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CURRENT RESEARCH

Our research program focuses on frontier mechanistic problems in bioinorganic chemistry that may be probed through reactivity and kinetic studies. Research at this interface requires the tools of both synthetic and physical inorganic chemistry. Specifically, we are interested in using small molecule chemistry to understand the catalytic activity of the nickel-containing enzymes carbon monoxide dehydrogenase (CODH) and acetyl coenzyme A synthase (ACS). These enzymes are found in anaerobic microorganisms that are capable of metabolizing small molecules, i.e. CO, CO₂ and acetate. Mononuclear zinc thiolates are also of interest in the laboratory as these species mimic a class of zinc proteins that activate sulfhydryl groups. Recently, we have shown that hydrogen-bonding to the thiolate can have a significant effect on reaction rates.

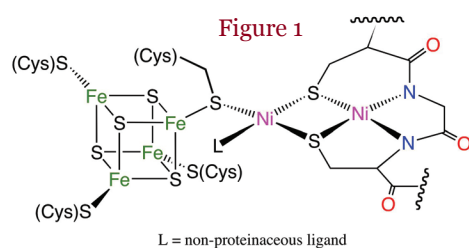
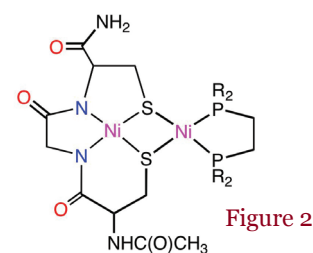
In another project, we are exploring the utility of nickel(I) complexes for the activation of dioxygen. Students in the laboratory are trained in the areas of synthesis, including anaerobic techniques, spectroscopy, reaction kinetics and mechanism.

ACETYL COENZYME

A SYNTHASE

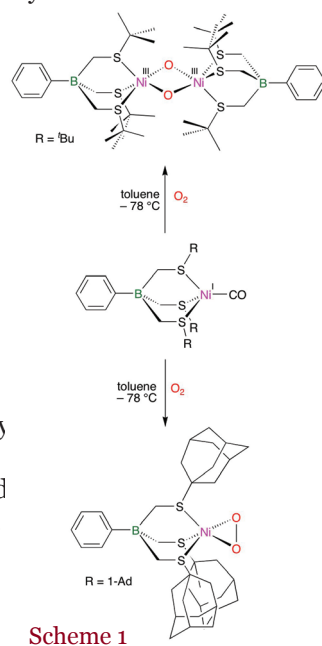
Recently three protein X-ray structures have been reported for the ACS enzyme providing the first glimpse of the active site (Fig. 1) responsible of acetate

synthesis via a bioorganometallic pathway. We have prepared small molecule representations of this cluster, for example Fig. 2 with the aim of interrogating relevant reaction chemistry.

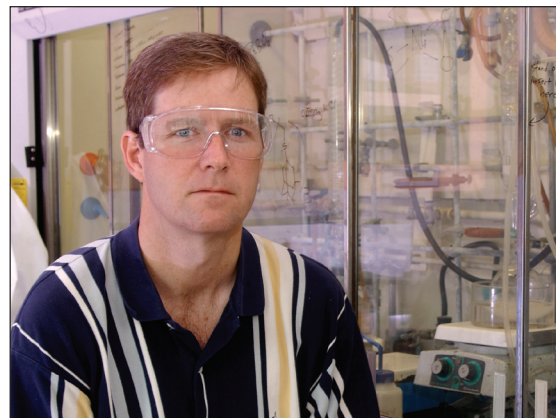


L = non-proteinaceous ligand

DIOXYGEN ACTIVATION O₂ is the ideal oxidant for a wide range of homogeneous catalytic processes. We have discovered that a series of readily accessible nickel(I) complexes react avidly with O₂, cleaving the O=O bond to generate metastable intermediates, Scheme 1. These species are competent in oxidizing exogenous substrates. A surprising observation is that the sulfur-containing ligand is



not oxidized during the reaction. Consequently, we are exploring the utility of these ligand systems for O₂ activation with a range of transition metal ions.



RECENT PUBLICATIONS

- R. Krishnan, C. G. Riordan, "Cys-Gly-Cys Tripeptide Complexes of Nickel: Binuclear Analogues for the Catalytic Site in Acetyl Coenzyme A Synthase" *Journal of the American Chemical Society* (2004) **126**, 4484-4485.
- Charles G. Riordan, "Acetyl Coenzyme A Synthase: New Insights into One of Nature's Bioorganometallic Catalysts" *Journal of Biological Inorganic Chemistry* (2004) **9**, 509-510.
- Matthew T. Kieber-Emmons, Ralph Schenker, Thomas C. Brunold and Charles G. Riordan, "Spectroscopic Elucidation of a Peroxo Ni₂(μ-O₂) Intermediate Derived from a Nickel(I) Complex and Dioxygen" *Angewandte Chemie International Edition* (2004) **43**, 6716-6718.
- Ralph Schenker, Matthew T. Kieber-Emmons, Charles G. Riordan and Thomas C. Brunold, "Spectroscopic and Computational Studies on the Trans-μ-1,2-Peroxo Bridged Dinickel(II) Species [Ni²⁺(tmc)₂(O₂)](OTf)₂: Nature of End-On Peroxo-Ni(II) Bonding and Comparison with Peroxo-Cu(II) Bonding" *Inorganic Chemistry* (2005) **44**, 1752-1762.
- Matthew T. Kieber-Emmons, Jamespandi Annaraj, Mi Sook Seo, Katherine M. Van Heuvelen, Takehiko Tosha, Teizo Kitagawa, Thomas C. Brunold, Wonwoo Nam and Charles G. Riordan, "Identification of an "End-on" Nickel-Superoxo Adduct, [Ni(tmc)O₂]⁺" *J. Am. Chem. Soc.* 2006, **128**, 14230-14231.
- Julie A. DuPont, Michael B. Coxey, Peter J. Schebler, Christopher D. Incarvito, William G. Dougherty, Glenn P. A. Yap, Arnold L. Rheingold and Charles G. Riordan, "High Spin Organocobalt(II) Complexes in a Thioether Environment" *Organometallics* 2007, **26**, 971-979.
- Matthew T. Kieber-Emmons and Charles G. Riordan, "Dioxygen Activation at Monovalent Nickel" *Acc. Chem. Res.* 2007, **40**, 618-625.