

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

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論文内容要旨

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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, $[\text{Pt}^{\text{IV}}(\text{amp})_2\text{Br}_2][\text{Pt}^{\text{II/IV}}(\text{amp})_2\text{Br}]_2\text{Y}$ ($\text{Y} = (\text{HSO}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (**3**), $(\text{H}_2\text{PO}_4)_6 \cdot 8\text{H}_2\text{O}$ (**4**)) and $[\text{Pt}^{\text{II/IV}}(\text{amp})_2\text{Br}]_2(\text{TsO}) \cdot \text{Br} \cdot 5\text{H}_2\text{O}$ (**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 (Me_2OMeamp). These studies identify the mixed valence PtBr chains as the first, characterised, with Me_2OMeamp 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 $\{[\text{Pt}(\text{dien})(\text{dmap})_{0.96}\text{I}_{0.04}]_2\text{I}_3\}_2(\text{I}_3)_{2.62}(\text{I})_{3.22}$ ($\text{dien} = \text{diethylenetriamine}$, $\text{dmap} = N,N$ -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 be belongs to class III of Robin-Day classification.

論文審査の結果の要旨

擬一次元ハロゲン架橋金属錯体 (MX 錯体) において、多様な電子状態の創出は、低次元電子系の理解を深化させる上で極めて重要である。これまでの研究では、平均原子価 (AV) 状態と混合原子価 (MV) 状態の二つが着目されてきたが、金属イオン間の相互作用に基づく Robin-Day の分類によれば、前者はクラス III、後者はクラス II または I となる。しかしながら、これまでクラス I に属する MX 錯体の報告は皆無であった。Unjila Afrin 氏は、MX 錯体の M-X-M 距離をさらに延ばしてクラス I を実現することを目的として研究を行った。

Unjila Afrin 氏は、M-X-M 距離の伸長のためには、 π 積層相互作用が有効と考え、2-アミノメチルピリジンを用いた面内配位子とすることで、単鎖の MX 錯体としては初めて芳香族性の配位子を導入することに成功した。MX 錯体の化学的合成法では、予想外に 4 価の Pt 錯体が鎖間に挿入されており、これは MX 錯体として初めての現象であった。この手法によって得られた MX 錯体はクラス II に属していた (3 章)。一方、Unjila Afrin 氏は電気化学的な合成法にも取り組み、見事に隣り合う鎖同士の芳香族性配位子が入れ子状になった直鎖状 MX 錯体 $[\text{Pt}(\text{amp})_2\text{Br}](\text{H}_2\text{PO}_4)_2$ の合成に成功した。この錯体の Pt-Br-Pt 距離は約 6.7 Å となり、既存の PtBr 錯体の記録を 0.5 Å 以上も更新した。この錯体のラマン散乱スペクトルや吸収スペクトルの測定より、クラス I であることを確認することができた (4 章)。

Unjila Afrin 氏はジエチレントリアミン配位子とパラ置換ピリジン誘導体を配位子に持つ MX 錯体の合成にも成功した (5 章)。この過程で、ジメチルアミノピリジンを用いた場合には、 Pt_2I_3 構造を持つ新規化合物が得られることを発見し、種々の測定や計算化学的手法により、AV 状態にあることを強く示唆する結果を得た。このような短いクラスターは、0 次元と 1 次元の狭間の電子系とみなすことができ、基礎科学的な観点から非常に興味深い (6 章)。

以上の研究成果は、博士論文として相応しい新規性を有しており、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、Unjila Afrin 提出の博士論文は、博士 (理学) の学位論文として合格と認める。