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# Pressure-Induced Metal–Semiconductor–Metal Transitions in an MMX-Chain Complex, $Pt_2(C_2H_5CS_2)_4I$

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The electrical conductivity and X-ray diffraction measurements were performed for a highlyconductive halogen-bridged binuclear-metal mixed-valence complex (the so-called MMX chain), $Pt_2(C_2H_5CS_2)_4I$, under high pressure up to 2.5 GPa. The complex exhibited pressure-induced metal–semiconductor–metal transitions at 0.5 and 2.1 GPa. The X-ray diffuse scatterings were observed at $k = n+0.5$ ($n$: integer) under ambient pressure, which are derived from the charge-density wave (CDW: $\cdots Pt^{2+}–Pt^{2+}\cdots I–Pt^{3+}–Pt^{3+}–I\cdots$) fluctuation in the MMX chain. Above 0.5 GPa, where the pressure-induced metal–semiconductor transition occurred, these scatterings disappeared. The electronic phases under high pressure ($P$) were found to be attributable to the metallic averaged-valence state (AV: $–Pt^{2.5+}–Pt^{2.5+}–I–Pt^{2.5+}–Pt^{2.5+}–I–$) with CDW fluctuation of $P < 0.5$ GPa, semiconducting charge-polarization state (CP: $\cdots Pt^{2+}–Pt^{3+}–I\cdots Pt^{2+}–Pt^{3+}–I\cdots$) of $0.5 < P < 2.1$ GPa, and metallic AV state of $P > 2.1$ GPa. The electronic state of $Pt_2(C_2H_5CS_2)_4I$ is very sensitive to pressure, which implies that the phase competition among the CP, CDW, and AV phases is present in the MMX chain.

## Introduction

One-dimensional (1D) halogen-bridged mixed-valence binuclear-metal complexes (MMX chain) have drawn much attention because of their various electronic structures that originate from the internal degree of freedom of charge distribution in metal-dimer units as follows:[1–2]

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

$Pt_2(C_2H_5CS_2)_4I$, which is an MMX chain complex as shown in Figure 1, exhibits a high electrical conduction and a metal–insulator (M–I) transition at 205 K.[3] This M–I transition temperature ($T_{MI}$) is relatively lower than typical 1D $d$-electron conductors in comparison with transition-metal complexes such as $K_2Pt(CN)_4Br_{0.3}\cdot nH_2O$ (commonly called KCP(Br); $T_{MI}$ = 250 K at 0 GPa).[4] It was revealed that the electronic state changes variously with decreasing temperature; the AV phase occurs with CDW fluctuation

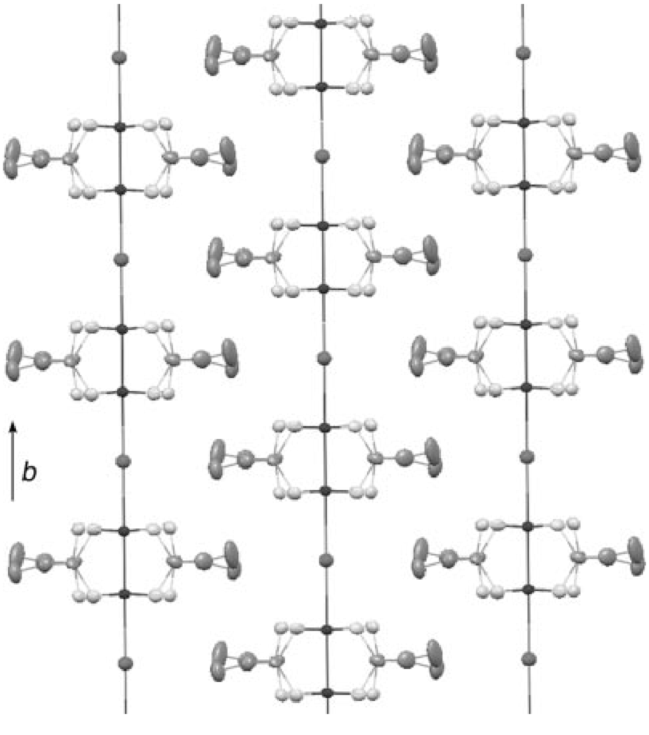

Figure 1. Chain structure of $Pt_2(C_2H_5CS_2)_4I$.

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above 205 K, the CP phase between 160–205 K, and the ACP phase below 160 K.[3,5] This phase competition is derived from the fact that the several interactions, such as the electron transfer integral (*t*), electron correlation (on-site (*U*) and inter-site (*V*) Coulombic repulsive energies), and electron-lattice interaction (*S*) are antagonistic to each other in this complex.[1d,1e,6]

The application of a high pressure to low-dimensional complexes gives rise to a drastic change in their physical properties because of an increase in the electron transfer integral *t* and a suppression of electron-lattice interaction *S*.[7] For example, $(CH_3)_4N[Ni(dmit)_2]_2$ shows a pressure-induced transition at 0.32 GPa from the normal metallic state to the superconducting state below 3 K.[8] Since the title complex exhibits various electronic states, the application of pressure may create a novel electronic phase. Therefore, we have investigated the electronic state of the MMX-chain complex under high pressure by electrical resistivity and X-ray diffuse scattering measurements.

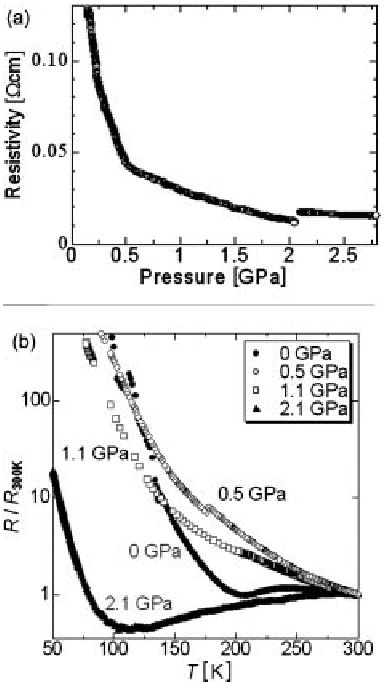

Figure 2. (a) Pressure dependence of the electrical resistivity at 298 K up to 2.5 GPa. (b) Temperature dependence of the electrical resistivity under several pressures (0, 0.5, 1.1 and 2.1 GPa).

## Results and Discussion

Figure 2(a) shows the pressure dependence of the electrical resistivity along the *b*-axis (parallel to the 1D chain) at 298 K. As the pressure is increased, the resistivity decreases rapidly up to 0.5 GPa and gradually between 0.5 and 2.1 GPa. The pressure coefficients of the resistivity below and above 0.5 GPa are –1.8 and –0.16 $GPa^{-1}$, respectively. Above 2.1 GPa, the resistivity is almost constant. The change in the pressure coefficients at 0.5 and 2.1 GPa implies that some phase transitions occur at these pressure points. A small resistance jump observed at 2.1 GPa is due to the resistance hysteresis derived from a cycle of cooling and heating processes in the electrical conductivity measurements.

The temperature dependences of the electrical resistivity at 0, 0.5, 1.1, and 2.1 GPa along the *b*-axis are shown in Figure 2(b). The resistivity is normalized at 300 K. At ambient pressure, $Pt_2(C_2H_5CS_2)_4I$ exhibited metallic conduction (≈ 5 $S\,cm^{-1}$ at 300 K) and underwent a metal–insulator transition at 205 K, which is consistent with our previous work.[3] As a little pressure was applied, a pressure-induced metal–semiconductor transition occurred at 0.5 GPa; the metallic conduction disappeared and a behavior consistent with a semiconductor was observed in the whole temperature range. This pressure-induced metal–semiconductor transition is in agreement with the discontinuity of the pressure coefficient observed at 0.5 GPa [Figure 2(a)]. The activation energy decreased with applied pressures from 72 meV at 0.5 GPa to 54 meV at 1.1 GPa, which is considered to be due to an increase in the bandwidth *W* (≈ 4*t* for 1D electronic system). At 2.1 GPa, metallic behavior was again observed, and an M–I transition occurred at 114 K. This pressure-induced semiconductor–metal transition is also in agreement with the discontinuity of the pressure coefficient observed at 2.1 GPa. Compared with the $T_{MI}$ = 210 K of KCP(Br) under 3.2 GPa,[4d] the transition temperature 114 K is a significantly lower value, which means that the metallic state of $Pt_2(C_2H_5CS_2)_4I$ is very stable as a 1D electronic system.

To clarify the electronic state under high pressure, an X-ray diffraction measurement was performed on a single-crystal with a diamond-anvil cell at room temperature.[8] Figure 3(a) shows the X-ray diffraction photograph taken at 0.1 GPa. Diffuse scatterings were clearly observed at $k = n + 0.5$ (*n*: integer), which corresponds to the CDW fluctuation that exists at ambient pressure as mentioned above. The intensities of the pixels located on the solid-line arrow from A to B in Figure 3(a) are shown in Figure 3(b). These scatterings observed at $k = n + 0.5$ disappeared gradually with increasing pressure, and were hardly observed above 0.5 GPa. The disappearance of these diffuse scatterings indicates that the CDW fluctuation is lost above 0.5 GPa where the pressure coefficient changed, as shown in Figure 2. Since no remarkable change in X-ray diffraction photographs was observed in the pressure region between 0.5 and 2.5 GPa, the superstructures with twofold periodic ordering such as CDW or ACP are absent in the high-pressure range.

In general, the application of high pressure to the complex suppresses the electron-lattice interaction *S* and increases the electron transfer integral *t* because of the increase in the elastic energy and the decrease in the interatomic distance. This in turn results in an increase in the conductivity, and the behavior of the complex tends to change from an insulator to a semiconductor or a metallic species.[7] Actually, with pressure the conductivity of

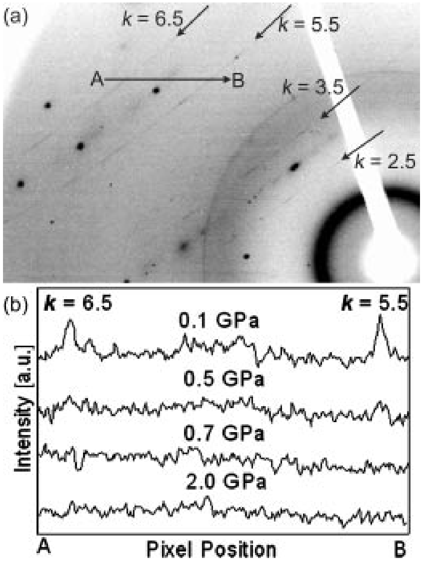

Figure 3. (a) X-ray diffraction photograph under 0.1 GPa at room temperature. (b) Intensity on the solid-line arrow from A to B in Figure 3(a) under several pressures (0.1, 0.5, 0.7 and 2.0 GPa).

$Pt_2(C_2H_5CS_2)_4I$ increased drastically and the CDW fluctuation of $\cdots Pt^{2+}–Pt^{2+}\cdots I–Pt^{3+}–Pt^{3+}–I\cdots$ was suppressed, which would disturb the itinerancy of the conduction of the electrons. The pressure-induced metal–semiconductor transition was nevertheless observed at 0.5 GPa. Recent theoretical calculations performed by Yamamoto et al. pointed out that the inter-site Coulombic repulsive energy $V$ increases as the interatomic distance is decreased with pressure, and in the case of $V > t$, the CP phase of $\cdots Pt^{2+}–Pt^{3+}–I\cdots Pt^{2+}–Pt^{3+}–I\cdots$ could be stabilized.[6a,6b] The CP phase can be regarded as a charge-ordered (or charge-localized) state, that is, a Mott insulating state.[9] With the consideration of the absence of any twofold structures, the semiconducting state of the complex in the region of 0.5–2.1 GPa is attributable to the CP phase. Above 2.1 GPa, the metallic phase appeared again in the temperature range of 114–300 K, which would be derived from the AV state of $–Pt^{2.5+}–Pt^{2.5+}–I–Pt^{2.5+}–Pt^{2.5+}–I–$ under the delicate competitive condition of $t > V$. No twofold structures were observed, which is not in conflict with the AV state.

In summary, the electrical conductivity and X-ray diffraction measurements under high pressure have been performed for a highly conductive MMX-chain complex, $Pt_2(C_2H_5CS_2)_4I$. Pressure-induced metal–semiconductor–metal transitions were observed at 0.5 and 2.1 GPa, which is considered to be derived from the phase transitions of the metallic AV state with CDW fluctuation to the semiconducting CP state, and from the CP state to the metallic AV state, respectively. The electronic state of $Pt_2(C_2H_5CS_2)_4I$ is very sensitive to pressure, which implies that the phase competition among the CP, CDW, and AV phases is present in the MMX chain. To determine the origin of these metal–semiconductor–metal transitions, theoretical calculations, Raman and IR spectroscopic studies under high pressure, are in progress.

## Experimental Section

**Synthesis:** Single-crystals of $Pt_2(C_2H_5CS_2)_4I$ were prepared according to the literature (see ref.[3a]).

**Electrical Conductivity:** The dc electrical resistivity of $Pt_2(C_2H_5CS_2)_4I$ along the *b*-axis (parallel to the 1D chain) was measured for several single-crystals with the four-probe-method with the use of a clump-cell and a cubic-anvil press system at the ISSP, the University of Tokyo.

**X-ray Diffraction:** X-ray diffraction measurements under high pressure were performed with a diamond-anvil cell at the BL-1B beamline in KEK-PF ($\lambda$ = 0.688 Å). Pressure was calibrated by the ruby luminescence technique.

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