Crystal Structure of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ at High Pressure

Yoshinori Okano, Takafumi Adachi,*[#] Bakhyt Narymbetov,[##] Hayao Kobayashi,* Biau Zhou, and Akiko Kobayashi[†]
Institute for Molecular Science and CREST, JST, Myodaiji, Okazaki 444-8585
[†]*Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-00333*

(Received May 7, 2004; CL-040512)

The high-pressure crystal structure determination was performed on $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$, which is a unique molecular superconductor with pressure-induced insulating phase above about 7 kbar. The structure analysis at 10 kbar revealed the pressure-induced cation ordering coupled with the doubling of the unit cell.

$[M(dmit)_2]$ (M = Ni, Pd; dmit = 4,5-dimercapto-1,3-dithiole-2-thion) superconductors occupy a unique position because most of the molecular superconductors so far developed are the systems composed of organic π donor molecules having TTF-like skeletons.[1] Only $M(dmit)_2$ conductors can be pure π acceptor superconductors without TTF-type π donors.[2] $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ is a molecular conductor consisting of π acceptor molecules and closed-shell cations, whose superconducting transition was observed around 2–7 kbar.[3] The crystal of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ belongs to the triclinic system. The lattice constants at ambient pressure are given in Table 1.[4] Since the $(C_2H_5)_2(CH_3)_2N^+$ cation is on the inversion center, the cation is disordered with taking two possible positions randomly at ambient pressure. The $Pd(dmit)_2$ molecules are stacked face-to-face to form dimeric columns along the *a* direction.[3,4] Despite of the high room-temperature conductivity, the crystal becomes semiconducting at low temperature. But as mentioned above, the system shows a superconducting transition at high pressure.[3,5] However, in contrast to most of the molecular superconductors with stable metallic states above the critical pressures where the superconducting phases are suppressed, the insulating state appears above 7 kbar. Similar unique phase diagram has been reported in β'-$[(C_2H_5)_2(CH_3)_2P][Pd(dmit)_2]_2$.[6]

Since the superconducting transitions of all the $M(dmit)_2$ conductors with closed-shell anions have been observed only at high pressure, the high-pressure crystal structure analysis is very important in the studies of $M(dmit)_2$ systems. However, only very limited information has been reported on the crystal structures of $M(dmit)_2$ conductors at high pressure.[7] Here, we report the crystal structure of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ at 10 kbar.

The high-pressure X-ray experiments were made by using a specially designed diamond anvil cell (Figure 1). The mixed silicone oil was used as a pressure medium. The pressure was determined by the standard ruby fluorescence method. The crystals with typical dimensions of about 0.3 × 0.2 × 0.04 mm^3 were used. The X-ray diffraction spots were detected by X-ray imaging plate system equipped with a rotating anode X-ray generator (Mo Kα).

The lattice constants are listed in Table 1. New diffraction spots indicating the doubling of the lattice constant *a* were observed above about 8 kbar. The crystal structure determination at 10 kbar was made using the 815 reflections ($I > 3\sigma(I)$). The correction for X-ray absorption by diamond anvil was not made. Because of the limited number of the observed reflections and the relatively large number of crystallographically independent atoms (41 non-hydrogen atoms of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$), the anisotropic temperature factors were used only for two Pd atoms. The structure refinements gave the final *R*-value of 0.105. The crystal structure is shown in Figure 2. At 10 kbar, the ammonium cation is ordered and $Pd(dmit)_2$ molecules are stacked to form tetrameric column along the *a* axis. Compared with the ambient-pressure structure, the molecular plane of $Pd(dmit)_2$ became relatively flat (Figure 3). The crystal structure determination was also made at 3 and 5 kbar where the crystal structures were essentially the same as the ambient-pressure structure.

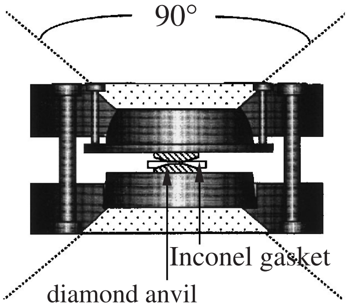

Figure 1. Side view of the diamond anvil cell. Unlike usual X-ray diamond anvil cell, Be disks were not used to reduce the back ground X-ray diffraction. Specially designed very flat diamond anvils were used to get large window angle (90°), which were supported directly by the steel disks of the high-pressure cell.

As mentioned before,[5] in the pressure-temperature phase diagram, the superconducting phase of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ appears around 2–7 kbar and the pressure-induced insulating phase develops above 7 kbar. Thus, the appearance

Table 1. The lattice constants of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$

	1 bar	3 kbar	5 kbar	10 kbar
a/ Å	7.908	7.883	7.848	15.336(5)[a]
b	18.492	18.460	18.376	18.226(6)
c	6.291	6.247	6.227	6.054(3)
α/°	96.92	96.85	96.54	96.89(3)
β	109.83	109.93	109.85	109.17(4)
γ	84.57	84.28	84.26	83.59(3)
V/ Å^3	857.7	846.8	837.4	1582.1(5)
Z	1	1	1	2

[a] The standard deviations at 1 bar, 3 kbar and 5 kbar are omitted for simplicity.

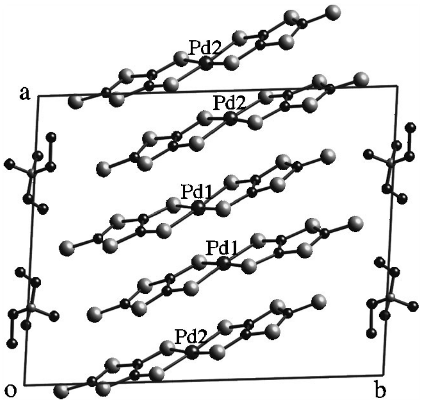

Figure 2. The crystal structure of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ at 10 kbar.

of new X-ray diffraction around 8 kbar is considered to be coupled with the appearance of the pressure-induced insulating phase. It is well known that the strongly dimerized $Pd(dmit)_2$ column producing the "HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) energy level inversion" is one of the characteristic features of the $Pd(dmit)_2$ conductor. If the HOMO–LUMO inversion is weakened at high pressure, the 1-D nature of the band structure (and therefore, the 1-D metal instability) will be enhanced because the nature of LUMO will tend to dominate the band character near Fermi level. At first, this was considered to give a plausible scenario of the development of the pressure-induced insulating state above 7 kbar.[5] However, the examination of the crystal structure and intermolecular overlap integrals of the frontier orbitals revealed that the strong dimeric nature of $Pd(dmit)_2$ column is retained even at 10 kbar. The intra-dimer Pd···Pd distance (d Å) is shortened with increasing pressure: $d =$ 3.161 (1 bar); 3.153 (3 kbar); 3.140 (5 kbar); 3.121 and 3.101 (10 kbar). The intra- and inter-dimer distance (Å) between the least-squares planes of $Pd(dmit)_2$ molecules are: 3.327, 3.750 (1 bar); 3.339, 3.702 (3 kbar); 3.329, 3.693 (5 kbar); 3.290 (average), 3.557 (10 kbar). Interestingly, the calculated orbital levels of HOMO and LUMO (ε_H, ε_L) at ambient pressure were significantly lower than those at 5 and 10 kbar,[7] which is considered to be related to the increase of planarity of $Pd(dmit)_2$ molecule (or π conjugation of the molecule) at high pressure (Figure 3): ε_H $\varepsilon_L = -9.456, -9.100$ eV (1 bar); -9.592, -9.238 (3 kbar); -9.660, -9.335 (5 kbar); -9.660, -9.316 (average) (10 kbar).

The intra- and inter-dimer HOMO···HOMO (S_{H1}, S_{H2}) and LUMO···LUMO (S_{L1}, S_{L2}) overlap integrals along the $Pd(dmit)_2$ stack are: S_{H1}, S_{L1}, S_{H2}, S_{L2} $(\times 10^3) = 46.3, -41.2, 8.8, 1.0$ (1 bar); 39.4, -37.8, 8.5, 0.9 (3 kbar); 43.4, -44.8, 6.2, 3.7 (5 kbar); 49.8 (average), -46.5 (average), 9.2, 5.3 (10 kbar). The maximum inter-stack interactions is less than 5×10^{-3} even at 10 kbar. Thus, it is said that the $Pd(dmit)_2$ column retains strong dimeric character even at high pressure, which is not consistent with the above-mentioned scenario based on the possible disappearance of HOMO–LUMO inversion at high pressure. On the other hand, the pressure-induced tetrameric columns is consistent with the periodicity of Peierls insulating phase of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$. Therefore, it may be said that due to the pressure-induced cation ordering coupled with the doubling of the lattice constant a, the high-pressure phase of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ is located near the boundary between metallic and insulating phases. It might be possible that the system transforms into insulating state if the role of tetrameric potential produced by ordered ammonium cations becomes more important at low temperature.

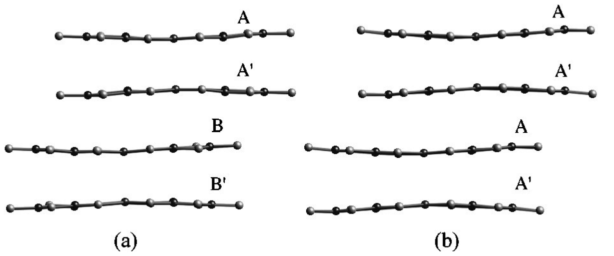

Figure 3. (a) The side view of $Pd(dmit)_2$ dimer at 10 kbar, indicating that the molecular plane tends to be flat at high pressure. (b) Two periodic units at ambient-pressure are given for comparison.

This work was supported by CREST (Core Research for Evolutional Science and Technology of JST (Japan Science and Technology Corporation)). This study was also 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.

References and Notes

\# Present address: Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto Mikazuki-cho Sayo-gun Hyogo 679-5198 Japan.

\## Present address: Complex Institute of Natural Sciences, Karakalpak Branch of Uzbek Academy of Science, Nukus 742000, Uzbekistan.

1 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A Clark, and A. E. Underhill, *Coord. Chem. Rev.*, **110**, 115 (1991).

2 For example, A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, *Chem. Lett.*, **1987**, 1819; A. Kobayashi, A. Miyamoto, R. Kato, A. Sato, and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **71**, 997 (1998); R. Kato, N. Tajima, and M. Tamura, *Phys. Rev. B*, **66**, 20508 (2002).

3 H. Kobayashi, K. Bun, T. Naito, R. Kato, and A. Kobayashi, *Chem. Lett.*, **1992**, 1909.

4 In this paper, the crystal axes are taken so as to make the a direction parallel to the $Pd(dmit)_2$ column. The relation between the lattice vectors ($\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$) and those reported in Ref. 3 ($\boldsymbol{a}'$, $\boldsymbol{b}'$, $\boldsymbol{c}'$) are: $\boldsymbol{a} = \boldsymbol{a}' + \boldsymbol{c}'$, $\boldsymbol{b} = -\boldsymbol{b}'$, $\boldsymbol{c} = -\boldsymbol{c}'$. The lattice constants at 1 bar are those determined by using the high-pressure X-ray cell.

5 A. Kobayashi, R. Kato, R. A. Clark, A. E. Underhill, A. Miyamoto, K. Bun, T. Naito, and H. Kobayashi, *Synth. Met.*, **55–57**, 2927 (1993).

6 R. Kato Y. Kashimura, S. Aonuma, N. Hanasaki, and H. Tajima, *Solid State Commun.*, **105**, 561 (1998).

7 For example, J. Yamaura, A. Nakao, and R. Kato, *J. Phys. Soc. Jpn.*, **73**, 976 (2004).

8 The molecular orbitals and the tight-binding band calculation were made on the basis of the extended-Hückel approximation. Slater type atomic orbitals were used. 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.