Séminaire DCM/ICMG/Labex ARCANE

Mardi 12/06/2018 - 14h à 17h00

Amphi Rassat – 470 rue de la chimie

Campus Saint Martin d'hères

Programme :

14h - 15h

"Copper and Heme-Copper Dioxygen Binding, Structures and Reactivity"

Prof. K. Karlin
Johns Hopkins University
Baltimore, USA

The study of ligand-copper or heme-copper reactions with molecular oxygen is of intrinsic interest; there is a need to establish fundamental aspects of Cu-O2 or heme-Cu-O2 complex formation, structures and associated physical properties. Such chemistries occur in biological systems, those involving O2-transport, O-atom insertion into organics or catalytic O2-reduction to water (i.e., fuel-cell chemistry).

Via the examination of synthetically derived chemical model systems, and in the context of metallobiochemistry, recent results on the following topics will be presented:

(i) Primary Cu-dioxygen species, cupric-superoxide complexes, can be stabilized through ligand-design features and cryogenic conditions. These will be described including complexes with ligands possessing a thioether donor-ligand or H-bonding moieties. Accompanying spectroscopic characterization, and reactivity with potential O–H or C–H containing substrates and/or reduction-protonation chemistries may also be expounded.

(ii) Model systems for heme-copper oxidases (e.g., cytochrome c oxidase, involving O2-binding and reduction are being pursued. Dioxygen reactions with reduced (heme)FeII…CuI ensembles lead to peroxo-bridged FeIII-(O22–)-CuII complexes. The significant effect of the nature of the copper-ligand on the FeIII-(O22–)-CuII structure, physical properties and reactivity will be emphasized.

The synthesis of reduced (heme)FeII…CuI(ligand) ensembles is described; their reactions with O2 gives high-spin (iron) peroxo-bridged FeIII-(O22–)-CuII(ligand); conversion to low-spin analogues occurs by addition of an heme axial-ligand (B) giving (B)FeIII-(m-1,2-O22–)-CuII(ligand) peroxo species. The nature of the Cu-ligation dictates the physical properties and subsequent reactivity of these assemblies. We also describe reactions with proton-electron sources (e.g., acids-reductants, catechols) which effect differing reactivity, such as metal-O bond cleavage releasing hydrogen peroxide and biomimetic reductive O-O cleavage.

Kenneth D. Karlin is the Ira Remsen Professor of Chemistry and the current department Chair at Johns Hopkins University in Baltimore, Maryland, USA. He grew up in Palo Alto, California, and was educated at Stanford University (B.S. 1970) and at Columbia University, New York (Ph.D. 1975; Preceptor, S. J. Lippard). He was a N.A.T.O. postdoctoral fellow at Cambridge University in England before being appointed Assistant Professor of Chemistry at the State University of New York at Albany (SUNY Albany) in 1977. He moved to The Johns Hopkins University as Professor in 1990, where he was appointed as Ira Remsen Professor of Chemistry in 1999. Dr. Karlin is Editor-in-Chief of Progress in Inorganic Chemistry (John Wiley & Sons) and holds or has held advisory or administrative positions with the Society for Biological Inorganic Chemistry (SBIC), the Petroleum Research Fund (PRF) (of the American Chemical Society (ACS)) and the Division of Inorganic Chemistry (DIC) of the ACS, most recently as 2013 DIC Chair (elected)). He is also a Fellow of the American Association for the Advancement of Science and was elected as an ACS Fellow in 2014. For research accomplishments, he won a 2009 ACS National Award, the F. Albert Cotton Award in Synthetic Inorganic Chemistry. He has been Organizer/Chair of a number of international meetings on copper and/or bioinorganic chemistry, the 1998 Metals in Biology Gordon Research Conference and the 1989 International Conference on Bioinorganic Chemistry (ICBIC-4). Dr. Karlin's bioinorganic research focuses on the design, synthesis and study of coordination complexes whose chemistry is relevant to biological processes, mainly metalloenzyme active site chemistry, involving copper and/or heme (porphyrin-iron) complexes and their chemistry with molecular oxygen, its reduced derivatives, and nitrogen oxide compounds.

15h - 15h20 **"A thiolate-supported iron complex for catalytic reduction of dioxygen to hydrogen peroxide"**

Marcello Gennari

DCM, équipe Cire

15h20 - 15h40 **"New heterogeneous biocatalysts for oxidation reactions: crystals of artificial metalloenzymes."**

Sarah Lopez

LCBM, équipe catalyse bioinorganique et environnement /DCM, équipe Serco

15h40 - 16h00 **"Challenging the $[Ru(bpy)_3]^{2+}$ photosensitizer with a robust triazatriangulenium organic dye for photocatalytic hydrogen production in water"**

Jérôme Fortage

DCM, équipe Cire

16h - 17h Discussion around a drink