Laboratory for Coordination Chemistry

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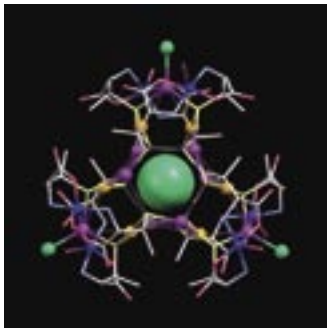
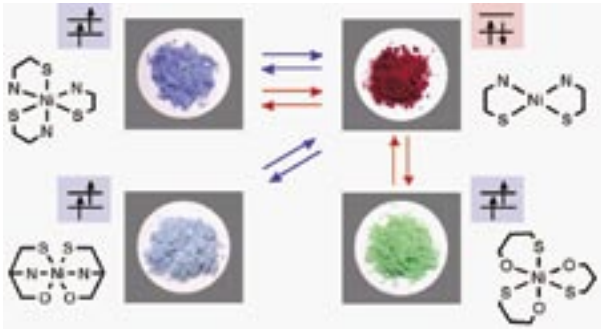
Creation of Metalloaggregates Based on Metalloligands

The design and creation of homometallic and heterometallic molecular aggregates that possess unique structures and properties have attracted increasing attention. While the most common approach to creating metalloaggregates is the use of functional organic ligands that can bridge two or more metal centers, our efforts have concentrated on the use of thiolato metal complexes as an S-donating metalloligand. Recently, we have shown that $[Au(D\text{-Hpen-}S)_2]^-$ (D-H_2pen = D-penicillamine) reacts with Ag^I to produce a photoluminescent $Au^I_2Ag^I_2$ complex, which further reacts with Cu^{II} in the presence of Cl^- to produce a metallo-supramolecular compound containing all three coinage metals. Remarkably, this product was found to be composed of monocationic 20-nuclear $Au^I_6Ag^I_8Cu^{II}_6$ and monoanionic 21-nuclear $Au^I_6Ag^I_9Cu^{II}_6$ supramolecular cages, which are coupled to each other to form an unprecedented 1:1 supramolecular salt with a 'rock-salt'-like lattice structure. In addition, we have shown that red $Au^I_2Ni^{II}_2$, purple $Au^I_3Ni^{II}_2$, light blue $Au^I_2Ni^{II}_2$, and green $Au^I_3Ni^{II}_2$ complexes are created only from $[Au(D\text{-pen-}S)_2]^{3-}$ in combination with Ni^{II}. It was found that the red complex is triply reversible with the purple, light blue, and green complexes in response to $Ni^{II}[Au(D\text{-pen-}S)_2]^{3-}$ stoichiometry and solution pH, accompanied not only by the readily detectable color change, but also by drastic switches in magnetism and chirality.

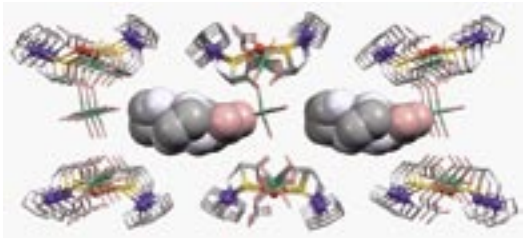




Chiral Recognition and Aggregation of Metal Complexes

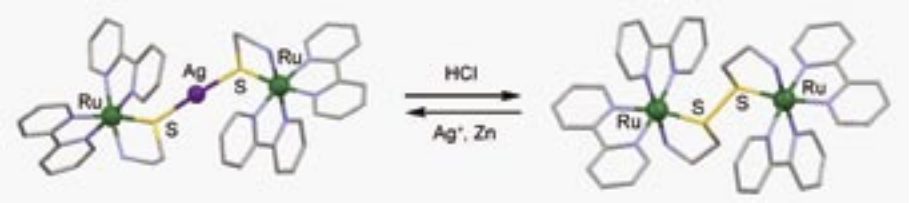
Considerable attention has been paid to the rational synthesis of chiral metal compounds in the field of coordination stereochemistry. This has been stimulated by the growing interest in the design and creation of well-organized metallo-supramolecular species, the overall structures of which can be controlled by the chirality of their building blocks. Our research interest has been directed toward this subject, focusing on the metal-assisted aggregation of chiral octahedral complex-units containing aminothiolate-type ligands. Recently, we have shown that the reaction of *trans*(*N*)-$[Co(D\text{-pen-}N,O,S)_2]^-$ with $[PtCl_2(CH_3NH_2)_2]$

produces $Co^{III}Pt^{II}_2$ trinuclear and $Co^{III}_2Pt^{II}_2$ tetranuclear complexes and that their structures are controlled by the anions employed. The $Co^{III}Pt^{II}_2$ trinuclear complex was found to serve as a 'chiral molecular nipper' that enantioselectively catches a chiral complex-molecule. In addition, we have shown that the Δ_L isomer of $[Co(L\text{-cys-}N,S)(en)_2]^+$ binds with Mn^{II} and Ag^I ions to produce a novel chiral $Co^{III}Mn^{II}Ag^I$ coordination polymer that diastereoselectively accommodates complex-molecules in its 1D channel.



Development of S-Bridged Polynuclear Complexes

We have been interested in the development of sulfur-bridged polynuclear complexes with various thiolate ligands, which exhibit unique molecular structures, electronic states, and chemical properties. Recently, we have found that the reaction of $[Ru(solvent)_2(bpy)_2]^{2+}$ (bpy = 2,2'-bipyridine) with Haet (2-aminoethanethiol) results in the formation of a $Ru^{II}Ru^{II}$ dinuclear complex, in which two $[Ru(bpy)_2]^{2+}$ moieties are bridged by two S atoms. Conversely, a thiolato-bridged $Ru^{II}Ag^{I}Ru^{II}$ trinuclear complex consisting of two $[Ru(aet)(bpy)_2]^+$ units was produced when a similar reaction was carried out in the presence of Ag^+. It was found that this $Ru^{II}Ag^{I}Ru^{II}$ trinuclear complex can be reversibly converted into a rare single-disulfide-bridged $Ru^{II}Ru^{II}$ dinuclear complex.



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