

Effect of Hydroxy Groups of In-Plane Ligand upon Electronic States and Physical Properties of One-Dimensional Metal Complexes

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論文内容要旨

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学位論文の 題 目	Effect of Hydroxy Groups of In-Plane Ligand upon Electronic States and Physical Properties of One-Dimensional Metal Complexes (一次元金属錯体の電子状態及び物性に対する面内配位子のヒドロキシ基の効果)		

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The chemistry of one-dimensional halogen-bridged metal (Ni, Pd and Pt) chain complexes (MX chains) 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. So far, all Ni-based MX chains form Ni(III) averaged valence (AV) state, whereas Pd/Pt-based MX chains form M(II)/M(III) mixed valence (MV) state. The chemistry of Pd/Pt in its 0, +II, and +IV oxidation states is well-known; by comparison, the chemistry of Pd/Pt in its +III oxidation state is in its infancy. The aim of the thesis involves a new synthetic strategy for preparing previously unknown M(III)X chains, including applications in materials chemistry.

Chapter 3 describes the first example of halogen-bridged Pd(III) chains by using triple hydrogen bonds. These Pd(III)X have been isolated up to their decomposition temperature. A new synthetic strategy (multiple-hydrogen-bond approach) was applied for synthesizing new Pd(III)X chains. An in-plane ligand with an additional hydrogen donor group (hydroxy group), (2S,3S)-2,3-diaminobutane-1,4-diol (dabdOH), was used to create a multiple-hydrogen-bond network, which effectively shrinks the Pd–X–Pd distance, stabilizing the Pd(III) state up to their decomposition temperature. Additionally, physical and optical properties have been studied. The Pd(III)X shows semiconducting behavior with a highest electrical conductivity ($3\text{--}38\text{ S cm}^{-1}$ for $[\text{Pd}(\text{dabdOH})_2\text{Br}]\text{Br}_2$ at room temperature) of all MX chains. The precise positional control of ions via a multiple-hydrogen-bond network is a useful method for controlling the electronic states, thermal stability and conductivity of linear coordination polymers.

Chapter 4 describes the preparation of halogen-bridged Pt chains by using multiple-hydrogen-bond approach. The M–X–M distance are increasing by replacing Pd to Pt. X-ray structural analysis and spectroscopic studies revealed that PtX chains exist in an Pt(II)/Pt(IV) MV state. However, additional hydrogen bond effectively works in PtX chains. In other words, the shortest Pt–X–Pt distances are realized in PtX chains, and the highest conductivity of all PtBr chains reported to date was observed in $[\text{Pt}(\text{dabdOH})_2\text{Br}]\text{Br}_2$.

Chapter 5 describes the development of new strategy for synthesizing unusual +II/+III mixed oxidation state in NiBr chains. This chapter represents the first example of mixed valence NiBr chains. Unusual hydrogen bonding system stabilizes the chain structure. Physical and optical properties of the chain were studied.

Chapter 6 describes the development of new strategy for synthesizing Magnus-type salt. The largest size of single crystals of Magnus-type salt was prepared by using dabdOH ligand. The higher solubility of $[\text{M}(\text{dabdOH})_2]^{2+}$ ions compared with those of analogous $[\text{ML}_2]^{2+}$ ions (L: in-plane ligand without OH group) enables the slow crystallization of Magnus-type salts.

別 紙

論文審査の結果の要旨

一次元 d 電子系を有する擬一次元ハロゲン架橋金属錯体 (MX 錯体) において、平均原子価 (AV) 状態を Pd 及び Pt 錯体で実現することは、新たな電子物性の創出という観点から極めて重要である。Mohammad Rasel Mian 氏は、面内配位子にヒドロキシ基を導入し、水素結合を強化することで、金属-ハロゲン-金属間距離 $d(\text{MXM})$ を縮め、AV 状態を安定化することを目的として研究を行った。

Mohammad Rasel Mian 氏は、L-酒石酸からヒドロキシ基を有する面内配位子 (2*S*,3*S*)-2,3-diaminobutane-1,4-diol (dabdOH) を合成し (2 章)、これを用いて Pd 錯体 (3 章)、Pt 錯体 (4 章)、Ni 錯体 (5 章) の合成を行った。 $[\text{Pd}(\text{dabdOH})_2\text{Br}]\text{Br}_2$ の結晶構造解析から、ヒドロキシ基と対アニオンとの間にもう一つ水素結合が追加されることで、対アニオンが MX 鎖から離れ、これが一次元鎖方向に働く化学的な圧力となり、 $d(\text{MXM})$ が 5.1818(4) Å (93 K) と、PdBr 錯体では過去最短となった。この結晶のラマン散乱スペクトルや STM 測定により、電子状態が AV 状態であることが確かめられた。この AV 状態は、分解が始まる 443 K という高温まで安定で、既知の PdBr 錯体の最高記録を 133 K も上回った。さらに、結晶の電気伝導率は室温で 3–38 S cm⁻¹ にも達し、既存のあらゆる MX 錯体の中で最高値を記録した。

同様の合成及び物性測定から、PdCl 錯体でも初の AV 状態が達成され、Pt 錯体でも単結晶構造解析結果が得られた錯体としては最も $d(\text{MXM})$ を縮めることができた。このように、「多重水素結合を用いたアプローチ」は、一次元鎖を圧縮する極めて有効な手法であることが確かめられた。さらに、Ni 錯体では Ni(II/III)混合原子価状態という極めて珍しい電子状態を実現している。また、一般に大きな結晶を合成することが難しいマグヌス塩の合成に dabdOH 配位子を用いることで、最大で 1~2 mm 程度の巨大単結晶の合成にも成功した (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、Mohammad Rasel Mian 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。