X-ray Diffuse Scattering of the Halogen-bridged Mixed-valence Diplatinum(II,III) Complex, $Pt_2(EtCS_2)_4I$

Koshiro TORIUMI, Yoshiki OZAWA, Minoru MITSUMI, Kumiko AKASHIKA, and Tetsuya YOSHINARI
Department of Material Science, Himeji Institute of Technology

1. Introduction

Halogen-bridged mixed-valence diplatinum complexes $Pt_2(RCS_2)_2I$ (R=CH_3 (**1**), C_2H_5 (**2**), n-C_3H_7 (**3**)) with linear chain structures of repeating units {-I–Pt–Pt–I-} (Fig.1) are particular interest because they are possible to take a variety of valence ordering as follows [1].

(a) –I—Pt^{2+}–Pt^{2+}—I–Pt^{3+}–Pt^{3+}–I–
(b) –I—Pt^{2+}–Pt^{3+}–I–Pt^{3+}–Pt^{2+}—I–
(c) –I—Pt^{2+}–Pt^{3+}–I—Pt^{2+}–Pt^{3+}–I–
(d) –I–$Pt^{2.5+}$–$Pt^{2.5+}$–I–$Pt^{2.5+}$–$Pt^{2.5+}$–I–

The crystals of **1** which was first reported by Bellitto *et al.* [2] exhibit anomalous electrical conducting behavior (T < 300 K, semiconductor; 300 K < T < 340 K, metallic) [3]. The variable temperature crystal structure analyses revealed dynamic disorder of the $CH_3CS_2^-$ ligands above 270 K [4].

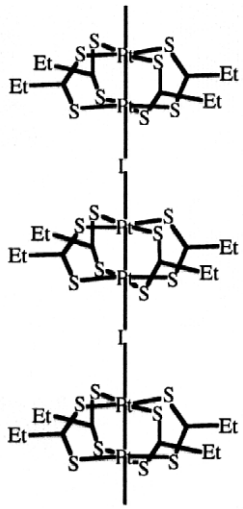

Fig. 1. Linear chain structure of $Pt_2(EtCS_2)_4I$ (**2**).

In order to elucidate the relation between the solid state behavior and the valence ordering of Pt atoms on the linear chain, the compounds **2** and **3** were synthesized and their crystal structure analyses and electrical conducting measurements were carried out [5]. The M-I transition was observed for **2** at about 200 K.

Since only the averaged structures have been provided the crystal structure analyses, we tried to measure the diffuse scattering corresponding to low-dimensional valence ordering of Pt atoms.

2. Experiment

Single crystal X-ray photographs of the compounds **1-3** were taken with a flat IP cassette or a vacuum type X-ray IP camera mounted on a 7-circle diffractometer at SPring-8 BL02B1 station. A Rigaku cold N_2 gas stream type low temperature apparatus was installed. X-ray photographs were taken by rotating crystals around the chain axes, by using 30 keV X-ray beam monochromated by a Si(111) double crystals and focused by a mirror. X-ray rotation photographs were also taken at temperature region 24 - 300 K by using the vacuum type low-background X-ray camera developed by MAC Science Co., Ltd. and us.

3. Results and Discussion

On the rotation photographs measured for the crystals **1-3** at room temperature, diffuse scattering corresponding to twice the original cell along the linear chain structures were clearly observed (Fig. 2).

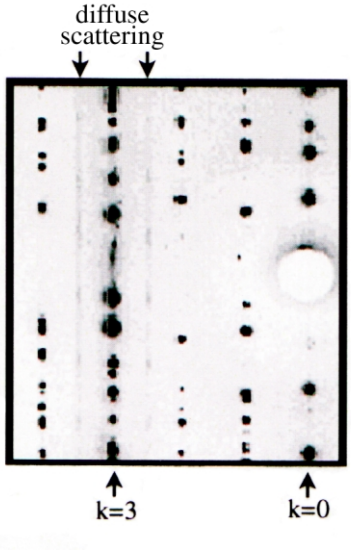

Fig. 2. Rotation photograph of $Pt_2(EtCS_2)_4I$ (**2**) at room temperature.

This strongly indicates that Pt^{2+} and Pt^{3+} are arranged alternately along the linear chain such as the valence ordering of (a) or (b) described above.

It was also revealed that although the diffuse scatterings were observed for **2** above 200 K (metallic state), but changed to the Bragg spots below 100 K (semiconductive state). Similar phenomena were observed for the crystals of **3**. These results suggest that the valences of Pt atoms are three-dimensionally ordered in the low temperature below 100 K, and seem to be consistent with the semiconductive behavior of **2**.

References

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[2] C. Bellitto *et al.*, Inorg. Chem. **22** (1983) 444.
[3] H. Kitagawa *et al.*, Synth. Met. **86** (1997) 1931.
[4] K. Toriumi *et al.*, 33rd. ICCC Abstract, 419 (1998).
[5] M. Mitsumi *et al.*, 33rd. ICCC Abstract, 385 (1998).