

Effects of Aromatic In-Plane Ligands on the Structures and Electronic States of Quasi-One-Dimensional Halogen-Bridged Platinum Complexes

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博士論文

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(擬一次元ハロゲン架橋白金錯体の構造及び
電子状態に対する芳香族性面内配位子の効果)

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Abstract

The chemistry of one-dimensional (1D) electron systems has been extensively studied in the field of both pure and applied sciences for a long time by chemists and physicists. This is because of their unique conducting and optical properties. For example, gigantic third-order nonlinearities and ultrafast optical switching has been discovered in Ni(III) chains, so-called Averaged valence (AV) (Robin-Day class III). On the other hand, Pd and Pt-based MX chains usually show M(II)/M(IV) mixed valence (MV) (Robin-day Class II) state due to the small on-site coulomb repulsion. No one has realized Robin-Day class I materials yet. On the other hand, development of the strategy to achieve Pt(III) AV state for the first time in MX chains has been important challenge because it definitely provides greater or unprecedented physical properties. Moreover, Pt ions are substitutionally inert, Pt-based MX chains are promising for new strongly-correlated electron systems with supramolecular structures. Therefore, a new synthetic strategy is necessary.

Chapter 3 describes syntheses, characterizations and physical properties of Quasi 1D halogen-bridged Pt chains with aromatic in-plane ligand. Bromide-bridged Pt chains, $[\text{Pt}^{\text{IV}}(\text{amp})_2\text{Br}_2][\text{Pt}^{\text{IIIV}}(\text{amp})_2\text{Br}]_2\text{Y}$ ($\text{Y} = (\text{HSO}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (**3**), $(\text{H}_2\text{PO}_4)_6 \cdot 8\text{H}_2\text{O}$ (**4**)) and $[\text{Pt}^{\text{IIIV}}(\text{amp})_2\text{Br}]_2(\text{TsO}) \cdot \text{Br} \cdot 5\text{H}_2\text{O}$ (**5**) were prepared by using 2-aminomethylpyridine (amp) for the first time. These chains with aromatic in-plane ligands are stabilized by two different non-covalent interactions. First, aromatic interactions occur between two benzene rings. Second, hydrogen bonding network forms between amino groups and counteranions. A discrete Pt(IV) complex has been isolated in MX chains which is tilted in the chain. To the best of my knowledge, **3**, **4** are the first MX chains containing discrete Pt(IV) complex as the counteranions via π -stacking.

Chapter 4 describes syntheses, characterizations and physical properties of a Q1D halogen-bridged Pt chain with aromatic in-plane ligand that belongs to Robin-Day Class I. So far, most of the known and fully characterized complexes of this type are either class II or class III according to Robin-Day classification. In this chapter, A PtBr chain exhibits emergent

Robin-Day class I behavior (no IVCT) $[\text{Pt}(\text{amp})_2\text{Br}](\text{H}_2\text{PO}_4)_2$ (6), was prepared for the first time.

Chapter 5 describes the syntheses, characterizations and physical properties of a Q1D halogen-bridged Pt chain with aromatic in-plane ligand 2,4-dimethyl-5-methoxy-2-(aminomethyl)Pyridine (dmmamp). These studies identify the mixed valence PtBr chains as the first, characterised, with dmmamp and investigate the effect of bulky substituents on the structure.

Chapter 6 describes the first halogen-bridged Pt(III) complex with a single unsupported bridging iodide ligand. The complex $\{[\text{Pt}(\text{dien})(\text{dmap})_{0.96}\text{I}_{0.04}]_2\text{I}_3\}_2(\text{I}_3)_{2.62}(\text{I})_{3.22}$ (dien = diethylenetriamine, dmap = *N,N*-dimethylpyridin-4-amine) can be obtained as shiny green crystals by oxidation of $[\text{Pt}(\text{dien})\text{dmap}]\text{I}$ in water/ethanol. The structure was controlled by the steric hindrance of in-plane dmap ligand. It is assumed that the chain length and oxidation state of Pt ions are controlled by in-plane dmap ligand. X-Ray structure analysis, X-ray photoelectron spectroscopy, Raman spectroscopy, IR, elemental analysis and X-ray absorption near edge spectra revealed that the charge of both Pt ions is +3. The complex represents the first halogen-bridged Pt complexes to belong to class III of Robin-Day classification.