Intermediate-spin iron(IV)-oxido species with record reactivity

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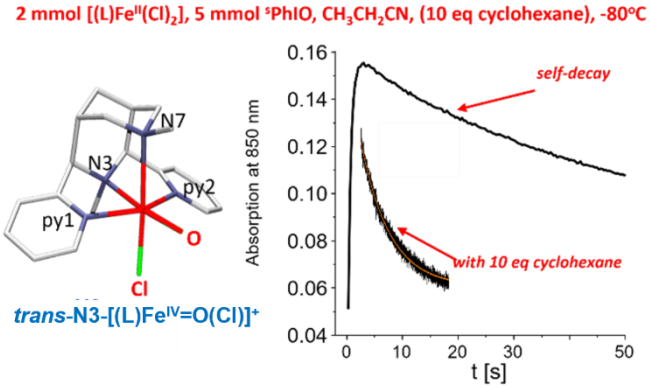
The lecture will start with a short discussion of a range of current projects in the Comba group from various areas of bioinorganic and coordination chemistry and then wiil concentrate on high-valent nonheme iron chemistry.
The iron(IV)-oxido complex *trans*-N3-[(L)Fe^{IV}=O(Cl)]$^{+}$, with a tetradentate bispidine as supporting ligand (see Figure), has an *S* = 1 electronic ground state (in contrast to enzymes with an *S* = 2 ground state), is the most reactive nonheme iron model system known so far, with a reactivity similar to nonheme iron enzymes (C-H abstraction of cyclohexane, -90°C (propionitrile), $t_{1/2}$ = 3.5 sec), and with 100% selectivity produces cyclohexyl chloride.[1-3] In absence of organic substrates, there are various self-decay pathways, one leading to an oxido-bridged diiron(III) species. The reactivity of this "resting state" as well as reasons for the unprecedented reactivity of *trans*-N3-[(L)Fe^{IV}=O(Cl)]$^{+}$ are discussed on the basis of temperature-dependent kinetics, a thorough spectroscopic analysis of the ferryl complex and the analysis of the electronic ground state involving ligand field and quantum-chemical methods.



1 Abu-Odeh, M.; Bleher, K.; Britto, N. J.; Comba, P.; Gast, M.; Jaccob, M.; Kerscher, M.; Krieg, S.; Kurth, M. *Chem. Eur. J.* **2021**, *27*, 11377-11390. http://dx.doi.org/10.1002/chem.202101045 'Pathways of the extremely reactive iron(IV)-oxido complexes with tetradentate bispidine ligands.'
2 Bleher, K.; Comba, P.; Faltermeier, D; Gupta, A.; Kerscher, M.; Krieg, S.; Martin, B.; Velmurugan, G.; Yang, S. *Chem. Eur. J.,* **2022** ,e202103452. http://dx.doi.org/10.1002/chem.202103452 'Non-heme-iron-catalyzed selective halogenation of unactivated carbon-hydrogen bonds.'
3 Comba, P.; Nunn, G.; Scherz, F.; Walton P. H. *Faraday Discussion,* **2022**. https://doi.org/10.1039/D1FD00073J 'Intermediate-spin iron(IV)-oxido species with record reactivity.'