

Preface

Material Designs and New Physical Properties in MX- and MMX-Chain Compounds

The history of quasi-one-dimensional halogen-bridged Pt complexes began at the end of the nineteenth century when Wolfram reported a Cl-bridged complex, $\text{Pt}(\text{etn})_4\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (etn=ethylamine), which is called Wolfram's red salt because of its lustrous red color. This complex was considered to be a Pt^{III} complex, but it has been shown that it is actually a $\text{Pt}^{\text{II}}\text{--Pt}^{\text{IV}}$ mixed valence complex $[\text{Pt}(\text{etn})_2][\text{PtCl}_2(\text{etn})_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$. Since then, many Pt complexes as well as Pd complexes have been synthesized. In 1981, $\text{Ni}(\text{chxn})_2\text{Br}_3$ (chxn=1R,2R-diaminocyclohexane) was synthesized. X-ray structure analysis revealed that it was not a $\text{Ni}^{\text{II}}\text{--Ni}^{\text{IV}}$ complex, but a Ni^{III} complex. Theoretically, these compounds are thought to be extended Peierls–Hubbard systems, where the electron–phonon interaction (S), the transfer integral (T), and the on-site and nearest-neighbor Coulomb repulsion energies (U and V , respectively) strongly compete with each other. The electronic states of these complexes depend mainly on the competition between U and S . When S is larger than U , $\text{M}(\text{II})\text{--M}(\text{IV})$ mixed valence states or charge density wave states (CDW), where the bridging halide ions are displaced from the midpoints between two neighboring metal ions, (represented as $\text{--X--M}^{\text{II}}\text{--X--M}^{\text{IV}}\text{--X--}$), are stabilized. On the other hand, when U is larger than S , an $\text{M}(\text{III})$ average valence or Mott–Hubbard (MH) state, where the bridging halide ions are located at the midpoint between two neighboring metal ions (represented as $\text{--X}^{\text{III}}\text{--X--M}^{\text{III}}\text{--X--}$), becomes stable. These Pt, Pd, and Ni complexes show very interesting chemical and physical properties, such as intense and dichroic charge transfer bands, progressive overtones in resonance Raman spectra, midgap absorptions attributed to solotons and polarons, and gigantic third-order nonlinear optical susceptibilities, and have applications in field effect transistor (FET) devices.

In the 1980s, a new type of complex composed of binuclear metal complexes and bridging halogens, represented as $\text{--M--M--X--M--M--X--}$, was reported. They

have a variety of electronic states and undergo various phase transitions by temperature, pressure, as well as photo irradiation.

In this book, we describe these complexes, including experimental results and theoretical treatments.

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