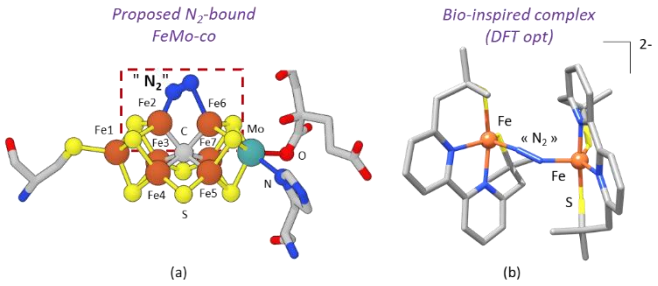
PhD thesis at the Univ. Grenoble Alpes from October 2022 (ANR funding, coll. LCC Toulouse and TU Darmstadt)

Topic: 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.

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 N2S2-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, etc.) will be explored, both in the absence and presence of electrons and/or protons (stoichiometric reactivity vs chemical/electro-/photo-catalysis). In collaboration with Antoine Simonneau from the LCC of Toulouse, the M/S complexes will be combined with phosphine-supported group VI M^0-N_2 adducts to access to new d-block based N_2-bridged push-pull dyads. DFT calculations will contribute to rationalize the observed reactivity (coll. with Vera Krewald, TU Darmstadt).



Methods & materials: Reactivity of complexes under inert atmosphere (glove box, Schlenk techniques), structural characterization by single crystal X-ray diffraction, characterization in solution (IR, NMR, EPR, mass spectrometry), electrochemistry (cyclic voltammetry, bulk electrolysis), (chemical, electro-, photo-) catalysis. Possibility to perform DFT calculations.

Required skills: Knowledge/experience in coordination chemistry will be appreciated. Interest in DFT calculations will be a plus.

Place: Département de Chimie Moléculaire (DCM) de Grenoble**.**

Dates: from October 2022 (ANR funding available, coll. LCC Toulouse and TU Darmstadt).

Application requirements: a CV including the names of two referees and a short letter describing the main expertise of the candidate.

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Deadline: 08/04/2022.