

RESEARCH ACTIVITIES VIII

Coordination Chemistry Laboratories

Prof. Kazushi Mashima (Osaka Univ.) and Assoc. Prof. Masato Kurihara (Yamagata Univ.) took the position of Laboratory of Complex Catalyst from April 2004. Prof. Masahito Yamashita (Tokyo Metropolitan Univ.) and Prof. Naoto Chatani (Osaka Univ.) finished their term as Adjunct Prof. of Complex Catalyst in March 2004. Their effort during their term is gratefully appreciated. Prof. Hiroyuki Matsusaka (Osaka Prefecture Univ.) and Prof. Keiji Ueno (Gunma Univ.) continue the position of the Laboratory of Coordination Bond.

VIII-A Nano-Sciences of Advanced Metal Complexes

Recently, nano-sciences or nano-technologies have been attracting much attention because they show very interesting physical properties based on the non-linearity and quantum effect. There are two methods to obtain the nano-size materials, that is, "top-down" and "bottom-up" methods. The top-down method such as laser abrasion has a limitation to make particles with the sizes less than 100 nm. On the other hand, the bottom-up method is promising to control the nano-size since the chemical reactions are available. However, the researches based on the bottom-up methods are rare and such methods have not been accomplished so far. Then, I would like to focus on the bottom-up methods. As for the bottom-up methods, there are three types of the target materials such as inorganic compounds, organic compounds, and metal complexes. The inorganic compounds easily take three-dimensional bulk structures. The organic compounds easily take 0- and 1-dimensional bulk materials. Therefore, neither inorganic nor organic compounds are suitable for the nano-sciences. On the other hand, the metal complexes easily take nano-size clusters where they are surrounded with the organic ligands. Therefore, the nano-sciences of the advanced metal complexes are most promising. As for the non-linearity, we focus on the gigantic third-order optical non-linearity. As for the quantum effect, we focus on the single-molecule magnets, nano-wire molecule-magnets, and nano-network molecule-magnets.

VIII-A-1 A Three-Dimensional Ferrimagnet Composed of Mixed-Valence Mn_4 Clusters Linked by an $\{Mn[N(CN)_2]_6\}^{4-}$ Unit

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A ferrimagnet with a 3D molecular network has been synthesized and characterized. This compound is composed of units of mixed-valence Mn_4 clusters, a unit that is well known for its single-molecule magnet properties, and Mn^{II} paramagnetic units. Both building blocks are linked by dicyanamide bridging ligand to form a covalent-bonded three-dimensional network. The compound becomes a ferrimagnet at 4.1 K that exhibits a spin-flip phenomenon under the influence of a magnetic field.

VIII-A-2 A Dimeric Manganese(III) Tertdentate Schiff Base Complex as a Single-Molecule Magnet

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[*Angew. Chem., Int. Ed.* **43**, 2801–2805 (2004)]

The complex $[Mn_2(\text{saltmen})_2(\text{ReO}_4)_2]$ ($\text{saltmen}^{2-} = N,N'-(1,1,2,2\text{-tetramethylethylene})\text{bis}(\text{salicylideneimine})$) is a simple out-of-plane dimer of Mn^{III} ions that unambiguously exhibits single-molecule magnetic behavior. To date, this compound is the smallest magnetic unit which has been reported to behave as a magnet at the molecular level and to show quantum tunneling.

VIII-A-3 Tuning the Electronic Structure from Charge-Transfer Insulator to Mott-Hubbard and Peierls Insulators in One-Dimensional Halogen-Bridged Mixed-Metal Compounds

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[*Phys. Rev. B* **70**, 035204 (6 pages) (2004)]

The electronic structures of one-dimensional (1D) halogen-bridged mixed-metal compounds, $[Ni_{1-x}Pd_x(\text{chxn})_2X]X_2$ ($\text{chxn} = \text{cyclohexanediamine}$; $X = \text{Cl, Br}$; $0 < x < 1$), are investigated through optical and magnetic measurements. The results reveal that the system changes from charge-transfer (CT) insulator to Mott-

Hubbard (MH) insulator at around $x \sim 0.3$, and from MH insulator to Peierls insulator at $x \sim 0.9$ with increasing x . From the analysis of optical conductivity spectra using the 1D two-band extended Peierls-Hubbard model, electronic parameters such as Coulomb repulsion energy, pd hybridization, CT energy, and electron-lattice interaction are determined.

VIII-A-4 A Square Cyclic Porphyrin Dodecamer: Synthesis and Single-Molecule Characterization

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[*Chem. Lett.* **33**, 578–579 (2004)]

We prepared a square cyclic porphyrin dodecamer via the tetramerization of a trimer shaped like a right angle. The molecule was visualized by scanning tunneling microscopy to be square.

VIII-A-5 Visualization of Local Valence Structure in Quasi-One-Dimensional Halogen-Bridged Complexes $[\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}]\text{Br}_2$ by STM

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[*Angew. Chem., Int. Ed.* **43**, 3171–3175 (2004)]

we have visualized the Mott-Hubbard and CDW states in quasi-1D halogen-bridged Ni and Pd complexes, respectively. In addition, we succeeded in visualizing the propagation of CDW coherence and the spin soliton in real space in the mixed-metal complexes $[\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}]\text{Br}_2$ for the first time.

VIII-A-6 A Dinuclear Ruthenium(II) Chelating Amido Complex: Synthesis, Characterization, and Coupling Reaction with Carbon Monoxide

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[*Organometallics* **23**, 3587–3589 (2004)]

$[\text{CpRuCl}]_4$ (Cp = $\eta^5\text{-C}_5\text{Me}_5$) reacts with 2 equiv of dilithium 2,3-naphthalenediamide to afford the dinuclear bridging amido complex $[(\text{CpRu})_2\{\mu_2\text{-(NH)}_2\text{-C}_{10}\text{H}_6\}]$ (**1b**) in moderate yield. Treatment of **1b** with CO (1 atm) resulted in the incorporation of three molecules of CO into the diruthenium core to give the carbamoyl amido bis(carbonyl) complex $[\text{CpRu}(\mu_2\text{-CO})\text{-}\{\mu_2\text{-2,3-(CONH)(NH)C}_{10}\text{H}_6\}\text{RuCp(CO)}]$.