Stanford

Daniel Stack

Associate Professor of Chemistry

CONTACT INFORMATION

- **Administrative Contact**

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Bio

BIO

Research in the Stack group focuses on the mechanism of dioxygen activation and the subsequent oxidative reactivity with primarily copper complexes ligated by imidazoles or histamines. Specifically, the group is interested in substrate hydroxylations and full dioxygen reduction. The remarkable specificity and energy efficiency of metalloenzymes provide the inspiration for the work. Trapping and characterizing immediate species, primarily at low temperatures, provide key mechanistic insights especially through substrate reactivity along with spectroscopic and metrical correlation to DFT calculations. Our objective is to move these efficient enzymatic mechanisms into small synthetic complexes, not only to reproduce biological reactivity, but more importantly to move the oxidative mechanism beyond that possible in the protein matrix.

Daniel Stack was born, raised and attended college in Portland Oregon. He received his B.A. from Reed College in 1982 (Phi Beta Kappa), working with Professor Tom Dunne on weak nickel-pyrazine complexes. In Boston, he pursued his doctoral study in synthetic inorganic chemistry at Harvard University (Ph.D., 1988) with Professor R. H. Holm, investigating site-differentiated synthetic analogues of biological Fe4S4 cubanes. As an NSF Postdoctoral Fellow with Professor K. N. Raymond at the University of California at Berkeley, he worked on synthesizing new, higher iron affinity ligands similar to enterobactin, a bacterial iron sequestering agent. He started his independent career in 1991 at Stanford University primarily working on oxidation catalysis and dioxygen activation, and was promoted to an Associate Professor in 1998. His contributions to undergraduate education have been recognized at the University level on several occasions, including the Dinkelspiel Award for Outstanding Contribution to Undergraduate Education in 2003.

Areas of current focus include:

Copper Dioxygen Chemistry

Our current interests focus on stabilizing species formed in the reaction of dioxygen with Cu(I) complexes formed with biologically relevant imidazole or histamine ligation. Many multi-copper enzymes ligated in this manner are capable of impressive hydroxylation reactions, including oxidative depolymerization of cellulose, methane oxidation, and energy-efficient reduction of dioxygen to water. Oxygenation of such complexes at extreme solution temperatures (-125°C) yield transient

Cu(III) containing complexes. As Cu(III) is currently uncharacterized in any biological enzyme, developing connections between the synthetic and biological realms is a major focus.

Surface Immobilization of Catalysts in Mesoporous Materials

In redox active biological metal sites, the ligation environment is coupled tightly to the functional chemistry. Yet, the metal sites are also site-isolated, creating species that may only have a transient existence in a homogeneous solution. Site isolation of synthetic complexes can be achieved synthetically by supporting the metal complex on a solid matrix. Movement of these complexes into silica based materials or onto electroactive carbon electrodes represent a new direction for the group in the development of bio-inspired metal-based catalysts.

ACADEMIC APPOINTMENTS

- Associate Professor, Chemistry

HONORS AND AWARDS

- Dinkelspiel Award for Outstanding Contribution to Undergraduate Education, Stanford University (2003)
- Hoefer Teaching Award, Stanford University (1997)
- Bing Foundation Teaching Award, Stanford University (1995-98)
- Shell Foundation New Faculty Award, Shell Foundation (1993-95)
- Harvard Danforth Distinguished Teaching Award, Harvard University (1983, 1984)

PROFESSIONAL EDUCATION

- NSF Postdoctoral Fellow, University of California at Berkeley , Inorganic Chemistry (1988)
- PhD, Harvard University , Inorganic Chemistry (1988)
- BA, Reed College , Chemistry (1982)

LINKS

- Stack Research Group: http://stacklab.stanford.edu/

Teaching

COURSES

2020-21

- Inorganic Chemistry I: CHEM 151 (Win)
- Structure and Reactivity of Organic Molecules: CHEM 33 (Aut, Spr)

2019-20

- Inorganic Chemistry I: CHEM 151 (Win)

2018-19

- Inorganic Chemistry I: CHEM 151 (Win)
- Structure and Reactivity of Organic Molecules: CHEM 33 (Spr)

2017-18

- Inorganic Chemistry I: CHEM 151 (Win)
- Structure and Reactivity of Organic Molecules: CHEM 33 (Spr)

STANFORD ADVISEES

Doctoral Dissertation Reader (AC)

Augustin Braun, Ariel Jacobs, Ioannis Kipouros, Rebecca McClellan, Chu Zheng

Doctoral Dissertation Advisor (AC)

Jasper Ainsworth, Will Keown, Tao Large

Publications

PUBLICATIONS

- **Simplest Monodentate Imidazole Stabilization of the oxy-Tyrosinase Cu2 O2 Core: Phenolate Hydroxylation through a Cu(III) Intermediate.** *Angewandte Chemie (International ed. in English)*
  Chiang, L., Keown, W., Citek, C., Wasinger, E. C., Stack, T. D.
  2016; 55 (35): 10453-10457
- **Direct Copper(III) Formation from O2 and Copper(I) with Histamine Ligation.** *Journal of the American Chemical Society*
  Gary, J. B., Citek, C., Brown, T. A., Zare, R. N., Wasinger, E. C., Stack, T. D.
  2016; 138 (31): 9986-9995
- **Manganese(II)/Picolinic Acid Catalyst System for Epoxidation of Olefins** *ORGANIC LETTERS*
  Moretti, R. A., Du Bois, J., Stack, T. D.
  2016; 18 (11): 2528-2531
- **Metal complex assembly controlled by surface ligand distribution on mesoporous silica: Quantification using refractive index matching and impact on catalysis** *JOURNAL OF CATALYSIS*
  Smith, B. J., Gallegos, P. A., Butsch, K., Stack, T. D.
  2016; 335: 197-203
- **Catalytic Phenol Hydroxylation with Dioxygen: Extension of the Tyrosinase Mechanism beyond the Protein Matrix** *ANGEWANDTE CHEMIE-INTERNATIONAL EDITION*
  Hoffmann, A., Citek, C., Binder, S., Goos, A., Ruebhausen, M., Troeppner, O., Ivanovic-Burmazovic, I., Wasinger, E. C., Stack, T. D., Herres-Pawlis, S.
  2013; 52 (20): 5398-5401
- **Self-assembly of the oxy-tyrosinase core and the fundamental components of phenolic hydroxylation** *NATURE CHEMISTRY*
  Citek, C., Lyons, C. T., Wasinger, E. C., Stack, T. D.
  2012; 4 (4): 317-322
- **Tyrosinase reactivity in a model complex: An alternative hydroxylation mechanism** *SCIENCE*
  Mirica, L. M., Vance, M., Rudd, D. J., Hedman, B., Hodgson, K. O., Solomon, E. I., Stack, T. D.
  2005; 308 (5730): 1890-1892
- **Structure and spectroscopy of copper-dioxygen complexes** *CHEMICAL REVIEWS*
  Mirica, L. M., Ottenwaelder, X., Stack, T. D.
  2004; 104 (2): 1013-1045
- **Efficient epoxidation of electron-deficient olefins with a cationic manganese complex** *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*
  Murphy, A., Dubois, G., Stack, T. D.
  2003; 125 (18): 5250-5251
- **C-H bond activation by a ferric methoxide complex: Modeling the rate-determining step in the mechanism of lipoxygenase** *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*
  Goldsmith, C. R., Jonas, R. T., Stack, T. D.
  2002; 124 (1): 83-96
- **Aryl C-H activation by Cu-II to form an organometallic Aryl-Cu-III species: A novel twist on copper disproportionation** *ANGEWANDTE CHEMIE-INTERNATIONAL EDITION*
  Ribas, X., JACKSON, D. A., Donnadieu, B., Mahia, J., Parella, T., Xifra, R., Hedman, B., Hodgson, K. O., Llobet, A., Stack, T. D.

2002; 41 (16): 2991-2994

- **Stereospecificity and self-selectivity in the generation of a chiral molecular tetrahedron by metal-assisted self-assembly** *ANGEWANDTE CHEMIE-INTERNATIONAL EDITION*
  Enemark, E. J., Stack, T. D.
  1998; 37 (7): 932-935

- **Catalytic galactose oxidase models: Biomimetic Cu(II)-phenoxyl-radical reactivity** *SCIENCE*
  Wang, Y. D., Dubois, J. L., Hedman, B., Hodgson, K. O., Stack, T. D.
  1998; 279 (5350): 537-540

- **Irreversible reduction of dioxygen by simple peralkylated diamine-copper(I) complexes: Characterization and thermal stability of a [Cu-2(mu-O)(2)](2+) core** *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*
  Mahadevan, V., Hou, Z. G., Cole, A. P., Root, D. E., Lal, T. K., SOLOMON, E. I., Stack, T. D.
  1997; 119 (49): 11996-11997

- **C-H bond activation by a ferric methoxide complex: A model for the rate-determining step in the mechanism of lipoxygenase** *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*
  Jonas, R. T., Stack, T. D.
  1997; 119 (36): 8566-8567

- **Trinuclear intermediate in the copper-mediated reduction of O-2: Four electrons from three coppers** *SCIENCE*
  Cole, A. P., Root, D. E., Mukherjee, P., SOLOMON, E. I., Stack, T. D.
  1996; 273 (5283): 1848-1850