

## Thursday 14<sup>th</sup> December

- 09.00-09:40 **Keynote: Anna Company**  
*Characterization and reactivity studies on a terminal copper-nitrene species.*
- 09:40-10:00 **Erik Hedegard**  
*Challenges in targeting spin states for theoretical chemistry: progress and new methods.*
- 10.00-10:20 **Christian Enachescu**  
*Theoretical approach for elastically driven cooperative switching of spin-cross-over compounds.*
- 10:20-10:25 **Group Picture**
- 10:25-10:50 **Coffee**
- 10.50-11:10 **Ana Vicente**  
*Strategies to improve the cooperativity in iron(III) spin crossover complexes.*
- 11:10-11:30 **Rafal Kulmaczewski**  
*LIESST in a family of isostructural Fe(II) spin crossover complexes.*
- 11:30-11:50 **Christina Wegeberg**  
*Light-induced oxygen activation by a mononuclear iron(III) complex.*
- 11:50-12:10 **Peter Weinberger**  
*Halogenated alkyltetrazoles for rational design of Fe(II)-spin crossover materials-fine tuning of the ligands size.*
- 12:15-13:40 **Light lunch**
- 13:40-14:00 **Lorenzo D'Amore**  
*Modulation of a weakly coupled peroxo-dicopper(II) complex by interaction with alkali metal ions.*
- 14:00-14:20 **Marco Seifried**  
*Functionalization of N-substituted 1H-tetrazoles: towards an easy library synthesis.*
- 14:20-14:40 **Hélène Jamet**  
*Theoretical studies of dinuclear copper centers.*
- 14:40-15:00 **Giovanni La Penna**  
*Copper catalysts and structural disorder.*
- 15:00-15:20 **Federico Martins**  
*Harnessing the spin crossover phenomenon: a study on the anion and halogen effects.*
- 15:20-15:40 **Simon Hallaert**  
*The reactivity of the  $\alpha$ -O in Fe-zeolites: a multireference approach.*
- 15:40-16:00 **Christine McKenzie**  
*Tuning peroxide activation by non-heme complexes.*

- 16:00-16:30 **Coffee**  
 16:30-17:00 **WGs meeting**  
 17:00-19:00 **Posters**  
 19:00-21.30 Informal Drinks/Hotel time  
 20.45 Meet at hotel to walk to Milano restaurant  
 21:30 **Conference dinner, Milano, Dawson Street**

### **Friday 15<sup>th</sup> December**

- 09:00-09:40 **Keynote: Sam de Visser**  
*What is the origin of the regio- and stereoselectivity of nonheme iron enzymes? A computational study?*
- 09:40-10:00 **Federica Arrigoni**  
*DFT study of CO<sub>2</sub> activation promoted by a class of thiolate bridged di-iron complexes with a [Cp\*Fe(μ-SR)<sub>2</sub>FeCp\*] scaffold.*
- 10:00-10:20 **Franc Meyer**  
*Bio-inspired mono- and dinuclear iron/NO complexes: electronic structure contributions to reactivity.*
- 10:20-10:50 **Coffee**
- 10:50-11:10 **Irene Kühne**  
*Investigation on ligand substituent effects on Mn(III) chelates.*
- 11:10-11:30 **Hans-Jörg Krüger**  
*Effect of coordinated radical ligands on the rate of spin crossover processes in iron(II) complexes.*
- 11:30-11:50 **Quan Phung**  
*Dinuclear iron(II) spin crossover compounds: a theoretical study.*
- 11:50-12:10 **Ivan Salitros**  
*Iron(III) complexes with pentadentate Schiff based-structural and magnetic investigation.*
- 12:15-13:40 **Light lunch**
- 13:40-14:00 **Vera Krewald**  
*Progress in understanding dinitrogen photocleavage.*
- 14:00-14:20 **Davide Angelone**  
*Transient formation and reactivity of a high-valent nickel(IV) oxido complex.*
- 14:20-14:40 **Julianne Olah**  
*Redox potential-basicity relationship of compound II of heme enzymes: A QM/MM study.*
- 14:40-15:00 **Rob Deeth**  
*Ab Initio ligand field molecular mechanics for iron(II) bis-pyrazolylpyridine spin crossover complexes.*
- 15:00-15:10 **Closing of the workshop**
- 20.00-23.00 **Informal dinner**

# **Oral Presentations**

# CHARACTERIZATION AND REACTIVITY STUDIES ON A TERMINAL COPPER-NITRENE SPECIES

Teresa Corona,<sup>1</sup> Lidia Ribas,<sup>1</sup> Mireia Rovira,<sup>1</sup> Erik. R. Farquhar,<sup>2</sup> Xavi Ribas,<sup>1</sup> Kallol Ray,<sup>3</sup> Anna Company<sup>1</sup>

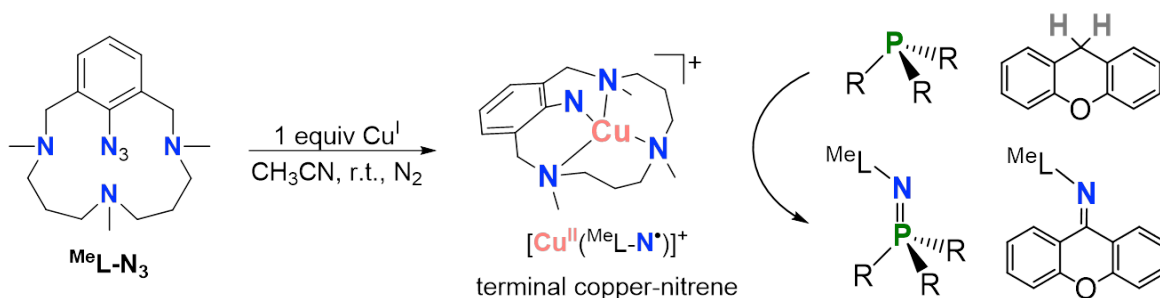
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High-valent copper-nitrene species have been postulated as key intermediates in several copper-catalyzed reactions such as aziridination and amination reactions.<sup>[1]</sup> The high reactivity of these intermediates has eluded their characterization for decades, thereby making the mechanism ambiguous. However, seminal works have evidenced their formation. For instance, Warren et al. could crystallize a dicopper(II)-nitrene complex as a precursor of a terminal copper(III)-nitrene species.<sup>[2]</sup> Very recently, the Lewis acid adduct of a copper-nitrene intermediate has been trapped at -90 °C and shown to be active in various oxidation reactions.<sup>[3,4]</sup>

Herein, we describe for the first time the synthesis and spectroscopic characterization of a room temperature stable terminal copper(II)-nitrene radical species in the absence of any Lewis acid (see Scheme).<sup>[5]</sup> The azide derivative of a triazamacrocyclic ligand has been employed as an ancillary ligand in the study, which has previously been utilized in the stabilization of aryl-Cu<sup>III</sup> intermediates. This copper-nitrene species is able to perform nitrene-transfer to phosphines and H-atom abstraction from weak C-H bonds leading to the formation of oxidized products in modest yields.



[1] R.T. Gephart, T. H. Warren. *Organometallics* **2012**, *31*, 7728.

[2] Y. M. Badié, A. Krishnaswamy, M. M. Melzer, T. H. Warren. *J. Am. Chem. Soc.* **2006**, *128*, 15056.

[3] S. Kundu, E. Micelli, E. Farquhar, F. F. Pfaff, U. Kuhlmann, P. Hildebrandt, B. Braun, C. Greco, K. Ray. *J. Am. Chem. Soc.* **2012**, *134*, 14710

[4] S. L. Abram, I. Monte-Pérez, F. F. Pfaff, E. R. Farquhar, K. Ray. *Chem. Commun.* **2014**, *50*, 9852.

[5] T. Corona, L. Ribas, M. Rovira, E. R. Farquhar, X. Ribas, K. Ray, A. Company. *Angew. Chem. Int. Ed.* **2016**, *55*, 14005.

# CHALLENGES IN TARGETING SPIN STATES FOR THEORETICAL CHEMISTRY: PROGRESS AND NEW METHODS

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A hallmark of transition metals and their complexes is their partially filled d-shell, which gives rise to a multiplet of possible spin-states. Depending on the surrounding ligands and the corresponding ligand field, the spin-states can both be well-separated or close in energy. The ability to change spin state depending on the ligand sphere can be utilized by enzymes to induce a specific reactivity. Theoretical methods for bio-inorganic chemistry must therefore deal with spin-state energetics. Unfortunately, this is a large challenge for theoretical methods. Density Functional Theory (DFT) is often insufficient, occasionally even failing to predict the correct ground state. Further, none of the commonly employed DFT methods can rigorously describe spin-coupled systems. *Ab-initio* wave function methods can rigorously describe *all* spin states, but are often prohibitively expensive for transition-metal complexes. In this talk I, will illustrate inaccuracies of DFT using some of the bio-inorganic systems we are currently investigating.<sup>[1,2]</sup> I will further discuss which *ab initio* methods we employ to benchmark DFT for these systems.<sup>[1,3]</sup> Finally, I will describe a new method that combines DFT with *ab-initio* methods to make the latter more efficient<sup>[4]</sup> without compromising the accuracy severely.

- 1) G. Dong, Q. M. Phung, S. D. Hallaert, K. Pierloot and U. Ryde, *Phys. Chem. Chem. Phys.* **2017**, *19*, 10590.
- 2) E. D. Hedegård and U. Ryde, *J. Biol. Inorg. Chem.* **2017**, *22*, 1029.
- 3) G. Dong, U. Ryde, and E. D. Hedegård, In prep.
- 4) E. D. Hedegård, J. Toulouse and H. J. Aa. Jensen, *J. Chem. Phys.* To be submitted.

# THEORETICAL APPROACH FOR ELASTICALLY DRIVEN COOPERATIVE SWITCHING OF SPIN-CROSSOVER COMPOUNDS

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Here we apply the mechanoelastic model [1] with realistic parameters in order to discuss recent experimental data in spin crossover materials, such the elastic step after photoexcitation [2]. This model is based on the idea that the difference of molecular volumes in the low spin (LS) and high spin (HS) states is at the origin of elastic interactions, accounted by springs which elongations produce different local pressure on every molecule inducing a shift of the molecules in the system during the transition. The molecules are arranged at the vertices of a triangular tiling, in 2D or 3D lattices of various shapes. The switching of molecules during the spin transition is decided by way of a Monte Carlo standard procedure. The elastic step is produced by the propagation of the elastic distortions, even before the increase of the crystal volume and implies the triggering of a further change of the electronic states of the molecules after switching off the light. We have successfully reproduced the experimental dependence of the elastic step of the photoexcitation percentage and temperature and we predict the behaviour of the system in the case of the variation of some parameters, such as the elastic constant, the size of the system or the homogeneity of the photoexcitation. The delay in the evolution of the surface and the contribution of the reorganisation of the molecular states during elastic steps, leading to clusters of HS molecules towards edge or corners is also revealed. (see figure).

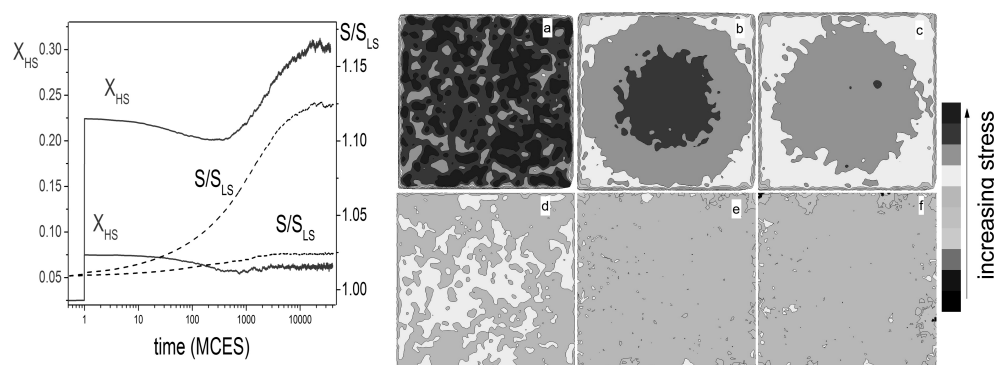


Figure: Variation of the fraction of HS molecules,  $X_{HS}$ , and of the area during elastic step for two photoexcitation rates (left) Map of stress inside the sample during the elastic step. (right)

## References

[1] C.Enachescu, A. Hauser, *PhysChemChemPhys*, **2016**, 18, 20591

[2] R. Bertoni, M. Lorenc, H. Cailleau, A. Tissot, J. Laisney, M. L. Boillot, L. Stoleriu, A. Stancu, C. Enachescu, E. Collet, *Nature Materials* **2016**, 15, 606

[3] C. Enachescu, L. Stoleriu, M. Nishino, S. Miyashita, A. Stancu, M. Lorenc, R. Bertoni, H. Cailleau and E. Collet, *Phys Rev B*, **2017**, 95, 224107

# STRATEGIES TO IMPROVE THE COOPERATIVITY IN IRON(III) SPIN CROSSOVER COMPLEXES

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The construction of complex hybrid materials which combine different properties, i.e. multifunctional materials, has been at the heart of research in recent years. Among these, our interest is focused upon polymeric complexes that have the potential of featuring switching magnetic properties combined with electrical conductivity. Thus, our ultimate goal is the usage of an external electric field to control the bistability in magnetic molecules and materials. For that, we wish to pursue the fabrication of multifunctional materials using a common strategy for electrochemical synthesis of electropolymerised films with conducting polymers attached onto spin crossover cations.

As a polymerisable units, 3'-bromo-2,2':5',2"-terthiophene and aniline are particularly attractive because of their electrochemical stability and high conductivity, both properties indispensable for preparing conducting polymers.<sup>[1]</sup> As switching unit, the  $[\text{Fe}(\text{salEen})_2]^+$  was selected due to its known spin crossover (SCO) behaviour.<sup>[2]</sup> Here we report the synthesis of both ligands and iron(III) complexes that are used for materials development through electropolymerisation of both the thiophene and aniline units. The magnetic properties of both complexes and polymers are investigated.

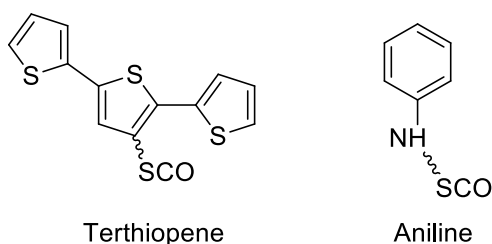


Figure 1. Electropolymerisable units.

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- 2) A. I. Vicente, A. Joseph, L. P. Ferreira, M. D. Carvalho, V. H. N. Rodrigues, M. Duttine, H. P. Diogo, M. E. M. Piedade, M. J. Calhorda, P. N. Martinho, *Chem. Sci.*, **2016**, 7, 4251

# LIESST IN A FAMILY OF ISOSTRUCTURAL FE(II) SPIN CROSSOVER COMPLEXES

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E. Collet,<sup>b</sup> and G. Chastanet<sup>c</sup>

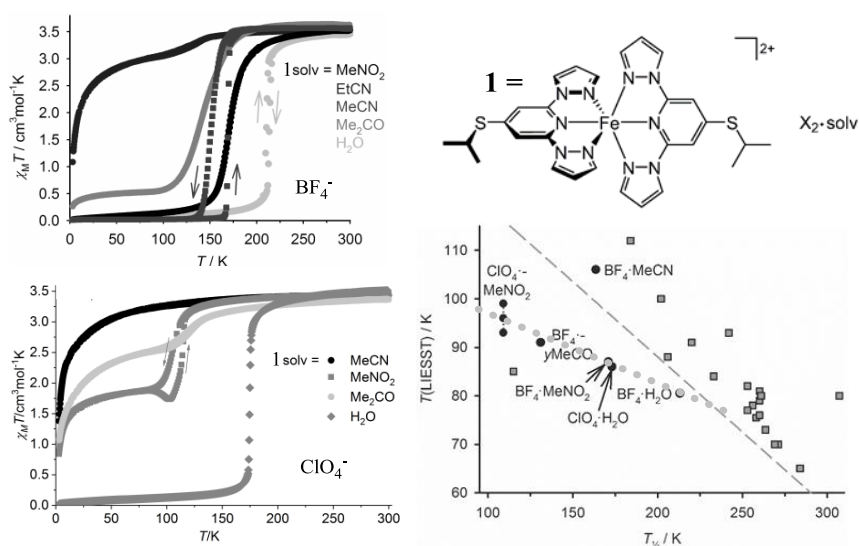
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Spin crossover (SCO) compounds at cryogenic temperatures can be excited from their low spin (LS) ground state to the metastable high spin (HS) state using light irradiation. This effect is called light induced electron spin state trapping (LIESST) and it has been known for over 30 years.<sup>(1)</sup> A family of isostructural  $1X_2 \cdot \text{solv}$  complexes has been produced exhibiting a wide range of spin state behaviors. Some compounds are HS while others undergo SCO upon cooling with different degrees of cooperativity or completeness.<sup>(2)</sup> The  $\text{ClO}_4^-$  salts in the series have lower  $T_{1/2}$  values than the corresponding  $\text{BF}_4^-$  salts while SCO cooperativity correlates with the lattice solvent. LIESST experiments conducted on SCO complexes from the family result in an excellent linear correlation between  $T_{1/2}$  vs  $T_{(\text{LIESST})}$  for five complexes. However, the most cooperative material  $1(\text{BF}_4)_2 \cdot \text{MeCN}$  has  $T_{(\text{LIESST})}$  20K higher than expected. Additional photocrystallographic studies conducted on the three of the complexes shed light on the possible explanation and will be discussed during the meeting.



## References:

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- 2) L. J. K. Cook, R. Kulmaczewski, O. Cespedes, M. A. Halcrow, *Chem. Eur. J.* **2016**, *22*, 1789
- 3) R. Kulmaczewski, G. Chastanet, E. Trzop, E. Collet and M.A. Halcrow, submitted for publication

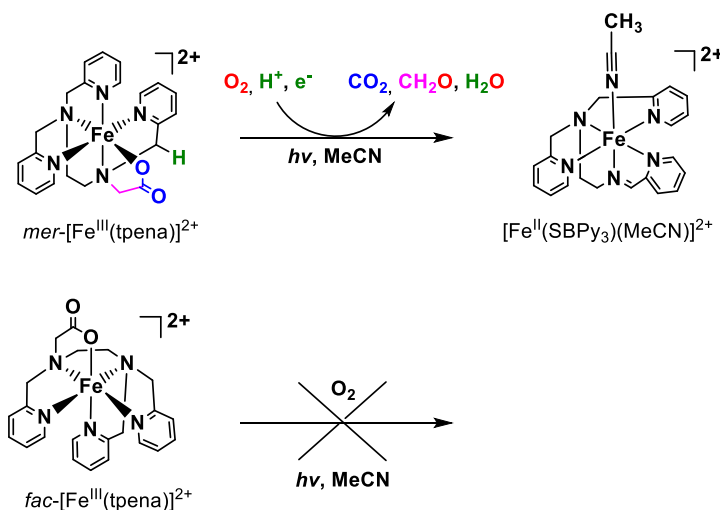


# LIGHT-INDUCED OXYGEN ACTIVATION BY A MONONUCLEAR IRON(III) COMPLEX

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The hexadentate carboxylato ligand of an iron(III) complex<sup>[1-3]</sup> undergoes decarboxylation, oxidative C-N cleavage and subsequent imine formation, when dissolved in organic solvents under ambient conditions. The imine formation is a two-step process, where the first step is light-dependent, and the second is oxygen-dependent. DFT calculations suggest that the light-initiated process occurs through the *mer*-diastereoisomer of  $[\text{Fe}(\text{tpena})]^{2+}$  to form an iron(II)-methylene complex upon carbon dioxide release, which in turn can activate oxygen to form a reactive intermediate and ultimately C-N cleavage with the release of formaldehyde to form  $[\text{Fe}(\text{SBPy}_3)(\text{MeCN})]^{2+}$ . The release of carbon dioxide and formaldehyde has experimentally been detected, and the conversion with its transient intermediates has been tracked with time-resolved UV-visible, Mössbauer, resonance Raman and EPR spectroscopy.



## References

- [1] A. Lennartson, C. J. McKenzie, *Angew. Chem. Int. Ed.* **2012**, *51*, 6767-6770.
- [2] M. S. Vad, A. Lennartson, A. Nielsen, J. Harmer, J. E. McGrady, C. Frandsen, S. Morup, C. J. McKenzie, *Chem. Commun.* **2012**, *48*, 10880-10882.
- [3] D. P. de Sousa, C. Wegeberg, M. S. Vad, S. Mørup, C. Frandsen, W. A. Donald and C. J. McKenzie, *Chem., Eur. J.* **2016**, *22*, 3810-3820

# HALOGENATED ALKYL TETRAZOLES FOR RATIONAL DESIGN OF FE(II)-SPIN CROSSOVER MATERIALS – FINE-TUNING OF THE LIGANDS SIZE

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1-(3-halogenpropyl)-1H-tetrazoles (3-X-3tz) and their corresponding Fe(II) spin crossover complexes  $[\text{Fe}(3\text{-X-3tz})_6](\text{BF}_4)_2$  (see Figure 1-left) will be presented in a combined experimental and theoretical study. The halogen substitution was found to positively influence the spin transition, up-shifting the transition temperature about 70 K towards room-temperature in comparison to their parent compound without halogen substitution (see Figure 1-right).<sup>[1]</sup> Located in the  $\omega$ -position it was shown, that the halogen is too far away from the coordinating tetrazole-moiety to have an electronic impact on the spin transition. The subtle variation of a ligands steric demand within a homologous series was found to have a comparably big impact on the spin transition behavior, highlighting the sensitivity of the effect.

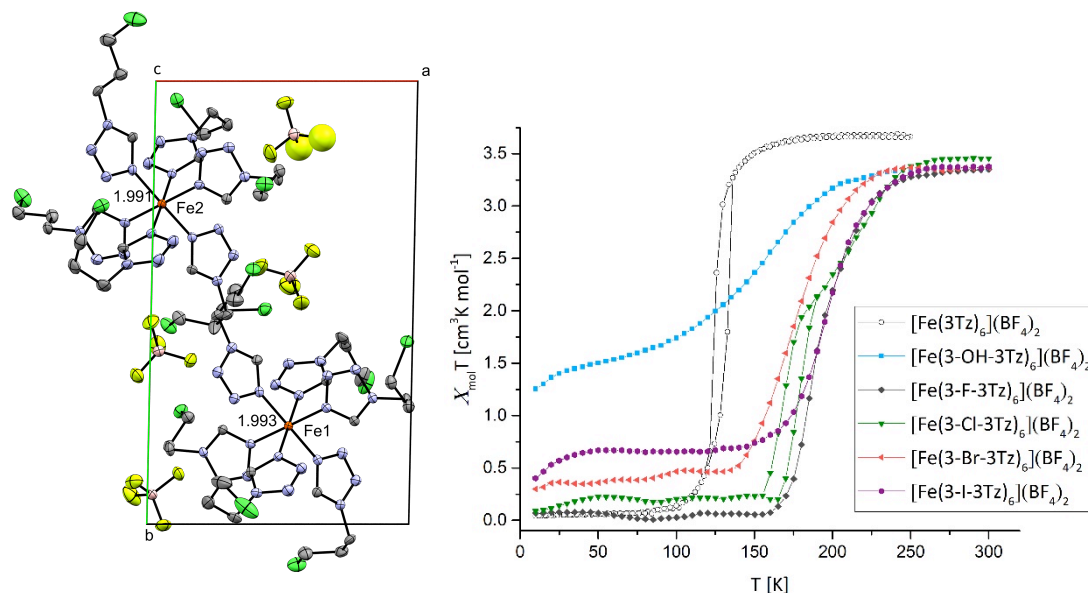


Figure 1: Crystal structure of LS  $[\text{Fe}(3\text{-Cl-3tz})_6](\text{BF}_4)_2$  (left) and a comparison of the SCO behavior of the 3-halo-complexes with the parent compound  $[\text{Fe}(3\text{tz})_6](\text{BF}_4)_2$ <sup>[2]</sup>

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# MODULATION OF A WEAKLY COUPLED PEROXO-DICOPPER(II) COMPLEX BY INTERACTION WITH ALKALI METAL IONS

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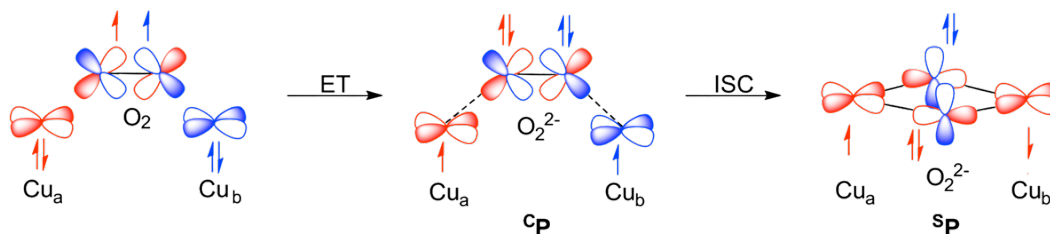
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The dicopper center is the active site of many type III Cu proteins, which play an important role in the transport and activation of oxygen in many biological systems. Among all the different species that occur upon O<sub>2</sub> binding in these metalloproteins, the <sup>sP</sup> motif is the most commonly detectable one. In this work we investigated through DFT calculation the synthetic, fully characterized Cu<sup>II</sup><sub>2</sub>(μ-η<sup>1</sup>:η<sup>1</sup>-O<sub>2</sub>) complex, featuring an unusual cis-peroxo binding (<sup>cP</sup>) and weak antiferromagnetic coupling,<sup>[1]</sup> comparable with that of a theoretically predicted transition state for O<sub>2</sub> binding to T3Cu centers,<sup>[2,3]</sup>. Conjoined UV/vis spectroscopy and computational studies allowed us to demonstrate how the electronic structure of the complex can be tuned by introducing different alkali metal ions (namely Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>) which interact with the peroxo moiety. Furthermore, the binding of diverse alkali cations was also found to modulate the magnitude of the antiferromagnetic coupling, by modifying the extent of overlap in copper and oxygen centered orbitals through variations in (i) coordination environments of the Cu(II) ions and (ii) Cu-O-O-Cu torsion angle.

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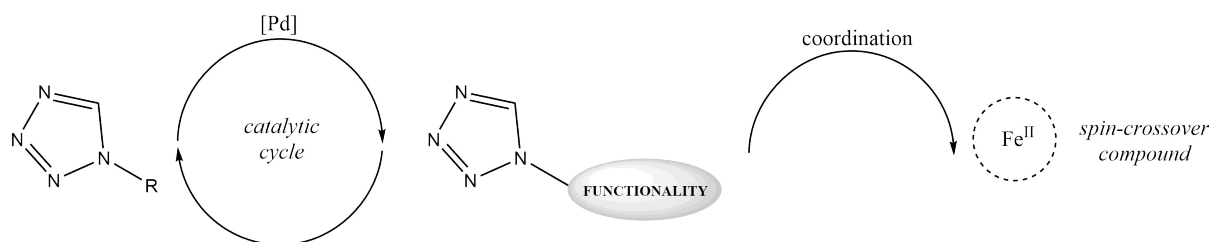


# FUNCTIONALIZATION OF N-SUBSTITUTED 1H-TETRAZOLES – TOWARDS AN EASY LIBRARY SYNTHESIS

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Substituted tetrazoles are mainly known for their applicability as carboxylic acid bioisosteres in drug design and as ligands for spin crossover complexes. The substitution pattern is commonly introduced by using an appropriate substituted precursor, namely the primary amine or isonitrile, for the ring formation, instead by a subsequent post-functionalization after tetrazole synthesis. In this context, the biggest hindrance regarding a bigger variety of substitution patterns is the limited availability or often tedious synthetic preparation of the necessary precursor. Therefore, we focused on possible post-functionalization procedures based on cross-coupling protocols to introduce functionality after ring closure. Frequently used coupling reactions, such as Suzuki<sup>[1]</sup>, Heck and Sonogashira, were adapted to work on corresponding tetrazole derivatives and were used to produce a variety of ligands with different functionalities and substitutional patterns. This drastically helps to systematically investigate the influence of substitution effects on the spin crossover behaviour of the respective iron(II) spin crossover compounds.



1) M. Seifried, et al., *Eur. J. Org. Chem.* **2017**, 17, 2416-2424

# THEORETICAL STUDIES OF DINUCLEAR COPPER CENTERS

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Dinuclear copper active sites are common feature in enzymes. In this communication, two theoretical studies in relation with Cu<sub>2</sub>-containing monooxygenases are presented.

The first concerns mixed-valence species Cu<sub>2</sub>O<sub>2</sub>(II,III) which are proposed as key intermediates in C-H activation for particulate methane monooxygenase. From a serie of phenoxo- and hydroxo-bridged dicopper(II) model complexes, calibration of DFT calculations for the first oxidation potential will be described.<sup>[1]</sup> The good agreement between experimental and theoretical results allows us in the following to use the developed protocol to design and characterize new dinuclear complexes.

The second involves interaction between an inhibitor, the kojic acid, and a bacterial tyrosinase. QM/MM calculations which confirm and refine a proposed binding mode by-spectroscopy will be described.<sup>[2]</sup>

These two theoretical studies, one on biomimetic complexes, the second on a whole enzyme, highlights our approaches to study such systems.

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# COPPER CATALYSTS AND STRUCTURAL DISORDER

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The catalytic properties of transition metal ions and metal/metal oxide surfaces are influenced by the presence of structural disorder. In a first approximation, an efficient catalysis occurs when the sites can easily host more oxidation states around a resting one. On the other hand, a preference for a given oxidation state prevents the cycling of oxidation states and electron shuttling via the site, hindering the catalysis.

We show how combining different models, it is possible to understand if ligand distortions or defect in surfaces shift a system from reactive to silent states.

One example is the activation of dioxygen by complexes of Cu with b-amyloid disordered peptides, favoring cell oxidation in neurodegeneration.<sup>[1]</sup> A second example is the hindering of proton reduction by Cu electrodes, favoring CO<sub>2</sub> reduction from water solution.<sup>[2]</sup>

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# HARNESSING THE SPIN CROSSOVER PHENOMENON: A STUDY ON THE ANION AND HALOGEN EFFECTS

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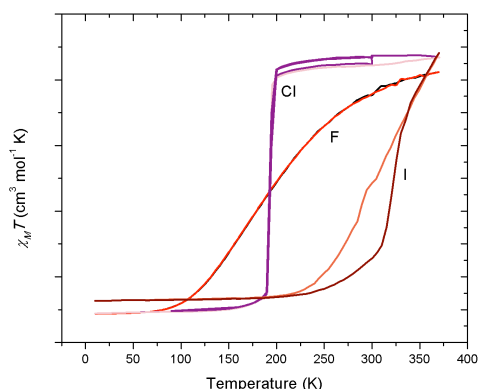
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Technological advances have been pushing the limits of chemistry for the last few years towards creating more efficient and multifunctional molecules and materials. A phenomenon that shows great promise in molecular electronics is spin crossover (SCO).<sup>[1]</sup> This switching can be harnessed to develop materials with a wide range of possible applications such as memory or sensing nano-devices.<sup>[2]</sup> Halogen derivatised SCO molecules are of great interest as they can interact with neighbouring molecules through either halogen or hydrogen bonds and additionally they can be modified through substitution or coupling reactions conferring additional properties and high versatility to the SCO molecules.<sup>[3,4]</sup>

Here we report the synthesis and characterisation of halogen derivatised SCO compounds with an Fe(III) metallic centre coordinated to tridentate (N<sub>2</sub>O) Schiff-base ligands and several tetrahedral anions (ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>). We have found that all compounds exhibit SCO with profiles ranging from gradual to abrupt with hysteresis. DFT calculations using spin state specific functionals are used to further understand the halogen and anion influences on these profiles.



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# THE REACTIVITY OF THE $\alpha$ -O IN FE-ZEOLITES: A MULTIREFERENCE APPROACH.

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Heme and non-heme iron enzymes ability to activate inert C-H bonds at ambient temperatures has inspired men to mimic this reactivity by making model complexes.<sup>[1]</sup> However, most of these model complexes have a reactivity that is much lower compared to the reactivity of real enzymes. An exception to this are Fe-containing zeolites, such as Fe-\*BEA and Fe-ZSM-5. These zeolites are able to oxidize methane to methanol stoichiometrically after activation with N<sub>2</sub>O.<sup>[2]</sup> Only recently, the structure of the reactive intermediates in these zeolites has been elucidated using VTVH-MCD spectroscopy and quantum chemical calculations.<sup>[3]</sup> The reactive species, called  $\alpha$ -O, is a high spin square pyramidal Fe(IV)=O moiety.

In this work the reactivity of the  $\alpha$ -O core is investigated using multireference ab initio calculations (CASSCF/CASPT2). The calculations identified two low lying, thermally accessible <sup>5</sup>E excited states. Analysis of the CASSCF wave function shows that the oxyl character in these <sup>5</sup>E states is much higher than in the <sup>5</sup>A ground state. In the literature it is proposed that oxyl character of Fe(IV)=O is related to its reactivity in hydrogen atom transfer (HAT) <sup>[4,5]</sup>, this indicates that the <sup>5</sup>E states are more reactive than the ground state. The remarkable reactivity of  $\alpha$ -O in methane hydroxylation may be explained by the involvement of low lying excited states. These findings may guide scientist in the synthesis of new reactive catalyst for C-H bond activation.

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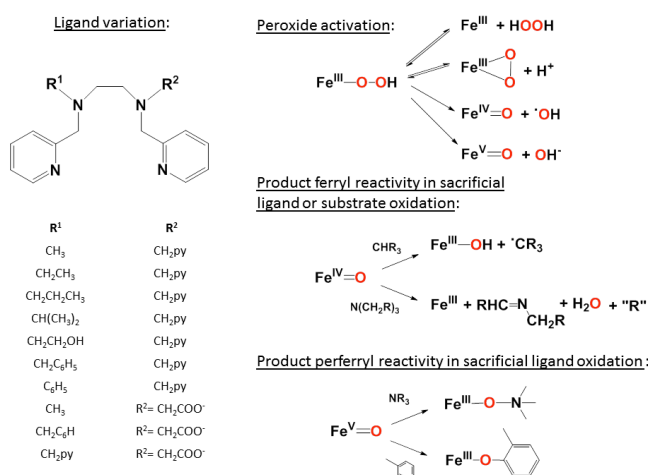


# TUNING PEROXIDE ACTIVATION BY NON-HEME COMPLEXES

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Ethylenediamine-backed penta- and hexa-dentate aminopyridyl ligands have been useful for accessing biomimetic non-heme iron<sup>[1-7]</sup> manganese<sup>[8]</sup> and chromium<sup>[9]</sup> complexes that can activate peroxides (and other terminal oxidants<sup>[10]</sup>). Little by little trends have emerged in the stability and reactivity of the Fe(III)peroxide adducts. Whether or not activation results in homolytic or heterolytic FeO-OH cleavage depends on the particular supporting ligand system. These reactions produce powerful iron-based oxidants whose reactivity can be directed towards the supporting ligand or substrates.



The supporting ligand matters: Pendant arm variations influence the extent to which a co-ligand hydroperoxido in iron complexes is activated. In turn, product high valent iron-oxo complexes can participate in HAT and OAT chemistry.

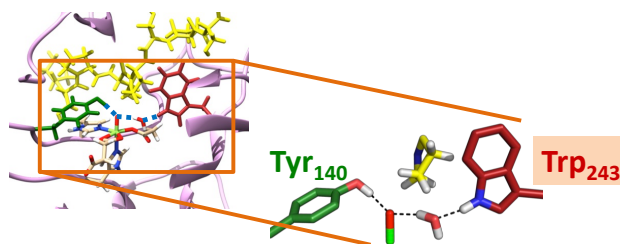
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# WHAT IS THE ORIGIN OF THE REGIO- AND STEREOSELECTIVITY OF NONHEME IRON ENZYMES? A COMPUTATIONAL STUDY.

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Nonheme iron enzymes catalyze a range of vital reactions for human health, including the biosynthesis of hydroxyproline, the catabolism of cysteine as well as DNA repair mechanisms.<sup>[1]</sup> There are many facets to the catalytic reaction mechanism of these enzymes that are still elusive, which is partially due to their high reactivity but also as a result of multiple spin states interfering into the reaction mechanism. In this presentation, I will give an overview of recent quantum mechanics/molecular mechanics and density functional theory studies of our group on the mechanism and function of a nonheme iron hydroxylase (prolyl-4-hydroxylase)<sup>[2]</sup> and a nonheme iron halogenase (hectochlorin biosynthesis protein).<sup>[3]</sup> Both enzymes contain a nonheme iron active center that is bound to the protein through interactions with two histidine side chains and in addition have an anionic ligand: aspartate in the hydroxylases and halide in the halogenases. Using  $\alpha$ -ketolutarate and molecular oxygen both enzymes react to form a high-valent iron(IV)-oxo species, which is the active oxidant. In both enzymes the catalyst triggers a regio- and stereospecific reaction mechanism and the calculations were focused on understanding the reactivity patterns. We performed detailed computational studies on the mechanisms leading to products and by-products for wildtype as well as mutants. The work highlights the importance of the secondary structure of the protein to guide the regio- and stereospecific product formation through proper substrate positioning but also through electrostatic interactions.



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# DFT STUDY OF CO<sub>2</sub> ACTIVATION PROMOTED BY A CLASS OF THIOLATE-BRIDGED DI-IRON COMPLEXES WITH A [Cp\*Fe(μ-SR)<sub>2</sub>FeCp\*] SCAFFOLD.

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Thiolate-bridged diiron clusters have been widely synthesized and structurally determined especially in the form of Fe<sub>2</sub>S<sub>2</sub> clusters, due to their close similarity to hydrogenase active site.<sup>[1]</sup> Only in recent years the idea of using such Fe<sub>2</sub>S<sub>2</sub> systems as nitrogenases functional analogues has taken root. Indeed, diiron sulfide/thiolate compounds are also suitable candidates to replicate the minimal functional subunit of Mo(V)-nitrogenase active site, the so called FeMo(V)-co.<sup>[2]</sup> In this context, a class of systems with a common [Cp\*Fe<sup>II</sup>(μ-SR)<sub>2</sub>Fe<sup>II</sup>Cp\*] (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) scaffold has proved to possess excellent catalytic activity towards N-N bond reductive cleavage of nitrogenase-relevant substrates, such as hydrazine and derivatives.<sup>[3][4][5]</sup> Additional interest in these bioinspired systems stems from the fact that nitrogenases are promiscuous enzymes, having the remarkable property of catalyzing the reduction of a series of substrates beside N<sub>2</sub>, such as protons (to form H<sub>2</sub>) and unsaturated hydrocarbons/CO (to form alkanes).<sup>[6]</sup> The most fascinating “alternative” reducing reactivity is certainly that exerted towards CO<sub>2</sub>, the more abundant greenhouse gas. In this scenario, it would be a fascinating and promising strategy to assess the proposed FeMo(V)-co analogues towards CO<sub>2</sub> activation and conversion, especially in light of the recent progresses in the field of noble-metal-free CO<sub>2</sub> homogeneous reduction.<sup>[7][8]</sup> Thus, the present work aims to understand if, at least in principle, a CO<sub>2</sub> reduction reactivity could be retained or exhibited by biomimetic Fe<sub>2</sub>S<sub>2</sub> systems, such as various [Cp\*Fe<sup>II</sup>(μ-SR)<sub>2</sub>Fe<sup>II</sup>Cp\*] complexes. DFT has been used in order to study in detail CO<sub>2</sub> binding modes and affinity to these systems, with the aim of highlighting the role that this class of complexes plays in CO<sub>2</sub> activation. Additionally, theoretical studies regarding putative electrochemical/chemical reductive applications will be also proposed.

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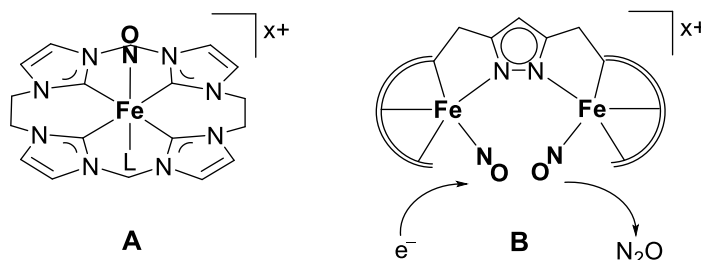
# BIOINSPIRED MONO- AND DINUCLEAR IRON/NO COMPLEXES: ELECTRONIC STRUCTURE CONTRIBUTIONS TO REACTIVITY

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The interaction of NO with Fe-containing metalloenzyme active sites and conversion of NO by such metalloenzymes of both, the heme and non-heme types, have important roles in biochemistry. Unravelling the electronic structures of key iron nitrosyl and nitroxyl intermediates, which form during those processes, provides fundamental insight that contributes to our understanding of the mechanisms of biological NO transformations. In this short presentation, recent results from one or both of the following projects will be briefly discussed:

- (i) the stabilization of a series of Fe/NO intermediates that are topologically related to heme/NO systems, but with macrocyclic N-heterocyclic carbene scaffolds imparting unusual electronic structures to the key reactive species (**A**);<sup>[2]</sup>
- (ii) structure-activity correlations for reductive coupling of NO to give N<sub>2</sub>O, using pyrazolate-based model systems with two adjacent {FeNO}<sup>7</sup> units (**B**) akin to flavodiiron nitric oxide reductases (FNORs), and comparison with recently reported phenolate-based FNOR model systems.<sup>[4]</sup>



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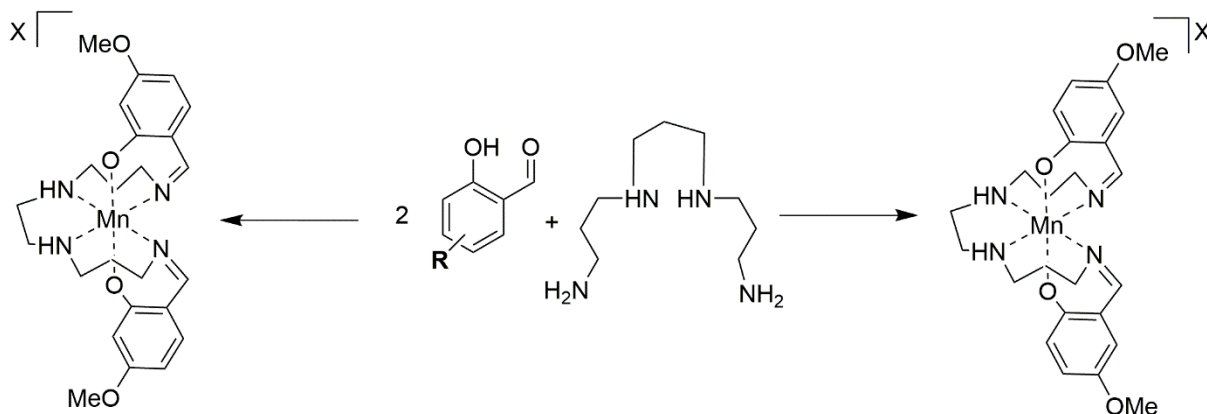
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# INVESTIGATION ON LIGAND SUBSTITUENT EFFECTS ON MN(III) CHELATES

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The phenomenon of spin crossover in metal complexes is known since the early 1930s,<sup>[1]</sup> and has since then attracted a lot of interest. Through their possible hysteretic effects, potential applications of these molecules include their use as molecular switches in data storage and in displays.<sup>[2-4]</sup> At low temperatures, it is energetically favorable for spin crossover compounds to be in a low spin state, and by application of an external stimulus, such as heat, light, pressure or applied magnetic field,<sup>[5,6]</sup> it is possible for the spins to occupy the energetically higher orbitals, resulting in a high-spin state of the molecule. We have synthesized different coordination Mn(III) complexes based 4-Methoxy- vs. 5-Methoxy-salicylaldehyde Schiff base ligands (see Figure) and have investigated their different magnetic behavior based on the position of the methoxy group. We have synthesized two families of complexes containing the same cationic metal complex, but with different counterions to understand this additional influence.



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# EFFECT OF COORDINATED RADICAL LIGANDS ON THE RATE OF SPIN CROSSOVER PROCESSES IN IRON(II) COMPLEXES

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Spin crossover (SCO) processes are entropy-driven redistributions of electrons among the d-orbitals of metal ions induced by a change in temperature or pressure or by light irradiation. The most intensively studied SCO complexes contain iron(II) ions. Among the various physical methods to study the SCO transition in these complexes, especially Mössbauer spectroscopy is a very valuable tool. SCO processes of iron(II) complexes below 250 K are generally slower than the time scale of the Mössbauer experiment.

We are interested in SCO complexes in which the metal ion is coordinated to radical ligands.<sup>[1]</sup> As part of this study we prepared iron(II) complexes containing the tetradentate N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane and radical anions of N,N'-diphenyl-acenaphthene-1,2-diimine derivatives as ligands. Characterization of the resulting octahedral iron(II) radical complexes by structural (Fig. 1a), magnetochemical and spectroscopic methods reveal that spin crossover equilibria occur between an  $S = 1/2$  ground state and an  $S = 3/2$  excited spin state. Using Mössbauer spectroscopy (Fig. 1b) it can be shown that the spin interconversion rate at the iron(II) site is considerably enhanced by the presence of a coordinated radical.

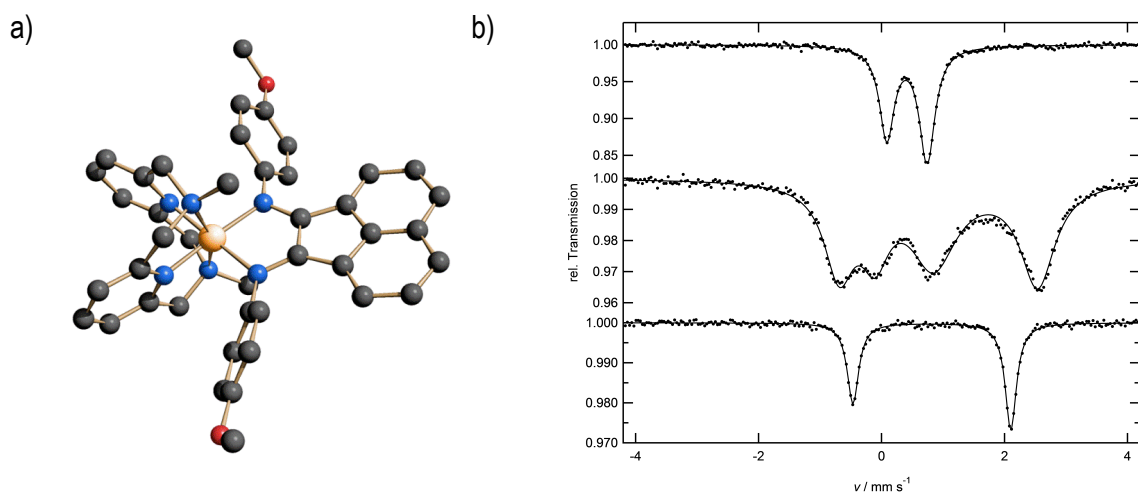


Figure 1: a) Perspective view of the complex cation in the SCO iron(II) radical complex; b) Mössbauer spectra at different temperatures.

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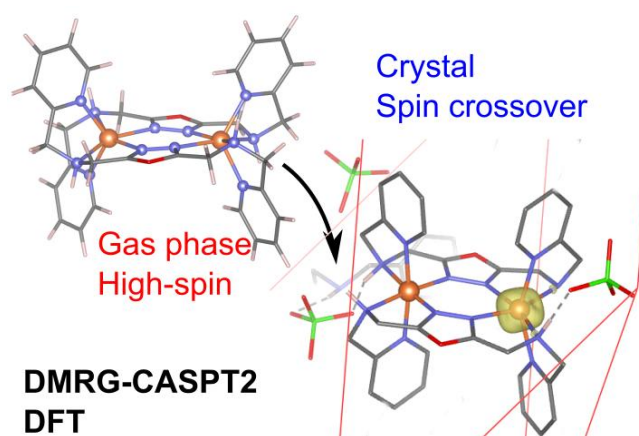
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# DINUCLEAR IRON(II) SPIN CROSSOVER COMPOUNDS: A THEORETICAL STUDY

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In this work, we present a theoretical study of structures and spin state energetics of two novel spin crossover di-iron(II) complexes based on thiadiazole and oxadiazole ligands,<sup>[1,2]</sup> using second-order perturbation theory based on density matrix renormalization group (DMRG-CASPT2)<sup>[3-6]</sup> and density functional theory (DFT). We showed that in order to correctly predict the spin crossover behavior of the complexes, different contributions to the gas-phase relative energy  $\Delta E_{\text{gas-phase}}$  must be taken into account. We illustrated that the contribution from crystal-stabilization energy ( $\epsilon = \Delta E_{\text{crystal}} - \Delta E_{\text{gas-phase}}$ ), which is usually neglected in theoretical works, is extremely important. This work also demonstrates that DMRG-based techniques are mature and have great potential for studying spin state energetics of multinuclear transition metal complexes.



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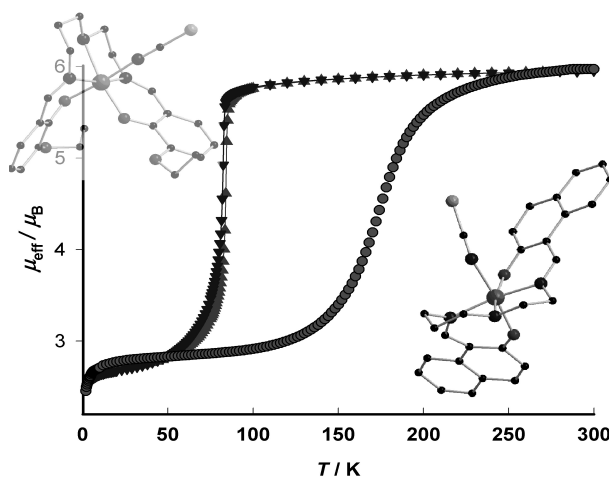
# IRON(III) COMPLEXES WITH PENTADENTAD SCHIFF BASE – STRUCTURAL AND MAGNETIC INVESTIGATION

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The pentadentate  $N_3O_2$ -donor ligands prepared from aliphatic triamines and aromatic aldehydes or ketones present outstanding family of Schiff bases capable to coordinate ferric salts and to form mononuclear complexes of  $[Fe(L^5)Cl]$  type. In the next step, weakly bonded chlorido ligand allows preparation of modified complexes either with terminal or with bridging N-donor moieties. In the line with such strategy of synthesis, we report the series of iron(III) complexes in which the ligand field was tuned by chlorido or pseudohalido terminal ligands. Depending on the length and symmetry of aliphatic part, ferric central atoms exhibit either permanent high spin behavior or show thermally induced spin crossover.

Magnetic anisotropy was compared with the degree of angular distortion of corresponding coordination polyhedra and obtained results were confronted with computational calculations. Magnetic anisotropy was investigated by several experimental techniques and obtained D parameters were confronted with the degree of angular distortion of corresponding coordination polyhedra. Spin crossover investigation was focused on the detection of thermal hysteresis and on the reflection of structural changes arisen upon the low spin – high spin transformation



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# PROGRESS IN UNDERSTANDING DINITROGEN PHOTOCLEAVAGE

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The identification of homogeneous catalysts for the fixation of dinitrogen has been a long-standing target in inorganic chemistry. While it is unclear whether homogeneous catalysts that produce ammonia from N<sub>2</sub> will ever become economically competitive with the Haber-Bosch process, such catalysts will open up new synthetic routes for the incorporation of N-atoms derived from dinitrogen into industrially relevant chemicals that are not sourced from fossil resources.

A less well explored alternative to thermal nitrogen fixation with homogeneous catalysts is the photochemical cleavage of dinitrogen, which has been established with several synthetic catalysts featuring linear metal-nitrogen-nitrogen-metal cores.<sup>[1]</sup> The photocleavage of dinitrogen is a particularly attractive as sunlight energy is used to cleave the strong dinitrogen bond and stored in the metal-nitrogen bonds that are formed during this process. In some cases, the splitting of the nitrogen-nitrogen bond upon irradiation with light from the solar spectrum competes with the scission of the metal-nitrogen bond. However, the precise photochemical and photophysical processes that induce either process are poorly understood, hampering the systematic improvement of these catalysts.

A quantum chemical analysis of the electronic structures of dinitrogen photocleavage catalysts and the bond cleavage processes will help in designing improved catalysts. We present our progress in describing and understanding dinitrogen photocleavage with complexes containing osmium and molybdenum cations using density functional theory as well as multireference methods (CASSCF, CASPT2, DMRG).<sup>[2]</sup> We evaluate similarities and differences between different dinitrogen photocleavage catalysts and discuss the implications for possible pathways towards the improvement of their efficiencies.

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# TRANSIENT FORMATION AND REACTIVITY OF A HIGH-VALENT NICKEL(IV) OXIDO COMPLEX

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Recent attention has been turned on synthetic nickel-based complexes due to both enzymes such as NOD (nickel oxide dismutase)<sup>[1]</sup> and their potential in the activation of small molecules, including H<sub>2</sub>O<sub>2</sub>.<sup>[2]</sup>

A reactive high-valent dinuclear nickel(IV) oxido bridged complex is reported that can be formed at room temperature by reaction of [(L)<sub>2</sub>Ni(II)<sub>2</sub>(μ-X)<sub>3</sub>]X (X = Cl or Br) with NaOCl in methanol or acetonitrile (where L = 1,4,7-trimethyl-1,4,7-triazacyclononane).<sup>[3]</sup> The unusual Ni(IV) oxidospecies is stabilized within a dinuclear tris-μ-oxido-bridged structure as [(L)<sub>2</sub>Ni(IV)<sub>2</sub>(μ-O)<sub>3</sub>]<sup>2+</sup>. Its structure and its reactivity with organic substrates are demonstrated through a combination of UV-vis absorption, resonance Raman, <sup>1</sup>H NMR, EPR, and Xray absorption (near-edge) spectroscopy, ESI mass spectrometry, and DFT methods. The identification of a Ni(IV)-O species opens opportunities to control the reactivity of NaOCl for selective oxidations.

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# REDOX POTENTIAL-BASICITY RELATIONSHIP OF COMPOUND II OF HEME ENZYMES: A QM/MM STUDY

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The heme group is probably the most important prosthetic group in nature that is central to the oxygen management of aerobic organisms.<sup>[1]</sup> The nature of the axial ligand of iron greatly influences the properties of the heme centre: cysteine-ligated cytochrome P450 enzymes have the remarkable ability to directly oxidize strong C–H bonds via hydrogen atom transfer mechanisms, while histidine-ligated peroxidases primarily act upon phenol-like substrates following proton-coupled electron transfer reaction mechanisms. Interestingly, compound I, (cpd-I, an iron(IV)–oxo porphyrin radical cation) and its one electron reduced form cpd II, are central to the catalytic activity of both groups of enzymes. The  $pK_a$  value of cpd-II of P450 enzymes is about 12<sup>[2]</sup> in contrast to the value of 3-5 reported for histidine-ligated enzymes.

We investigated the basicity and redox potential relationships of heme enzymes by performing MD simulations and QM/MM calculations on three thiolate-ligated (P450119, P450158A2, and an aromatic peroxygenase) and two histidine-ligated (horseradish and lignin peroxidases) enzymes. We calculated protonation energies and electron affinities and also determined the  $pK_a$  of Fe=O functionality and the reduction potential of the active site. We found that a high cpd-II basicity is always coupled to a suppressed redox potential and we offer intuitive support for the notion that P450 enzymes avoid non-productive PCET reactions by shifting their active site properties to a low-redox-potential – high  $pK_a$  regime. By plotting density difference distributions for vertical electron attachment processes we revealed two conceptually distinct redox scenarios; namely, the reduction is sulphur-based in cysteine ligated enzymes while porphyrin-based in the case of histidine-ligated proteins.

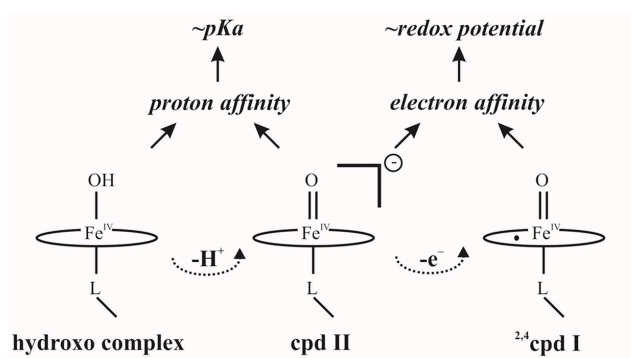


Fig.1. Relationship among the hydroxo complex, Cpd-II, and quartet/doublet Cpd-I of heme enzymes. The ellipse indicates the porphyrin ring and L can be either a Cys or a His residue.

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# AB INITIO LIGAND FIELD MOLECULAR MECHANICS FOR IRON(II) BIS-PYRAZOLYLPYRIDINE SPIN CROSSOVER COMPLEXES

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Parameterisation is a perennial problem in force field design. For ligand field molecular mechanics (LFMM)[1], it is especially challenging. On the one hand, the angular overlap model (AOM) d-electron energy term is crucial to LFMM's success while, on the other, the AOM requires additional parameters.[2] These are normally derived by fitting to experiment. However, in many cases, the data are either not available or not of sufficient resolution. In addition, there may be more than one set of AOM parameter values capable of reproducing the same d-orbital energy levels. A remedy for these issues is illustrated here for the spin-crossover (SCO) complex  $[\text{Fe}(\text{bpp})_2]^{2+}$  (bpp = 2,6-di(pyrazol-1-yl)pyridine). There are not enough experimental data to fit all the AOM parameters so instead, we use a complete set of theoretical d-orbital energies computed using ab initio ligand field theory based on CASSCF/NEVPT2 wavefunction theory.[3] Two reasonable AOM parameter sets emerge and the ambiguity is resolved by using the LFMM to compute the sense of Jahn-Teller distortion for the high spin case. This refined 'ab initio' LFMM approach can then be used to model the effects of  $[\text{BF}_4]^-$  or  $[\text{PF}_6]^-$  counter ions, plus the spin state energetics for 3-pyrazolyl substituents, where the interactions are mainly steric, and for 4-pyridyl or 4-pyrazolyl substituents, where there is an electrostatic effect plus a dominant electronic effect. Overall, the LFMM performs very well but the electronic effects particularly of 4-pyridyl substituents is not captured fully. Potential future developments to resolve this issue will be outlined.

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# Posters

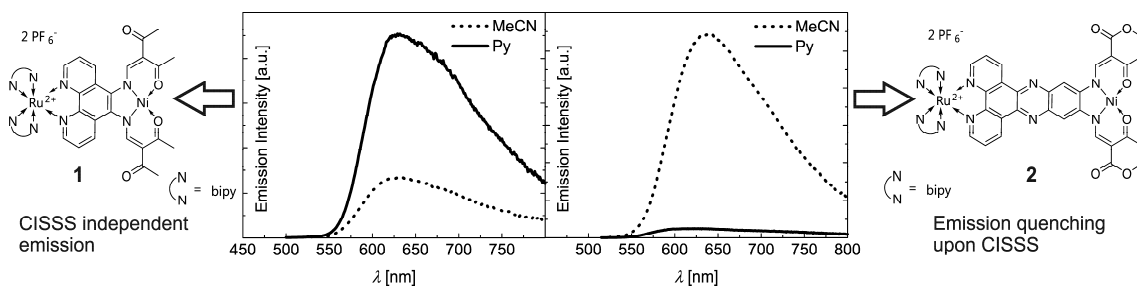
# SYNTHESIS AND OPTICAL PROPERTIES OF PHENANTHROLINE-DERIVED SCHIFF BASE-LIKE DINUCLEAR RU(II)-NI(II) COMPLEXES

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Nowadays, there is a high demand for multifunctional switchable materials, which feature on the one hand responsive behaviour to chemical or physical stimuli and on the other hand read out possibilities. Molecules that can change their spin state upon external stimuli are interesting for this approach. Two well-known phenomena, which include a spin state change, are spin crossover (SCO) and coordination induced spin state switching (CISS). CISS denotes the phenomenon that complexes are responsive to coordinating guest molecules.<sup>[1]</sup> The coupling of CISS with the read out possibility photoluminescence offers great application potential in the field of bio-sensors.<sup>[2]</sup> Therefore, both features can be combined in one molecule by covalently linking of a photoluminescent unit to the molecular switch.<sup>[3]</sup>

Here we present two new ligand systems in which a phosphorescent Ru(II) unit is linked covalently over a bridging unit to a Schiff base-like ligand system. Two dinuclear Ni(II)-Ru(II) complexes were synthesised to investigate the influence of the spin state of Ni(II) on the photophysical properties. Upon addition of the coordinating solvent pyridine to an acetonitrile solution, both Ni(II) complexes showed a CISS. It was demonstrated that the photophysical behaviour is strongly influenced by the nature of the bridging ligand. The photophysical properties of the Ni(II) complex **1** is independent on the CISS. The crystal motif of **1** revealed that the Ni(II) metal centre is not included in the  $\pi$ -system of the Ru(II) unit due to bending of the molecule. In contrast, a photoluminescence quenching upon CISS was observed for the Ni(II) complex **2**.<sup>[4]</sup>



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# SYNTHESIS, CHARACTERIZATION AND ULTRASOUND-ASSISTED DELAMINATION OF TWO 2-D CADMIUM-BASED COORDINATION POLYMERS

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Synthesis, characterization and exfoliation of 2D coordination polymers having cadmium as metallic center were investigated. Ultrathin nanoflakes and thin films were obtained by optimization of liquid phase exfoliation in different solvents, assisted by ultrasound. Results on the exfoliation of the two different complexes synthesized proved the need of weak bonds with the entrapped solvent molecules and robust structure in the layers in order to succeed in exfoliation.

Physical and chemical characterization of the exfoliated flakes and films was provided. Results on the characterization suggested larger exfoliation yields using an ultrasound bath as ultrasound source than a probe tip. Besides, differences on the morphology of flakes obtained with different solvents were investigated.

# TOWARDS THE OXIDATIVE DEGRADATION OF GRAPHENE USING BIOMIMETIC IRON COMPLEXES

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Graphene has been cited as the next 'wonder material' and possesses excellent thermal and electronic conductivity, high tensile strength, and is extremely light and flexible. Despite this, it is both hard to produce en masse and does not disperse easily in polar solvents. Altering the structure of graphene via functionalisation overcomes some of these problems and enables the use of graphene in transistors, biosensors, inkjet printing, and many other applications.<sup>[1]</sup> However, the possible industrial use of graphene in future raises the question of how it will interact with, and could be broken down by, bacterial enzymes when released in the environment.<sup>[2]</sup>

To this end, we investigated the reactivity of some biomimetic Fe catalysts towards dispersed few-layer graphene and graphene oxide, using hydrogen peroxide as an oxidant. The complexes<sup>[3,4]</sup> used in this study were initially developed by Que's group to mimic Rieske dioxygenases,<sup>[5]</sup> which are known to be capable of breaking down aromatic compounds in bacteria via a  $\text{Fe}^{\text{V}}(\text{O})(\text{OH})$  oxidant. Viewing graphene as an extended polyaromatic system, these catalysts should hold the potential to catalytically functionalise or degrade graphene and other carbon nanomaterials as well.

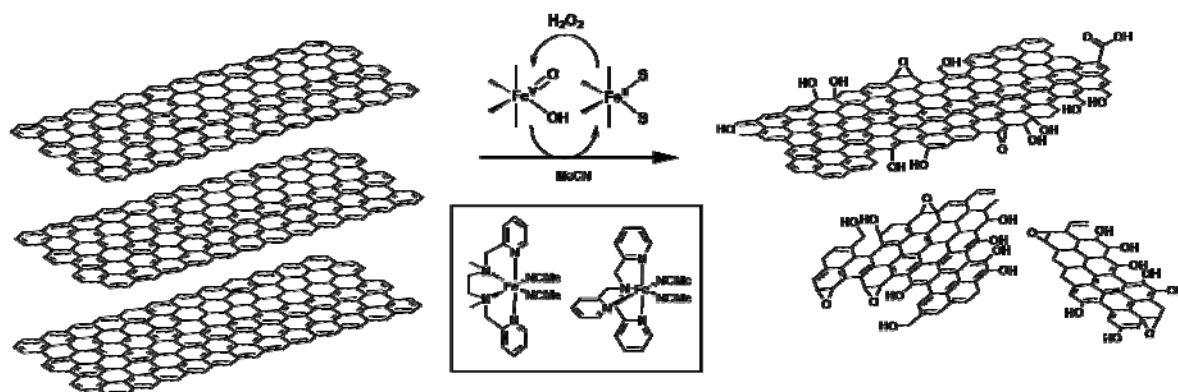


Figure: Postulated oxidation of graphene by  $\text{H}_2\text{O}_2$ ,  $[\text{Fe}^{\text{II}}(\text{BPMEN})(\text{MeCN})_2]^{2+}$  and  $[\text{Fe}^{\text{II}}(\text{TPA})(\text{MeCN})_2]^{2+}$ .<sup>[6]</sup>

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# COUPLED CLUSTER AND CASPT2 CALCULATIONS ON NON-HEME IRON COMPLEXES

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Heme and nonheme mononuclear iron oxygenases and their synthetic analogues are known to perform a wide range of catalytic oxidative transformations in chemistry and biochemistry.<sup>[1]</sup> The most typical reaction is the C-H hydroxylation which has been proposed to be performed by an iron-oxo Fe<sup>IV</sup>O active intermediate. The rate limiting step in these reactions was found to be the hydrogen atom abstraction process. These systems are also known for their two-state reactivity. The triplet state is the ground state, but the quintet state is a low lying state. The transition state on the quintet surface has a lower barrier and modulates the reaction.

However, these systems can show some multireference character. Therefore, we compared canonical coupled cluster calculations with multireference DMRG-CASPT2 calculations with large active space. It has been seen earlier that if one uses Kohn-Sham orbitals in coupled cluster calculations the T1 diagnostic shows smaller multireference character.<sup>[2]</sup> Thus, we investigated the influence of chosen orbitals on coupled cluster results. Restricted and unrestricted Hartree-Fock and Kohn-Sham orbitals have been tested, but also natural and pseudo-canonical CASSCF orbitals.

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# INVESTIGATING THE STRUCTURE OF *C. ELEGANS* MANGANESE SUPEROXIDE DISMUTASES BY X-RAY CRYSTALLOGRAPHY AND MOLECULAR DYNAMICS SIMULATIONS

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Superoxide dismutases (SODs) act as the first line of defense against reactive oxygen species (ROS), by dismutating superoxide into hydrogen peroxide and molecular oxygen. The catalytic mechanism of SOD is complex to decipher. Therefore, reverse engineering was performed to generate a *C. elegans* H30 mutant, in order to investigate its structure and understand small structural differences in MnSOD-3 that may have pronounced effects on catalysis.

Optimal crystallization conditions were determined at the University of Malta and the structures of native MnSOD-3 and a H30 mutant were solved to 1.77 and 1.52Å, respectively via X-ray crystallography performed at the Diamond Synchrotron Light Source, Oxfordshire, UK. The structure of the H30 mutant revealed changes in active site geometry, since the latter was observed to change from the penta-coordinated geometry usually observed in MnSOD proteins, to hexa-coordinated geometry. Such changes in the active site of the mutant, potentially affect the functionality of this mutant enzyme. Results from metal analysis of the mutant protein also revealed the spontaneous uptake of Fe in addition to Mn, which is the natural cofactor of the native SOD. The structures of the native and mutant proteins determined by X-ray crystallography were subsequently used as a starting point for molecular dynamics (MD) simulations to study structural properties which cannot be elucidated via X-ray crystallography. Molecular dynamics simulations of the MnSOD-3 His30 mutant were performed using the Amber 16 package at various temperatures, using the 12-6-4 LJ-type non-bonded model AMBER force field, which includes parameters for Mn and Fe in the 2+ state. Post-processing and analysis were carried out using VMD<sup>1</sup>. Trajectory analysis performed in the H30 mutant revealed differences in the binding modes of particular inner-sphere residues in the protein being investigated.

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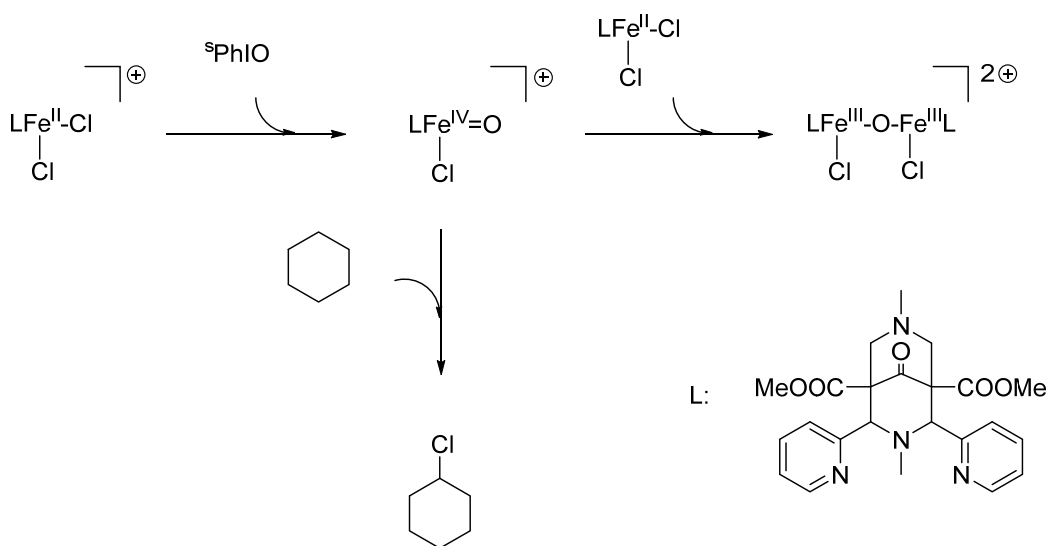
# A HIGH-SPIN IRON(IV)OXO-COMPLEX FOR SELECTIVE HALOGENATION OF ALKANES

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High-valent iron-oxo complexes have been in focus of research, since both enzymes as well as model complexes are known to catalyze a wide range of oxidation and halogenation reactions.<sup>[1,2,3]</sup> The  $[(N_2py_2)Fe=O(Cl)]^+$ -complex reported here has shown activity in both reactions mentioned above. With an excess of oxidant, rapid oxidation of thioanisole was observed. However, no reaction was observed with a stoichiometric amount of oxidant. This is due to a fast reaction of the active high-valent iron-oxo compound with residual iron(II)-complex to an iron(III)- $\mu$ -oxo-bridged species, which was observed via mass spectrometry. Both, the reactivity towards sulfoxidation reactions and the observation of the  $\mu$ -oxo-bridged species indicate, that the active species is an iron(IV)oxo-complex.

In addition, this complex shows reactivity towards the chlorination of cyclohexane with a high selectivity to the halogenated product (close to 100% selectivity). Here again, the use of a stoichiometric amount of oxidant leads to no product formation.



**Figure 1:** Reaction scheme of the halogenation reaction of cyclohexane with the  $[(N_2py_2)Fe=O(Cl)]^+$  - complex.

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# BIOMIMETIC DINUCLEAR MANGANESE COMPLEXES AND SUPEROXIDE

Adriana M. Magherusan,<sup>a</sup> Ang Zhou,<sup>b</sup> Erik R. Farquhar,<sup>c</sup> Max García-Melchor,<sup>a</sup> Brendan Twamley,<sup>a</sup> Lawrence Que, Jr.,<sup>b</sup> Aidan R. McDonald<sup>\*a</sup>

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Ribonucleotide Reductases (RNRs) are proteins that are involved in DNA biosynthesis. We are mainly interested in class Ib RNRs which can contain either a diiron or dimanganese cofactor. While dioxygen is the active oxidant for class Ib diiron RNRs, superoxide has been shown to only activate class Ib dimanganese RNRs. A Mn<sup>II</sup>Mn<sup>III</sup> intermediate has been postulated to form after the reaction of superoxide with the Mn<sup>II</sup><sub>2</sub> cluster. Cleavage of the O-O bond has been proposed to generate a Mn<sup>III</sup>Mn<sup>IV</sup> intermediate that oxidises tyrosine to tyrosyl.<sup>[1]</sup> We used biomimetic complexes to gain insight into the reactivity of dimanganese complexes towards superoxide.

A series of Mn<sup>II</sup><sub>2</sub> complexes were synthesised and characterised (Figure 1b). The treatment of complexes with superoxide at -40 °C formed a metastable species with an absorbance band at ~460 nm (Fig. 1a) in the electronic absorption spectrum. The peroxo-Mn<sup>II</sup>Mn<sup>III</sup> has also been characterised by EPR (inset Figure 1a), direct injection ESI-MS and XANES. Similarly, when a Mn<sup>II</sup><sub>2</sub> complex (Figure 1c) supported by a polyridine ligand ([Mn<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(BPMP)](ClO<sub>4</sub>)) has been reacted with superoxide at -90 °C, an adduct with a weak absorbance band at λ<sub>max</sub> = 440 nm was observed by electronic absorption spectroscopy. Very interestingly, when this adduct has been warmed up at room temperature, a 16-line EPR signal has been observed by EPR. Such features are characteristic of Mn<sup>III</sup>Mn<sup>IV</sup> complexes. Our findings provide support for the postulated mechanism of O<sub>2</sub><sup>·-</sup> activation at class Ib Mn<sub>2</sub> RNRs.

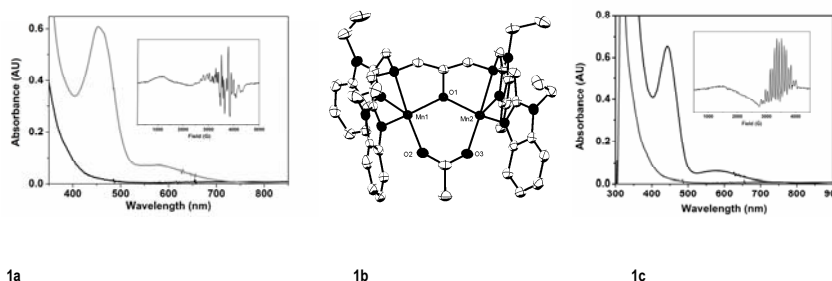


Figure 1- a) UV-Vis spectra of the Mn<sup>II</sup>Mn<sup>III</sup>-peroxo species formed at ~460 nm (black trace = complex in Figure 1b, red trace = metastable species), inset = EPR spectrum of metastable species b) ORTEP plot of ([N-Et-HPTB](Mn<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>))(ClO<sub>4</sub>)<sub>2</sub> (H atoms and perchlorate anions omitted for clarity) c) UV-Vis spectra of another Mn<sup>II</sup>Mn<sup>III</sup>-peroxo species formed at λ<sub>max</sub> = 440 nm (red trace in figure 1c), inset = EPR spectrum of the decayed Mn<sup>II</sup>Mn<sup>III</sup>-peroxo.

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# RATIONAL DESIGN OF TETRADENTATE TRANSITION METAL LIGANDS FOR ATMOSPHERIC PRESSURE AMMONIA SYNTHESIS

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Ammonia (NH<sub>3</sub>) is one of the most important compounds produced in industry. NH<sub>3</sub> production adds up to approximately 140 million tons per year. Still, the production in its present form is not efficient. Converting N<sub>2</sub> to NH<sub>3</sub> via the Haber-Bosch process accounts for about 3% of the world's greenhouse gas emission and more than 1% of the world's annual energy consumption due to the high pressure and temperature (150-300 atm, 400-500°C). In order to produce ammonia in a more environment-friendly and energy efficient way, one should find a method that could operate at room temperature and atmospheric pressure.

Interestingly, microorganisms in nature can fix dinitrogen and produce ammonia at ambient conditions. Thus, it would be reasonable to mimic the active site of nitrogenase enzymes and design artificial catalysts that could be competitive alternatives to the Haber-Bosch process. In this work we investigate recently synthesized biomimetic catalysts<sup>1-3</sup> with DFT methods to understand their catalytic activity. These complexes contain a central metal atom surrounded by tetradentate trisphosphino scorpionate ligands (Figure 1). In recent years numerous similar complexes have been successfully synthesized that reduce dinitrogen into ammonia in the presence of proton and electron sources at atmospheric pressure. Since the experimental characterization of the intermediates is challenging, the exact steps of the catalytic cycle are not clear yet. By studying the Gibbs free enthalpy profile, we determine the exact reaction paths of these catalysts and identify the critical steps. Our results indicate that the reduction of N<sub>2</sub> most likely proceeds via the so-called hybrid pathway (-N<sub>2</sub> → -NNH<sub>2</sub> → -NH<sub>2</sub>NH<sub>2</sub> → 2 NH<sub>3</sub>) and that the thermodynamical driving force disappears in the last steps of the cycle (-NH<sub>2</sub>NH<sub>2</sub> → 2 NH<sub>3</sub>). These observations enable the rational re-design of the tetradentate ligands based on the destabilization of the intermediates located in the energy valleys of the obtained profile.

The exploration of the catalytic mechanism requires careful examination of the spin states of all intermediates as the molecular spin quantum number of the experimentally characterized structures ranges from 0 to 2. Thus, we computed all (theoretically) possible spin states of a given intermediate in order to find the thermodynamically most stable species. This process was preceded by extensive test calculations based on experimental data (e.g. Mössbauer spectra) to confirm the reliability of the chosen density functional.

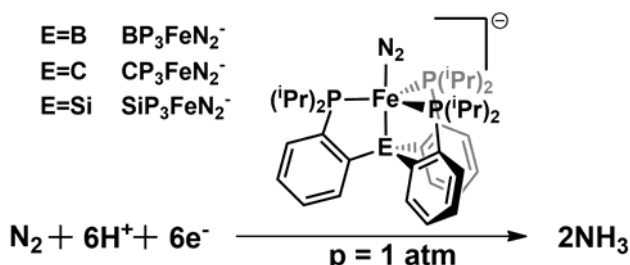


Figure 1. Reduction of dinitrogen to ammonia by EPPP scorpionate complexes at atmospheric pressure.

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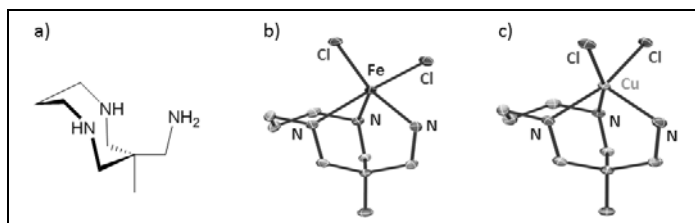
# COORDINATION PROPERTIES OF BIOINSPIRED MESOCYCLIC TRIPODAL LIGANDS

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In the quest to continuously develop more energy efficient processes, and to further reduce greenhouse gas emissions, activating low molecular weight hydrocarbons to convert them into compounds of interest is highly important. Nature has developed various metalloenzymes using transition metals to perform these tasks. Particulate Methane Monooxygenase (pMMO) is one of such metalloenzymes, capable of activating alkanes up to C5 at an N-coordinated Cu dimer.<sup>[1]</sup> Another family of metalloenzyme, capable of activating a large range of substrate, is based on non-haem iron centres where the cation is coordinated by the 2-His-1-Carboxylate facial triad.<sup>[2]</sup> The active species in iron enzymes have been identified has  $\text{Fe}^{\text{IV}}=\text{O}$ ,<sup>[3]</sup> and it has been proposed that terminal  $\text{Cu}^{\text{III}}=\text{O}$  or dimeric  $\text{Cu}^{\text{III}}-(\mu\text{-O})_2\text{-Cu}^{\text{III}}$  are responsible for hydrogen atom abstraction (HAA) in pMMO.<sup>[4]</sup>

In this project, we are dedicated to develop models of the active site of these two kinds of enzyme. Indeed, if many  $\text{Fe}=\text{O}$  species have been described,<sup>[5]</sup>  $\text{Cu}^{\text{III}}=\text{O}$  complexes remain elusive.<sup>[6]</sup> To fulfill this goal, we synthesized original ligands based on tripodal diazacyclooctane (DACO) derivatives.<sup>[7]</sup> These tridentate ligands should favor, through the presence of the facially capping 8-membered mesocycle and the dangling arm (figure a), low coordinate geometries, hence stabilizing high-valent oxo species of late transition metals such as copper. The coordination properties of these ligands have been investigated towards various first row transition metals (Fe, Co, Ni, Cu, Zn). We have successfully isolated a number of complexes of low-valent metals (figure b, c) which constitute interesting precursor to high-valent species.<sup>[8]</sup>



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# SPIN STATES OF TRIAZINE AND PYRIMIDINE DERIVED IRON II COMPLEXES

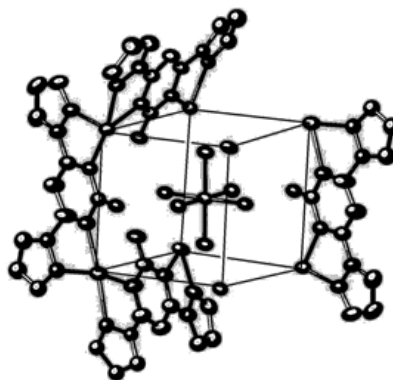
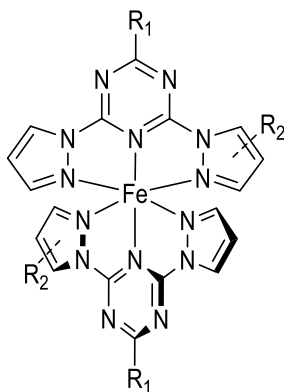
Izar Capel Berdiell, Prof. Malcolm Halcrow.

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Spin Crossover (SCO) is a well known phenomenon for  $d^4$  to  $d^7$  transition metal complexes which is frequently shown by iron(II) N-donor hexacoordinated salts. Those complexes undergo a spin transition triggered by external stimuli such as variation of temperature, pressure, light or magnetic field. Such materials have been used in prototype display and memory devices and in nanoscience, and are also good testbeds for new theories and techniques in crystal engineering and solid state science. [1]

A number of 2,4-di(pyrazol-1-yl)-6-R-1,3,5-triazine bptR-containing complexes of the type  $[\text{Fe}(\text{bptR})_2] \cdot 2\text{X}$  (where R is isopropylsulfanyl, ethoxide, dimethyl or diethyl amine and  $\text{X} = \text{BF}_4$  or  $\text{ClO}_4$ ) have been synthesized as a new family of potentially easily modifiable SCO iron(II) complexes. They have been analysed by different methods including X-ray crystallography, Uv-Visible spectroscopy and SQUID magnetometry. Contrary to what was expected, it has been demonstrated that none of those complexes exhibit SCO either in solid or liquid state, and show strong distortion from the ideal  $D_{2d}$  geometry. [2]

2,4-Di(4,5,6,7-tetrahydro-2-indazol-2-yl)-6-chloro-1,3,5-triazine reacted with iron(II) tetrafluoroborate as a bis-bidentate ligand yielding a cubic-shaped structure where 12 hydrolysed ligands act as edges of the cube while iron(II) atoms are the vertices. A similar structure was reported before containing cobalt [3]. 2-Methyl-4,6-di(pyrazol-1-yl)-1,3-pyrimidine and 2-methyl-4,6-di(pyrazol-1-yl)-1,3-pyrimidine produced mono-dimensional coordination polymers when react with iron(II) salts.



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# RU<sup>II</sup> PHOTOSENSITIZER FUNCTIONALIZED TWO-DIMENSIONAL MOS<sub>2</sub> FOR LIGHT-DRIVEN HYDROGEN EVOLUTION

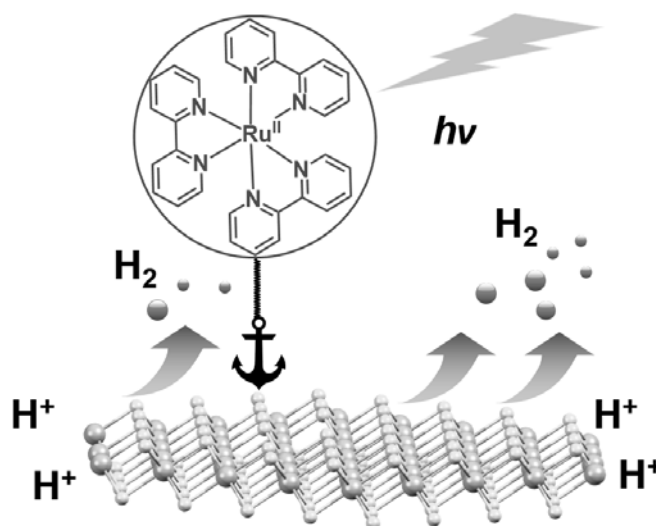
Xin Chen,<sup>\*a,b</sup> David McAteer,<sup>a,c</sup> Cormac McGuinness,<sup>a,c</sup> Aidan R. McDonald<sup>\*a,b</sup>

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Metallic-phase molybdenum disulfide (1T-MoS<sub>2</sub>) nanosheets synthesized by a lithium intercalation and exfoliation method have proven to be highly active in electrocatalytic hydrogen evolution reaction (HER) [1-3]. We describe an approach to constructing a Ru<sup>II</sup> photosensitizer functionalized 1T-MoS<sub>2</sub> device by covalently tethering the molecular photosensitizer [Ru<sup>II</sup>(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine) onto 1T-MoS<sub>2</sub> nanosheets. This was achieved by first covalently tethering the free bpy ligand to 1T-MoS<sub>2</sub> nanosheets, and subsequent complexation with [Ru<sup>II</sup>(bpy)<sub>2</sub>Cl<sub>2</sub>] on the nanosheet surface to yield [Ru<sup>II</sup>(bpy)<sub>3</sub>]-MoS<sub>2</sub>. The obtained [Ru<sup>II</sup>(bpy)<sub>3</sub>]-MoS<sub>2</sub> was characterized using X-ray photoelectron, Raman, and Infrared spectroscopies and electron microscopy. The fabricated material exhibited a significant improvement of photocurrent and HER performance, demonstrating the potential of the [Ru<sup>II</sup>(bpy)<sub>3</sub>]-MoS<sub>2</sub> covalent assembly in photosensitized HER.



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# A THIOLATE-SUPPORTED IRON(III)-PEROXO COMPLEX EN ROUTE TO CATALYTIC REDUCTION OF DIOXYGEN TO HYDROGEN PEROXIDE

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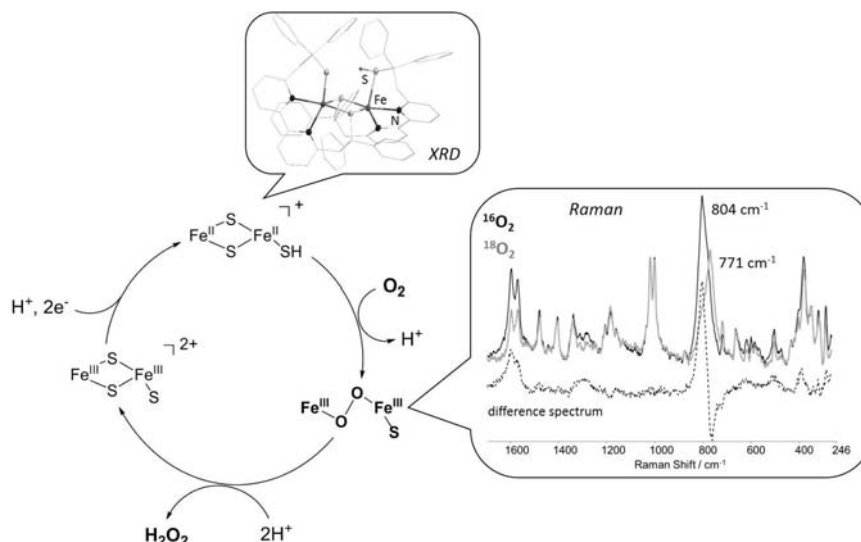
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Transition metal ions are known for their ability to facilitate and control the reductive activation of dioxygen. Among them, iron exhibits extremely rich oxygen chemistry in both biological and synthetic systems.<sup>[1-2]</sup> In parallel, thiolate ligation in metal complexes has been shown to promote activation of O<sub>2</sub>.<sup>[3-5]</sup> In this context, we report on the synthesis and dioxygen reactivity of an iron(II)-thiolate dinuclear. In the presence of a proton source (2,6-lutidinium) and electrons, this complex acts as a catalyst for O<sub>2</sub> reduction to H<sub>2</sub>O<sub>2</sub>. The two-electron reduction process is 100% selective when a one-electron reducing agent (octamethylferrocene) is employed, while selectivity decreases to 20% when the process is driven electrochemically. During mechanistic investigations, an iron(III)-peroxo intermediate has been initially detected by ESI-mass, and then isolated and definitively identified by Raman and Mossbauer spectroscopies.



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# INSPECTING THE EFFECT OF SUBSTITUTION ON SCHIFF BASE LIGAND ON SPIN GAP IN IRON(III) COMPLEXES

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The spin crossover (SCO) materials based on coordination compounds of 3d metals are potentially interesting materials due to their possibility to change the spin state upon applying the external impetuses such as temperature, pressure or light.<sup>[1]</sup> So far, the iron complexes constitute the majority of SCO compounds, in which complexes of iron(II) dominates. However, iron(III) SCO compounds has received considerable attention in last few years.<sup>[2]</sup> The hexadentate Schiff-base ligand derived from reaction of variously substituted aromatic 2-hydroxy-aldehydes with triethylenetetramine (H<sub>2</sub>L6) provided already several series of SCO iron(III) compounds, e.g. [Fe(5-X-L6)]A (X = Me, i-Pr, t-Bu; A = NO<sub>3</sub>, PF<sub>6</sub>)<sup>[3]</sup> and [Fe(4-OH-L6)]A (A = Cl, Br and I).<sup>[4]</sup> Within these molecular systems, the SCO properties can be tuned by modification of H<sub>2</sub>L6 ligand and also by variation of non-coordinated anions (A). The presented work is focused on the theoretical study of various substitutions of H<sub>2</sub>L6 ligand and their impact on geometries of low-spin and high-spin [Fe(L6)]<sup>+</sup> complexes and on energy difference between these two spin states. The theoretical methods based on Density Functional Theory (DFT) and Complete Active Space Self Consistent Calculations (CASSCF) were employed to assess their electronic properties. The calculated trends of the spin gap based on ligand substitutions can thus serve as a tool for the synthesis of new SCO iron(III) compounds.

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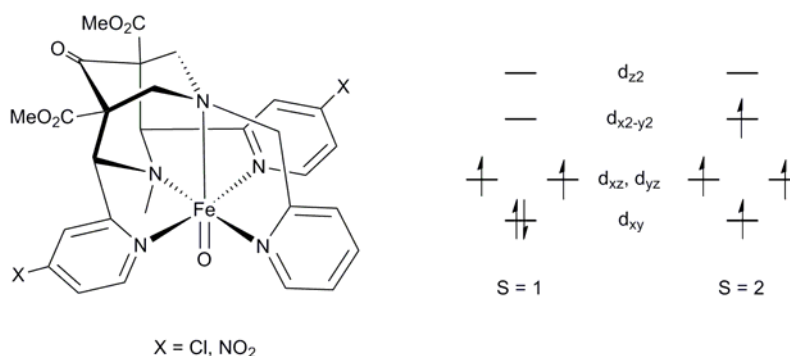
# SPIN STATES IN BISPIDINE-IRON(IV)OXO COMPLEXES

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In nature, a wide range of oxidations and halogenations are catalyzed by non-heme enzymes with a high-spin iron(IV)oxo intermediate ( $S = 2$ ) as active species.<sup>[1]</sup> In contrast, most published mononuclear iron(IV)oxo complexes have an intermediate-spin ground state ( $S = 1$ ).<sup>[2]</sup> To obtain high-spin iron(IV)oxo complexes with our bispidine ligand system,<sup>[3]</sup> electron-withdrawing groups (Cl, NO<sub>2</sub>) were introduced at the pyridine donors in para-position to weaken their donor strengths (see Figure 1). Due to the resulting weaker ligand field in equatorial position, it can be expected that the energy of the  $d_{x^2-y^2}$ -orbital is lowered, which could lead to a high-spin electronic configuration. Temperature-dependent UV-Vis-NIR spectroscopy is used to examine the electronic properties of the complexes. With both complexes we observed thermal spin-crossover of the iron(IV) complexes in the measured temperature range.



**Figure 1:** Bispidine-iron(IV)oxo complex and the d-orbital splitting diagram of iron(IV) in a distorted octahedral geometry.

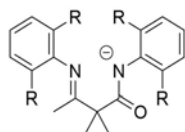
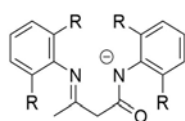
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# IMAM LIGANDS FOR LOW-COORDINATE LATE TRANSITION METAL COMPLEXES

Marta Lovisari, Brendan Twamley and Aidan R. McDonald\*

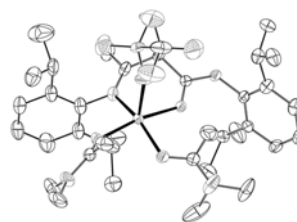
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The design of new catalysts for the functionalization of inert C-H bonds is a compelling goal to be able to take advantage of hydrocarbon-based feedstock in a more selective, cost-effective and environmentally friendly way.<sup>[1]</sup> The synthesis of biomimetic complexes inspired by active oxidant species involved in enzymatic catalytic cycles, notably metal-oxo intermediates, is one important route of investigation to overcome this limit.<sup>[2]</sup> Late transition metal-oxo complexes (groups 9, 10, 11) are postulated to be potentially stronger oxidants than early-transition ones, but they have so far been elusive due to electronic structural requirements.<sup>[3]</sup> One possible strategy to override this "Oxo Wall"<sup>[3]</sup> is to synthesize low-coordinate precursors in square planar, tetrahedral or trigonal planar geometries. Bulky  $\beta$ -diketiminato ligands are widely investigated in order to access metal complexes with low coordination numbers and have been used to synthesize trigonal planar mononuclear Ni(II)<sup>[4]</sup> and Cu(II) superoxo and bis( $\mu$ -oxo) complexes.<sup>[5]</sup> Herein we propose a novel IMAM (IMinoAMido) ligands family (**1**) to access low-coordinate precursors and bearing an anionic donor to stabilize the high-valent late transition metal-oxo species. The new compounds were fully characterized through IR, NMR, HRMS, and their coordination properties with Fe, Ni, Co and Cu (**2**) were explored.



H,H-IMAM1: R=iPr H,H-IMAM 2: R=Me Me,Me-IMAM1: R=iPr Me,Me-IMAM 2: R=Me

(1)



(2)

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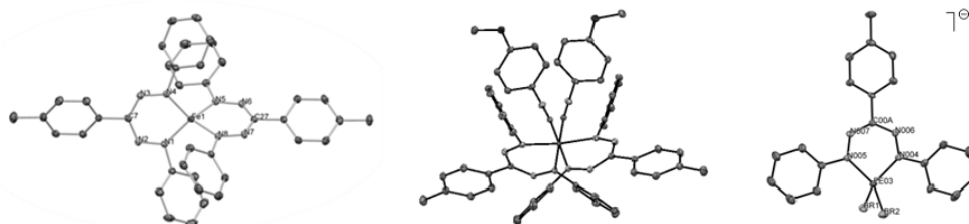
# ELECTRONIC AND STRUCTURAL PROPERTIES OF IRON COMPLEXES WITH FORMAZANATE LIGANDS

Francesca Milocco,\* Folkert de Vries, Raquel Travieso-Puente, Serhiy Demenshko, Franc Meyer, Edwin Otten

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Complexes that show spin-crossover are well known for 6-coordinate, octahedral geometries. Due to a much weaker ligand field in 4-coordinate complexes, these (with very few exceptions)<sup>[1]</sup> lead to high spin-states only. Here, we present 4-coordinate iron(II) complexes with formazanate ligands ( $L_2Fe$ ), some of which show spin-crossover. The strong  $\pi$ -acceptor properties of these ligands leads to an unusual d-orbital splitting pattern that stabilizes the low-spin ( $S = 0$ ) state in these compounds.<sup>[2]</sup> We investigated the effect of steric and electronic changes in the ligand framework and a range of spectroscopic, magnetic and computational techniques is used to understand the origin of spin-crossover in these compounds. The redox behavior of the bis(formazanate) iron complexes has also been studied by cyclic voltammetry and isolation and characterization of the reduced compounds have been carried out, when possible. Furthermore, the reactivity of isocyanide with  $L_2Fe$  leads to the formation of an octahedral diamagnetic complex. Moreover, attempted oxidative addition of alkyl halides to the Fe(I) complex  $[L_2Fe]^-$  allows the isolation of a high-spin mono(formazanate) iron complex, for which a rational synthesis was developed.



**Figure1.** Iron formazanate complexes.

- 1) a) J. J. Scepaniak, T. D. Harris, C. S. Vogel, J. Sutter, K. Meyer, J. M. Smith, *J. Am. Chem. Soc.* **2011**, 133, 3824; (b) A. C. Bowman, C. Milsmann, E. Bill, Z. R. Turner, E. Lobkovsky, S. DeBeer, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2011**, 133, 17353.
- 2) R. Travieso-Puente, J. O. P. Broekman, M.-C. Chang, S. Demeshko, F. Meyer, E. Otten, *J. Am. Chem. Soc.* **2016**, 138, 5503.