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

| | |
|---|---|
| 著者 | MIAN Mohammad Rasel |
| 学位授与機関 | Tohoku University |
| 学位授与番号 | 11301甲第18268号 |
| URL | http://hdl.handle.net/10097/00124052 |

博士論文

# 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）

Mohammad Rasel Mian

平成３０年

# Contents of Doctoral Thesis

## Chapter 1: General Introduction

### I. Quasi-one-dimensional (Q1D) halogen-bridged (Ni, Pd and Pt) metal chain complexes (MX chains)



### II. 1D chain complexes with metal-metal interactions



### III. Purpose and Strategy



## Chapter 2: Syntheses of ligands

**Chapter 3: Pd-based MX chains**



**Chapter 4: Pt-based MX chains**



**Chapter 5: Ni-based MX chains**



**Chapter 6: Pd- and Pt-based Magnus-type of salt**

# Abstract

The chemistry of one-dimensional halogen-bridged metal (Ni, Pd and Pt) chain complexes (MX chain) 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 state (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 (3–38 S $cm^{-1}$ for $[Pd(dabdOH)_2Br]Br_2$ at room temperature) all of MX-type complexes. 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 spectroscopies studies reveal that PtX chains exist in an Pt(II)/Pt(IV) MV state. However, additional hydrogen bond effectively works in PtX chains. As a result the shortest Pt–X–Pt distance was observed in PtX, which the requirement for realizing Pd(III) ion.

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 valance 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 involving additional hydrogen bond.