CHRISTOU research group

MOLECULAR AND SUPRAMOLECULAR METAL-OXO CLUSTER CHEMISTRY

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

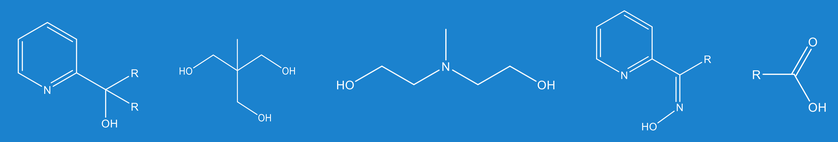
-Jalaluddin Rumi

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 polynuclear 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.

Acknowledgements

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

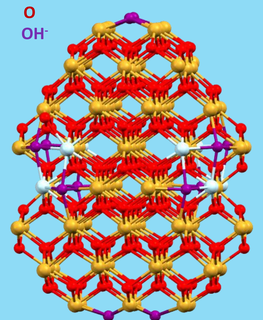
Reactions: comproportionation, reductive aggregation, ligand substitution, aerial oxidation, hydrolysis of metal ions.

Homometallic Molecular Clusters

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

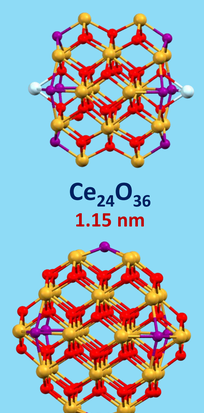
CeO_2 MNPs

Ce^{III} Ce^{IV} O OH^-



$Ce_{100}O_{167}$
2.25 nm

Russell-Webster, B. *et al. Angew. Chem. Int. Ed.*, **2021**, *60*, 12591-12596.

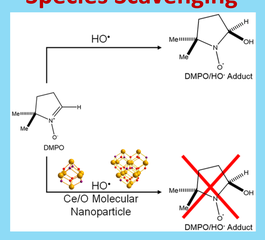


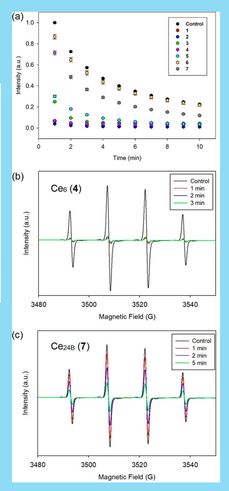
$Ce_{38}O_{62}$
1.20 nm

Mitchell, K. J. *et al. Nature Commun.*, **2017**, *8*, 1445.

$Ce_{24}O_{36}$
1.15 nm

Radical Oxygen Species Scavenging



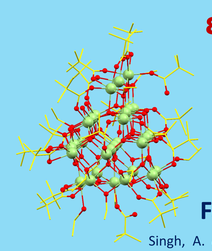


The redox capabilities of CeO_2 MNPs can be used to scavenge radical oxygen species, a hot topic in nanomedicine.

Mitchell, K. J. *et al. Inorg. Chem.*, **2021**, *60*, 1641-1653.

ε-Fe_2O_3 MNPs

Fe O C

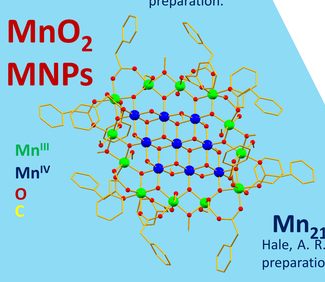


Fe_{29}

Singh, A. *et al.* In preparation.

MnO_2 MNPs

Mn^{III} Mn^{IV} O C



Mn_{21}

Hale, A. R. *et al.* In preparation.

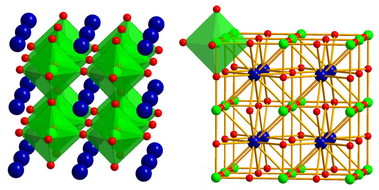
Only the Ce-O cores are shown - carboxylate and pyridine ligands are omitted for clarity.

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.

Heterometallic Molecular Clusters

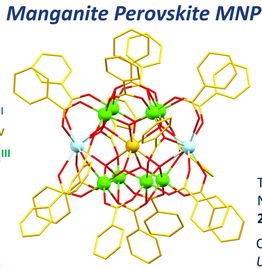
Similarly, in the heterometallic molecular nanoparticle projects we are synthesizing molecular analogues of heterometallic and composite oxides of bulk and nanoparticle metal oxides.

Perovskite Family, ABO_3



Mn_8Ce_3

Manganite Perovskite MNP



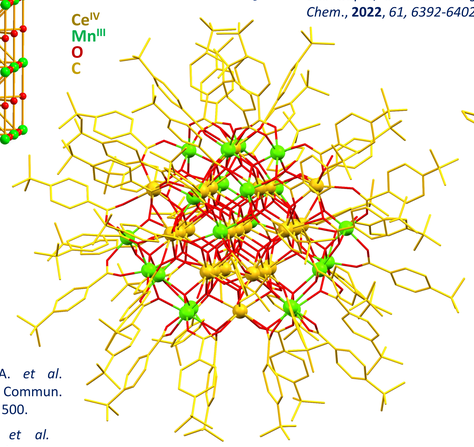
Thuijs, A. *et al.* Nature Commun. **2017**, *8*, 500.

Cao, T. *et al. Under review*.

$Ce_{23}Mn_{20}$

Ce MNP surrounded by a Mn monolayer

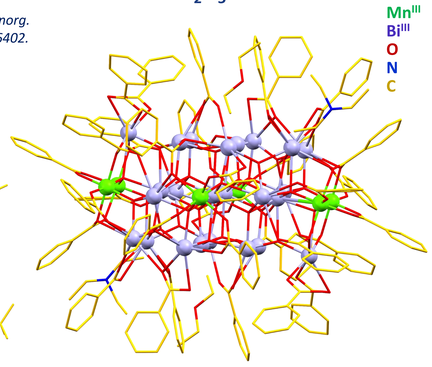
Das Gupta, S. *et al. Inorg. Chem.*, **2022**, *61*, 6392-6402.



$Bi_{24}Mn_6$

δ-Bi_2O_3 MNP

Daniels, E. *et al.* In preparation.



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 multiferroic behavior.

The interest in Ce/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.

The Diversity of Metal-oxo Clusters

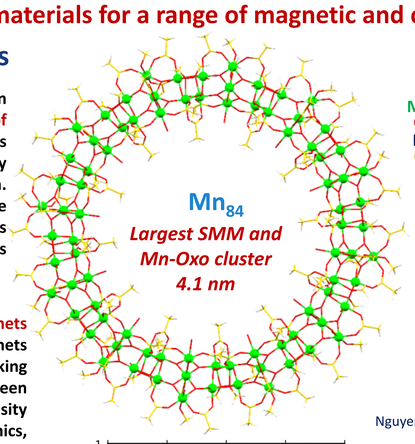
We synthesize homo- and heterometallic complexes spanning the periodic table to design new materials for a range of magnetic and catalytic applications.

Giant Molecules

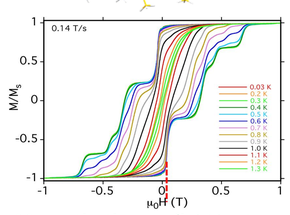
High nuclearity clusters can resemble small pieces of bulk materials, allowing us to gain insight into the early stages of their formation. We are also able to compare and contrast the properties of bulk materials vs. clusters of any size.

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.

Tasiopolous, A. *et al. Angew. Chem. Int. Ed.*, **2004**, *43*, 2117-2121.
Vinslava, A. *et al. Inorg. Chem.*, **2016**, *55*, 3419-3430.
Hale, A. *et al. Under Review.*



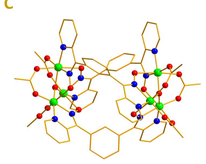
Mn_{84}
Largest SMM and Mn-Oxo cluster 4.1 nm



Magnetization vs. field hysteresis

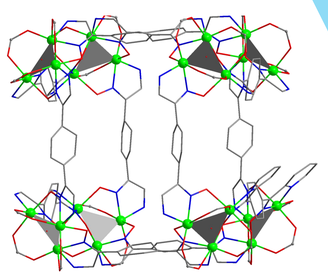
Supramolecular Aggregates of SMMs

Mn^{III} O N C



$\{Mn_3\}_2$

Nguyen, T. *et al. JACS*, **2015**, *137*, 7160-7168.

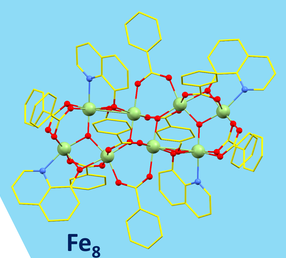


$\{Mn_3\}_8$

Ghosh, T. *et al.* In preparation.

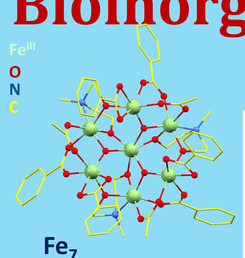
Supramolecular aggregates of SMMs are collections of weakly-coupled SMMs, which retain their intrinsic SMM properties. Dioximate and dicarboxylate linkers can be used to link two or more SMMs to form supramolecular aggregates of SMMs, for use as components of new technologies such as quantum computing.

Bioinorganic Chemistry



Fe_8

Mitchell, K. J. *et al. Inorg. Chem.*, **2016**, *55*, 6597-6608.



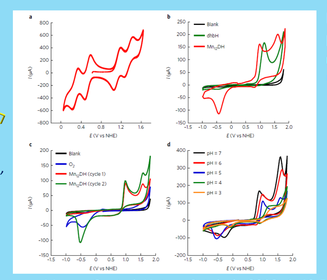
Fe_7

Hale, A. R. *et al. Inorg. Chem.*, **2022**, *61*, 11261-11276.

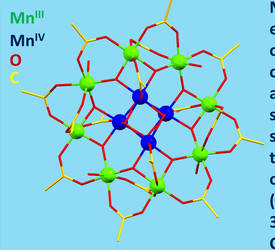
Fe^{III}-O Magnetostructural Correlations

Lower nuclearity clusters are desirable because it is possible to correlate their structures to physical properties (e.g., magnetic coupling, electrochemistry).

Water Oxidation Catalysis



Mayan, G. *et al. Nature Catalysis*, **2018**, *1*, 48-54.

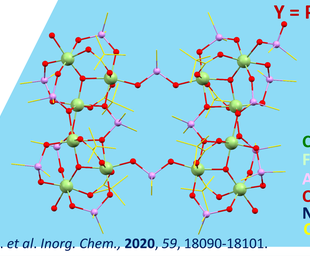


$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$

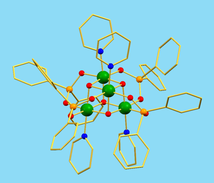
Nature's ability to achieve high-efficiency catalytic water oxidation in plants and cyanobacteria using earth-abundant metals Mn and Ca sets the standard for artificial systems in new energy technologies. The development of water oxidation catalysts (WOCs) using earth-abundant 3d metals such as Mn, Co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

"Pseudocarboxylate," $[R_xYO_y]^{z-}$, Cluster Chemistry

Y = P, S, Se, or As, x =1 or 2, y = 2 or 3, z = 1 or 2

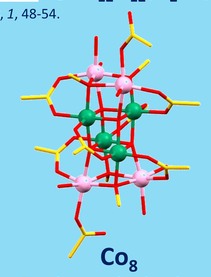


Lee, K. L. *et al. Inorg. Chem.*, **2020**, *59*, 18090-18101.



Brantley, C. L. *et al.* In Preparation.

Such underexplored ligands are an exciting frontier- they are structurally similar to carboxylates, but with new properties which have resulted in both familiar and new structural types.



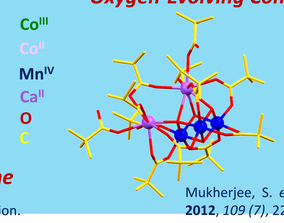
Co_8

Triple-stacked cubane

Brantley, C. L. *et al.* In Preparation.

Mn_3Ca_2

Synthetic mimic of the Oxygen-Evolving Complex



Mukherjee, S. *et al. PNAS*, **2012**, *109 (7)*, 2257-2262.