

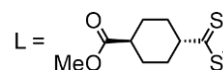
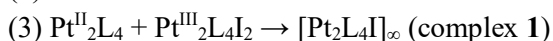
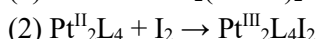
Synthesis and physical properties of a functionalized cyclohexane-dithiocarboxylate-based MMX-chain complex

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One-dimensional halogen-bridged mixed-valence dinuclear metal complexes (MMX-chains) show a wide variety of electronic states depending on the external stimuli such as temperature and pressure due to the high degrees of freedom of the charge polarization in dimerized metal unit. In particular, some dithiocarboxylate-based MMX-chains exhibit metallic conductivity¹. However, only the effect of alkyl chain length of the ligand has been systematically studied in this system. In this study, we have aimed to investigate the electronic states by introducing a rigid moiety to a dithiocarboxylate ligand.

The MMX-chain $\text{Pt}_2\text{L}_4\text{I}$ (complex **1**) based on *trans*-4-(methoxycarbonyl)cyclohexanedithiocarboxylate (L) as a ligand was synthesized by the following reactions:



The crystal structure of complex **1** was determined by the single crystal X-ray structural analysis at 100 K (Fig. 1(a)). Based on the observed $\text{Pt} \cdots \text{I}$ distances, the electronic state in a chain is in the charge-polarization state (CP state: $-\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}^-$). The electrical conductivity was measured by a two-terminal method along the chain direction. As the temperature increased, the conductivity changed from increasing to decreasing around 323 K, suggesting a structural phase transition at 323 K (Fig. 1(b)). From the variable temperature single crystal X-ray structure analysis, the bridging iodide ions exist at the midpoint between platinum dimer units above 323 K. This suggests that the electronic state in a chain is in the averaged-valence state (AV state: $-\text{Pt}^{2.5+}-\text{Pt}^{2.5+}-\text{I}^-$). Details are discussed.

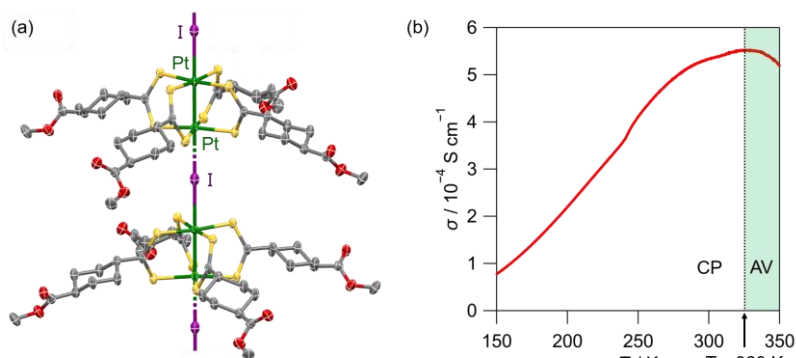


Fig. 1 (a) Molecular structure of complex **1** at 100 K. Hydrogen atoms are omitted for clarity. (gray: C, red: O, yellow: S, green: Pt, purple: I) (b) Electrical conductivity of complex **1**.

1) M. Mitsumi *et al*, *J. Am. Chem. Soc.* **2001**, 123, 11179-11192