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Department of Chemistry

Special MPIG Seminar

9:45 a.m. Tuesday, March 1 • 331 Smith Hall

Dow Corning Assistant Professor

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The Many Faces of the Coordination Chemistry of Nitric Oxide and its Significance for the Biosynthesis, Sensing and Detoxification of Nitric Oxide in Biological Systems

Research interests:

Coordination chemistry of nitric oxide as it pertains to biological systems,
in particular NO sensing and detoxification

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Abstract

Nitric oxide (NO) is a fascinating diatomic radical in the context of coordination chemistry due to its notorious non-innocent behavior in transition metal complexes. For example, NO adducts of ferrous iron complexes could have electronic structures that vary all the way from an Fe(I)-NO⁺ to an Fe(III)NO⁻ extreme with the Fe(II)-NO(radical) case being intermediate. This distinction is significant, as it can be expected that NO⁺, NO(radical), and NO⁻ will show very different reactivities. However, characterizing the exact electronic structures of transition metal nitrosyls has been difficult, which led to the establishment of the famous Enemark-Feltham notation that allows for a general classification of transition metal nitrosyls without the need to define an exact electronic structure. In the 1980s, nitric oxide evolved from being merely an air pollutant and curiosity of coordination chemistry to being a central signaling molecule in the cardiovascular and neuronal systems and a central anti-bacterial agent in immune defense in mammals. Correspondingly, the electronic structures and reactivities of transition metal nitrosyls have become of primary importance to understand the biosynthesis, sensing, regulation, transport, and detoxification of nitric oxide in biological systems. [1] All these functions are primarily mediated by metalloproteins, in particular iron and copper enzymes. An important goal of my work is to use the spectroscopic and theoretical methods at hand in the 21st century to go beyond the Enemark and Feltham classification in order to achieve more precise descriptions of the electronic structures of transition-metal nitrosyls that reflect the electron distribution in the complexes and the nature of the metal-NO bonds. This information allows one to draw conclusions with respect to the potential reactivities of these complexes in biological systems. My presentation will focus on the spectroscopic properties, electronic structures and reactivities of copper- and heme-nitrosyl complexes as they pertain to the biosynthesis, sensing, transport, and detoxification of NO in biology. For this purpose, vibrational (IR, resonance Raman, and nuclear resonance vibrational spectroscopy), electron paramagnetic resonance, and magnetic circular dichroism spectroscopy, among others, have been applied to investigate the properties of NO complexes of relevant synthetic model systems and enzymes. Coupled to density functional theory (DFT) calculations, the obtained spectroscopic data are analyzed in detail to determine the electronic structures of the complexes. This information is then related to the known (or proposed) functions of the corresponding metalloproteins in biology. As the journey continues, many more exciting discoveries with respect to the biological functions and the coordination chemistry of NO and its siblings, the NO_x derivatives, can be expected in the future.

[1] N. Lehnert, W. R. Scheidt, guest editors, 'Inorganic Chemistry FORUM: The Coordination Chemistry of Nitric Oxide and its Significance for Metabolism, Signaling and Toxicity in Biology', 2010, in press

Host: Regents Professor Larry Que
Refreshments will be served prior to the seminar.