and in the direction of [1 0 0] and [1 0 $\bar{1}$].

The electrical resistivity of the compressed pellet sample of [Pd(dt)$_2$] was measured by the usual four-probe method down to 50 K. The room temperature conductivity was 0.3 S cm^{-1}. [Pd(dt)$_2$] showed a semiconducting behavior with an activation energy of 94 meV. Thus, the conductivity of [Pd(dt)$_2$] is higher than that of the analogous palladium complex, [Pd(C3-tdt)$_2$] (C3-tdt = di-*n*-propylthiotetrathiafulvalenedithiolate), which has more bulky *n*-propylthio groups in the terminal site of the ligands.[7]

The extended Hückel type tight-binding band structure calculation of [Pd(dt)$_2$] was carried out by use of Slater-type atomic orbitals.[8] Figure 2a shows schematic drawings of the HOMO and the LUMO of [Pd(dt)$_2$]. The [Pd(dt)$_2$] molecule has approximately D_{2h} symmetry. The calculation resulted in the HOMO and the LUMO with b_{1u} and b_{2g} symmetry, respectively. the HOMO of [Pd(dt)$_2$] has the same sign on every chalcogen atom. On the other hand, the LUMO has a nordal plane on the central palladium atom. Figure 2b shows the obtained density of state (DOS). The band structure was calculated for various values of a HOMO–LUMO gap ($\mathcal{E}_{HL}$), 0.0–1.0 eV. The calculations suggest that the semiconducting state exists when $\mathcal{E}_{HL} <$ 0.2 eV, but slightly metallic state exists when $\mathcal{E}_{HL} >$ 0.25 eV. At first sight, these results seems to show an extremely small HOMO–LUMO gap, which is considered the most essential requirement for highly conducting single-component molecular systems, is not a dominant factor for producing the Fermi surfaces in this complex. The existence of a band gap for $\mathcal{E}_{HL} <$ 0.2 eV is consistent with the large HOMO–LUMO interaction compared to the HOMO–HOMO and the LUMO–LUMO interactions, which tend to produce the energy gap, especially when $\mathcal{E}_{HL}$ is small. Two large peaks of DOS separated by about 0.85 eV (Figure 2b) are consistent with the broad maximum of the electronic absorption spectra of [Pd(dt)$_2$] around 1 eV.[9] The semiconducting properties of [Pd(dt)$_2$] suggests $\mathcal{E}_{HL}$ is less than 0.2 eV.[10]

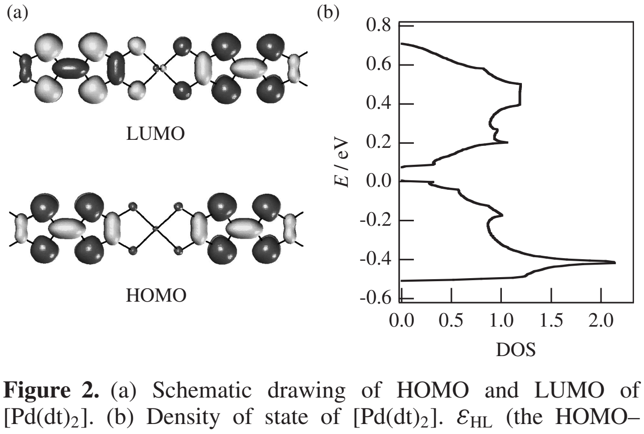


Figure 2. (a) Schematic drawing of HOMO and LUMO of [Pd(dt)$_2$]. (b) Density of state of [Pd(dt)$_2$]. $\mathcal{E}_{HL}$ (the HOMO–LUMO gap) is 0.1 eV.

In conclusion, we have prepared a new single-component TTF dithiolato palladium complex, [Pd(dt)$_2$] and determined the crystal structure using the synchrotron radiation X-ray powder experiments. Neutral [Pd(dt)$_2$] exhibits a relatively high conductivity compared to the single-component extended-TTF dithiolate complexes with bulky substituents. The semiconducting behavior of [Pd(dt)$_2$] is consistent with the result of the tight-binding band structure calculation, suggesting a large HOMO–LUMO interaction.

This study was supported by a Grant-in-Aid for Scientific Research (S) (14103005) and for the 21st Century COE Program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science and Technology. This work was also supported by CREST (Core Research for Evolutional Science and Technology of JST (Japan Science and Technology Corporation)). The synchrotron radiation experiments were performed at the BL02B2 at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI).

References and Notes

1 N. L. Narvor, N. Robertson, E. Wallace, J. D. Kilburn, A. E. Underhill, P. N. Bartlett, and M. Webster, *J. Chem. Soc., Dalton Trans.*, **1996**, 823; N. L. Narvor, N. Robertson, T. Weyland, J. D. Kilburn, A. E. Underhill, M. Webster, N. Svenstrup, and J. Becher, *Chem. Commun.*, **1996**, 1363; K. Ueda, M. Goto, M. Iwamatsu, T. Sugimoto, S. Endo, N. Toyota, K. Yamamoto, and H. Fujita, *J. Mater. Chem.*, **8**, 2195 (1998); K. Ueda, Y. Kamata, M. Iwamatsu, T. Sugimoto, and H. Fujita, *J. Mater. Chem.*, **9**, 2979 (1999); A. Kobayashi, H. Tanaka, M. Kumasaki, H. Torii, B. Narymbetov, and T. Adachi, *J. Am. Chem. Soc.*, **121**, 10763 (1999); H. Tanaka, H. Kobayashi, and A. Kobayashi, *J. Am. Chem. Soc.*, **124**, 10002 (2002); W. Suzuki, E. Fujiwara, A. Kobayashi, Y. Fujishiro, E. Nishibori, M. Takata, M. Sakata, H. Fujiwara, and H. Kobayashi, *J. Am. Chem. Soc.*, **125**, 1486 (2003).

2 H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki, and A. Kobayashi, *Science*, **291**, 285 (2001).

3 A. J. Moore, M. R. Bryce, A. S. Batsanov, J. N. Heaton, C. W. Lehmann, J. A. K. Howard, N. Robertson, A. E. Underhill, and I. F. Perepichka, *J. Mater. Chem.*, **8**, 1541 (1998); H. Moriyama, S. Nagayama, T. Mochida, and H. Kobayashi, *Synth. Met.*, **120**, 973 (2001); Y. Misaki, Y. Tani, M. Taniguchi, T. Maitani, K. Tanaka, and K. Bechgaard, *Mol. Cryst. Liq. Cryst.*, **343**, 59 (2000).

4 The elemental analysis of [Pd(dt)$_2$] is: Found: C, 22.81; H, 0.93; N, 0.00 %. Calcd for $C_{12}H_4S_{12}Pd$: C, 22.54; H, 0.63; N, 0.00 %. The ratio of Pd:S determined by electron probe X-ray microanalysis (EPMA) was 1:12.4.

5 E. Nishibori, M. Takata, and M. Sakata, to be published.

6 X-Ray crystallographic data of [Pd(dt)$_2$]: $C_{12}H_4S_{12}Pd$, $M_r = 810.05$, monoclinic, space group $P2_1/m$, $a = 10.0465(2)$, $b = 11.5882(2)$, $c = 7.9613(3)$ Å, $\beta = 96.7677(5)°$, $V = 920.41(2)$ Å^3, $Z = 2$, $R_{wp} = 0.039$, $R_I = 0.071$.

7 W. Suzuki, E. Fujiwara, A. Kobayashi, A. Hasegawa, T. Miyamoto, and H. Kobayashi, *Chem. Lett.*, **2002**, 936.

8 Slater type atomic orbitals were used to calculate the molecular orbitals. The ionization potentials (eV) and the exponent ζ are: Pd 5s, -9.194, 2.190; Pd 5p, -5.304, 2.150; Pd 4d, -12.91, $0.5264\chi_1(5.98) + 0.6372\chi_2(2.613)$; S 3s, -22.03, 2.122; S 3p, -10.47, 1.827; C 2s, -21.39, 1.625; C 2p, -11.40, 1.625; H 1s, -13.60, 1.000.

9 A. Kobayashi, M. Sasa, W. Suzuki, E. Fujiwara, H. Tanaka, M. Tokumoto, Y. Okano, H. Fujiwara, and H. Kobayashi, to be published.

10 Recently, we calculated the electronic absorption spectra of [Pd(dt)$_2$] based on the tight-binding band parameters, which also suggested $\mathcal{E}_{HL}$ is less than 0.2 eV (A. Kobayashi et al., to be published).

Published on the web (Advance View) November 3, 2003; DOI 10.1246/cl.2003.1106