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Most Stable Metallic Phase of the Mixed-Valence MMX-Chain, $Pt_2(dtp)_4I$ (dtp = $C_2H_5CS_2^-$), in Purely *d*-Electronic Conductors Based on the Transition-Metal Complex

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Quasi-one-dimensional stacks of planar molecules displaying mixed valency, such as KCP(Br) ($K_2Pt(CN)_4Br_{0.3}\cdot nH_2O$),[1] TTF-TCNQ (TTF = tetrathiafulvalene, TCNQ = tetracyanoquinodimethane),[2] and $(TMTSF)_2PF_6$ (TMTSF = tetramethyltetraselenafulvalene),[3] have provided a very rich chemistry and physics. These include various electronic states, such as charge density wave,[4] spin density wave,[5] Mott insulating,[6] and spin-Peierls,[7] due to the electron-lattice, electron-electron, and spin-lattice interactions. Among them is the Peierls instability, which is a periodic lattice distortion of wavevector $2k_F$, resulting in an energy gap at the Fermi level in one-dimensional (1-D) metallic chains having a half-filled band.[8] To overcome this instability, pressure is used to increase weak transverse transfer integrals, thus stabilizing the metallic state down to low temperatures and, in some cases, leading to superconductivity.[9] For example, $(TMTSF)_2$-PF_6 exhibits a metal-superconductor transition at 1.2 K under 0.65 GPa.[10] Among the quasi-1-D systems, the family of halogen-bridged mixed-valence binuclear metal complex, the so-called MMX-chain, is of particular interest and has been attracting much attention. This is because of its wide variety of structural and physical properties derived from the 1-D *d*-electron system which is well-confined.[11] Consequently, MMX-chain complexes are semiconductors, and few exhibit metallic conduction.[12] The binuclear metal units provide an additional internal degree of freedom of charge polarization, resulting in four possible electronic ground states as follows:

(1) Averaged-valence (AV) state
$-M^{2.5+}-M^{2.5+}-X-M^{2.5+}-M^{2.5+}-X-$
(2) Charge-polarization (CP) state
$\cdots M^{2+}-M^{3+}-X\cdots M^{2+}-M^{3+}-X\cdots$
(3) Charge density wave (CDW) state
$\cdots M^{2+}-M^{2+}\cdots X-M^{3+}-M^{3+}-X\cdots$
(4) Alternate charge-polarization (ACP) state
$\cdots M^{2+}-M^{3+}-X-M^{3+}-M^{2+}\cdots X\cdots$

$Pt_2(dtp)_4I$ (Figure 1) is a special case among this family of compounds; it exhibits a high electrical conductivity (~5 Scm^{-1}) and a metal-insulator transition at 205 K under ambient pressure.[12b] Its electronic state changes with temperature: AV state with CDW fluctuation above 205 K, CP state between 160 and 205 K, ACP state below 160 K.[12c] Since $Pt_2(dtp)_4I$ has various fluctuations derived from the 1-D electronic system, such as spin, charge, and lattice, novel electronic states are expected to exist under high pressure. In this work, we report that $Pt_2(dtp)_4I$ exhibits the most stable metallic state in the 1-D *d*-electronic metal-complex-based system, and furthermore, we evidence a novel pressure-induced metal-insulator transition at 3.0 GPa.

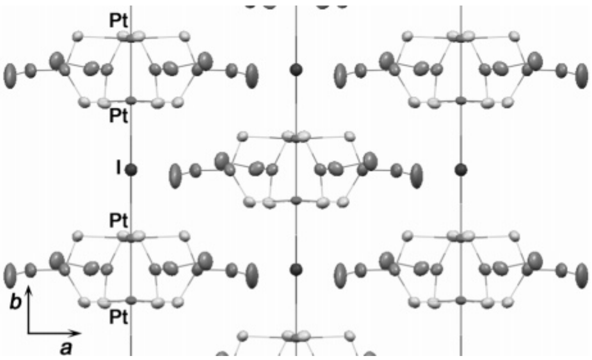

Figure 1. Projection of the crystal structure of $Pt_2(dtp)_4I$ along the *c*-axis.

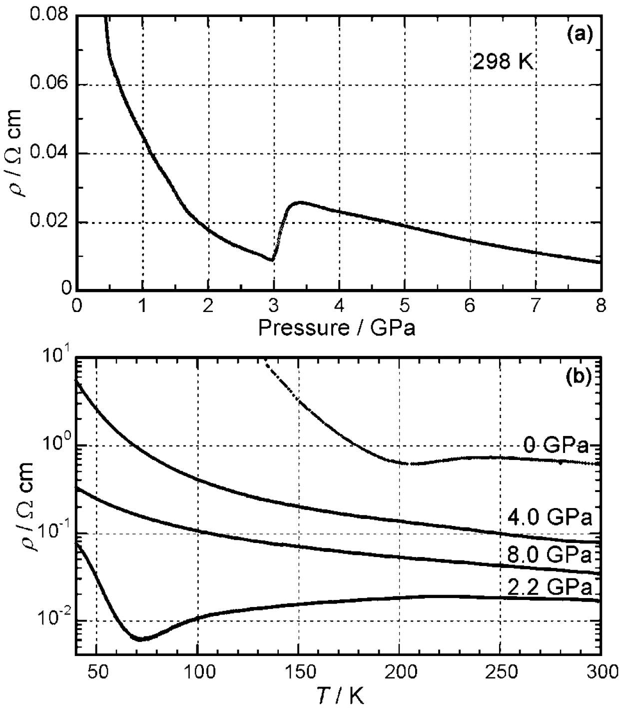

Figure 2. (a) Pressure dependence of the electrical resistivity of $Pt_2(dtp)_4I$. (b) Temperature dependences of the electrical resistivity at 0, 2.2, 4.0, and 8.0 GPa.

Figure 2a shows the pressure dependence of the electrical resistivity of $Pt_2(dtp)_4I$ along the *b*-axis (// 1-D chain) at 298 K.[13] Upon increasing the pressure, the resistivity decreases rapidly

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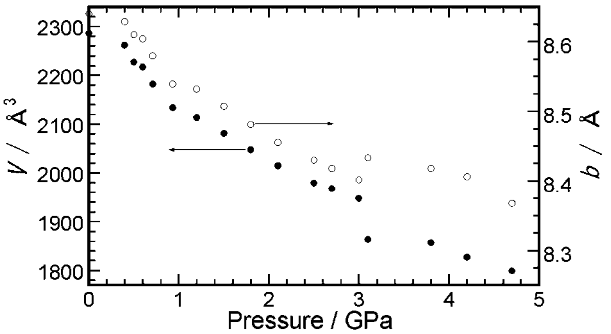

Figure 3. Pressure dependences of the lattice parameter b (open circle) and unit cell volume V (closed circle) of $Pt_2(dtp)_4I$.

followed by a sharp transition at 3.0 GPa to a more resistive state and a gradual decrease up to 8.0 GPa.

Temperature dependences of the electrical resistivity at 0, 2.2, 4.0, and 8.0 GPa are shown in Figure 2b.[13] At ambient pressure (0 GPa), the metal-insulator transition was observed at 205 K, which is consistent with the previous report.[12b] Under 2.2 GPa, metallic conduction is maintained down to 70 K; that is, the metallic AV state is stabilized under pressure, surviving down to 70 K. This metal-insulator transition temperature ($T_{MI} = 70$ K) is the lowest value in the 1-D *d*-electronic conductors based on transition-metal complexes; in other words, $Pt_2(dtp)_4I$ is the most stable metal in 1-D *d*-electronic transition-metal complexes. As is well-known, the first molecular conductor $K_2Pt(CN)_4Br_{0.3}\cdot nH_2O$[1a,b] (often abbreviated KCP(Br)) had so far held the lowest T_{MI} (= 210 K under 3.2 GPa).[9a] Compared to KCP(Br), the T_{MI} of $Pt_2(dtp)_4I$ is lowered by 140 K and its 1-D metallic state is much more stabilized. Above 3.0 GPa, on the contrary, the electrical transport behavior changed to be narrow-gap semiconductor in the whole temperature region, where the activation energies are 17 meV at 4.0 GPa and 10 meV at 8.0 GPa. These results indicate that the resistivity jump at 3.0 GPa is due to a pressure-induced metal-insulator transition.

To clarify the origin of the pressure-induced metal-insulator transition, X-ray oscillation photographs were taken under high pressure at room temperature.[14] Any diffuse scatterings or superlattice reflections at $k = n + 0.5$ (n being an integer) originating from the 2-fold periodic charge ordering, such as CDW or ACP states, were not observed above 2.0 GPa,[12b,15] suggesting that the electronic state above 2.0 GPa is not CDW or ACP but AV or CP. Pressure dependences of the lattice parameter b and unit cell volume V up to 5.0 GPa are shown in Figure 3. The parameters b and V decreased monotonically with applied pressure, while the discontinuous jump was observed for each parameter at 3.0 GPa, where the pressure-induced metal-insulator transition occurs. The pressure-induced metal-insulator transition at 3.0 GPa is, therefore, attributable to the first-order structural phase transition with elongation of the *b*-axis (// chain), resulting in a lowering of the electron transfer integral (t).

In general, the resistivity decreases with pressure because of an increase of the bandwidth ($W \sim 4t$ for 1-D system). The metallic AV state is stabilized with pressure up to 3.0 GPa due to the increases of W and the elastic energy. As opposed to these enhancements, $Pt_2(dtp)_4I$ undergoes the metal-insulator transition at 3.0 GPa, which can be related to the elongation of the interdimer distance in $-Pt_2(dtp)_4-I-Pt_2(dtp)_4-I-$.

In summary, the electrical resistivity and the X-ray diffraction measurements for the MMX-chain complex, $Pt_2(dtp)_4I$, were performed under high pressure. We observed the suppression of the metal-insulator transition to 70 K, the lowest known for any 1-D purely *d*-electronic conductors based on transition-metal complexes, at 2.2 GPa. The pressure-induced metal-insulator transition associated with an elongation of the chain axis b was observed at 3.0 GPa. Full structural X-ray single-crystal analysis and Raman spectroscopic study under high pressure are in progress.

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Supporting Information Available: X-ray oscillation photographs under 0.02, 0.45, 2.5, and 4.3 GPa (PDF) are available. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Krogmann, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 35. (b) Kuse, D.; Zeller, R. H. *Phys. Rev. Lett.* **1971**, *27*, 1060. (c) Williams, M. J.; Schultz, J. A.; Underhill, A. E.; Carneiro, K. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982; Vol. 1, p 73.

(2) (a) Ferraris, F.; Cowan, O. S.; Walatka, V.; Perlstein, H. J. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Cohen, J. M.; Coleman, B. L.; Garito, F. A.; Heeger, J. A. *Phys. Rev. B* **1974**, *10*, 1298.

(3) (a) Bechgaard, K.; Jacobsen, S. C.; Mortensen, K.; Perdersen, H. J.; Throrup, N. *Solid State Commun.* **1980**, *33*, 1119. (b) Throrup, N.; Rindorf, G.; Soling, H.; Bechgaard, K. *Acta Crystallogr. B* **1981**, *37*, 1236.

(4) Heeger, J. A. In *Highly Conducting One-Dimensional Solids*; Devrees, T. J., Evrand, P. R., van Doren, E. V., Eds.; Plenum: New York, 1979; p 69.

(5) (a) Overhauser, W. A. *Phys. Rev.* **1963**, *128*, 1437. (b) Nasu, K. *J. Phys. Soc. Jpn.* **1983**, *52*, 3865. (c) Nasu, K. *J. Phys. Soc. Jpn.* **1983**, *53*, 302.

(6) Mott, F. N. *Metal-Insulator Transitions*; Taylor and Francis: New York, 1974.

(7) (a) Jacobs, S. I.; Bray, W. J.; Hart, R. H.; Interrante, V. L.; Kasper, S. J.; Watkins, D. G.; Prober, E. E.; Bonner, C. J. *Phys. Rev. B* **1976**, *14*, 3036. (b) Huizinga, S.; Kommandeur, J.; Sawatzky, G. A.; Kopinga, K.; de Jonge, M. J. W. In *Quasi One-Dimensional Conductors II*; Barisic, S., Bjelis, S., Cooper, R. J., Leotic, B., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1979; p 45.

(8) (a) Peierls, E. R. *Quantum Theory of Solids*; Clarendon: Oxford, 1974. (b) Bernasconi, J.; Bruesch, P.; Zeller, R. H. *J. Phys. Chem. Solids* **1974**, *35*, 145. (c) Ishiguro, T.; Kagoshima, S.; Anzai, H. *J. Phys. Soc. Jpn.* **1976**, *41*, 351. (d) Kobayashi, K.; Mori, T.; Inokuchi, H.; Kato, R.; Kobayashi, H. *Synth. Met.* **1988**, *27*, B275.

(9) (a) Thielemans, M.; Deltour, R.; Jerome, D.; Cooper, R. J. *Solid State Commun.* **1976**, *19*, 21. (b) Shirotani, I.; Onodera, A.; Anzai, H. *J. Solid State Chem.* **1981**, *36*, 246. (c) Shirotani, I.; Kawamura, A.; Yamashita, M.; Toriumi, K.; Kawamura, H.; Yagi, T. *Synth. Met.* **1994**, *64*, 265. (d) Jerome, D. *Science* **1991**, *252*, 1509. (e) Cassoux, P. *Coord. Chem. Rev.* **1999**, *185−186*, 213.

(10) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, L95.

(11) (a) Bellito, C.; Flamini, A.; Gastaldi, L.; Scaramuzza, L. *Inorg. Chem.* **1983**, *22*, 444. (b) Che, C. M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, B. H. *J. Am. Chem. Soc.* **1983**, *105*, 4606. (c) Matsuzaki, H.; Kishida, H.; Okamoto, H.; Takizawa, K.; Matsunaga, S.; Takaishi, S.; Miyasaka, H.; Sugiura, K.; Yamashita, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3240.

(12) (a) Kitagawa, H.; Onodera, N.; Sonoyama, T.; Yamamoto, M.; Fukawa, T.; Mitani, T.; Seto, M.; Maeda, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10068. (b) Mitsumi, M.; Murase, T.; Kishida, H.; Yoshinari, T.; Ozawa, Y.; Toriumi, K.; Sonoyama, T.; Kitagawa, H.; Mitani, T. *J. Am. Chem. Soc.* **2001**, *123*, 11179. (c) Mitsumi, M.; Kitamura, K.; Morinaga, A.; Ozawa, Y.; Kobayashi, M.; Toriumi, K.; Iso, Y.; Kitagawa, H.; Mitani, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2767. (d) Wakabayashi, Y.; Kobayashi, A.; Sawa, H.; Ohsumi, H.; Ikeda, N.; Kitagawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 6676.

(13) The single crystals of $Pt_2(dtp)_4I$ were prepared according to the previous report (see ref 12b). The dc electrical resistivity measurements of $Pt_2(dtp)_4I$ along the *b*-axis were performed on several single crystals with a four-probe method using a cubic anvil press system at the ISSP, the University of Tokyo.

(14) X-ray oscillation photographs of $Pt_2(dtp)_4I$ were taken using a diamond anvil cell at the KEK-PF BL-1B. The pressure was calibrated by ruby luminescence technique.

(15) See Supporting Information.

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