Forschungsschwerpunkte – Professor Dr. Kazuyuki Tatsumi

Dr. Tatsumi was established as a theoretical chemist early in his academic carrier. This theoretical background and concepts provided him with foundation to carry out experimental/synthetic research successfully in emerging areas of inorganic chemistry. For instance, the study on the synthesis of unprecedented transition metal chalcogenide complexes has been extended to bioinorganic chemistry of enzymes containing metal sulfide clusters. Including this specific subject of cluster chemistry, his current research group has been engaged in (1) chemical synthesis and reactions of the cluster active sites of various reductases, (2) the development of catalytically active coordinatively unsaturated organometallic compounds, in particular iron/rhodium/iridium/ruthenium complexes bearing bulky thiolates or N-heterocyclic carbenes, and (3) the synthesis of transition metal supramolecular complexes via tinker-toy construction and self-assembly reactions.

Dr. Tatsumi has been aiming at a comprehensive and fundamental understanding of the role that transition metals play in various inorganic systems. One topical example is transition metal elements in proteins and enzymes. Metalloenzymes are essential for all organisms on earth, and their metal-incorporating active centers regulate highly efficient/selective chemical transformations under mild conditions. An important and urgent mission of chemists has been to synthesise model active-sites in vitro and to elucidate the mechanisms of the biological functions, which would eventually lead to artificial enzymes equivalent or even superior to nature's. Although the study on metalloenzymes has long been centered on oxygenases, the investigation of reductases has made a rapid progress in recent years, unfolding novel structures and functions of the cluster active centers, greatly expanding our established knowledge of chemistry. Newly discovered reductases commonly contain unprecedented transition metal sulfide/thiolate clusters at the active sites. They show remarkable activities as exemplified by CO-dehydrogenases generating protons and electrons from CO and water, hydrogenases converting dihydrogen into protons and electrons reversibly, and nitrogenases catalysing the reduction of dinitrogen into ammonia. On the other hand, the structure of photosystem II has been determined, revealing a unique manganese oxide cluster structure at the oxygen-evolving center. The sophisticated functions of these cluster active centers provide excellent concepts and bio-inspired models to meet pressing needs for establishment of a sustainable society, which include 1) production of dihydrogen without use of oil, 2) new concepts for fuel cell, 3) energy-saving production of nitrogen fertiliser, and 4) water splitting under mild conditions.

The cluster active sites of the enzymes are so unusual that they have been thought difficult to synthesise chemically, and they are noticed as key target molecules in chemistry. Topical examples of recent achievements by Dr. Tatsumi in this research topic are itemised below.

(1) A new method to synthesise Fe/S clusters in anon-polar solvent has been developed, which resulted in a series of unprecedented cluster structures, which are relevant to the active sites of nitrogenase. The newly synthesised clusters include the unusual [8Fe-7S] inorganic core structure of P-cluster (PN) of nitrogenase, another type of [8Fe-7S] clusters, the structures of which may link topologically the FeMo-co and P-cluster of nitrogenase.

(2) Various dinucler Ni-Fe complexes have been synthesised as excellent structural models for the active site of [NiFe] hydrogenase. For instance, the synthesis of a series of dinuclear Fe(CO)3-Ni complexes was attained from a preformed tetranuclear Fe2Ni2 cluster. Although introduction of CN onto the Fe site of the Fe-Ni dinuclear complexes had been thought difficult, the group has successfully synthesized dinuclear Fe(CO)2(CN)2-Ni, and Fe(CO)(CN)2-Ni complexes, which are the best structural models of the [Ni-Fe] hydrogenase active site.

(3) A series of S- and O-bridged dinuclear W-Ru and Ge-Ru complexes were synthesised, and these complexes have been found to promote heterolytic cleavage of molecular hydrogen under mild conditions. These reactions mimic the function of [Ni-Fe] hydrogenase, and provide insights into the mechanism of hydrogenase. For example, an S(OH)-bridged dinuclear Ge-Ru complex reacts with H2 reversibly under mild conditions to generate a hydride complex and H2O.

(4) A dinuclear nickel complex, in which one nickel site (Nid) is coordinated by an N4 cyclic ligand and the other site (Nip) carries methyl and thiolate ligands, has been synthesised as a Nid-Nip active site model of acetyl-CoA synthase (ACS). The study on the reactions of the model complex revealed the mechanism of the ACS function.