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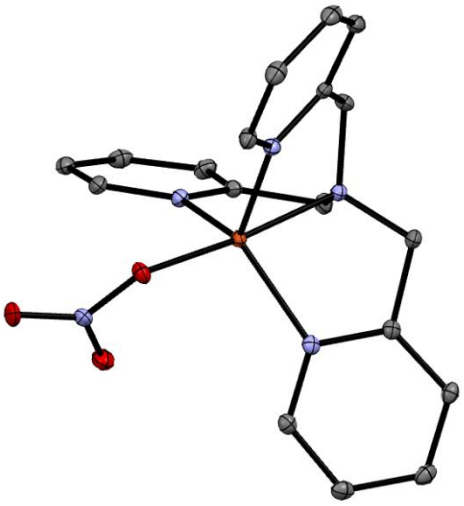
ELECTRO-ASSISTED REDUCTION OF NITROGEN OXYANIONS (NO_x^-) IN WATER: NEW COPPER-BASED ELECTROCATALYSTS

Large-scale use of nitrogen containing fertilizers, relying on the Haber-Bosch process, has allowed to supply food to an ever-growing world population. However, of the 135 million tons of agricultural nitrogen that are spread every year on farmlands, only 17% is finally converted into proteins. Most of the remaining is converted by soil micro-organisms into **nitrogen oxyanions (NO_x^-)**, and particularly nitrates (NO_3^-) and nitrites (NO_2^-). Environmental accumulation of NO_x^- is of particular concern. High concentration of NO_x^- have been shown to be significant drivers of water eutrophication inducing uncontrolled algae bloom in contaminated environment. When routinely ingested by humans, NO_x^- can also contribute to the development of serious diseases such as ovarian and bladder cancers, as well as non-Hodgkin's lymphoma.[1]



Electro-assisted reduction of NO_x^- is a promising mitigation strategy to convert these harmful products into benign (N_2) or useful compounds (NH_3). Such multi-electron, multi-proton processes are complex and often suffer from lazy kinetics. Transition metal catalysts usually favour the desired multielectron processes, owing to their ability to accommodate multiple reduction steps within the range of considered potentials. Highly tuneable through ligand design, molecular electrocatalysts are capable to ensure control over reactant and product selectivity, together with in-depth mechanistic understanding. Such molecular systems capable to effectively reduce nitrate ions are, nevertheless, still rare.[1–4] **In this internship, new molecular systems capable to electro-assist the reduction of nitrogen oxyanions, and particularly nitrates, will be developed**. We recently demonstrate the ability of some copper(II) complexes to interact with nitrates to form stable, isolable adducts (*Figure*). A series of copper(II) complexes relying on the tris(2-pyridylmethyl)amine (TMPA) platform will thus be prepared and characterised. Special attention will be given to the study of the electrocatalytic behaviour of these compounds towards **NO_x^- reduction**. Synthetic, spectroscopic and electrochemical tools will be used to gain some insight on the catalytic mechanism.

The internship will be supervised by Dr. N. Queyriaux and Dr. C. Esmieu. Solid skills in coordination chemistry, and common electrochemical techniques will be acquired, as well as a background in analytical chemistry (NMR, UV-Vis and infrared spectroscopy, X-ray diffraction).

To apply, please attach a CV, M1 results and the most recent internship report to your application.

[1] S. Partovi, Z. Xiong, K. M. Kulesa, J. M. Smith, *Inorg. Chem.* **2022**, *61*, 9034–9039.
[2] H.-Y. Kwon, S. E. Braley, J. P. Madriaga, J. M. Smith, E. Jakubikova, *Dalton Trans.* **2021**, *50*, 12324–12331.
[3] S. Xu, D. C. Ashley, H.-Y. Kwon, G. R. Ware, C.-H. Chen, Y. Losovyj, X. Gao, E. Jakubikova, J. M. Smith, *Chem. Sci.* **2018**, *9*, 4950–4958.
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