



RESNICKINSTITUTE
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RESEARCH HIGHLIGHTS

From the Resnick Sustainability Institute
Graduate Research Fellows at the
California Institute of Technology

**Model Complexes for Studying
Heterometallic Effects Relevant
to Fuel Cell Chemistry**

Daide Lionetti

Model Complexes for Studying Heterometallic Effects Relevant to Fuel Cell Chemistry

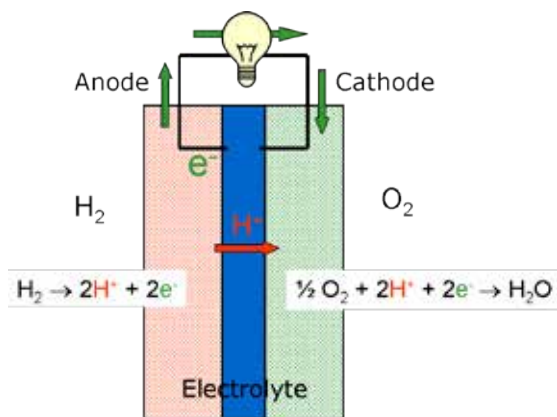
Davide Lionetti

Global Significance

The introduction of alternative energy sources to fossil fuels is the touchstone of a sustainable approach to rising world-wide energy demands. One of the key challenges of implementing these novel energy sources is the development of efficient fuel cells to convert fuels obtained from renewable sources into power. Fuel cells that rely on oxygen to convert fuel into electricity are of particular interest, as oxygen is abundant in our atmosphere and the byproduct of its consumption is harmless water.

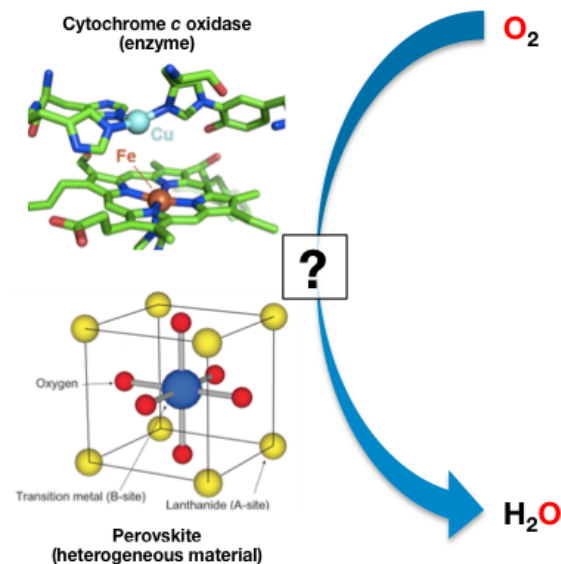
Metal catalysts have been studied to improve fuel cell efficiency, but their advancement is often hindered by lack of information on how catalysts, both natural and artificial, carry out the chemical reaction to convert oxygen to water. This project focuses on the development of models of metal catalyst systems known to carry out these reactions. From the models, we aim to be able to accurately identify the features relevant to improving catalyst design.

Fusing synthetic bioinorganic chemistry and electrochemistry, this project focuses on the development of small-molecule models of systems known to reduce oxygen to water. This approach allows us to study relevant systems at the molecular level in order to gain insight into the design elements that may lead to improved catalysts for fuel cells.



Overall: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$

General Schematic for an H_2/O_2 fuel cell. Fuel cells require metal catalysts for both fuel oxidation and reduction of a sacrificial oxidant. An ideal terminal oxidant is dioxygen (O_2) from air, because of its abundance and of the harmless nature of its reduction product -water (H_2O).



Known metal-containing enzymes and heterogeneous materials that perform the reduction of dioxygen to water include cytochrome c oxidase and perovskites. While these systems are effective catalysts, the interactions between the metals is not fully understood. Our project aims to gain insight into this reactivity via the study of metal cluster complexes.

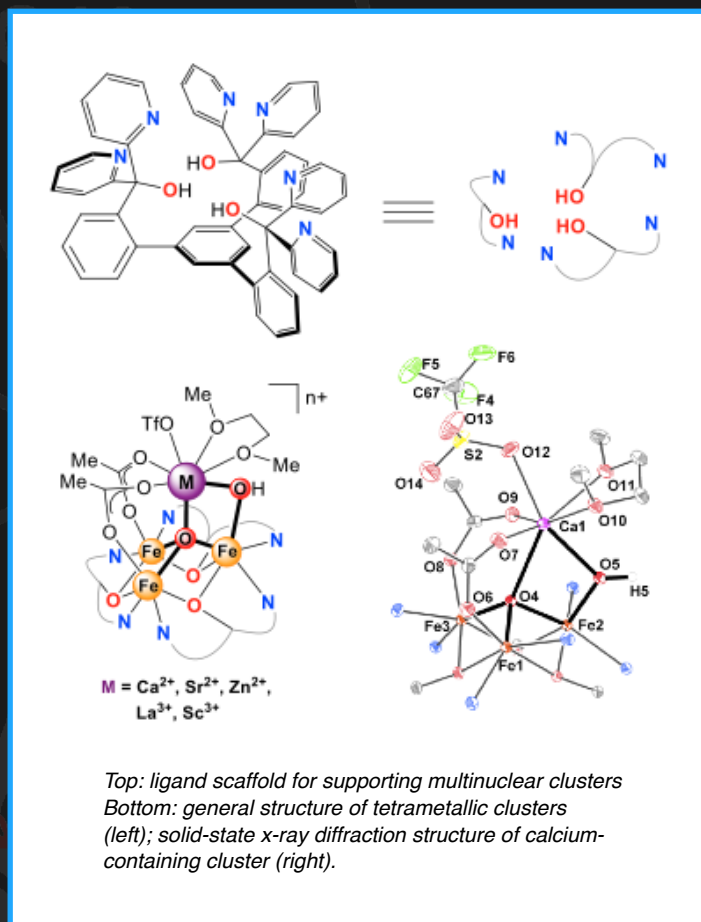
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Project Summary

To understand how different metals interact in systems that can perform the oxygen reduction reaction, we modeled metal cluster complexes to allow us to observe what properties and characteristics may prove relevant to reactivity. Specifically, we designed a ligand scaffold that supports multiple metal centers in close proximity. Based on this framework, we developed synthetic protocols to control the identity of the metals incorporated, allowing access to a series of complexes each containing four metals, three of which are iron centers while the fourth one is a metal incapable of transferring electrons. Using various techniques, we studied the effects of changing metal composition on the properties of the cluster, discovering that the ease of transfer of electrons to/from the clusters is strongly influenced by the identity of the fourth metal.

- Optimized synthetic protocols afford the ability to systematically vary cluster composition while maintaining an analogous structure.
- Use of small-molecule models allows accurate structural characterization, simplifying drawing connections between structural changes and properties.

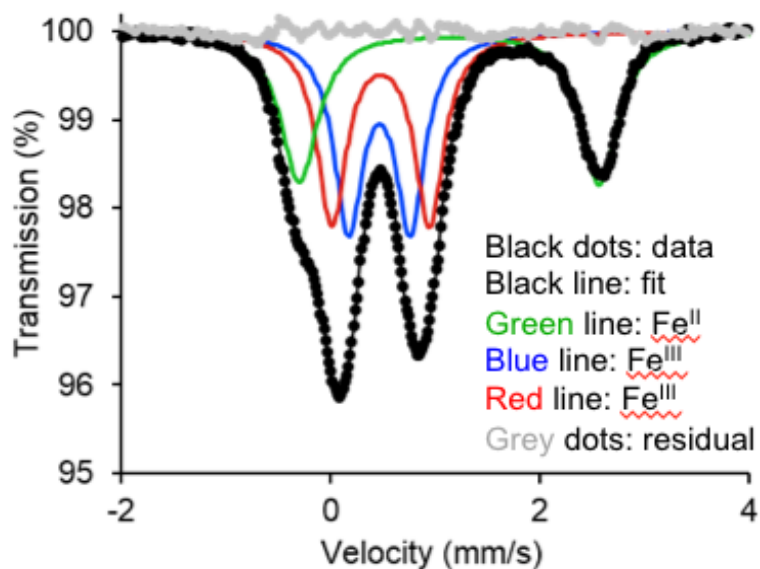
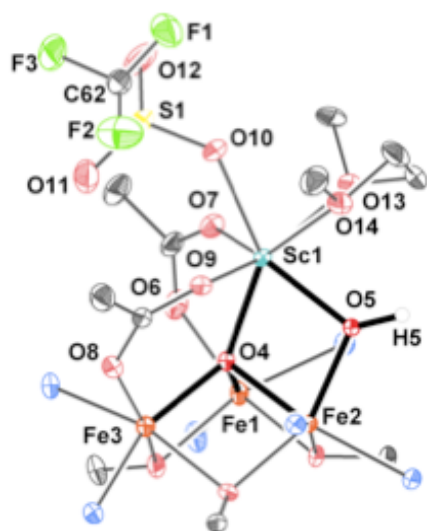


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Potential Impact

Through small-molecule modeling we hope to accurately understand the mechanisms driving reactions analogous to those found in fuel cells; gaining insight into their structure and function. If successful, these fundamental studies may point to systematic methods for designing more efficient catalysts and therefore improve the viability of fuel cell technology.



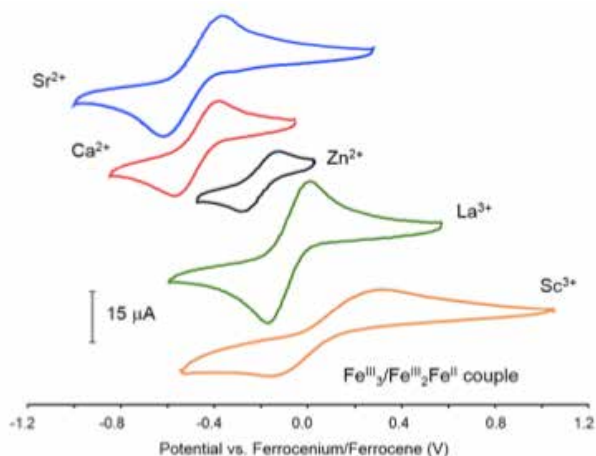
Structure and Mössbauer spectrum of scandium-containing cluster. Mössbauer spectroscopy allows precise assignment of the oxidation state of the iron centers. The overall signal (black dots) is deconvoluted into individual components corresponding to each iron center (red, blue, green lines).

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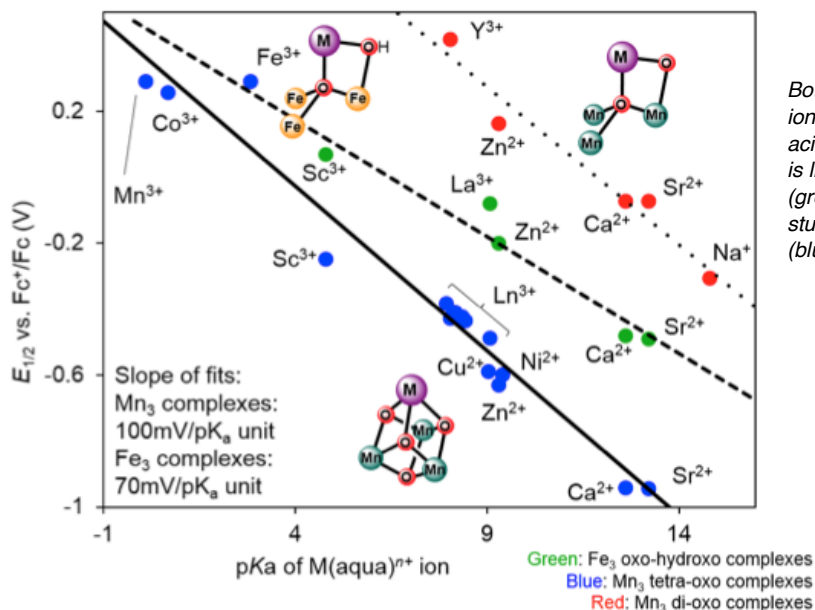
The Science

Tetranuclear, triiron complexes were accessed in which the fourth metal center could be introduced in a controlled fashion to give a series of structurally analogous clusters with different metal composition (clusters containing Ca^{2+} , Sr^{2+} , Zn^{2+} , La^{3+} , and Sc^{3+} were prepared). The structure of each cluster was confirmed via x-ray diffraction, which affords structural information at the atomic level. The clusters contain an oxido ligand bridging across all four metal centers and a hydroxide ligand bridging between an iron center and the redox-inactive metal. The redox-inactive metals can act as Lewis acids, drawing electron density through bridging ligands and therefore affecting electron transfer at the iron centers. Using the pK_a of metal-aquo ions as a measure of Lewis acidity, it was found that the cluster redox potential correlates linearly with the Lewis acidity of the redox-inactive metal.



M^{n+}	$E_{1/2}$ (V, vs. Fc^+/Fc)
Sc^{3+}	+0.07
La^{3+}	-0.08
Zn^{2+}	-0.21
Ca^{2+}	-0.49
Sr^{2+}	-0.49

Top: cyclic voltammograms of tetrametallic, triiron clusters and table of redox potentials observed



Bottom: Plot of redox potential vs. pK_a of the aqua ion of the redox inactive metal, a measure of Lewis acidity. The correlation between the two sets of values is linear for the iron complexes in the present work (green dots, dashed line) as well as for previously studied manganese clusters with different structures (blue dots, solid line and red dots, dotted line).

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Key Results

The correlation between Lewis acidity and redox potential suggests that, although they do not participate directly in electron transfer, redox-inactive metals can tune the redox potential of metal clusters, suggesting they may play a similar role in catalytic systems in which they are present.

Future Steps

While to date studies have focused on electron transfer, we would like to extend our studies to chemical reactivity. The transfer of oxygen atoms from the clusters to suitable substrates will therefore be investigated, and the effects of the identity of the redox-inactive metal on these reactions will be determined to provide further insight into how these components affect processes relevant to reduction of oxygen.

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Publications

- Herbert, D. E.; Lionetti, D.; Rittle, J.; Agapie, T. (2013) Heterometallic Triiron-Oxo/Hydroxo Clusters: Effect of Redox-Inactive Metals. *J. Am. Chem. Soc.* 135, 19075