MOLECULAR AND SUPRAMOLECULAR METAL-OXO CLUSTER CHEMISTRY

Homometallic Molecular Clusters

Molecular Nanoparticles (MNPs) – molecular clusters with the same structure as a bulk metal oxide and greater than 1 nm in size.

Only the Ce-O cores are shown - carboxylate and pyridine ligands are omitted for clarity.

In the homometallic molecular nanoparticle projects we are synthesizing molecular analogues of bulk and nanoparticle metal oxide materials. These molecular products allow us to study the structure by X-ray crystallography allowing for elucidation of the exact structure, the oxidation state of each metal ion, the location of H+ on the surface, and greater insights into the structures of their larger counterparts.

The Diversity of Metal-oxo Clusters

We synthesize homo- and heterometallic complexes spanning the periodic table to design new materials for a range of magnetic and catalytic applications.

Giant Molecules

High nuclearity clusters can resemble small pieces of bulk materials, allowing us to gain insight into the early stages of their formation. We are also able to compare and contrast the properties of bulk materials vs. clusters of any size.

Single-molecule magnets (SMMs) are permanent magnets below a specific blocking temperature. They have been proposed for higher density information storage, spintronics, and quantum technologies.

Supramolecular Aggregates of SMMs

Supramolecular aggregates of SMMs are collections of weakly-coupled SMMs, which retain their intrinsic SMM properties. Dissinate and dicarboxylate linkers can be used to link two or more SMMs to form supramolecular aggregates of SMMs, for use as components of new technologies such as quantum computing.

Bioinorganic Chemistry

Water Oxidation Catalysis

Nature's ability to achieve high-efficiency catalytic water oxidation in plants and cyanobacteria using earth-abundant metals Mn and Ca sets the standard for artificial systems in new energy technologies. The development of water oxidation catalysts (WOCs) using earth-abundant 3d metals such as Mn, Co and Cu has become more intensely investigated.

Synthetic Methods

Ligands: simple oxygen and nitrogen donor ligands with the ability to bind in multiple chelating and bridging modes.

Precursors: simple metal salts and preformed clusters

Reactions: comproportionation, reductive aggregation, ligand substitution, aeration, oxidation, hydrolysis of metal ions.

Heterometallic Molecular Clusters

Similarly, in the heterometallic molecular nanoparticle projects we are synthesizing molecular analogues of heterometallic and composite oxides of bulk and nanoparticle metal oxides.

The interest in Ca/Mn heterometallic MNPs is due to the synergistic effect of their composite oxides in various catalytic processes, such as oxidation of VOCs and dissolved organic pollutants.

Homometallic Bi-oxo chemistry is highly attractive due to the impressive photocatalytic activity of the bulk alpha and beta forms, and the bulk delta form has the highest known conductivity for a metal oxide. The interest in Bi/Mn compounds is due to their potential multifaceted behavior.

Acknowledgements

Distinguished Professor George Christou's Research Group is a synthetic, bioinorganic and physical inorganic group. Our main research interests are in metal-oxo coordination chemistry, focused on the synthesis and characterization of polymeric cluster (complexes with more than two metal centers). We use a variety of techniques, as needed, to study our compounds, including FT-IR, paramagnetic NMR, electrochemistry, SQUID magnetometry, X-ray crystallography, EPR spectroscopy, and/or DFT calculations, some of them with expert collaborators.

“Do not be satisfied with the stories that come before you. Unfold your own myth.”

-Jalaluddin Rumi