

Master internship + PhD thesis in Chemistry

Host laboratory/institution: Département de Chimie Moléculaire (DCM), Univ. Grenoble Alpes.
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Internship/PhD supervisor: Marcello GENNARI, CNRS researcher
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Title: Mimicking nitrogenase chemistry with bio-inspired thiolate-supported transition metal complexes.

Objectives: Study of the reactivity of metal-thiolate complexes towards molecular nitrogen and other N-containing small molecules.

Pedagogical interest and targeted skills: The subject is multidisciplinary, the student will have the opportunity to discover different fields of chemistry, mainly bio-inspired coordination chemistry, activation of small molecules by metal complexes, molecular electrochemistry and homogeneous catalysis. She/he will become familiar with different techniques of characterization in solution.

Abstract: Ammonia (NH_3), essential to manufacture fertilizers and emerging as a portable energy vector, is produced industrially from N_2 and natural-gas-generated H_2 in the strongly CO_2 emissive Haber-Bosch process, where a thermally-activated iron surface acts as heterogeneous catalyst. On the other hand, in nature the reduction of N_2 to NH_3 is performed at room temperature and pressure by a class of metalloenzymes named nitrogenases. In their most common form, the active site contains a unique iron-molybdenum cluster (FeMo-co) including a diiron unit that is responsible for N_2 binding and activation (Fig. a). Inspired by nitrogenases, we propose to study bimetallic complexes (Fe, etc.) supported by a thiolate-rich N_2S_2 -donor ligand as potential synthetic catalysts for mild N_2 -reduction (Fig. b). This family of complexes has been previously reported by our group as molecular oxygen reduction catalysts (JACS 2015, 137, 8644; JACS 2019, 141, 8244). During the internship, complexes from this series will be synthesized, their protonation/reduction properties and their reactivity towards N_2 and other N-substrates (like hydrazine, diazenes) will be explored, both in the absence and presence of electrons and protons (stoichiometric reactivity vs chemical/electro-/photo-catalysis). DFT calculations will contribute to rationalize the observed reactivity (coll. Darmstadt).

