Structural Phase Transition and Valence Fluctuation Observed in a New MMX Chain Compound, $Pt_2(n\text{-}PrCS_2)_4I$

Minoru Mitsumi,* Shunsuke Umebayashi, Yoshiki Ozawa, Koshiro Toriumi,* Hiroshi Kitagawa,[†,#] and Tadaoki Mitani[†]
Department of Material Science, Himeji Institute of Technology, 3-2-1 Kouto, Kamigori-cho, Hyogo 678-1297
[†]*Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-1292*

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A new one-dimensional iodo-bridged mixed-valence diplatinum(II,III) complex (MMX chain compound) with dithiobutanoate ($n\text{-}PrCS_2^-$) as a ligand, $Pt_2(n\text{-}PrCS_2)_4I$, was found to undergo a structural phase-transition at 358–359 K by the differential scanning calorimetry (DSC) measurement and X-ray crystal structure analyses. In X-ray diffraction photographs measured using synchrotron radiation of the SPring-8 facility, the weak but distinct Bragg spots corresponding to the periodicity of 2-fold repetition length of a –Pt–Pt–I– unit were observed at 300 K and changed to diffuse scattering at 350 K. The electric conductivity deviates from the typical semiconducting behavior in the temperature region above 330 K.

Recently, one-dimensional (1-D) halogen-bridged mixed-valence dinuclear metal complexes, MMX chain compounds, have attracted much attention. Previously, two families of MMX chain compounds, namely $A_4[Pt_2(pop)_4X]\cdot nH_2O$ (pop = $P_2O_5H_2^{2-}$, A = Li, K, Cs, NH_4, X = Cl, Br, I)[1] and $Pt_2(RCS_2)_4I$ (R = Me, Et)[2–4] have been reported. An important feature of MMX compounds is the increase in internal degrees of freedom upon introducing a dinuclear unit in the mixed-valence linear chain system, allowing it to assume a variety of electronic structures.

(a) averaged valence state:

$$-M^{2.5+}-M^{2.5+}-X^{-}-M^{2.5+}-M^{2.5+}-X^{-}-$$

(b) charge-polarization state:

$$—M^{2+}–M^{3+}\text{-}X^{-}—M^{2+}–M^{3+}\text{-}X^{-}—$$

(c) charge density wave (CDW) state:

$$—M^{2+}—M^{2+}—X^{-}\text{-}M^{3+}\text{-}M^{3+}\text{-}X^{-}—$$

(d) alternate charge-polarization state

$$—M^{2+}–M^{3+}\text{-}X^{-}\text{-}M^{3+}–M^{2+}–X^{-}—$$

The periodicity of the 1-D chains in the valence-ordering states (a) and (b) are –M–M–X–, whereas those in (c) and (d) are doubled. The valence state taken in the 1-D chain system may depend not only on electron correlation, transfer energy, and electron–lattice interaction in the 1-D chain but also on weak, but effective, interchain interactions, such as Coulomb interactions.[4] If the interchain interaction in a crystal could be changed by chemical modification of the 1-D system, while retaining the basic skeleton, the valence ordering and/or fluctuation state would be changed and yield new solid-state properties.

Black needle crystals of $Pt_2(n\text{-}PrCS_2)_4I$ (**1**) were grown by slow cooling of a toluene solution of equimolar amounts of $[Pt_2(n\text{-}PrCS_2)_4]$ (**2**) and $[Pt_2(n\text{-}PrCS_2)_4I_2]$ (**3**).[5]

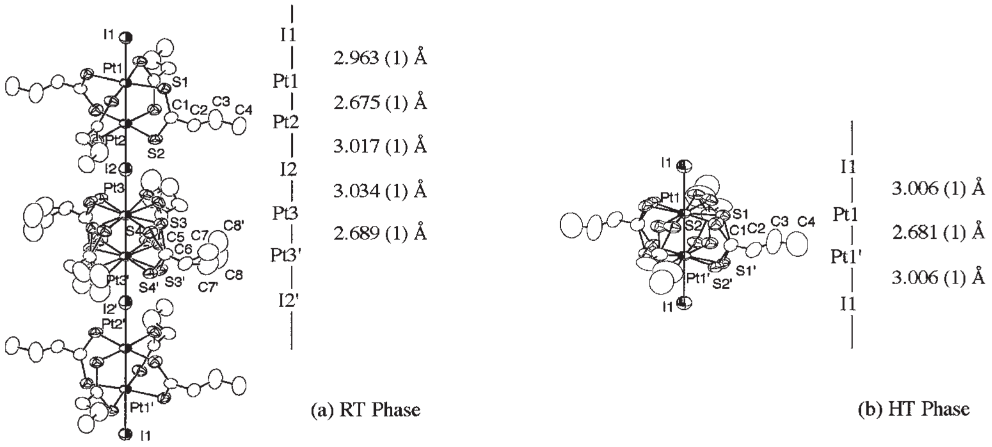
In the differential scanning calorimetry (DSC) measurement of compound **1**, the latent heat was observed at 358–359 K, indicating the first-order phase-transition at the temperature and two phases of room temperature (RT) and high-temperature (HT).[6]

X-ray crystal structure analyses of **1** were carried out at 293 K (RT phase) and 377 K (HT phase).[7,8] ORTEP diagrams of both phases are shown in Figure 1. The space groups of both phases are the same $I4/m$, and the crystal consists of only a neutral 1-D chain with a –Pt–Pt–I– repeating unit lying on the crystallographic 4-fold axis parallel to the c axis. However, the unit cell dimension c along the 1-D chain direction changes from 3-fold of a –Pt–Pt–I– period at RT phase to 1-fold at HT one. In the RT phase, the ligand moieties including S atoms of one of the three diplatinum units are positionally disordered at two positions related by the crystallographic mirror plane perpendicular to the 1-D chain and passing through the midpoint of Pt(3) and Pt(3'), whereas in the HT phase all the sulfur atoms of ligands are disordered.[9] The shortest interchain S···S distances in RT phase is S(2)···S(2) (1/2–x, 1/2–y, 1/2–z) = 4.569 (4) Å, indicating no interchain S···S contact.

All the Pt–Pt and Pt–I bond distances in HT phase are crystallographically equivalent respectively, and hence the valence states of platinum atoms can be regarded as the average of +2.5. All the iodine atoms in the RT phase are placed at almost midpoint between two diplatinum units, but Pt(2)–I(2) and Pt(3)–I(2) distances (3.017 (1) and 3.034 (1) Å) are slightly lengthened compared with Pt(1)–I(1) (2.963 (1) Å). It is noteworthy that the average temperature factor U_{33} of I atoms (0.054) directed along the linear chain is significantly larger than those of Pt and S atoms (0.021 for Pt, 0.031 for S on average). This suggests that the iodine atoms are positionally disordered or vibrate with large amplitude.

Single crystal electrical resistivity measured along the c axis (1-D chain direction) shows a thermally activated behavior with activation energy of 363 meV in the temperature range of 245–320 K but an apparent deviation from the thermally activated behavior in the temperature range of 320–359 K. Resistivity jump due to the first-order phase-transition was also observed at 359 K. On the other hand, the thermoelectric power shows almost temperature independent behavior ($-40\,\mu V\,K^{-1}$) in the range of 330–360 K. Above the phase-transition temperature, the thermoelectric power tends to increase slightly with increasing temperature.

X-ray diffraction photographs of compound **1** were measured in the temperature range of 300–380 K using synchrotron radiation (30.0 keV, $\lambda = 0.413$ Å) at BL02B1 beam line of the SPring-8 facility, and are shown in Figure 2. In the oscillation photographs rotated around the c axis at 300 K, weak but distinct Bragg spots were observed in the reciprocal positions indexed as $l \pm 1/3$ and $l + 1/2$, where the lattice parameter c_{HT} of the HT phase is corresponding to the repetition length of a –Pt–Pt–I– unit. The structural analysis including the weak intensities of $l \pm 1/3$ revealed the super structure of $c_{RT} = 3c_{HT}$ as shown in Figure 1(a). However, the super structure corresponding to 6-fold of a –Pt–Pt–I– unit have not been determined yet, since reflections indexed as $l \pm 1/6$ are entirely absent. This seems to suggest that the super



(a) RT Phase (b) HT Phase

Figure 1. ORTEP diagrams with 50% thermal ellipsoids and relevant interatomic distances of $Pt_2(n\text{-}PrCS_2)_4I$ (**1**): (a) RT phase (293 K), (b) HT phase (377 K).

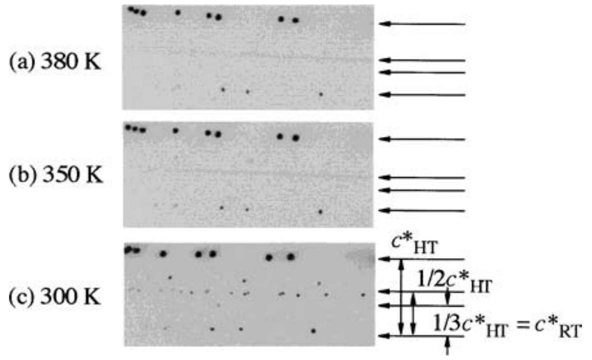


Figure 2. Portions of X-ray diffraction photographs of $Pt_2(n\text{-}PrCS_2)_4I$ (**1**). The chain axis c is vertical. (a) At 380 K in HT phase. (b) At 350 K in RT phase. (c) At 300 K in RT phase.

structure corresponding to 3-fold of a –Pt–Pt–I– is independent to that of 2-fold one. The intensities of reflections of $l \pm 1/3$ decrease above 300 K and disappear at 380 K. This is well interpreted by the order-disorder structural change of the ligands accompanied by the first-order phase transition at 358–359 K. On the other hand, it should be noted that the Bragg spots of $l + 1/2$ change to diffuse scattering around 350 K, of which the intensities are clearly visible even at 380 K. The diffuse scattering corresponding to two-fold repetition length of a –Pt–Pt–I– unit was also observed for the analogous compounds of $Pt_2(RCS_2)_4I$ (R = Me, Et) and well attributable to the lattice distortion arising from the valence ordering of (c) or (d).[4,10] The large temperature factors U_{33} of I atoms at 293 K can be interpreted by the valence-ordering structure.

It should be noted that the temperature dependence of electric conductivity is well corresponding to the change of diffraction pattern due to the valence ordering. In the typical semiconducting region, the diffraction photographs show Bragg spots corresponding to the three-dimensional valence ordering, that is, the valence localization state. On the other hand, in the temperature region in which the electric conductivity is deviated from the typical semiconducting behavior, the diffuse scattering has been observed and suggests the one-dimensional periodic valence ordering along the linear chain structure. This may suggest that the valence fluctuation plays an important role for the electric conducting behavior of compound **1**. Further crystallographic and spectroscopic characterization of **1** is now in progress.

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\# Present address: Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan.

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5 Synthesis of **1**: The compounds **2** (41 mg, 0.047 mmol) and **3** (53 mg, 0.047 mmol) were dissolved in 5.5 mL of toluene at 70 °C. After being slowly cooled to 3 °C, black needles separated from the solution were collected by suction filtration: yield 58 mg (62%). Anal. Calcd for $C_{16}H_{28}IPt_2S_8$: C, 19.33; H, 2.84%. Found: C, 19.50; H, 2.88%.

6 DSC measurement was carried out using a MAC Science DSC3200 system. The measurement was performed for 10.150 mg of **1** at a scanning rate of 5 K min^{-1} in the temperature range of 153–403 K.

7 Crystallographic data for $Pt_2(n\text{-}PrCS_2)_4I$ at 293 K: $C_{16}H_{28}IPt_2S_8$, fw = 993.96, black, tetragonal, space group $I4/m$, $a = 12.634$ (1) Å, $c = 26.066$ (2) Å, $V = 4160.5$ (3) $Å^3$, $Z = 6$. The final $R1$ factor was 0.0276 for 1392 reflections $|F_o| > 4\sigma(F_o)$ ($wR2 = 0.0824$ for 3101 all reflections). GOF = 0.853.

8 Crystallographic data for $Pt_2(n\text{-}PrCS_2)_4I$ at 377 K: $C_{16}H_{28}IPt_2S_8$, fw = 993.96, black, tetragonal, space group $I4/m$, $a = 12.777$ (1) Å, $c = 8.692$ (1) Å, $V = 1419.0$ (1) $Å^3$, $Z = 2$. The final $R1$ factor was 0.0572 for 853 reflections $|F_o| > 4\sigma$ (Fo) ($wR2 = 0.1374$ for 1094 all reflections). GOF = 1.212. The large temperature factors of C3 and C4 atoms indicate that these atoms are positionally disordered or vibrate with large amplitude.

9 The two PtS_4 planes of the dinuclear unit in the HT phase are twisted by 21.8 (2) ° from the eclipsed D_{4h} structure.

10 Y. Ozawa, M. Kim, K. Takata, and K. Toriumi, manuscript to be submitted.