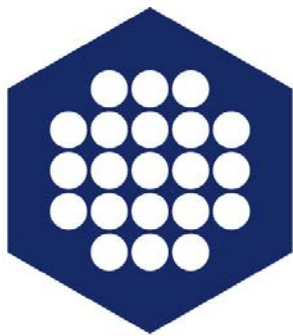
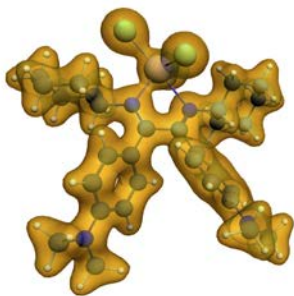


**ECOSTBio: Fourth scientific  
workshop: Prague, April 13-15, 2016**

**Information package:**  
Introduction, Travel, Venue, Book  
of Abstracts, List of Participants



**ÚOCHB  $\frac{AV}{\check{C}R}$**   
**IOCB PRAGUE**



**COST Action CM1305**

**ECOSTBIO**

**Explicit Control Over Spin-states  
in Technology and Biochemistry**

# **ECOSTBio: Fourth scientific workshop: Prague, April 13-15, 2016**

## **Venue**

IOCB, Prague, Czech Republic

## **Organizing Committee**

Jana Roithová

Lubomír Rulíšek (**mobile : +420-731-447-872**)

## **Local Organizing Committee**

Ondrej Gutten

Martin Srnec

Prokopis Andrikopoulos

## **Supported by**

IOCB: Institute of Organic Chemistry and Biochemistry AS  
CR

Fourth scientific workshop  
Prague, April 13-15, 2016

***Dear participant of the 4th scientific workshop of the ECOSTBio.***

*Welcome in Prague!*



*Welcome at IOCB, Institute of Organic Chemistry and Biochemistry, AS CR!*



*Following previous successful meetings in Girona (2014), Marseille (2015), Belgrade (2015), we expect the Prague workshop to be fruitful, relaxed, and pleasant exchange of ideas in (not only) bioinorganic chemistry where members of the ECOSTBio action reunite and meet with international experts and colleagues (this time Kara Bren, Ed Solomon, Andy Borovik, and Larry Que). In an early spring atmosphere, students and professors, experimentalists and theoreticians may discuss the recent progress and challenges in the field. Thus, the meeting perfectly fulfils the aim of the COST action which is to establish a working network of scientists focused on the “chemistry of spin-states”.*

*The meeting begins with an **informal dinner on Tuesday, April 12**. Organizers booked some 40 places in the **restaurant Pod Juliskou** ([www.podjuliskou.cz](http://www.podjuliskou.cz)) that is some 100 meters from the Hotel Internacional where most of the participants stay. When exiting the main entrance of the hotel, turn left and you will not miss it. Martin Srnec and Lubomír Rulíšek will be there **since 19:00 till at least 22:00** (the restaurant closes at 24:00). It is not really in the Prague centre, but we thought it might be very convenient for people arriving at various times to the hotel just to walk in (the restaurant), have some meal and beer and then leave at their leisure. We will bring the conference badges (electronic door passes to IOCB) and other registration materials (e.g., confirmation of attendance, confirmation of the lunch/dinner payment) with us so we can slightly diminish queues at the IOCB entrance on Wednesday morning. Please note that the dinner is not covered by the organizers, have some Czech crowns (or credit card) ready to cover the cost of the dinner (8-15 EUR in total, unless you aim for a truly unique experience with Czech food and beer ☺). Those that will be reimbursed by the COST action (Wes Browne is responsible for that) may claim the dinner as the “refundable expense”. The registration brings me to the very important point: there is no conference fee, but the organizers **provide three lunches and one conference dinner**. You will be requested to **pay 20 EUR/meal (i.e. 80 EUR in total, in most cases) or equivalent in Czech crowns (local currency) – 540 CZK/meal** - to the organizers (in cash, no credit cards) in the more or less same way as in previous meetings. The lunch and dinner tickets will be issued and will serve as the “entrance ticket” to lunches (always at IOCB, in the form of the buffet) and to the **conference dinner (Restaurant Nebozizek, [www.nebozizek.cz](http://www.nebozizek.cz), near Prague castle) on Wednesday evening**.*

*The meeting begins on Wednesday, April 13, 9:00 at IOCB. IOCB is within a walking distance from the Hotel Internacional (5 min max). Please be there **at least half an hour before (8:30)**, especially those not registered on Tuesday. The meeting **ends with the lunch on Friday, April 15**. This leaves us with the Thursday evening to be filled by some activity. We plan to organize an informal dinner in the very center of Prague, but at the same time, we are aware that many people might prefer the individual programs, such as evening sightseeing. This will be decided on Wednesday.*

*We wish you a safe flight to and from Prague! We look forward to meeting you soon and enjoying together adventurous journey over the spin-states in technology and biochemistry.*

*Marcel Swart,  
ECOSTBio Chair*

*Jana Roithová, Lubomír Rulíšek (**helpline: +420-731-447-872**)  
Conference Chairs*

## Travel Information

Prague International Airport (Vaclav Havel Airport) lies 15 km west of the city center.

### **PUBLIC TRANSPORT FROM THE AIRPORT**

The best option is to take **Bus 119 that takes you** in about 15 minutes **to metro (underground) station Nadrazi Veleslavin** (which is the final stop of the Bus 119). Bus departs from airport from both Terminals 1 and 2

Timetable for Bus 119 can be found at e.g. [www.dpp.cz](http://www.dpp.cz); it goes every 5-10 minutes until 11:45 pm (bus 510 then goes every ca. 30 mins afterwards, but you have to change to tram at the stop Divoka Sarka)

Tickets (< 1.50 €) can be purchased from the ticket machines at the stop/terminal or from the driver. The standard ticket is for 90 minutes, valid on all public transport in Prague

### **From Nadrazi Veleslavin to the hotel Internacional and to IOCB.**

Continue from Nadrazi Veleslavin by underground (metro), direction to "Depo Hostivar" and exit at the second stop - Dejvicka. Exit the platform of Dejvicka metro station in the direction of the train ("no escalators" side of the platform) and being one level up, follow the sign "Bus (Suchdol/Lysolaje)". This will get you to the "ground level". To IOCB, it is an easy 10 mins walk (see the map) while to the hotel, bus stop(s) are some 50 meters in front of you (marked by black dot in the map)

Take bus 107, 147, or 160 and exit on the first stop (Cinska); the hotel Internacional is the largest building in front of you (ca. 2 mins walk from the bus stop). If you prefer walking, it is ca. 10-15 mins walk down the street "Jugoslavskych partizanu": you may see the tip of the hotel (in the style of Lomonosov University) already from Dejvicka station.

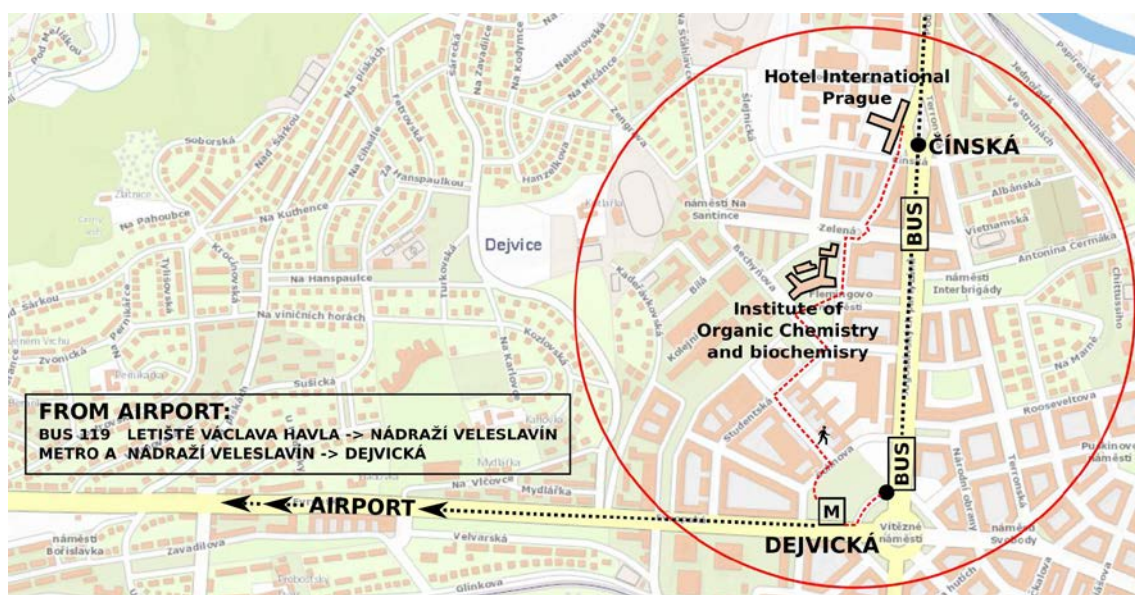
### **TAXI**

AAA Taxi or Fix Airport Cars are the recommended taxis at the [www.prg.aero](http://www.prg.aero) Airport web pages

Price from the Airport to the IOCB (Flemingovo namesti 2) or Hotel Internacional (Koulova 15) should be around 15 €

It is advisable to ask for the receipt

## MAP



## HOTEL

Hotel International  
Koulova 15  
16000 Praha 6  
Czech Republic  
TEL: (+420) 296 537 111  
FAX: (+420) 296 537 535  
E-MAIL: [hotel@internationalprague.cz](mailto:hotel@internationalprague.cz)

Reservations Office:  
TEL: (+420) 296 537 854  
FAX: (+420) 296 537 266  
E-MAIL: [hotel@internationalprague.cz](mailto:hotel@internationalprague.cz)

## VENUE

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the  
Czech Republic  
Flemingovo náměstí 2  
166 10, Praha 6





# Programme of Prague Meeting

IOCB, Lecture Hall

## Wednesday April 13

- 8.30-9.00 Registration  
9.00-9.20 Opening of the meeting (ECOSTBio Chair and Conference Chairs)

### Session 1 (Chairwoman: Jana Roithová)

- 9.20-10.00 **E. I. Solomon**  
*Structure/Function Correlations over Non-Heme Iron Enzymes.*
- 10.00-10.20 S. Padamati  
*The Conflicting Role of Water in the Activation of H<sub>2</sub>O<sub>2</sub> and the Formation and Reactivity of Non-Heme Fe(III)-OOH and Fe(III)-O-Fe(III) Complexes at Room Temperature.*
- 10.20-10.40 Q. Phung  
*Density matrix renormalization group (DMRG) study of spin-state energetics of ironoxo porphyrins.*
- 10.40-11.10 Coffee

### Session 2 (Chairman: Jeremy Harvey)

- 11.10-11.30 S. Bonnet  
*Stabilization of the low-spin state in a mononuclear iron(II) complex and high temperature cooperative spin crossover mediated by hydrogen bonding.*
- 11.30-11.50 R. Herchel  
*Iron(III) spin crossover compounds with schiff-base ligands.*
- 11.50-12.20 **F. Neese**  
*Spin States and Molecular Magnetism.*
- 12.20-14.00 Light lunch

### Session 3 (Chairman: Rob Deeth)

- 14.00-14.30 **M. Gruden**  
*Density functional approximations for spin-state chemistry.*
- 14.30-14:50 T. Corona  
*Characterization and reactivity studies of A terminal copper-nitrene species.*
- 14:50-15.10 B. Sarkar  
*Click-derived tripodal ligands for spin crossover and bond activation reactions.*
- 15:10-15.30 D. Brazzolotto  
*Dioxygen activation and catalytic reduction by a thiolate-bridged dimanganese(II)*

- 15:30-15:50 *complex with a pendant thiol.*  
C. de Graaf  
*Managing the computational chemistry big data problem: the ioChem-BD platform.*
- 15.50-16.30 Database discussion
- 16.30-17.15 Discussion time WGs
- 17.15-18.30 Poster session (+ pica pica)

## Thursday April 14

### Session 4 (Chairman: Tomasz Borowski)

- 9.00-9.40 **L. Que Jr.**  
*The Amazing High-Valent Iron-Oxo Reaction Landscape.*
- 9.40-10.00 E. Andris  
*Reactivity of stereoisomeric iron(IV) complexes with a different spin state studied in the gas phase.*
- 10.00-10.20 C. Enachescu  
*Matrix-assisted relaxation in Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> spin-crossover microparticles: theoretical and experimental investigations.*
- 10.20-10.40 A. R. McDonald  
*Nickel(III)-oxygen adducts that oxidize inert hydrocarbons.*
- 10.40-11.10 Coffee + Group Picture

### Session 5 (Chairman: Matthias Stein)

- 11.10-11.30 **M. Radoń**  
*Accurate spin-state energetics of Fe(III) and Ru(III) aquo complexes evidence significant solvation effects.*
- 11.30-11.50 M.C. Kafentzi  
*Heterometallic Nickel-Copper dioxygen complexes: electronic structure and reactivity.*
- 11.50-12.20 **P. Maldivi**  
*Quantum chemical analysis of iron complexes highly active in H abstraction and nitrene insertion reactions.*
- 12.20-14.00 Light lunch

### Session 6 (Chairman: Wesley Browne)

- 14.00-14.40 **A. Borovik**  
*A Bioinspired Approach to Synthetic Iron and Manganese Complexes with Oxido and Hydroxido Ligands.*
- 14.40-15.00 S. DeVisser

- Quantum mechanics/molecular mechanics studies of cytochrome P450 peroygenases for the biosynthesis of biofuels.
- 15.00-15.20 J. Klein  
*The aqueous chemistry of the  $[FeIV(O)TMC]^{2+}$  complex: determining the pKa of an aqua ligand bound to an  $FeIV=O$  unit.*
- 15.20-15.40 A. Kochem  
*Polynuclear methane monooxygenase bioinspired copper complexes.*
- 15.40-16.00 R. Travieso-Puente  
*Reversible spin state changes in a tetrahedral iron complex with redox-active formazanate ligands.*
- 16.00-16.30 **K. Pierloot**  
*Describing oxygen atom transfer with DFT and multiconfigurational methods.*
- 16.35-18.00 MC meeting

## Friday April 15

### Session 7 (Chairman: Ricardo Louro)

- 9.00-9.40 **K. Bren**  
*Effects of Heme Conformation on Spin State, Spin Distribution, and Electron Transfer in Cytochromes.*
- 9.40-10.00 P. Weinberger  
*Variable temperature ATR-IR spectroscopy as a valuable tool for the in situ spin state detection of iron(II) spin crossover complexes.*
- 10.00-10.20 D. Luneau  
*Valence tautomerism in 2D manganese-nitronyl nitroxide radical systems.*
- 10.20-10.40 P. Kyritsis  
*Mononuclear single molecule magnets: the case of manganese(III), Iron(II) and Cobalt(II) complexes bearing imidodiphosphinato chelating ligands.*
- 10.40-11.10 Coffee

### Session 8 (Chairman: Jon McGrady)

- 11.10-11.30 G. La Penna  
*Reactive oxygen species and the Cu[Amyloid-Beta] complex.*
- 11.30-11.50 H. J. Krüger  
*Intermediate-spin state in six-coordinate iron complexes with a pseudo-octahedral coordination environment.*
- 11.50-12.20 **K. Meyer**  
*Uranium-mediated electrocatalytic H<sub>2</sub> production from water.*
- 12.20-14.00 Light lunch



Fourth scientific workshop  
Prague, April 13-15, 2016

# INVITED and KEYNOTE LECTURES

## Structure / Function Correlations Over Non-Heme Iron Enzymes

Edward I. Solomon

*Department of Chemistry, Stanford University*

Six classes of ferrous enzymes activate dioxygen for H-atom abstraction and electrophilic attack on substrates. We have developed near IR variable-temperature, variable – field magnetic circular dichroism (VTVH MCD) spectroscopy as a probe of non-Kramers' ions and used this to define a general mechanistic strategy of O<sub>2</sub> activation, requiring the presence of all cosubstrates. For some classes, O<sub>2</sub> activation is at the Fe(III)OOH level, while for others this involves Fe(IV)=O intermediates. We have used Nuclear Resonance Vibrational Spectroscopy (NRVS) to define geometric structure and VTVH MCD to define electronic structure and the frontier molecular orbitals (FMOs) of these intermediates. For the hydroperoxo-ferric intermediates we showed that non-heme iron is fundamentally different from heme iron in dioxygen activation and that there is a significant spin state dependence in peroxo activation. For the Fe(IV)=O intermediates, we used structurally defined models to define the FMOs and their spin state dependence and correlated these models to Fe(IV)=O enzyme intermediates for insight into how the Fe(IV)=O S=2 pi and sigma FMOs enable selectivity in catalysis.

## Spin States and Molecular Magnetism

Mihail Atansov, Elizabeta Suturina, Daniel Aravena and Frank Neese

*Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

**Keywords:** *Magnetism, ab initio ligand field theory, multireference theory, spin states, spin-orbit coupling*

Rational design of molecules with tailored magnetic properties can presumably not be achieved without a thorough understanding of magnetostructural correlations. Such correlations can be established by theoretical or experimental means and must be formulated in a language that is accessible to synthetic chemists. Quantum chemistry can be of tremendous help in this context. In fact, modern first principles quantum chemical calculations can be of predictive accuracy for magnetic properties, can be used to understand actual experimental data and can be used to establish magnetostructural rules and trends. However, the method of density functional theory (DFT) that is dominating both molecular quantum chemistry and solid state physics has been found to be of rather limited accuracy in this context, in particular for the calculation of the all-important zero-field splitting (magnetic anisotropy). In our work, we have focused on multiconfigurational wavefunction based approaches that offer a more systematic and general theoretical approach for the calculation of magnetic properties. The lecture will discuss some methodological aspects and will then focus on recent examples to illustrate the fruitful interplay between theory and experiment.

- [1] M. Atanasov, D. Aravena, E. Suturina, E. Bill, D. Maganas, F. Neese, First principles approach to the electronic structure, magnetic anisotropy and spin relaxation in mononuclear 3d-transition metal single molecule magnets *Coord. Chem. Rev.* **2015**, *289*, 177-214.
- [2] Suturina, E. A.; Maganas, D.; Bill, E.; Atanasov, M.; Neese, F. Magneto-Structural Correlations in a Series of Pseudotetrahedral Co-II(XR)<sub>4</sub> (2-) Single Molecule Magnets: An ab Initio Ligand Field Study *Inorg. Chem.* **2015**, *54*, 9948-9961.
- [3] Zadrozny, J. M.; Xiao, D. J.; Long, J. R.; Atanasov, M.; Neese, F.; Grandjean, F.; Long, G. J. Mössbauer Spectroscopy as a Probe of Magnetization Dynamics in the Linear Iron(I) and Iron(II) Complexes [Fe(C(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>]<sub>1-0</sub> *Inorg. Chem.* **2013**, *52*, 13123-13131.
- [4] Zadrozny, J. M.; Xiao, D. J.; Atanasov, M.; Long, G. J.; Grandjean, F.; Neese, F.; Long, J. R. Magnetic blocking in a linear iron(I) complex *Nature Chemistry* **2013**, *5*, 577-581.
- [5] Zadrozny, J. M.; Atanasov, M.; Bryan, A. M.; Lin, C.-Y.; Rekker, B., D.; Neese, F.; Long, J. R. Slow magnetization dynamics in a series of two-coordinate iron(II) complexes *Chem. Sci.* **2013**, *4*, 125-138.
- [6] Atanasov, M.; Zadrozny, J. M.; Long, J. R.; Neese, F. A theoretical analysis of chemical bonding, vibronic coupling, and magnetic anisotropy in linear iron(II) complexes with single-molecule magnet behavior *Chem. Sci.* **2013**, *4*, 139-156.
- [7] Atanasov, M.; Ganyushin, D.; Sivalingam, K.; Neese, F. In *Struct. Bond.*; Springer-Verlag: Berlin Heidelberg, **2012**; Vol. 143, p 149-220.

# DENSITY FUNCTIONAL APPROXIMATIONS FOR SPIN-STATE CHEMISTRY

Maja Gruden,\* Marcel Swart

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Elucidating the role and effect of different spin states on the properties of a system is presently one of the most challenging endeavors both from an experimental and theoretical point-of-view. Computational studies, including Density functional theory (DFT) have shown that a correct description of the spin state is not trivial, and it is not always straightforward to predict the orbital occupation pattern. Although the DFT, in principle, gives an exact energy, a universal functional is still unknown, leading to density functional approximations (DFAs). These DFAs are parameterized for different properties and, noteworthy, spin-state energies were not included in the development for most of nowadays available DFAs.

For the reliable prediction of the correct spin ground state from a number of close lying states, OPBE and SSB-D have emerged to be one of the best DFAs for the task. Recently, Swart constructed a new density functional that combines the best of OPBE (spin states, reaction barriers) with the best of PBE (weak interactions) into the S12g<sup>[1]</sup>. Some of our recent validation studies<sup>[2-5]</sup> with the OPBE, SSB-D and S12g functionals, on number of complexes will be presented.

1) M. Swart, *Chemical Physics Letters* **2013**, 580, 166.

2) M. Gruden, S. Stepanovic, and M. Swart, *J. Serb. Chem. Soc.* **2015** 80(11), 1399.

3) M. Gruden-Pavlovic, S. Stepanovic, M. Peric, M. Güell and M. Swart, *Phys. Chem. Chem. Phys.* **2014**, 16, 14514

4) S. Stepanovic, L. Andjelkovic, M. Zlatar, K. Andjelkovic, M. Gruden-Pavlovic and M. Swart, *Inorg. Chem.* **2013**, 52, 13415

5) M. Zlatar, M. Gruden-Pavlovic, M. Güell and M. Swart, *Phys. Chem. Chem. Phys.* **2013**, 15, 6631



## The Amazing Nonheme High-Valent Iron-Oxo Reactivity Landscape

Lawrence Que, Jr.

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Biological oxidation reactions are often catalyzed by metalloenzymes via high-valent iron centers generated by dioxygen activation. Key nonheme iron examples are the mononuclear oxoiron(IV) oxidants associated with TauD and related oxygenases and halogenases and the  $\text{Fe}^{\text{IV}}_2\text{O}_2$  diamond core found for intermediate **Q** of soluble methane monooxygenase. In both types, the high-valent iron center has an  $S = 2$  ground spin state. Our recent efforts have led to the generation of  $S = 2$   $\text{Fe}^{\text{IV}}=\text{O}$  species that exhibit high rates of cyclohexane oxidation that are comparable to those associated with enzymatic  $\text{Fe}^{\text{IV}}=\text{O}$  intermediates. Extension of this effort to modeling the corresponding nonheme iron halogenases has resulted in the generation and spectroscopic characterization of  $[\text{Fe}^{\text{IV}}(\text{O})(\text{L})(\text{Cl}/\text{Br})]$  complexes. These complexes can halogenate hydrocarbon substrates, and both oxygenated and halogenated products are observed, thereby shedding light on the factors that control the relative rates of oxygen and halogen rebound.

## Quantum chemical analysis of iron complexes highly active in H abstraction and nitrene insertion reactions

Pascale Maldivi,<sup>a</sup> Jean-Marc Latour,<sup>b</sup> Eric Gouré,<sup>b, c</sup> Ranjan Patra<sup>a, b</sup>, Senthilnathan Dhurairajan<sup>a</sup>

<sup>a</sup> *Reconnaissance Ionique et Chimie de Coordination, INAC/LCIB (UMR-E 3 CEA/UJF), CEA Grenoble and Univ. Grenoble Alpes, Grenoble France*

*pascale.maldivi@cea.fr*

<sup>b</sup> *Physicochimie des Métaux en Biologie, iRTSV/LCBM (UMR UJF/CEA/CNRS 5249), CEA Grenoble and Univ. Grenoble Alpes, Grenoble France*

<sup>c</sup> *CIRE/Department of Molecular Chemistry, CNRS and Univ. Grenoble Alpes, Grenoble France*

Among well documented series of iron complexes coordinated by phenolato ligands and exhibiting mixed (N, O) coordination sphere, we have been able to identify and characterize complexes with very high activity towards H abstraction and NTs insertion reactions (Ts = tosylate).<sup>1</sup> Thanks to spectroscopic and analytical methods, some insights have been gained on its molecular structure and hypotheses about the activation mechanism have been proposed. Most importantly, Fe<sup>IV</sup> = NR (R = Ts = tosylate) species seems to be a key intermediate. Such Fe<sup>IV</sup> = NR species attract much interest nowadays, because of their analogy with long-time studied Fe<sup>IV</sup> = O systems, and because this moiety seems to be critical for reactivity mechanisms involving a NR group.<sup>2</sup>

The high reactivity of the present Fe<sup>IV</sup> intermediate has so far precluded its isolation for further characterizations, and we thus turned to theoretical calculations to get more insight into its structural and electronic properties. In order to be as reliable as possible, extensive calibrations on homolog complexes have first been performed, completed by the estimation of Mössbauer parameters. A special focus will be made on the proposed Fe<sup>IV</sup> = NTs intermediate, with a careful exploration of the various possible spin states and Fe<sup>IV</sup> = NTs bonding. Indeed, this intermediate exhibits very closely lying low-energy Fe<sup>IV</sup> high spin (S = 2) and intermediate (S = 1) spin state.<sup>3</sup> Interestingly, in both cases, analysis of the bonding reveals some Fe<sup>III</sup>-N\* character. Reaction pathways were also investigated on some species to get informations on the possible mechanism involved in the aziridination reaction. Some rationale gathering molecular electronic features (Figure 1) and reactivity properties will be proposed in the light of these calculations.

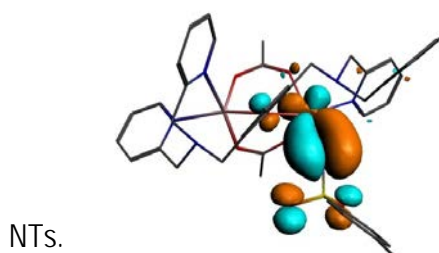


Figure 1. LUMO of electrophilic species Fe<sub>2</sub><sup>III,IV</sup> – NTs.

1. Avenier, F.; Latour, J.M. *Chem. Commun.* **2004**, 1544-1545. Avenier, F. et al. *Angew. Chem. Int. Ed.* **2008**, *47*, 715-717.
2. Kinkler et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 7394. Vardhaman, A. K. et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 12288-12292.
3. Gouré, E. et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 1580-1584.

## Metal-oxo and metal-hydroxo species in biology

Andy Borovik

*Department of Chemistry, University of California – Irvine*

The structure of active sites of proteins containing metal–oxo and hydroxo units has important consequences in metallobiochemistry. In many cases, they have been proposed to be key intermediates during catalysis, especially in proteins that utilize dioxygen for oxidative transformation. In addition, it has been proposed that intermediates formed during water oxidation at the oxygen-evolving complex within Photosystem II contain both metal–oxo and metal–hydroxo units. Developing synthetic systems having similar units has been challenging because of difficulties in replicating the structural components associated with active sites in metalloproteins. We develop synthetic systems that duplicate some of the structural complexity found in proteins, including hydrogen bonding networks that control the local environment around metal ions. This talk will describe our latest efforts in preparing and characterizing new metal-oxo and hydroxo complexes with a variety of biologically relevant metal ions. Included in the discussion will be methods to prepare heterometallic complexes containing hydroxo and oxo ligands. Our work suggests that high spin metal-oxo species can have a role in a variety of biochemical processes, including the conversion of water to dioxygen.

# DESCRIBING OXYGEN ATOM TRANSFER WITH DFT AND MULTICONFIGURATIONAL METHODS

Kristine Pierloot

*Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium  
kristin.pierloot@chem.kuleuven.be*

An important goal in the study of transition metal-mediated oxidative catalysis is to gain understanding of the relationship between the electronic structure of the metal-oxo species delivering the oxygen and its reactivity. Crucial factors are the radical character on the oxo-group, the availability of an empty metal-d-orbital, the presence of low-lying states with different spin and/or metal oxidation state. In this lecture, we will focus on the electronic structure of manganese-oxo porphyrins, and study the reactivity of such species in C-H bond hydroxylation. Due to the lack of oxyl character, the  $Mn^V$  singlet ground state is unreactive. Oxygen atom transfer reactions should therefore proceed through thermally accessible triplet and quintet states. The possibilities of multiconfigurational perturbation theory: CAS-PT2, RAS-PT2, and in particular the novel DMRG-PT2 approach, are explored and the results are used to benchmark a wide range of GGA and hybrid density functionals. With the latter functionals both the  $Mn^V \rightarrow Mn^{IV}$  promotion energy and the diradical character of the Mn–O  $\pi$  bond in the  $Mn^V$  triplet state are found to be extremely dependent on the contribution of exact exchange. For this reason, GGA functionals are to be preferred for further reactivity studies.

Reference:

S. A. V. Jannuzzi, Q. M. Phung, A. Domingo, A. L. B. Formiga, K. Pierloot, *Inorg. Chem.* **2016**, published online, DOI:10.1021/acs.inorgchem.5b02920

## Effects of heme conformation on spin state, spin distribution, and electron transfer in cytochromes

Kara L. Bren

*Department of Chemistry, University of Rochester*

Heme cofactors in proteins usually display distortions from planarity, and these distortions have been proposed to influence heme reactivity. In cytochromes *c*, the heme cofactor is ruffled, but the effect of ruffling on function has not been clear. To better understand the effects of ruffling on heme properties, cytochrome *c* variants with different amounts of ruffling have been prepared and studied using electrochemistry, nuclear magnetic resonance (NMR), nuclear resonance vibrational spectroscopy (NRVS), resonance Raman, and transient absorption spectroscopy. The results indicate that increasing ruffling increases porphyrin ligand field strength and decreases reduction potential. Furthermore, ruffling decreases delocalization of Fe  $d$  based molecular orbitals to the pyrrole carbons, resulting in decreased coupling to redox partners and slower electron transfer. In addition, ruffling influences iron vibrational dynamics, which are strongly coupled to polypeptide vibrations and influenced by interactions with other macromolecules. These results provide a basis for a hypothesis of how binding to redox partners may enhance electron transfer rates.

## Uranium-mediated electrocatalytic H<sub>2</sub> production from water

Karsten Meyer

*FAU Erlangen-Nuremberg*

Depleted uranium is a mildly radioactive waste product that is stockpiled worldwide. The chemical reactivity of uranium complexes is well documented, including the stoichiometric activation of small molecules of biological and industrial interest, such as H<sub>2</sub>O, CO<sub>2</sub>, CO, or N<sub>2</sub>, but catalytic transformations with actinides remain underexplored in comparison with transition-metal catalysis. For reduction of water to H<sub>2</sub>, complexes of low-valent uranium show the highest potential, but are known to react violently and uncontrollably to form stable bridging oxo or uranyl species. As a result, only a few oxidations of uranium with water have been reported so far, all stoichiometric. Catalytic H<sub>2</sub> production, however, requires the reductive recovery of the catalyst via a challenging cleavage of the uranium-bound oxygen-containing ligand. Here, we report the electrocatalytic water reduction observed with a trisaryloxo U(III) complex  $[(\text{Ad}, \text{MeArO})_3\text{mes}]\text{U}$ —the first homogeneous uranium catalyst for H<sub>2</sub> production from H<sub>2</sub>O. The catalytic cycle involves rare terminal U(IV)–OH and U(V)=O complexes, which have been isolated, characterized, and proved to be integral parts of the catalytic cycle. The recognition of uranium compounds as potentially useful catalysts suggests new uses for the light actinides. Hence, the development of uranium-based catalysts provides fundamentally new perspectives on nuclear waste management strategies, by suggesting that mildly radioactive and depleted uranium—an abundant waste product of the nuclear power industry—could be a valuable future resource.

# SCIENTIFIC TALKS

## The Conflicting Role of Water in the Activation of H<sub>2</sub>O<sub>2</sub> and the Formation and Reactivity of Non-Heme Fe(III)-OOH and Fe(III)-O-Fe(III) Complexes at Room Temperature

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Iron(II) complexes have been applied extensively in the epoxidation of alkenes as well as oxidation of alkyl C-H bonds to yield alcohols and ketones using H<sub>2</sub>O<sub>2</sub>.<sup>i,ii,iii,iv</sup> The complex [(MeN3Py)Fe<sup>II</sup>(CH<sub>3</sub>CN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**), can catalyze the oxidation of alkenes to 1,2-diols, as well as epoxides.<sup>v</sup> Here, the formation of an Fe<sup>III</sup>-OOH species by reaction of **1** with H<sub>2</sub>O<sub>2</sub> at room temperature is investigated by a combination of UV/vis absorption, EPR and resonance Raman spectroscopies and UV/vis absorption spectroelectrochemistry. The formation of the Fe<sup>III</sup>-OOH species, and its subsequent conversion to relatively inert Fe<sup>III</sup>-O-Fe<sup>III</sup> species, is shown to be highly dependent on the concentration of water, with excess water favoring the formation of the latter species. The presence of acetic acid increases the rate and extent of oxidation of **1** to its iron(III) state and inhibits the wasteful decomposition of H<sub>2</sub>O<sub>2</sub> but does not affect significantly the spectroscopic properties of the Fe<sup>III</sup>-OOH species formed.

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## DENSITY MATRIX RENORMALIZATION GROUP (DMRG) STUDY OF SPIN-STATE ENERGETICS OF IRON-OXO PORPHYRINS

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Despite of extensive studies, the correct description of the relative energies of low-lying states in the oxo-iron(IV) porphyrin  $\pi$ -cation radical  $(\text{Por}^+)\text{Fe}^{\text{IV}}=\text{O}(\text{Cys})$ , known as Compound I (Cpd I), is still a big challenge. Due to the strongly multireference character of Cpd I, density functional theory (DFT) can only give qualitative results for the electronic structure of Cpd I. On the other hand, in high accuracy *ab initio* multireference methods such as multireference perturbation theory (R)CASPT2, a large active space is required in order to quantitatively describe the relative energies. In this work, we have used a novel method known as Density matrix renormalization group (DMRG)<sup>[1]</sup>. Here, we report preliminary results obtained for the spin-state energetics of the Cpd I model. By comparing between CASSCF, RASSCF, DMRG-SCF and the multireference perturbation method RASPT2, we can conclude that:

- (i) DMRG-SCF is a good alternative to CASSCF for small active space calculations and is better than RASSCF with a large active space. This enables us to employ a large active space for Cpd I calculations. Furthermore, the results indicate that the RASSCF orbitals are already a very good approximation to the DMRG-SCF orbitals.
- (ii) In comparison with the best RASPT2 results<sup>[2]</sup>, CASSCF, RASSCF, and DMRG-SCF all predict the wrong ground state. This illustrates the importance of dynamic correlation for spin state energetics. To account for dynamic correlation, perturbation theories such as NEVPT2<sup>[3]</sup> on top of DMRG-SCF are being implemented and will be tested in the future.

### Acknowledgement

This work was done in the framework of the COST action CM1305 "Explicit Control Over Spin-states in Technology and Biochemistry (ECOSTBio)" (STSM reference: COST-ONLINE\_STSM-CM1305-27670). This investigation has been supported by grants from the Flemish Science Foundation (FWO).

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# STABILIZATION OF THE LOW-SPIN STATE IN A MONONUCLEAR IRON(II) COMPLEX AND HIGH-TEMPERATURE COOPERATIVE SPIN CROSSOVER MEDIATED BY HYDROGEN BONDING

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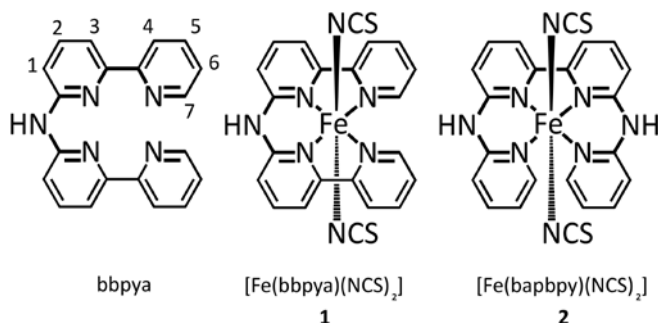
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The tetrapyrridyl ligand bbpya (bbpya = N,N-bis(2,2'-bipyrid-6-yl)amine) and its mononuclear coordination compound  $[\text{Fe}(\text{bbpya})(\text{NCS})_2]$  (**1**) were prepared. According to magnetic susceptibility, differential scanning calorimetry fitted to Sorai's domain model, and powder X-ray diffraction measurements, **1** is low-spin at room temperature, and it exhibits spin crossover (SCO) at an exceptionally high transition temperature of  $T_{1/2} = 418$  K. Although the SCO of compound **1** spans a temperature range of more than 150 K, it is characterized by a wide (21 K) and dissymmetric hysteresis cycle, which suggests cooperativity. The crystal structure of the LS phase of compound **1** shows strong  $\text{N} \cdots \text{H} \cdots \text{S}$  intermolecular H-bonding interactions that explain, at least in part, the cooperative SCO behavior observed for complex **1**. DFT and CASPT2 calculations under vacuum demonstrate that the bbpya ligand generates a stronger ligand field around the iron(II) core than its analogue bapbpy (N,N'-di(pyrid-2-yl)-2,2'-bipyridine-6,6'-diamine); this stabilizes the LS state and destabilizes the HS state in **1** compared with  $[\text{Fe}(\text{bapbpy})(\text{NCS})_2]$  (**2**). Periodic DFT calculations suggest that crystal-packing effects are significant for compound **2**, in which they destabilize the HS state by about  $1500 \text{ cm}^{-1}$ . The much lower transition temperature found for the SCO of **2** compared to **1** appears to be due to the combined effects of the different ligand field strengths and crystal packing.<sup>[2]</sup>



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## IRON(III) SPIN CROSSOVER COMPOUNDS WITH SHIFF-BASE LIGANDS

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Our recent work in the field of Fe(III) spin crossover molecular magnetism is summarized. Series of iron(III) mononuclear complexes are reported, in which the spin crossover phenomenon is tuned by i) coordinated pseudohalide anions (NCS<sup>-</sup>, NCS<sup>-</sup>, NCO, N<sub>3</sub><sup>-</sup>),<sup>[1]</sup> ii) non-coordinated halide anions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>),<sup>[2]</sup> iii) various substituents on Schiff-base ligands,<sup>[3]</sup> and iv) co-crystallized molecules of solvents (*N,N*-dimethylformamide, dimethyl sulfoxide, butanone).<sup>[4]</sup> Furthermore, the utilization of DFT methods both for predicting of the observed trend of  $T_{1/2}$  and quantification of the strength of hydrogen bonds affecting transition temperature are discussed.

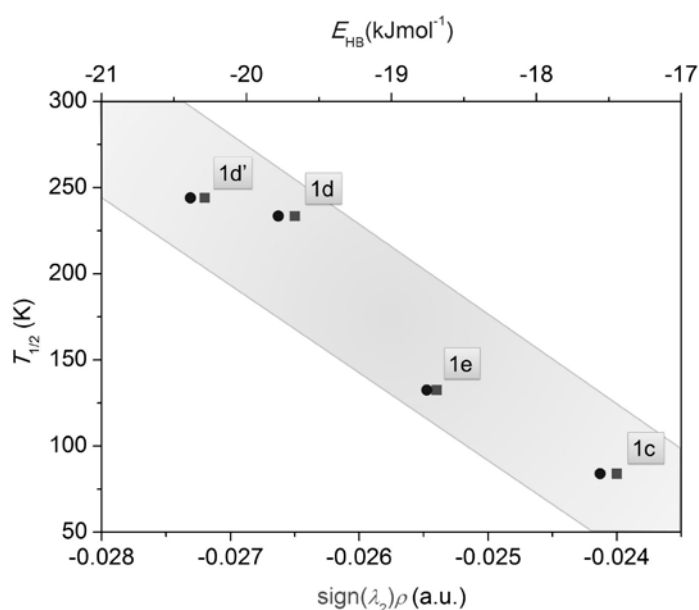


Fig.1 The plot of spin transition temperature  $T_{1/2}$  of SCO compounds with various co-crystallized solvent molecules as a function of strength of N–H...O contacts.<sup>[4]</sup>

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

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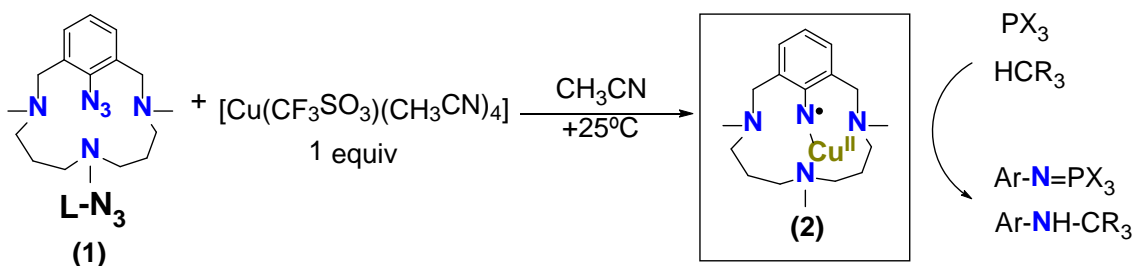
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High-valent copper-nitrene species have been postulated as key intermediates in several copper-catalyzed reaction such as aziridination and amination reactions.<sup>[1]</sup> However, due to their high reactivity, terminal copper-nitrene species have not been either isolated or spectroscopic characterized. 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>. Moreover, Ray *et al.* reported the spectroscopic and theoretical characterization of a copper(II)-nitrene radical stabilized by Sc(III)<sup>[3,4]</sup> and very recently, Bertrand *et al.* could crystallize a copper(II)-bis-nitrene complex<sup>[5]</sup>.

Herein, we describe the preparation and characterization of a well-defined terminal copper(II)-nitrene radical species (**2**), which is stable at room temperature, formed by reaction of L-N<sub>3</sub> (**1**) with [Cu(I)(CF<sub>3</sub>SO<sub>3</sub>)(CH<sub>3</sub>CN)<sub>4</sub>] in acetonitrile (Scheme 1). The nature of compound **2** has been established by spectroscopic and spectrometric technics together with theoretical methods. Moreover, compound **2** is able to perform nitrene-transfer reactions and H-atom abstraction reactions of phosphines and weak C-H bonds respectively in modest yields.



**Scheme 1:** Schematic representation of the mechanism of the reaction of **1** with copper(I) in CH<sub>3</sub>CN at +25°C.

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## CLICK-DERIVED TRIPODAL LIGANDS FOR SPIN CROSSOVER AND BOND ACTIVATION REACTIONS

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1,2,3-Triazoles derived from the copper(I) catalyzed azide-alkyne reaction are popular ligands in coordination chemistry.<sup>[1]</sup> In this contribution we will present tripodal ligands derived through the aforementioned reaction. It will be shown that spin crossover can be achieved for both iron(II)<sup>[2]</sup> and cobalt(II)<sup>[3]</sup> complexes using exactly the same click-derived tripodal ligand. Additionally, we will show that metal complexes of such tripodal ligands can be used for investigating bond activation reactions<sup>[4]</sup> including C-H activation.<sup>[5]</sup> Furthermore, the utility of cobalt(II) complexes with such ligands for activating dioxygen will also be addressed.

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## Dioxygen Activation and Catalytic Reduction by a Thiolate-Bridged Dimanganese(II) Complex with a Pendant Thiol

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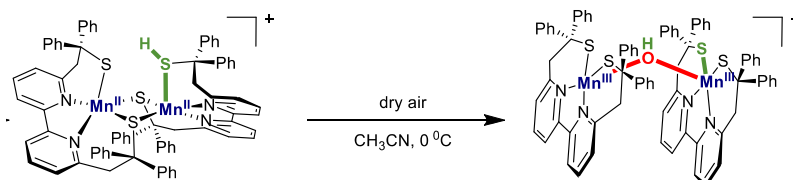
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Synthetic metal-oxygen complexes, such as metal -hydroperoxo and -oxo species, are of special interest for the communities of bioinorganic and biological chemists as key intermediates for dioxygen activation and oxidation reactions catalyzed by enzymes or their synthetic mimics.<sup>1</sup> In addition, activation of dioxygen represents a critical step in numerous fundamental biological and industrial processes.

How dioxygen can be activated and reduced by molecular transition metal complexes remains a central question, especially the determination of the factors that favour 4-electron reduction vs 2-electron reduction to yield water or hydrogen peroxide, respectively.<sup>2,3</sup>

We report here on a manganese complex that catalyses O<sub>2</sub> reduction in the presence of a one-electron reducing agent (decamethylferrocene) and a proton source (2,6-lutidinium tetrafluoroborate), in solution. The catalyst is a new dimanganese(II) complex, (Scheme 1), that shows two peculiar features. First, the presence of thiolates in the coordination sphere of the Mn ion should promote the activation of molecular oxygen and its reduction. Second, a pendant bound thiol can (i) promote reactivity *via* transient hydrogen bonding interactions, (ii) act as proton relay during a catalytic process or/and (iii) modulate the redox potential of the manganese center.<sup>4</sup>



Recently, new intermediates have been synthesized and characterized (X-ray, XAS, EXAFS, UV-Vis, IR) corresponding to high-valent oxo Mn complexes (scheme 2).



The conditions to generate these species and their reactivity toward different substrates have been investigated and will be presented.

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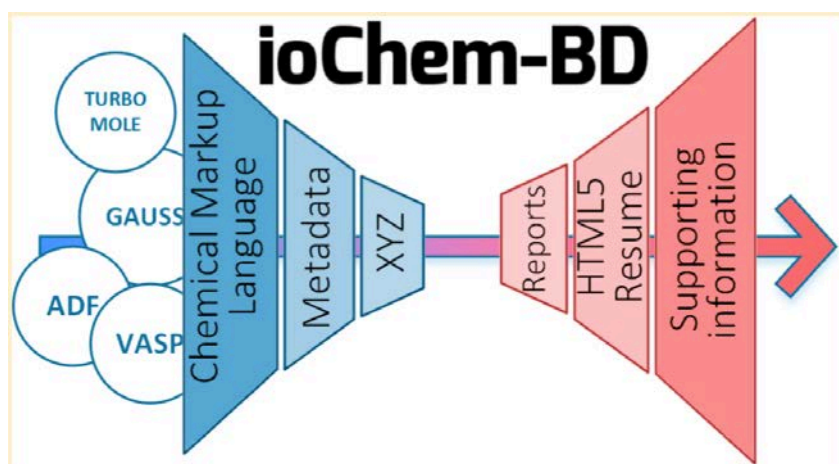
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## MANAGING THE COMPUTATIONAL CHEMISTRY BIG DATA PROBLEM: THE IOCHEM-BD PLATFORM

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We present the ioChem-BD platform ([www.iochem-bd.org](http://www.iochem-bd.org))<sup>[1]</sup> as a multiheaded tool to manage large volumes of quantum chemistry results from a diverse group of standard simulation packages. The platform has an extensible structure. The key modules managing the main tasks are (i) the upload of output files from computational chemistry packages, (ii) extract meaningful data from the results, and (iii) generate output summaries in user-friendly formats. A heavy use of the Chemical Mark-up Language (CML) is made in the intermediate files used by ioChem-BD. From them and using XSL techniques, we manipulate and transform such chemical data sets to fulfill researchers' needs in the form of HTML5 reports, supporting information, and other research media.



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## REACTIVITY OF STEREOISOMERIC IRON(IV) COMPLEXES WITH A DIFFERENT SPIN STATE STUDIED IN THE GAS PHASE

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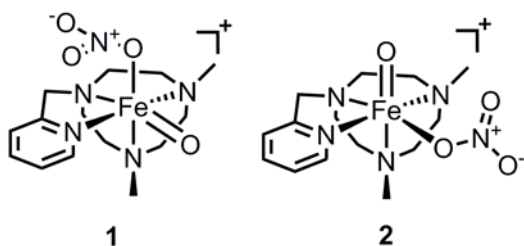
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We have found a method to generate different stereoisomers of an iron(IV) complex with PyTACN ligand (**1**, **2**) in the gas phase. It is based on different modes of electron ionization conditions. The isomers have been characterized by helium tagging infrared photodissociation (He@IRPD) spectroscopy and it was found that they are generated in different spin states.<sup>[1,2]</sup> The reactivity of the complexes has been probed under well-defined gas phase conditions. We have shown that the reactivities of the spin-isomers significantly differ in both, hydrogen-atom transfer reaction and oxygen-atom transfer reaction. The quintet isomer reacts about three to five times faster.



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## MATRIX-ASSISTED RELAXATION IN $\text{Fe}(\text{PHEN})_2(\text{NCS})_2$ SPIN-CROSSOVER MICROPARTICLES. THEORETICAL AND EXPERIMENTAL INVESTIGATIONS

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The influence of the embedding matrix on the relaxation of  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  (phen=1,10-phenanthroline) spin-transition microparticles analysed in the framework of an elastic model based on a Monte-Carlo method<sup>[1]</sup> is revealed here. With respect to bare particles, their dispersion in glycerol leads to less sigmoidal high-spin  $\rightarrow$  low-spin relaxation curves, associated with the dampening of cooperativity<sup>[2]</sup>. The hypothesis of interactions between the microparticles and their environment is satisfyingly supported by the model. The interactions between molecules are accounted by springs which elongations produce different local pressure on every molecule. A faster start of the relaxation for microparticles embedded in glycerol is reproduced by an initial positive local pressure acting on the edge spin-crossover molecules from the matrix side (see figure, left). This local pressure diminishes and eventually becomes negative during the relaxation, due to the decrease of volume of spin crossover microparticles during the high-spin  $\rightarrow$  low-spin relaxation. These features are accounted for by the glassy nature of matrix encapsulating the microparticles (rigid environment, ageing effect).

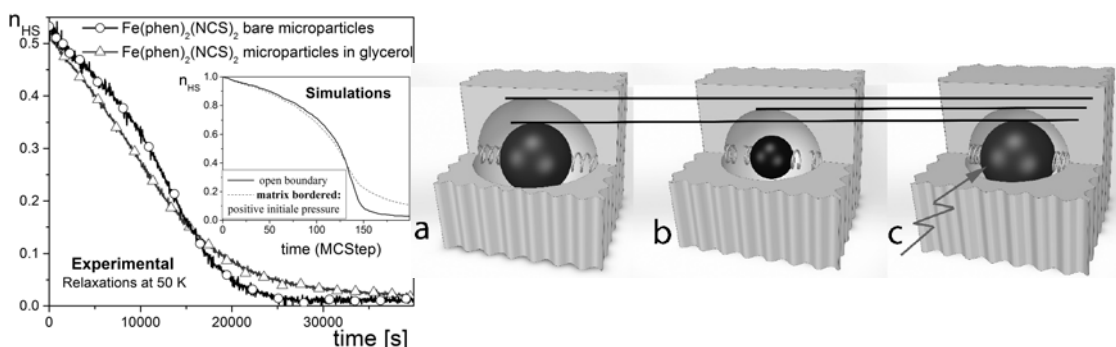


Figure: Relaxation curves on  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  spin-crossover microparticles and simulations within the mechanoelastic model (left) A spin crossover particle in its environment: (a) HS state at high-temperature (b) LS state at low temperature (c) HS state after photoexcitation at low temperature

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## Nickel(III)-Oxygen Adducts That Oxidize Inert Hydrocarbons

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High-valent terminal metal-oxygen adducts are hypothesized to be the potent oxidising reactants in late transition metal oxidation catalysis. In particular, examples of high-valent terminal nickel-oxygen adducts are sparse, meaning there is a dearth in the understanding of such oxidants. Herein we describe the preparation of a family of Ni(III)-oxygen adducts. Electronic absorption, electronic paramagnetic resonance, and X-ray absorption spectroscopies, and density functional theory calculations have been used to probe the electronic and structural properties of these compounds. Structure function relationships in a series of complexes have been elucidated, providing us with critical insight into the reactivity properties of high-valent nickel oxidants.

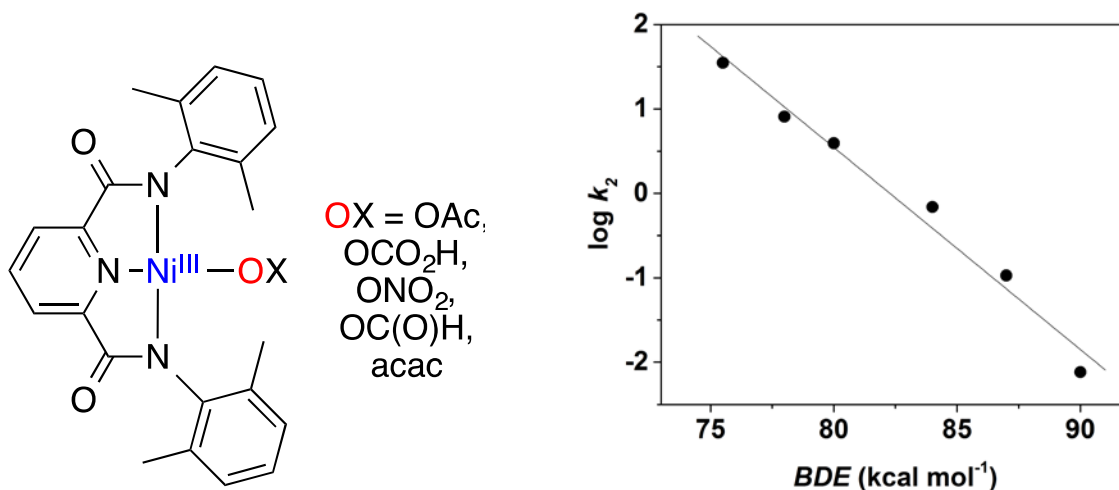


Figure 1. Nickel(III)-oxygen adducts (left) and a plot (right) of  $\log(k_2)$  versus C–H BDE for the reactions between a nickel(III)-oxygen adduct and various hydrocarbons.

## ACCURATE SPIN-STATE ENERGETICS OF FE(III) AND RU(III) AQUO COMPLEXES EVIDENCE SIGNIFICANT SOLVATION EFFECTS

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Some applications of high-level wave function theory methods to the problem of spin-state energetics are recalled,<sup>[1]</sup> with particular focus on our recent study of metal aquo complexes  $[M(H_2O)_6]^{n+}$  ( $M = Fe^{III}$  and  $Ru^{III}$ ),<sup>[2]</sup> for which there are reliable experimental data of spin-state energetics to compare with. In view of notable controversies for  $Fe^{III}$  aquo complex,<sup>[3,4]</sup> vertical energies of the lowest-energy spin states are critically studied by CASPT2, RASPT2, NEVPT2, and CCSD(T)-F12 methods. Moreover, comparative calculations are also presented for various CC methods up to full CCSDT. It is shown that spin-state energetics obtained from single- and multi-reference methods are consistent with each other, but they differ considerably from the experimental transition energies. Our results indicates that these discrepancies can be attributed to significant solvation effects, which were totally neglected in the previous theoretical studies.<sup>[3-5]</sup> To this end, DFT and CASPT2 calculations of spin-state energetics are reported for larger models with added a second shell of explicit water molecules,  $[M(H_2O)_6 \cdot (H_2O)_{12}]^{3+}$  ( $M = Fe$  and  $Ru$ ). It is shown that for the latter type of models, compared with unsolvated  $[M(H_2O)_6]^{3+}$  ones, the lower-spin state is stabilized by as much as  $(3-4) \cdot 10^3 \text{ cm}^{-1}$  ( $\sim 10 \text{ kcal/mol}$ ) with respect to the higher-spin state. This effect is due to the interaction of the first-shell water ligands with the second-shell water molecules, which leads to a contraction of the first coordination sphere and thus to an increase of the ligand field. The results suggest that solvation may affect the energies of d-d transitions, even for coordinatively-saturated complexes, more significantly than it is widely assumed. Some further examples are shown to indicate that similar solvation effects (due to the change of the solute geometry) may also be expected for other complexes, even those where ligands are not explicitly involved in H-bonding interactions with the solvent molecules, and that analogous medium effects may be important for crystalline phases too. The outcome of this research is important for correct interpretation of experimental spin-state energetics obtained in condensed phases and for development of reliable computational protocols.

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## HETEROMETALLIC NICKEL-COPPER DIOXYGEN COMPLEXES: ELECTRONIC STRUCTURE AND REACTIVITY

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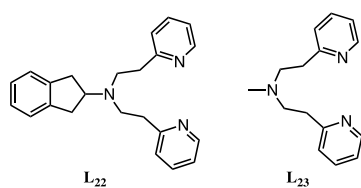
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Dioxygen binding and activation reactions at dimetal sites constitute chemical processes of fundamental interest, because of their implication in biology, chemical synthesis and catalysis. The study of heterobimetallic dioxygen complexes is highly interesting because of their potential in modelling structures and reactivities of metalloenzymes containing two different metal ions at their active sites<sup>[1]</sup>. The first high-valent bis- $\mu$ -oxo dimetal core has been characterized using a Cu<sup>I</sup> triamine complex and a stable Ni<sup>III</sup> superoxo complex where the oxo groups act as nucleophiles and react towards aldehydes<sup>[2]</sup>, in contrast to the electrophilic oxo groups of the homometallic  $[\text{Ni}_2(\mu\text{-O})_2]^{2+}$  and  $[\text{Cu}_2(\mu\text{-O})_2]^{2+}$  analogues which are unreactive towards electrophile substrates. On the other hand, our group has reported the stereoselective oxygen insertion to the nonreactive C-H bond of the ligand L22 through a homometallic core  $[\text{Cu}_2(\mu\text{-O})_2]^{2+}$  using amino pyridine type ligands<sup>[3]</sup>.

Herein, two heterometallic intermediates were characterized using Cu<sup>I</sup> complexes coordinated to the following ligands (in L22 the substrate is covalently bound to the ligand):



Therefore, in this study we report the synthesis and spectroscopic characterization of mixed-metal Ni-Cu intermediates which were identified by UV-Vis, EPR and resonance Raman spectroscopy. Also, we investigate the reactivity of those heterometallic complexes towards electrophile external substrates or internal substrates. This work has been carried out through an STSM CM1305.

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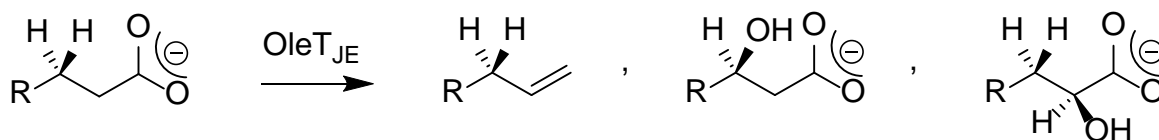
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## Quantum mechanics/molecular mechanics studies of cytochrome P450 peroxygenases for the biosynthesis of biofuels.

Sam P. de Visser, Abayomi S. Faponle, Matthew G. Quesne, Tomasz Borowski

Cytochrome P450 enzymes are versatile biocatalysts in human physiology that convert substrates to products efficiently. In the human body they have many functions, including the biosynthesis of hormones in the liver as well as the metabolism of drugs. Despite their biological functions, actually few P450 isozymes are being used in the Chemical Industry at the moment, which is due to the fact that they use expensive cofactors, such as NADPH. One specific class of P450 enzymes, however, utilize hydrogen peroxide as a terminal oxidant and act as peroxygenases. These lack the need of cofactors and, hence, are biotechnologically preferred. A recently discovered P450 isozyme, namely OleT<sub>JE</sub>, was found to utilize long chain fatty acids (C<sub>16</sub> – C<sub>20</sub>) and convert them to terminal olefins, hence paving the way for biofuels production. Unfortunately, the P450 OleT<sub>JE</sub> isozyme gives a considerable amount of by-products related to  $\square$  and  $\square$ hydroxylation processes. To understand the mechanisms for substrate activation leading to olefins as well as  $\square$  and  $\square$ hydroxylated products, we have performed a detailed quantum mechanics/molecular mechanics study. In recent years, we developed efficient protocols for running QM/MM calculations,<sup>1</sup> which we have applied, for instance, to the P450 peroxygenase reaction.<sup>2</sup> We show that the P450s have a fit-for-purpose substrate binding pocket that destabilize the thermodynamically favourable substrate hydroxylation reaction in preference of a desaturation reaction.



*Scheme 1: Products observed in the reaction of fatty acids with P450 OleT<sub>JE</sub>.*

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## The aqueous chemistry of the $[\text{Fe}^{\text{IV}}(\text{O})\text{TMC}]^{2+}$ complex: determining the $pK_a$ of an aqua ligand bound to an $\text{Fe}^{\text{IV}}=\text{O}$ unit

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Inspired by the high-valent chemistry of many iron containing non-heme enzymes an incredibly large array of Fe(IV)-oxo model complexes has been reported in the literature.<sup>[1]</sup> Examples include the Fe(IV)-oxo complex derived from the TMC-ligand (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), which was the first crystallographically characterized example.<sup>[2]</sup> Exploration of this complex in aqueous media allowed us to study the first example of an Fe(IV)-oxo complex in water with a *trans* labile site bearing an aqua ligand. This complex allowed us to determine the  $pK_a$  of the aqua ligand bound to an Fe(IV)-center. The  $pK_a$  measurement serves as a direct measurement of the Lewis acidity of the Fe(IV)-oxo unit. Experimental results were complemented by computational studies.

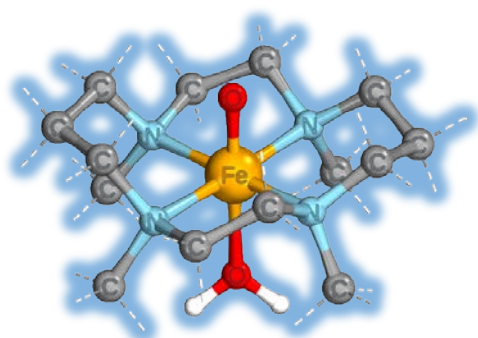


Figure 1: DFT-optimized structure of  $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{H}_2\text{O})]^{2+}$ .

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## POLYNUCLEAR MMO BIOINSPIRED COPPER COMPLEXES

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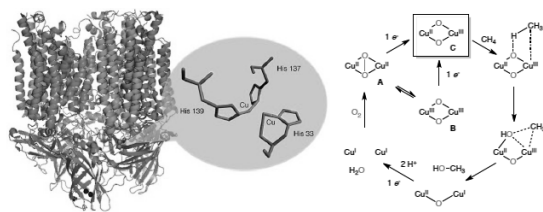
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Methane is a greenhouse gas that remains in the atmosphere for approximately 9-15 years. It is over 20 times more effective in greenhouse effect than carbon dioxide over a 100-year period. Methane is also a primary constituent of natural gas and an important energy source. To reduce its greenhouse gas effect and to increase its potential as a petroleum alternative for fuels and in the petrochemical industry, its transformation into a liquid form such as methanol is of current interest in chemistry.<sup>[1]</sup> Currently, industrial methanol production is accomplished by steam reforming of methane, which requires high temperatures and pressures. Therefore, alternative processes such as the selective direct oxidation of methane to methanol are of considerable interest. However, methane has the strongest CH bond of any hydrocarbon (104 kcal/mol), thus its selective oxidation to methanol without further oxidation is extremely challenging. In nature, methane particulate monooxygenases (pMMO) accomplish the direct conversion of methane into methanol at ambient temperature and atmospheric pressure allowing the harnessing of methane as an energy source and for the synthesis of the life required molecules (figure 1).<sup>[2]</sup> The most recent results propose a dinuclear copper center, which reacts with dioxygen to produce a  $\text{Cu}_2/\text{O}_2$  as active species in methane oxidation such as  $(\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo})\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ ,  $\text{bis}(\mu\text{-oxo})\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}$  or mixed-valent  $\text{bis}(\mu\text{-oxo})\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}$ . Herein, we report the synthesis and characterization of several polynuclear pMMO bio-inspired copper complexes. Electronic mapping of these species is of crucial importance and constitutes the first step to understand their potential reactivity. A deep understanding of their electronic structure will be provided by their characterization using several techniques (EPR, electrochemistry, magnetism) coupled with theoretical calculations.



**Figure. Structure of the pMMO from *Methylococcus capsulatus* and proposed catalytic cycle.**

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# REVERSIBLE SPIN STATE CHANGES IN A TETRAHEDRAL IRON COMPLEX WITH REDOX-ACTIVE FORMAZANATE LIGANDS

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Coordination complexes that show electronic bistability are of interest for applications such as molecule-based data-storage, switches and sensors.<sup>[1]</sup> In the case of iron compounds, most of these are based on 6-coordinate geometries, where switching between  $S = 0$  and  $S = 2$  states is observed. Due to the smaller ligand field in 4-coordinate (pseudo)tetrahedral complexes, these are usually high-spin and do not show changes in spin state.<sup>[2]</sup>

We recently developed formazanates (based on a [NNCNN] backbone) as a novel class of redox-active ligands that are accessible in the anionic ( $L^-$ ), radical dianionic ( $L^{2-}$ ) and trianionic ( $L^{3-}$ ) form.<sup>[3]</sup> Here, we report a bis(formazanate)iron complex ( $L_2Fe$ ) and present X-ray crystallographic and spectroscopic evidence for thermal switching between  $S=0$  and  $S=2$  states. Fitting of variable-temperature NMR data (Figure 1) suggests that transition to a high-spin Fe(II) electronic isomer takes place with  $T_{1/2} = 345$  K. Mössbauer spectroscopy and magnetic (SQUID) measurements provide insight in the nature of the spin transition both in the solid state and in solution. Chemical reduction of the neutral compound ( $L_2Fe$ ) yields a stable mono-anion ( $[L_2Fe]^-$ ) which has a  $S = 1/2$  ground state.

These results show that the 4-coordinate iron complex show reversible spin state changes due to the unique properties of the formazanate ligands.

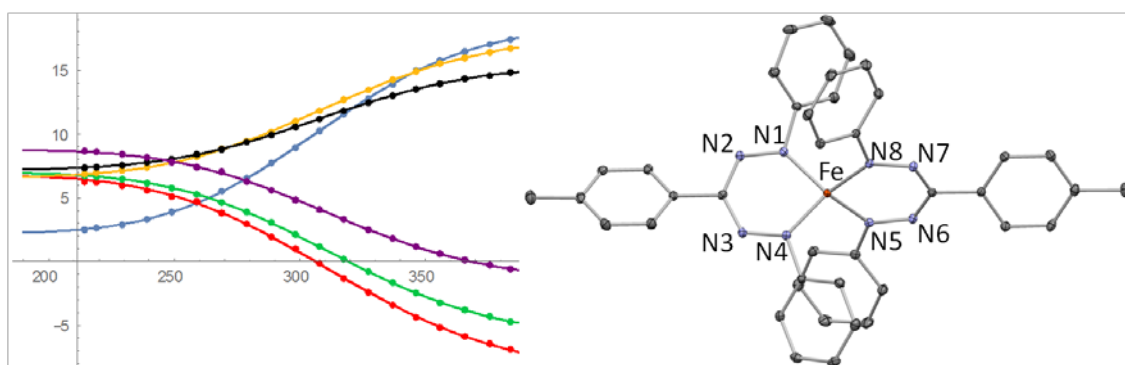


Figure 1 Temperature-dependence of <sup>1</sup>H NMR shifts of compound 1 (left) and X-ray crystal structure (right).

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## VARIABLE TEMPERATURE ATR-IR SPECTROSCOPY AS A VALUABLE TOOL FOR THE IN SITU SPIN STATE DETECTION OF IRON(II) SPIN CROSSOVER COMPLEXES

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Variable temperature vibrational spectroscopy has proved a valuable tool for structural characterization of iron(II) coordination compounds undergoing a high-spin (HS) ↔ low-spin (LS) transition. MIR- and FIR-spectroscopy of iron(II) compounds allows not only for the observation of the first order structural phase transition, but also concomitant for an in-situ detection of the spin state<sup>[1,2]</sup>. The reason for this is the drastic bond strength change of the Fe-N bonds due to the spin transition. Especially, temperature-dependent FIR-spectroscopy is an often neglected technique, mainly due to the obstacle of sensitivity and sample preparation. It has been shown that in the FIR region there is a vibrational mode of the iron(II) coordination center towards the centroids of the coordination octahedron formed by the six coordinating nitrogen atoms of the tetrazole ligands<sup>[3]</sup>. The calculations reveal that this N3-Fe-N3' vibrational mode is almost totally decoupled from any other atomic motions of the rest of the molecule. Therefore, this absorption feature can be used for the quantification of the high spin and low spin species, respectively, thus allowing for a very sensitive in-situ determination of the ratio between the high spin and low spin compounds. The molecular spin transition properties derived by variable temperature vibrational spectroscopy is compared to complementary physico-chemical characterizations by UV-VIS-NIR spectroscopy, SQUID/VSM and <sup>57</sup>Fe-Mössbauer spectroscopy<sup>[4]</sup> Herein we present an innovative custom-made setup for both temperature-dependent MIR and FIR-spectroscopy based on a PIKE Technologies ATR-Unit with a Perkin Elmer Spectrum 400 FT-MIR/FIR combination. The resulting spectra during the observation of a phase transition using the novel ATR-setup are compared to calculated spectra for detailed assignments using DFT. The DFT calculations implemented in the Gaussian 09 software package<sup>[5]</sup> used for the free ligands the basis set 6-311G++ (2d,3p) and SDD for the complexes for the B3LYP functionals.

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## Valence tautomerism in 2D manganese-nitronyl nitroxide radical systems

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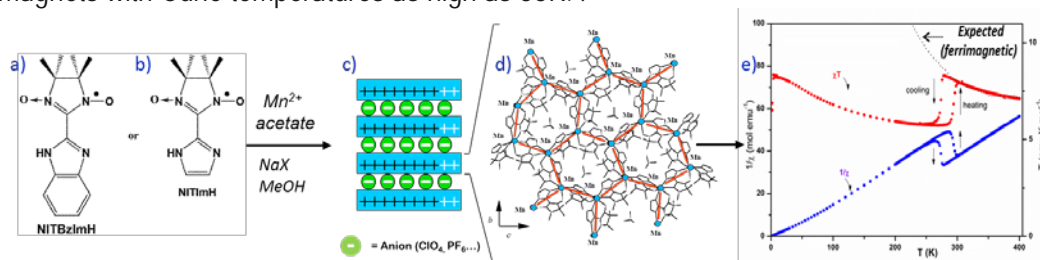
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Interest of nitronyl nitroxide free radicals in molecular magnetism holds in the possibility to use them as both spin carrier and as bridging ligand to build magnetic architectures. Their incorporation into chelates has enabled the development of a rich coordination chemistry dedicated to molecular magnetism.<sup>1</sup> Thus, when functionalized with imidazole or benzimidazole substituents (Figure 1a-b) they give with the Mn<sup>2+</sup> ions lamellar compounds (1c diagram) whose sheets are formed by the 2D coordination polymer, Mn-radical, of formula {[Mn<sup>II</sup><sub>2</sub> (NITR)<sub>3</sub>]}<sub>n</sub> (scheme 1d) between which are intercalated anions (X<sup>-</sup>).<sup>2,3,4</sup> Some of these compounds are magnets with Curie temperatures as high as 55K.<sup>4</sup>



Scheme 1

We recently discovered that some of these systems have a thermal-induced transition of magnetic susceptibility, with hysteresis, in the range of room temperature. This is attributed to a phenomenon of valence-tautomerism (redox isomerism) through which the Mn ions, which are in their +2 oxidation state at high temperature (> 320K), are oxidized in their +3 oxidation state upon cooling (<270K) while some nitronyl nitroxide radicals are reduced. The process is reversed on heating.

This family of Mn-radical compounds is therefore a new type of switchable materials with all the features required for potential applications such as the abrupt transition with hysteresis at room temperature and the layered structure that allows great flexibility.

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## MONONUCLEAR SINGLE MOLECULE MAGNETS: THE CASE OF MANGANESE(III), IRON(II) AND COBALT(II) COMPLEXES BEARING IMIDODIPHOSPHINATO CHELATING LIGANDS

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During the last few years, a large number of mononuclear metal complexes has been investigated as potential Single Molecule Magnets (SMMs).<sup>[1-3]</sup> The coordination chemistry of dichalcogenidoimidodiphosphinato type of ligands,  $R_2P(E)NHP(E')R'_2$  ( $E, E' = O, S, Se, Te; R, R' = \text{alkyl or aryl groups}$ ), towards both main group and transition metal elements, has been shown to be rather versatile, especially in their anionic  $L^-, [R_2P(E)NP(E')R'_2]^-$ , form.<sup>[4]</sup> Recent examples of high-spin  $S = 2$  Mn(III) and Fe(II), as well as  $S = 3/2$  Co(II) complexes, bearing these ligands and exhibiting SMM-like properties will be presented.

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# REACTIVE OXYGEN SPECIES AND THE CU[AMYLOID-BETA] COMPLEX

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Copper is required by living cells for moving electrons between organic molecules and reactive oxygen species (ROS). Free copper is toxic and copper reactivity is kept under control by well ordered macromolecules that carry copper and other metal ions.<sup>[1]</sup> When this control is lacking, copper ions are found in abnormal amount in several cellular and extracellular compartments, a process known as disohomeostasis.

When the compartment is populated by disordered proteins, these latter can interact with metal ions and behave as new catalysts. This occurs, for instance, in the synapse of neurons upon neurodegeneration: disordered amyloid- $\beta$  (Ab) peptides produced by a pathological cut of a precursor protein interact with copper and various monomeric, oligomeric and aggregated forms of Cu[Ab] exert different properties.<sup>[2]</sup> When dioxygen is present together with organic reducing agents, electron transfer to dioxygen is observed. Recently, the production of superoxide as an intermediate in O<sub>2</sub> reduction has been demonstrated in vitro.<sup>[3]</sup> Dioxygen activation to superoxide is explained by interactions with carboxylate anti to Cu(I)-O<sub>2</sub> binding position.<sup>[4]</sup> This interaction is allowed by the intrinsic disorder of the amyloid peptide.

In this contribution, we discuss how to use computational models to control, in the amyloid- $\beta$  context, the Cu-O<sub>2</sub> oxidation and spin state.

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## INTERMEDIATE-SPIN STATE IN SIX-COORDINATE IRON COMPLEXES WITH A PSEUDO-OCTAHEDRAL COORDINATION ENVIRONMENT

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For iron(III) complexes with a perfect octahedral coordination environment around the metal ion, ligand field theory predicts either a low-spin or a high-spin state as ground state for the iron(III) ion. Although deviations from the perfect octahedral ligand environment can be induced by an inhomogeneous ligand donor set, by distortions of the bond angles around the central metal ion or by a set of non-uniform metal-ligand bond lengths, these deviations are generally considered to be insufficient to perturb the electronic structure of the metal ion to such an extent that an intermediate-spin state can be observed as ground state. Only substantial deviations from an octahedral coordination environment such as changing the coordination number of the metal ion are known to result in an intermediate-spin state of the iron ion.

Here, we want to present strategies how an intermediate-spin ground state can be achieved in six-coordinate iron(III) complexes, where, however, the structural distortions from the octahedral coordination environment are by no means more severe than in any other pseudo-octahedral metal complex. The spin state of the iron(III) complex can be unambiguously established by structure analysis, magnetic susceptibility measurements, ESR and Mössbauer spectroscopy. These strategies are also applied towards the synthesis of an intermediate-spin iron(II) complex.

# POSTER PRESENTATIONS

<u>No.</u>	<u>Presenting Author</u>	<u>Title</u>
P1	Andjelkovic, Ljubica	<i>Spin States of Hepta-Coordinated Transition Metal Ion Complexes</i>
P2	Buta, Cristina	<i>The Fine Balance of Effects in Spin Cross-Over Processes. A Ligand Field Modeling</i>
P3	Yavuz, Dede	<i>Mimicking the Secondary Sphere Histidine of a Dioxygenase Active Site</i>
P4	Desage-El Murr, Marine	<i>Cooperative Catalysis with Redox Non-Innocent Ligands</i>
P5	Deville, Claire	<i>O<sub>2</sub> Activation and Double C-H Oxidation by a Mononuclear Manganese(II) Complex</i>
P6	Domingo, Alex	<i>Tuning the Electronic Structure of Fe(II) and Ru(II) Complexes with Imidazole Based Chelating Ligands</i>
P7	Feixas, Ferran	<i>Accelerating Metal-Directed Protein Dynamics with Enhanced Sampling Techniques</i>
P8	Fitzpatrick, Anthony	<i>Geometric Modulation of the Jahn-Teller Distortion in Highly Anisotropic Manganese(III) Complexes</i>
P9	Freitag, Leon	<i>On the Active Space Selection in Multiconfigurational Calculations of Excited States of [Ru(bpy)<sub>2</sub>]<sup>2+</sup></i>
P10	Gutten, Ondrej	<i>Metal-Ion Selectivity in Peptides and Model Complexes</i>
P11	Halcrow, Malcolm	<i>The Influence of Molecular Shape on Spin Transition in the Solid State</i>
P12	Hallaert, Simon	<i>A Combined Computational and Spectroscopic Investigation of <math>\alpha</math>-Fe in Fe-ZSM-5</i>
P13	Hunter, Gary	<i>Metal Selectivity and Specificity in Mononuclear Superoxide Dismutases</i>
P14	Jakobsen, Vibe	<i>Resolution of Chiral Spin States</i>
P15	Latour, Jean-Marc	<i>Amidines Synthesis from Tandem Nitrene Transfer and Nitrile Insertion</i>
P16	Murariu, Ioana	<i>Rationalizing the Magnetic Anisotropy with the Help of Ligand Field Concepts in Simple Lanthanide Units</i>
P17	Romero, Adrian	<i>New Method for the Prediction of Mössbauer Parameters for Iron Containing Complexes</i>
P18	Šalitroš, Ivan	<i>Bis-Tridentate Organic Ligands with Photoactive Anthracene Skeleton</i>
P19	Srnec, Martin	<i>Accurate Prediction of One-Electron Reduction Potentials in Aqueous Solution by Variable-Temperature H-Atom Addition/Abstraction Methodology</i>
P20	Stepniewski, Adam	<i>Interaction of NO and NH<sub>3</sub> with Cobalt Centers in Zeolites: Cluster and Periodic Calculations</i>
P21	Weber, Birgit	<i>Synergetic Effects between Spin State Change and Fluorescent Properties of Schiff Base-like 3D Metal Complexes</i>
P22	Wegeberg, Christina	<i>In Situ Insight into Reversible O<sub>2</sub> Gas-Solid Reactions</i>
P23	Borowski, Tomasz	<i>DFT Study of Nitroxygenase Activity of Manganese Quercetin 2,3-dioxygenase</i>
P24	Zoppellaro, Giorgio	<i>The Non-Innocent Nature of Graphene Oxide as Organic Platform for Biomedical Applications and its Reactivity Towards Metal-Based Anticancer Drugs</i>

## SPIN STATES OF HEPTA-COORDINATED TRANSITION METAL ION COMPLEXES

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Density Functional Theory study on the effect of the spin state and the ligand charge on the electronic structure and stereochemistry for Mn<sup>II</sup>, Fe<sup>II</sup>, Fe<sup>III</sup>, Co<sup>II</sup> and Ni<sup>II</sup> complexes with the 2,6-diacetyl-pyridine-bis(semioxamamide) ligand and its mono- and di-anionic analogues is presented. The calculated geometries are in excellent agreement with the available X-ray structures. Our calculations clarify some intriguing experimental observations. The absence of a nickel-complex in a hepta-coordination is confirmed, which is easily explained by inspection of the molecular orbitals that involve the central metal ion. Moreover, it is found that changes in spin state lead to completely different coordination modes, in contrast to the usual situation that different spin states mainly result in changes in the metal-ligand bond lengths. Both effects result from different occupations of a combination of  $\pi$ - and  $\sigma$ -antibonding, and non-bonding orbitals.

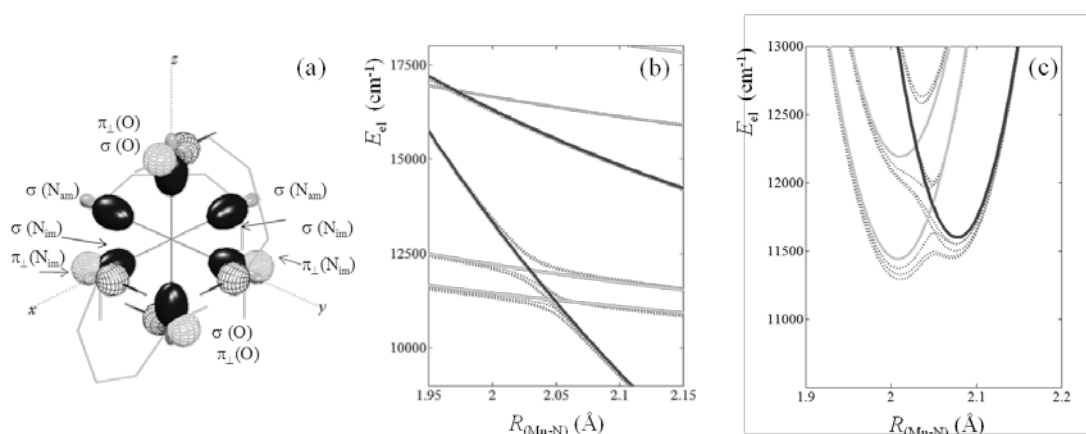
# THE FINE BALANCE OF EFFECTS IN SPIN CROSS-OVER PROCESSES. A LIGAND FIELD MODELING.

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The spin cross-over (SCO) is fascinating as a phenomenon taking effectively place at the ionic core of several classes of complexes, driven by factors of immediate environment (ligand field), next neighbor arrangements (supramolecular level) as well as from inner atomic structure (the spin-orbit coupling). Most efficient ion in achieving the SCO is the iron in Fe(II) complexes, a bit lesser in Fe(III) ones. Less frequent SCO manifestations are the in Co(II) systems, while Mn(III) is the most rare. We consider prototypic Co(II)<sup>[1]</sup> and Mn(III)<sup>[3-4]</sup> SCO systems as case studies of ligand field and spin coupling factors, based on the interpretation of Density Functional Theory calculations, attempting also the mechanisms that are making the difference between ions in the SCO occurrence. The synopsis in the Figure 1 shows the ingredients for the Ligand field modeling in Morgan-type complex units,<sup>[2,3]</sup> as well as the modelled diagrams for the SCO effect.



**Figure 1.** (a) The molecular skeleton and ligand field actors of a *cis*- [Mn<sup>III</sup>N<sub>4</sub>O<sub>2</sub>]. (b) and (c) the spin-crossing diagram with and without vibration terms, modeling with data fitted on a series of related compounds.

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## MIMICKING THE SECONDARY SPHERE HISTIDINE OF A DIOXYGENASE ACTIVE SITE

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Fe- Homoprotocatechuate Dioxygenase (HPCD) is a non-heme extradiol enzyme that operates in the oxidative ring opening pathways of aromatic compounds.<sup>[1,2]</sup> Recent studies showed that the proton transfer to afford **3** from **0** (Figure 1) is assisted by an His200 residue present in the secondary sphere of HPCD active site.<sup>[3,4]</sup> Thus, the main role of His200 is to act as a Brønsted base. Herein, we present a Density Functional Theory analysis of the energetics of a modified first coordination shell with the objective of mimicking the role of His200 by incorporation of various functional groups in lieu of one of the imidazole ligands, **L** (Figure 1). The aim is to build a proton transfer step which is thermodynamically and kinetically adequate when compared with the native enzyme environment. Figure 1 shows the reaction mechanism and possible functional groups capable for the proton shuttling.

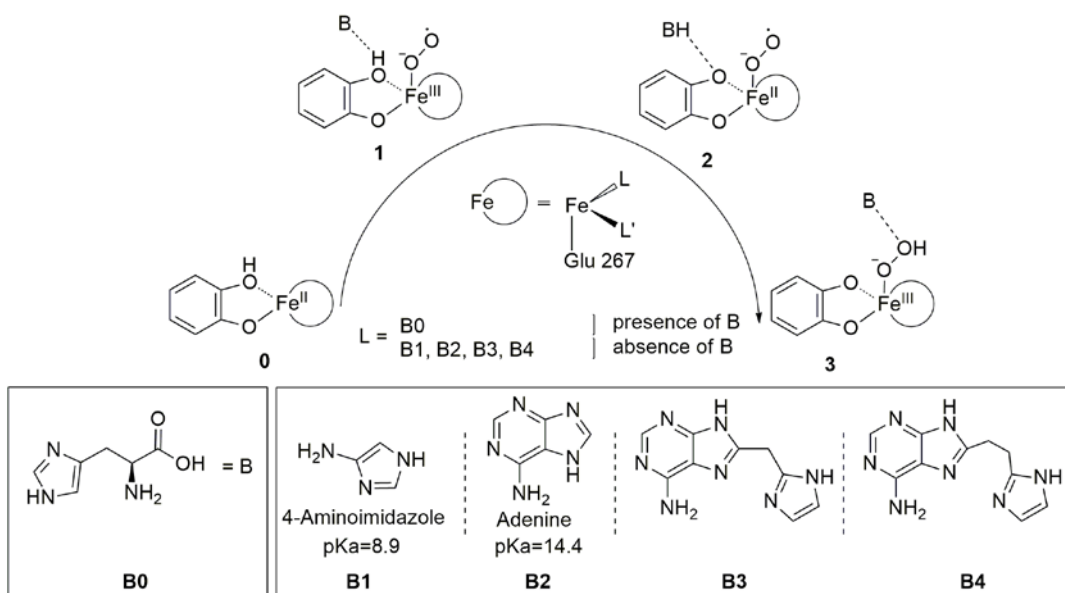


Figure 1. Species and reaction mechanism. **L'** is imidazole for **B0**, **B1** and **B2**. No **L'** is present for the bidentate ligands **B3** and **B4**.

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# COOPERATIVE CATALYSIS WITH REDOX NON-INNOCENT LIGANDS

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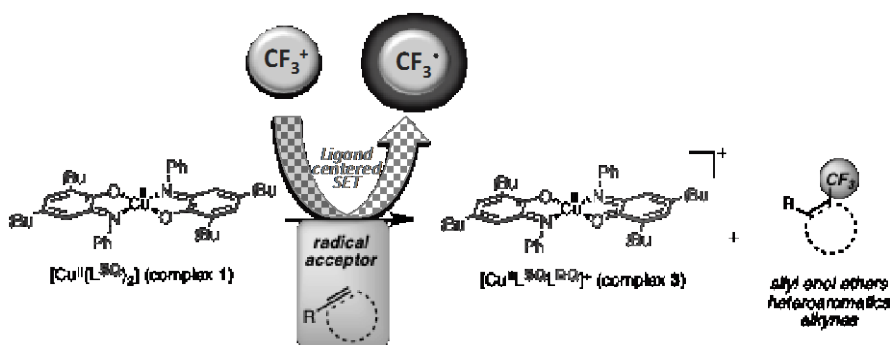
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Increasing concerns regarding sustainability and cost-related issues of noble metals are driving chemists to revisit the chemistry of first-row early transition metals (Fe, Co, Ni, Cu). Although widely used, these metals tend to be limited by their electronic structure, which makes them prone to mono-electronic transfers and limits their efficiency and selectivity.

An emerging area in catalysis is the use of redox non-innocent ligands, which can act as a storage and supply unit of electrons, allowing the metal to perform reactions once forbidden, thus imparting noble metal character and broadening the scope of their synthetic applications.<sup>[1]</sup> Catalytic relevance of these ligands is promising and new applications are being increasingly developed. Progress made in iron-catalyzed tandem catalytic C–H activation/arylation of unactivated arenes<sup>[2]</sup> and copper-catalyzed trifluoromethylation<sup>[3]</sup> will be presented.



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## O<sub>2</sub> ACTIVATION AND DOUBLE C-H OXIDATION BY A MONONUCLEAR MANGANESE(II) COMPLEX

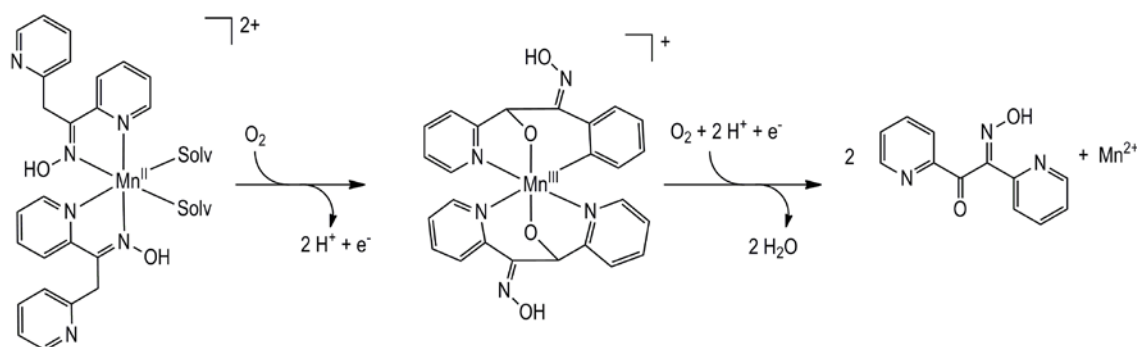
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Manganese plays crucial roles in the biological formation of O<sub>2</sub> at the Oxygen Evolving Center (photosynthesis), catalases (H<sub>2</sub>O<sub>2</sub> disproportionation) and superoxide dismutases (destruction of reactive oxygen species). These processes involve O<sub>2</sub> release from high valent Mn species. An example of the opposite reaction was caught here; O<sub>2</sub> activation by a Mn(II) species.<sup>[1]</sup> Molecular oxygen was found to be the source of the oxygen inserted into a C-H bond to form an alcohol in a first step and then a ketone derivative of the dipyridyloxime starting ligand.



The reaction was followed by UV-visible and Raman spectroscopy and the provenance of the oxygen atoms was demonstrated by mass spectrometry (<sup>18</sup>O-labelling). Relatives of the unoxidized starting material and final ketone containing complex as well as the reactive alcohol intermediate could be crystallized and characterized by single crystal X-ray diffraction.

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## TUNING THE ELECTRONIC STRUCTURE OF Fe(II) AND Ru(II) COMPLEXES WITH IMIDAZOLE BASED CHELATING LIGANDS

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Chelating aromatic N-heterocyclic ligands, such as bipyridines, coordinate with Fe(II) and Ru(II) centres typically forming complexes with rich photochemistry. Low-lying  $\pi^*$  orbitals on the ligand favour the spin allowed metal-to-ligand charge transfer (MLCT) that can lead to long-lived excited states and open new photoreactive channels. Aiming to achieve a better control over the electronic properties of such complexes, we combined an electron-rich imidazol with an electron-deficient pyridine or diazine on the 2-(1H-imidazol-2-yl)R ligand (R=pyridine,diazine). The opposite traits of the moieties forming this ligand confer to its complexes and enhanced electron density on the metal through  $\sigma$ -donation from the imidazol moiety and low-lying MLCT transitions to the pyridine or diazine moiety. By means of wave function based computational methods, we evaluate the low energy spectroscopy of an homoleptic Ru(II) complex with 2-(1H-imidazol-2-yl)pyridine, which is characterized by a MLCT manifold appearing below the metal-centred transitions. Moreover, we explore the effects of two diazine structural isomers, namely pyrazine and pyrimidine, on the electronic structure of their respective homoleptic Fe(II) complexes with 2-(1H-imidazol-2-yl)diazine. Even though these diazine isomers only differ on the position of a single N atom, the isomerization is capable of changing the spin multiplicity of the ground state of the complex, activating a spin transition at 100 K and completely altering its spectroscopy.

## ACCELERATING METAL-DIRECTED PROTEIN DYNAMICS WITH ENHANCED SAMPLING TECHNIQUES

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Some important processes such as biomolecular recognition, allosteric regulation, protein folding or signal transduction, usually take place on the micro- to millisecond or even longer time scales. Low-energy states relevant for these processes may be separated by high-energy barriers, which are rarely crossed over the course of conventional molecular dynamics simulations. Accelerated molecular dynamics (aMD) enhances sampling through modification of the system's Hamiltonian in a relatively simple way.<sup>[1,2,3]</sup> In addition, it does not rely on the definition of a reaction coordinate or a set of collective variables (a priori knowledge of the underlying free energy landscape is not needed), and it conserves the essential details of the free-energy landscape. Here we focus on the potential of aMD as a tool to efficiently explore the rough free energy landscape of proteins and other molecules and its applications to: 1) the study of protein folding and metal directed protein folding; 2) the study of biomolecular recognition and protein dynamics in metalloproteins.

First, folding of four fast-folding proteins, including chignolin, Trp-cage, villin headpiece, WW domain, and a Zn folding peptide is simulated via aMD. Free energy profiles calculated through improved reweighting of the aMD simulations using cumulant expansion to the 2nd order are in good agreement with those obtained from conventional MD simulations. This allows us to identify distinct conformational states (e.g. unfolded and intermediate) other than the native structure and the protein folding energy barriers.<sup>[4]</sup> Second, the potential of aMD as a tool to efficiently explore the free energy landscape of (metallo)proteins and its applications to the study of biomolecular recognition will be highlighted. In particular, we will study the role of the Fe<sub>4</sub>S<sub>4</sub> cluster in cytosolic aconitase. It is said that aconitase acts as a sensor of iron through a large conformational change associated with the assembly and disassembly of the Fe<sub>4</sub>S<sub>4</sub> cluster.

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## GEOMETRIC MODULATION OF THE JAHN-TELLER DISTORTION IN HIGHLY ANISOTROPIC MANGANESE(III) COMPLEXES

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High spin (HS) Mn<sup>III</sup> in an octahedral field exhibits a strong Jahn-Teller (JT) effect which can confer considerable magnetic anisotropy or directionality. Magnetic anisotropy and its effect on the overall assembly of spins has been widely exploited in the design of single molecule magnets.<sup>[1,2]</sup> We were particularly interested in exploring the magnetic anisotropy in Mn<sup>III</sup>, as our previous spin crossover complexes,<sup>[3-5]</sup> the JT distortion in the HS form is non-classical: we have typically observed a HS axial compression (equatorial elongation), due to either population of the  $d_{x^2-y^2}$  orbital or a dynamic axial elongation. The addition of strain on the flexible ligand backbone previously used<sup>[3]</sup> is explored here, leading to the formation of trigonal prismatic complexes, Figure 1, with varying degrees of geometrical distortion. The counter anion has a marked effect on the degree of distortion and therefore on the trigonal prismatic character of the complex. This rare geometry could be integral in yielding interesting complexes that are both; magnetically and electronically atypical. This is due to the JT distortion manifesting itself in a peculiar way, a *cis* Jahn-Teller distortion, which results in the elongation of both tertiary amine donors. The magnetic anisotropy has been probed by high field/frequency EPR, magnetization and, DC and AC susceptibility measurements.

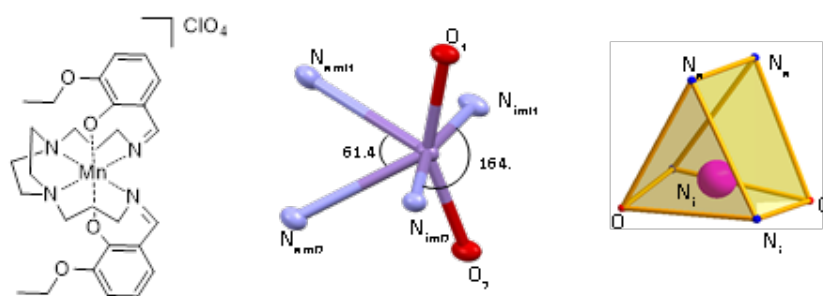


Figure 1 – Trigonal prism geometry of Mn(III) complex

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## On the active space selection in multiconfigurational calculations of excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$

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Tris(2,2-bipyridine)ruthenium (II),  $[\text{Ru}(\text{bpy})_3]^{2+}$  is the flagship of the ruthenium polypyridyl series of complexes, which have found their way to numerous applications such as dye-sensitised solar cells, artificial photosynthesis systems or photoredox catalysis. The promising photophysical properties of  $[\text{Ru}(\text{bpy})_3]^{2+}$  have led to a large number of spectroscopical studies (e.g. Ref. 1). To back up experimental results, high-accuracy ground and excited state electronic structure and dynamics calculations are needed.

Accurate descriptions of ground and excited states of many transition metal complexes often require multiconfigurational methods, based e.g. on complete active space self-consistent field (CASSCF). However, multiconfigurational calculations performed on transition metal complexes often require large active spaces, which are beyond reach for traditional multiconfigurational methods such as CASSCF. The density matrix renormalisation group (DMRG) method [2, 3] allows for larger active spaces than the traditional CASSCF method, while approaching its accuracy.

In addition, multiconfigurational methods require a careful manual selection of the active orbitals, which is often non-trivial, especially for computational chemists without prior experience with these methods, and even for experienced users when large active spaces and large number of states are involved.

Orbital entanglement analysis [4, 5] is a novel tool, which allows to characterise the amount of static and dynamic correlation present in single orbitals or bonds.[6] In this contribution we perform CASSCF and DMRG calculations on  $[\text{Ru}(\text{bpy})_3]^{2+}$  and demonstrate how orbital entanglement analysis can be used as a quantitative measure to systematise the selection of the active space for excited state multiconfigurational calculations.

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## Metal-ion selectivity in peptides and model complexes

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Deciphering mechanisms and factors underlying the metal-ion selectivity in biomolecules holds promise for *de novo* design and optimization of metal-binding and catalytic systems. Tackling the problem from a computational perspective, however, introduces requirements for proper representation of various metal-binding environments, electronic structure, and solvent effects.

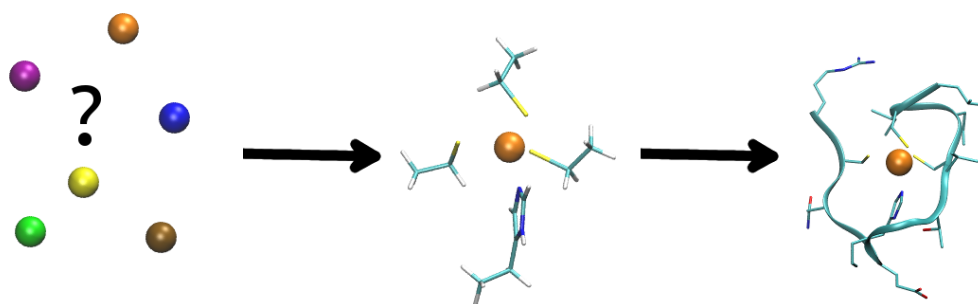


Figure 1: From selectivity principles to metallopeptides

The poster will present an overview of our endeavours to find an accurate, yet affordable protocol for evaluating differences in free energies of binding among a set of biologically relevant metal ions complexed with ligands representing amino acid side-chains. Our '*tour de force*' began by benchmarking a variety of density functional theory (DFT) functionals and wave function methods [1]. The combination of selected method with COSMO-RS solvation model has been tested for its ability to reproduce experimental stability constants of model complexes.[2] Finally, the relation of these small models to real [metal+peptide] complexes has been examined [3].

Building upon the earned experience, a database containing an exhaustive list of *in silico* designed metal-ion complexes is created with an intention of mining a wealth of metal-ion selectivity and structural information, as well as examining possible relations and trends among diverse groups of complexes.

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## THE INFLUENCE OF MOLECULAR SHAPE ON SPIN TRANSITIONS IN THE SOLID STATE

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Spin-crossover (SCO) involves the rearrangement of electrons in a metal ion, from a high-spin to a low-spin state.<sup>[1]</sup> Such transitions have a large impact on the physical properties of a solid material, including its magnetic moment, colour, dielectric constant and electrical resistance. Practical applications of molecular SCO switches have been demonstrated, including: display and memory devices, with switchable pixels of a SCO material; electrical and electroluminescent devices, employing changes in the electrical resistance of a SCO thin-film; and, in a temperature-sensitive MRI contrast agent.<sup>[2]</sup> The design of new spin-crossover molecular materials with technologically useful properties is an important problem of crystal engineering, which also has more general implications for the production of functional molecular crystals to undergo phase changes on demand.<sup>[3]</sup>

Using data from our lab and from the literature, we proposed that cooperative (abrupt and hysteretic) SCO can be promoted by two factors.<sup>[3]</sup> First, are molecules that undergo an anisotropic structural rearrangement between the spin states, such as a ligand conformational change. Second, is that such structure changes are propagated effectively between molecules that interdigitate in the crystal, to maximise mechanical coupling between the switching centres. This talk will describe the rationale behind these suggestions and will present recent examples of compounds that follow these rules,<sup>[4,5]</sup> as well as some that apparently do not.<sup>[5,6]</sup>

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## A COMBINED COMPUTATIONAL AND SPECTROSCOPIC INVESTIGATION OF $\alpha$ -FE IN FE-ZSM-5

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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 is Fe-ZSM-5. This zeolite is able to oxidize methane to methanol stoichiometrically after activation with N<sub>2</sub>O.<sup>[2]</sup> It is generally believed that an active oxygen species, called  $\alpha$ -O, formed out of a precursor Fe(II), called  $\alpha$ -Fe, is the oxidizing agent. Unfortunately, the presence of multiple iron species makes it hard to identify the active species amongst a variety of spectator Fe. Therefore, the exact nature of both  $\alpha$ -O and  $\alpha$ -Fe remains a matter of debate.<sup>[3,4]</sup> In order to understand the reactivity of active sites, it is of key importance to have insight in the molecular and electronic structure. Spectroscopy combined with computational methods can be a great tool to provide this insight.<sup>[5,6]</sup> In this work, at different stages in the reaction of Fe-ZSM-5 with methane and N<sub>2</sub>O, electronic spectra were obtained. These spectra revealed a band in the NIR region that is a feature of  $\alpha$ -Fe. Multi-reference ab initio calculations, i.e. CASPT2, of different Fe(II)-binding sites in ZSM-5 show that this band can only be attributed to a  $d_{z^2} \rightarrow d_{x^2-y^2}$  ligand field transition of Fe(II) in a square planar coordination environment.

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## Metal Selectivity and Specificity in Mononuclear Superoxide Dismutases

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The antioxidant superoxide dismutase (SOD) acts as the first line of defence against the deleterious effects of the superoxide radical in cells. The dismutation reaction releases hydrogen peroxide and molecular oxygen. In order to perform the reaction, mononuclear SODs depend on an iron or manganese ion located in their active site, which undergoes redox cycling between the 2<sup>+</sup> and 3<sup>+</sup> state during catalysis.

Despite a very high degree of structural homology between MnSOD and FeSOD of *E.coli*, each protein naturally selects its cognate metal during folding. This selectivity is apparent even when nascent proteins are provided with a choice between the two metals *in vivo*. If availability of the correct metal is low, these SODs may incorporate the incorrect metal but are rendered incapable of dismutation. What determines metal selectivity during protein folding and specificity toward the correct metal during catalysis is not at all understood. Whether or not there are small differences in the orientation of amino acids around the active site when the metal is reduced or oxidized is a difficult question to answer. Similarly the path of substrates and products to and from the active site, as well as their binding sites on the protein are poorly understood.

We have been examining the second sphere residues around the active site that may help determine these functions in SODs. Experiments have been devised and are on-going to decipher the 'metallation code' for these important enzymes. We hope that an *in-silico* approach to the same problems would be both complementary to the experiments and beneficial in suggesting further residues to explore.

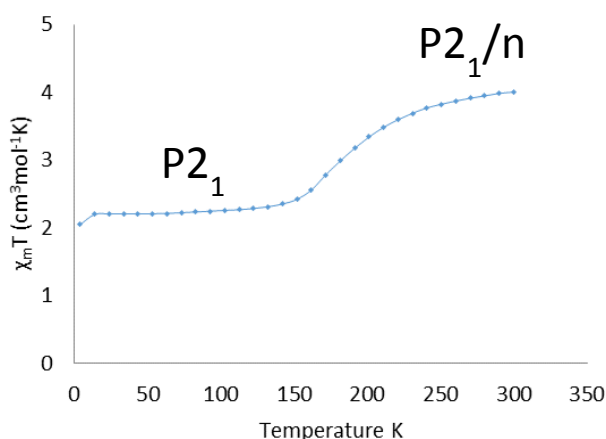
## RESOLUTION OF CHIRAL SPIN STATES

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Many small molecule complexes with chelating ligands have  $\Delta$  and  $\lambda$  optical forms depending on the direction of the ligand twist around the coordinated ion. Most of these crystallise in non-chiral space groups, with the pair of enantiomers related by an inversion centre. In our recent work we have studied several metal ligand combinations where spin crossover in either iron(III)<sup>[1]</sup> or manganese(III)<sup>[2]</sup> can be induced with judicious choice of chelating ligand. We now present a series of iron(III) complexes where spin crossover is accompanied by a structural phase transition which results in spin state ordering of high spin and low spin sites in a 1:1 ratio. During the ordering transition loss of the inversion centre between  $\Delta$  and  $\lambda$  forms also results in chiral resolution of the enantiomers, a rare example of combined spin state ordering and chiral resolution.<sup>[3]</sup> We report here our structural, magnetic and spectroscopic studies on the extent and reproducibility of the phenomenon in multiple crystals.



**Figure 1** Plot of  $X_M T$  versus  $T$  for mononuclear iron(III) complex showing spin state ordering and chiral resolution.

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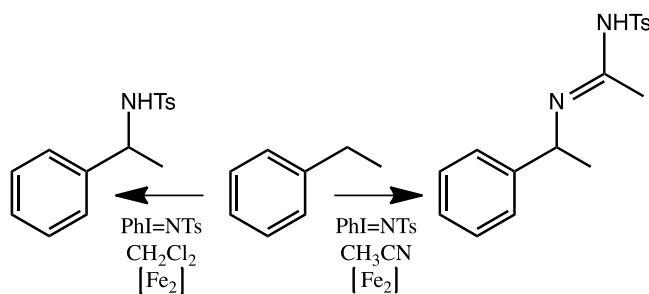
## AMIDINES SYNTHESIS FROM TANDEM NITRENE TRANSFER AND NITRILE INSERTION

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Nitrene transfer is attracting continuing interest as the most efficient and general tool to build various kinds of amine derivatives.<sup>[1]</sup> Whereas heavy metal catalysts (dirhodium tetracarboxylates, ruthenium porphyrins) were used in the past years, recent emphasis has been put on developing catalysts based on first row transition metals and especially iron to follow green chemistry incentives.<sup>[2]</sup> We have reported diiron complexes that can mediate aliphatic and aromatic<sup>[3]</sup> intramolecular aminations and efficiently catalyze aziridination and sulfimidation reactions.<sup>[4, 5]</sup> In the present work, we show that when nitrene transfer to aliphatic substrates is performed in the presence of nitriles, their insertion into the product occurs leading to amidines instead of the targeted amine (Scheme).



Scheme: amine vs amidine synthesis

We will present a mechanistic study of this tandem reaction .

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# RATIONALIZING THE MAGNETIC ANISOTROPY WITH THE HELP OF LIGAND FIELD CONCEPTS IN SIMPLE LANTHANIDE UNITS.

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The magnetic anisotropy is the basic ingredient that determines the formation of magnetization axis that drives a spin-carrier molecule into a nominal magnet. The attention on Single Molecule Magnet class was progressively shifted towards smaller species such as binuclear or even mononuclears, namely Single Ion Magnet cases. The molecular simplicity allows insight into structure-property relationships. In this spirit, we deliberately consider simple mononuclear unit, the  $[\text{Ln}(\text{NO}_3)_5]^{(2-)}$  units (Ln=Sm, Eu, Gd, Tb, Dy, Ho, Er) from a newly synthesized series of systems having complex counterions,  $[\text{M}(\text{phen})_3]^{2+}$  (M=Ni, Co). The calculation of lanthanide complexes faces the special problem of the non-*aufbau* nature of the *f* shell in the complex and the weakly interacting nature of the *f* electrons. We resolved the technical issues, having pioneering advances<sup>[1]</sup> in the treatment of electron structure of lanthanide complexes. With the help of computational tools we are able to analyse and even predict the magnetic properties of the units, the presented systems being clear examples. The magnetic anisotropy is suggestively accounted by our methodological invention,<sup>[2]</sup> namely the drawing of the polar maps for response of states (all spectral terms) with respect of magnetic field, scanned at all 3D orientations around the given site. The resulting lobes identify the easy magnetization axis and the magnitude of the carried magnetic moment, as illustrated in the Figure 1 for the Tb and Dy congeners.

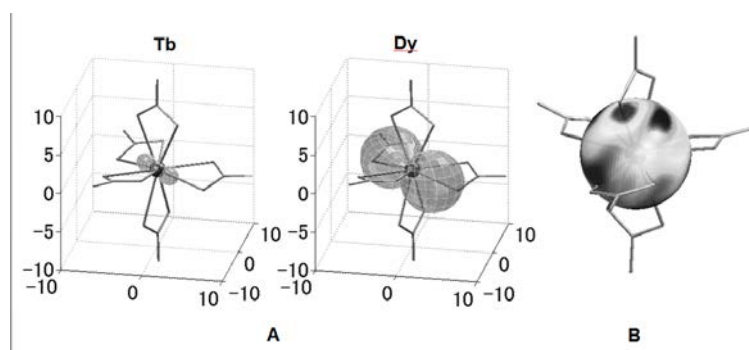


Figure 1. A) The polar maps of the state specific magnetization in the groundstates of the  $[\text{Ln}(\text{NO}_3)_5]^{(2-)}$  (Ln= Tb, Dy) units. B) The map of the ligand field, basically the same in the whole isostructural series.

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## NEW METHOD FOR THE PREDICTION OF MÖSSBAUER PARAMETERS FOR IRON CONTAINING COMPLEXES

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Mössbauer spectroscopy is a useful analytical spectroscopy technique for the analysis of iron containing complexes. Mössbauer spectroscopy is sensitive to the charge distribution of charge density around <sup>57</sup>Fe nuclei, leading to the quadrupole splitting ( $\Delta E_Q$ ) and the isomer shift ( $\delta$ ). The good point is that these parameters are closely related to the electronic density distribution of the iron nucleus, and hence can be used to determine the oxidation and spin state of iron.

During many years, DFT applications to predict the Mössbauer parameters have been used in order to compute these parameters and compared to experimental ones. This is particularly so for the isomer shift, which is directly proportional to the total electron density at the iron nuclei. There are different kind of studies trying to establish a linearity between the calculated electron density in the iron nuclei and the experimental isomer shift of different complexes iron complexes.

Here, we suggest a new method to predict the isomer shifts of iron containing complexes, which consists of having as a reference a single iron atom in equation (1), where parameters have been obtained using the same calibration complexes as Noodleman.<sup>[1,2]</sup> We use different functionals and basis sets to obtain average parameters of the linear equation (A and B), followed by the application of the calibrated linear equations to obtain the isomer shifts of a series of interesting iron complexes.<sup>[3,4]</sup>

$$\delta = A (\rho_{\text{iron of the structure}} - \rho_{\text{iron atom}}) + B \quad (1)$$

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## Bis-tridentate Organic Ligands with Photoactive Anthracene Skeleton

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The design, development and study of molecular materials with tailored physical properties are enduring goals for modern synthetic chemistry worldwide. Among a wide range of systems under investigation, materials that undergo spin state switching between distinct magnetic states have received very considerable interest for both their fundamental behavior and application potential in high density memory or display device applications. So called “*spin crossover*” (SCO) coordination compounds are able to reversibly change their spin states under various external triggers, for instance by temperature change or by light irradiation (LIESST effect). In particular, the phototransformation of SCO complexes present very convenient and cheap method for the alternation between the low and high spin states. However, the existence of photoexcited metastable states is usually observed at cryogenic temperatures only, therefore the investigation and better understanding of photoexcited metastable spin states is still challenge for us. On the other hand, an alternative to the LIESST effect is phenomenon called as *ligand driven light induced spin transition*, where spin state of the central atom is affected by reversible photochemical changes performed on the ligand environment.

With respect to this, we proposed sophisticated molecular design of bis(tridentate) ligands which consists of two peripheral shoulders containing 2,6-bis(pyrazol-1-yl)pyridine moiety introduced on 1,8-bis(acetylene)anthracene skeleton connected to the central aromatic unit -1,8-diethynylantraquinone for ligand **1a**, 1,8-diethynylantracene for ligand **1b**, and 4,5-diethynyl-9-methoxyanthracene for ligand **1c**. On the one hand, presence of 2,6-bis(pyrazol-1-yl)pyridine coordination embrace ensure formation of iron(II) complexes with room temperature SCO bistability. On the other hand, presence of two or more anthracene moieties allows to investigate reversible photocycloadditions, which might affect spin states of iron(II) central atoms. Herein, we present goal-directed synthesis of bis(tridentate) organic ligands **1a**, **1b** and **1c**, and their [4 +4] photocycloaddition and thermal decyclisation. In addition to this, prepared ligands and their photoisomers have been structurally characterized and their optical properties revealed investigated as well.



## Accurate Prediction of One-Electron Reduction Potentials in Aqueous Solution by Variable-Temperature H-Atom Addition/Abstraction Methodology

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A robust and efficient theoretical approach for calculation of the reduction potentials of charged species in aqueous solution is presented.<sup>1</sup> Within this approach, the reduction potential of a charged complex (with a charge  $|n| \geq 2$ ) is probed by means of the reduction potential of its neutralized (protonated/deprotonated) cognate, employing one or several H-atom addition/abstraction thermodynamic cycles. This includes a separation of one-electron reduction from protonation/deprotonation through the temperature dependence. The accuracy of the method has been assessed for the set of 15 transition metal complexes that are considered as highly challenging systems for computational electrochemistry. Unlike the standard computational protocol(s), the presented approach yields results that are in excellent agreement with experimental electrochemical data. Last but not least, the applicability and limitations of the approach are thoroughly discussed.

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## INTERACTION OF NO AND NH<sub>3</sub> WITH COBALT CENTERS IN ZEOLITES: CLUSTER AND PERIODIC CALCULATIONS

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Our work focuses on the description of the NO bonding to cobalt site in zeolites.<sup>[1]</sup> We use two protocols for this purpose: spin-resolved natural orbital for chemical valence<sup>[2]</sup> (DFT-based SR-NOCV method) and valence-bond expansion of multiconfiguration CASSCF wave function.<sup>[3]</sup> T1-based clusters<sup>[4,5]</sup> (T1 – single aluminium tetrahedron) are taken under considerations, including the structures labelled as [T1-Co(NO)(NH<sub>3</sub>)<sub>x</sub>]<sup>1+</sup> (where x = 0,2,3). In addition, [Co(NO)(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> adduct, well-known in the coordination chemistry<sup>[6]</sup> was investigated. Moreover, we study the structure and energetics of Co<sup>2+</sup> embedded in 6MR (six-membered ring) and 8MR (eight-membered ring) in the framework of periodic calculations with VASP.<sup>[7-10]</sup>

Proper wave function for cobalt centers involves more than one Slater determinant thus the SR-NOCV analysis (based on UDFT) may be safely used to compare adducts where similar electronic structure is expected. More robust explanation of the NO activation in ammonia-modified sites is based on a share of Co<sup>I</sup>NO<sup>+</sup>, Co<sup>II</sup>NO, Co<sup>III</sup>NO<sup>-</sup> resonance structures obtained from the analysis of multi-configuration wavefunction. Interestingly, NO and NH<sub>3</sub> co-adsorption leads to close-lying singlet and triplet states, exhibiting different ability to activate NO.<sup>[1,5]</sup>

The number of NH<sub>3</sub> ligands co-bound to the Co-NO center depends on its position in the framework, i.e. either 6MR or 8MR. Up to two or three NH<sub>3</sub> molecules are bonded, respectively. The co-adsorption induces the change of favourable location for cobalt from 6MR (non-modified site) to 8MR (full saturation by NH<sub>3</sub> ligands). Furthermore, we observe the formation of [Co(NO)(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> species interacting only with the framework oxygen atoms by hydrogen bonds. The geometry of cluster centers is in good agreement with those obtained for chabazite.<sup>[1]</sup>

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## SYNERGETIC EFFECTS BETWEEN SPIN STATE CHANGE AND FLUORESCENT PROPERTIES OF SCHIFF BASE-LIKE 3D METAL COMPLEXES

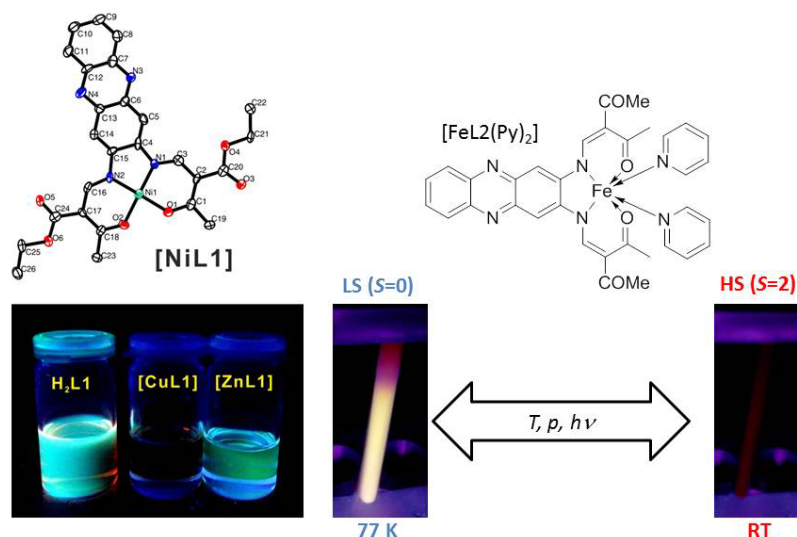
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Spin crossover (SCO) complexes belong to a type of molecules whose spin state can be switched by physical stimuli such as pressure or temperature change, or light irradiation.<sup>[1]</sup> Structural and electronic changes associated with this transition can be exploited for numerical data storage,<sup>[2]</sup> temperature and pressure sensors,<sup>[3]</sup> or display devices.<sup>[2]</sup> Fe(II) is the most widely used metal center for the synthesis of SCO complexes, however, the phenomenon itself is not limited to iron(II) or other 3d<sup>4-7</sup> metal centers with an octahedral coordination sphere. The coordination induced spin state change of Ni(II) complexes from diamagnetic ( $S = 0$ ) square planar to paramagnetic ( $S = 1$ ) square pyramidal or octahedral coordination sphere shifted recently back into focus.<sup>[4]</sup>



A new ligand system based on a Schiff base-like ligand bearing a phenazine fluorophore was synthesized, as well as the corresponding Fe(II), Ni(II), Cu(II), and Zn(II) complexes. The fluorescence properties of the  $S = 0 \leftrightarrow S = 1$

switchable Ni(II) complexes were investigated with steady-state extinction and fluorescence spectroscopy as well as time-resolved fluorescence spectroscopy.<sup>[5]</sup> The SCO Fe(II) complexes were investigated with respect to thermally induced synergetic effects.

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## IN SITU INSIGHT INTO REVERSIBLE O<sub>2</sub> GAS-SOLID REACTIONS

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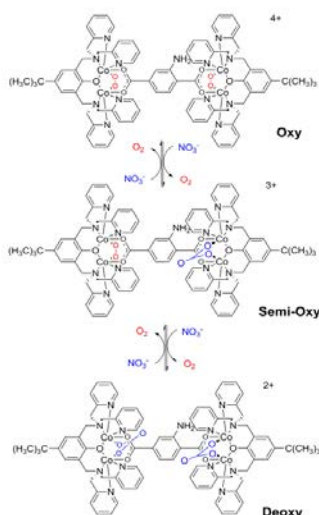
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Non-porous crystalline solids containing a series of cationic tetracobalt complexes reversibly, selectively and stoichiometrically chemisorb dioxygen in temperature/O<sub>2</sub> partial pressure induced processes involving the oxidation of cobalt with concurrent reduction of two equivalents of sorbed O<sub>2</sub> to form  $\mu-\eta^1, \eta^2$ -peroxide ligands.<sup>[1]</sup> The attenuation of O<sub>2</sub> affinity by the introduction of electron withdrawing or electron donating substituents into the supporting ligand framework, otherwise dominant in solution<sup>[2]</sup> is overridden in the crystalline state. Here O<sub>2</sub> affinity is tuned predominantly by phase and a two-step gas sorption isotherm is apparent.<sup>[1]</sup> By following in situ

*reversible single-crystal to single-crystal (SCSC) transformations<sup>[3]</sup> using a gas-crystal cell and synchrotron X-ray radiation we can show that two distinctive channels through the crystalline solids are operative under sorption and desorption processes<sup>[4]</sup>. The reaction proceeds via a semi-oxy form that we had been seeking for some time, and the results have enabled an updated hypothesis that the transient conduit for O<sub>2</sub> escapes from an oxy crystal, albeit a counteranion obstacle race, is lined by stacks of one end of the molecule. This is contrary to our original hypothesis<sup>[1]</sup> that communication between the binding sites caused an allostery or anti-cooperative effect: Crystal structure overrides molecule tweaking.*



**Figure 1.** Top: tetracobalt complex in oxy, semi-oxy and deoxy form. Bottom: crystals in oxy (right) and (almost) deoxy form (left).

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**DFT study of nitroxygenase activity of manganese quercetin 2,3-dioxygenase**Zuzanna Wojdyła<sup>a</sup> and Tomasz Borowski<sup>b</sup>

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Quercetin 2,3-dioxygenase (QDO) is an enzyme that cleaves the central heterocycle ring of flavonol quercetin by incorporation of both atoms of dioxygen into the substrate and release of carbon monoxide. *B. Subtilis* QDO is active with several transition metal ions. However, only Mn(II) containing enzyme exhibits nitroxygenase activity with nitroxyl (HNO) substituted for dioxygen. HNO is incorporated into quercetin in a specific manner, thus only one product of the reaction is observed. The nonenzymatic base-catalyzed reaction occurs at pH above 7 and yields the same product as the Mn-QDO catalyzed reaction. Hybrid density functional theory with dispersion correction (B3LYP-D3) was employed to investigate the nitroxygenase activity of Mn-QDO and the nonenzymatic nitroxylation reaction. The results suggest that the regioselectivity of the reaction is dictated by the intrinsic electronic features of the reactants, as the N atom of HNO is the preferred region for nucleophilic attack by quercetin. Fe(II)- and Co(II)-containing active site models were also considered. The outcome of this analysis indicates that the key to Mn-QDO nitroxygenase activity is weak binding of HNO to the cofactor ion. In case of Fe- and Co-QDO a strong preference for N(H) coordination of nitroxyl inhibits the nitroxygenase activity.

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## The non-innocent nature of graphene oxide as organic platform for biomedical applications and its reactivity towards metal-based anticancer drugs

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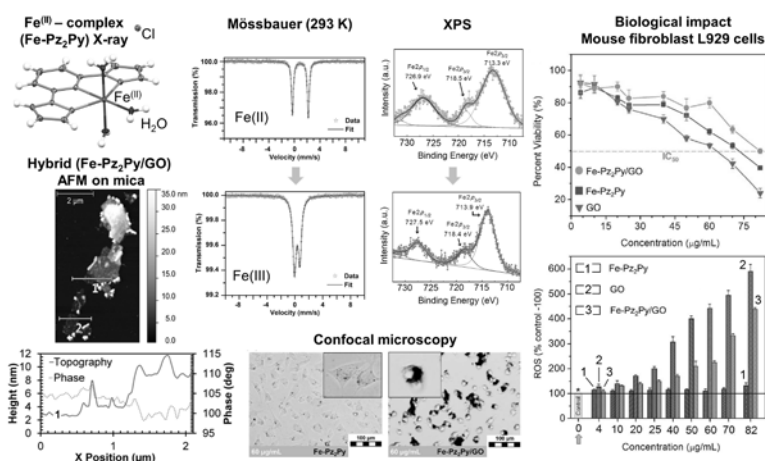
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The self-assembly process in solution of a high-spin ( $S=2$ ) mononuclear iron (II) complex based on the bispyrazolylpyridine scaffold (Fe-Pz<sub>2</sub>Py, Fig. 1) with graphene oxide (GO) micrometer-sheets allowed devising not only a new hybrid-architecture for GO-based materials suitable for nanomedicine (termed Fe-Pz<sub>2</sub>Py/GO), but also to disclose the reactive nature of the GO organic scaffold.<sup>[1]</sup> The bare iron (II) complex was found highly effective in disrupting cell's metabolism through DNA binding, with behaviour similar to that expressed by Ruthenium-complexes as well as antibiotic-drugs (e.g. doxorubicin). On the contrary, in the hybrid material (Fe-Pz<sub>2</sub>Py/GO), the proclivity of GO to produce reactive oxygen species (ROS) became down-regulated by the electron-buffering properties of the complex, evidencing the presence of an active electron transfer from the iron complex to GO upon loading, leading to an oxidized iron (III) high-spin ( $S=5/2$ ) system. These findings question the use of the neat GO platform as a suitable carrier for metal-based anticancer drugs in theranostic (medical) applications.

Fig. 1. Comparison of some physical properties and the biological impacts (*in vitro*) of the neat iron complex versus neat GO and the iron complex loaded onto the GO carrier.



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