O-I-M Seminar Series

Organic/Inorganic/Materials • https://chemistry.uoregon.edu/

Timothy Warren

Michigan State University

November 17, 2023 • 3:00 pm, WIL 110

Hosted by Mike Pluth

NITRIC OXIDE SIGNALING CHEMISTRY AT COPPER AND LEWIS ACID SITES

Nitric oxide (NO) plays numerous, disparate biological roles which range from signaling in the respiratory system to vasodilation in the cardiovascular system to host defense against microbial pathogens. Nonetheless, discrete molecular mechanisms involved are not well understood: molecular relatives such as nitrite (NO_2^-) can also serve as reservoirs of NO-like behavior. Thus, understanding the discrete mechanistic pathways by which NO and NO_2^- form, interconvert, and react with molecular targets of biological relevance is critical to understand the molecular basis for physiological effects ascribed to NO and its relatives.

Employing a family of biologically relevant copper model complexes, we examine the reactivity and interconversion of NO, RSNOs, NO_2^-, and NO_3^-. These studies offer mechanistic insight into the copper-catalyzed release (and uptake) of NO via RSNOs as well as conversion of NO_2^- and NO_3^- to NO that generate S-based signaling molecules. We also describe the reductive coupling of NO at copper(I) centers that involves novel reduced NO and *cis*-hyponitrite intermediates such as $\{[Cu](ONNO)[Cu]\}^-$ complexes and examine chemical triggers for N_2O release. These *cis*-hyponitrite complexes also reveal how copper sites can help release the tremendous oxidizing capability of NO, a more powerful oxidant than O_2. Additionally, we illustrate how Lewis acid sites may regulate important redox interconversions in nitric oxide signaling chemistry. Redox innocent Lewis acids greatly facilitate the reduction of RSNOs and NO_2^- and can change their signaling output upon reduction .