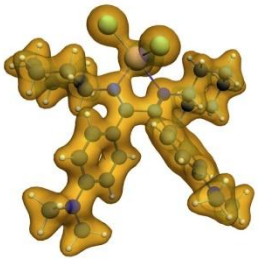
ECOSTBio: Fifth Scientific Workshop
Krakow, September 8–9, 2016

Information Package:

Introduction, Travel & Venue,
Book of Abstracts, List of Participants

Faculty of Chemistry
Jagiellonian University in Krakow

Institute of Catalysis and Surface Chemistry
Polish Academy of Sciences



COST Action CM1305
ECOST310
Explicit Control Over Spin-states
in Technology and Biochemistry

cost
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

ECOSTBio: Fifth Scientific Workshop. Krakow, September 8–9, 2016

Venue
Faculty of Chemistry, Jagiellonian University, Krakow, Poland

Organizing Committee
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Kamila Sobańska
Adam Stępniewski

Dear participant of the 5th Scientific Workshop of the ECOSTBio:

Welcome in Krakow!
Welcome at Faculty of Chemistry of Jagiellonian University in Krakow!

Following previous unforgettable meetings in Girona (2014), Marseille (2015), Belgrade (2015), and the last one in Prague (2016), we expect the Krakow workshop to be an excellent opportunity for exchange of ideas focused on the "chemistry of spin-states", within our COST action and beyond. Several features make the present meeting slightly different from the previous ones. First, in addition to excellent lectures (including those delivered by invited and keynote speakers: Marcel Swart, Stefan Grimme, Wesley Browne, Roman Boca, Rudi van Eldik, Piotr Pietrzyk, Dimitrios Pantazis), we will also have discussion panels concluding all sessions. We hope that this will provide extra opportunity for stimulating discussions and, thereby, it will accelerate the exchange of ideas within our scientific network. Second, the present workshop partly overlaps with theoretical chemistry conference CTTC VII (http://www.chemia.uj.edu.pl/cttc7) held at the same venue the days before. Hence, we have two overlapping sessions on Thursday morning (September 8) with good selection of speakers and an opportunity to meet during the dinner on Wednesday evening (see below). Last but not least, this time also a practical training on the usage of the spin-state database will be organized. This is hoped to further stimulate the involvement of all of us in the activity of WG1 "SPINSTATE database", fulfilling one of the aims of the COST action.

The meeting will take place at Faculty of Chemistry of Jagiellonian University. The venue is located close to the city center, within a walking distance (1 km, 15 min) from the Hotel IBIS, where most of the participants stay. As you may see below, our scientific program starts on Thursday morning at 9 a.m., but since most of you arrive the day before, you are kindly invited to an **informal dinner on Wednesday evening** (about 8 p.m.) in the restaurant Wanilia (Gołębia St. 6, http://wanilia-pieprz.pl/). Taking into account that some of you also participate in the CTTC VII conference, we decided to organize the informal dinner about the same time and next door to the official CTTC VII conference dinner (in the restaurant Kawaleria, Gołębia St. 4). In order to help you in getting to the restaurant Wanillia, we can walk there together, starting from the Hotel IBIS around 7:40 p.m. Please note that the informal dinner is not covered by the organizers. Therefore, please be prepared to pay by your own (with local currency PLN or credit card). Those that will be reimbursed by the COST action may claim the dinner as a "refundable expense".

Likewise the previous meetings, there will be no conference fee, but **since the organizers provide two lunches and one conference dinner, you will be requested to pay 20 EUR/meal to the organizers in cash** (no credit cards).[1] After making this payment, you will receive the "entrance tickets" to lunch breaks (organized in the form of buffet at Faculty of

[1] The total amount will be 60 EUR in most cases, except for regular participants of the CTTC VII conference who pay only 40 EUR, as the conference fee already includes the Thursday lunch.

Chemistry) and to the **conference dinner (organized at Restaurant Zakładka food & wine; http://zakladkabistro.pl/en) on Thursday evening**.

To speed-up all the registration formalities, **on Wednesday afternoon there will be a registration desk at the Hotel IBIS**, where you will be able to pick your conference badge and certificate of attendance, and also pay the lunch & dinner fees. Registering there right after your arrival on Wednesday is strongly recommended for those of you who stay in the Hotel IBIS. **The next opportunity to register will be on Thursday morning at Faculty of Chemistry. To register there, please, arrive at least half an hour earlier (8:30 a.m.).** Note that the morning session must start exactly at 9 a.m., since it overlaps with the CTTC VII conference; therefore, we kindly ask all of you to be on time (or ahead of time, if not registered yet).

The meeting is expected to conclude on Friday (September 9) at 6 p.m. After that, we plan to organize an informal dinner somewhere in the old town. We will be happy to spend this time with all of you, but we also take into account that some of you may have different plans, such like sightseeing or returning home on Friday.

We wish you a pleasant journey to and from Krakow, and a very enjoyable conference.
We look forward to meeting you soon!

With best regards,

Marcel Swart

(ECOSTBio Chair)

Ewa Broclawik, Tomasz Borowski, and Mariusz Radoń

(Local organizers)

Travel Information

Hotel

Hotel Ibis Krakow Centrum
ul. Syrokomli 2, 30-102 Krakow



Tel. +48-12-299-33-00
Fax. +48-12-299-33-33

E-mail: H3710@accor.com
Website: http://www.accorhotels.com/gb/hotel-3710-ibis-krakow-centrum/index.shtml

Venue

Faculty of Chemistry
Jagiellonian University in Krakow
ul. Ingardena 3, 30-060 Krakow



Tel: +48-12-6632215
Fax: +48-12-6340515

E-mail: sekretaria@chemia.uj.edu.pl
Website: www.chemia.uj.edu.pl

How to get from the airport to the hotel?

For people coming to Krakow by plane:

Krakow International Airport (John Paul II Airport) is located ~10 km west of the city center.

Official website of the Airport: www.krakowairport.pl/en | How to get to Krakow Airport

By public transport - option 1

- The best option is to take Bus 252. The bus departs roughly every 40 min from the bus stop located ~150 m from the the passenger terminal (exit Terminal 1, turn right and walk the sidewalk). The bus timetable can be found at e.g. mpk.krakow.pl.
- Exit the bus 252 at the stop "Jubilat". The hotel is within ca. 100 m distance from the "Jubilat" bus stop. See map (below) for the location of the hotel and bus stops.

By public transport - option 2

- Take train from the Airport to the Krakow city center. At the airport the train station is located near the passenger terminal, at the rear of the multi-storey car park. Current timetable is available here.
- Exit the train at station "Kraków Łobzów". After exiting the platforms turn left and walk ~100 m to reach the bus stop "Łobzów PKP" (you have to cross Wrocławska Street). From here, take bus 144 (direction: "Rżąka") or 194 (direction: "Czerwone Maki") to the bus stop "Jubilat". The hotel is within ca. 100 m distance from the "Jubilat" bus stop (for map see below).

By TAXI

- The taxi ranks are located in front of the passenger terminal.
- Krakow Airport Taxi is the official taxi service at the airport.

How to get from the central railway station ("Kraków Główny") to the hotel?

For people coming to Krakow by train:

Exit the railway station to Pawia Street, the bus stop "Dworzec Główny Zachód" is located 20 meters from the entrance. Take the bus 179 (direction: "Os. Kurdwanów"). Get off the bus at the "Jubilat" bus stop. The hotel is then within a walking distance (for map see below).

How to get from the hotel to the venue?

The suggested route is shown in the map below. The total distance to walk is about 1 km (15 min).

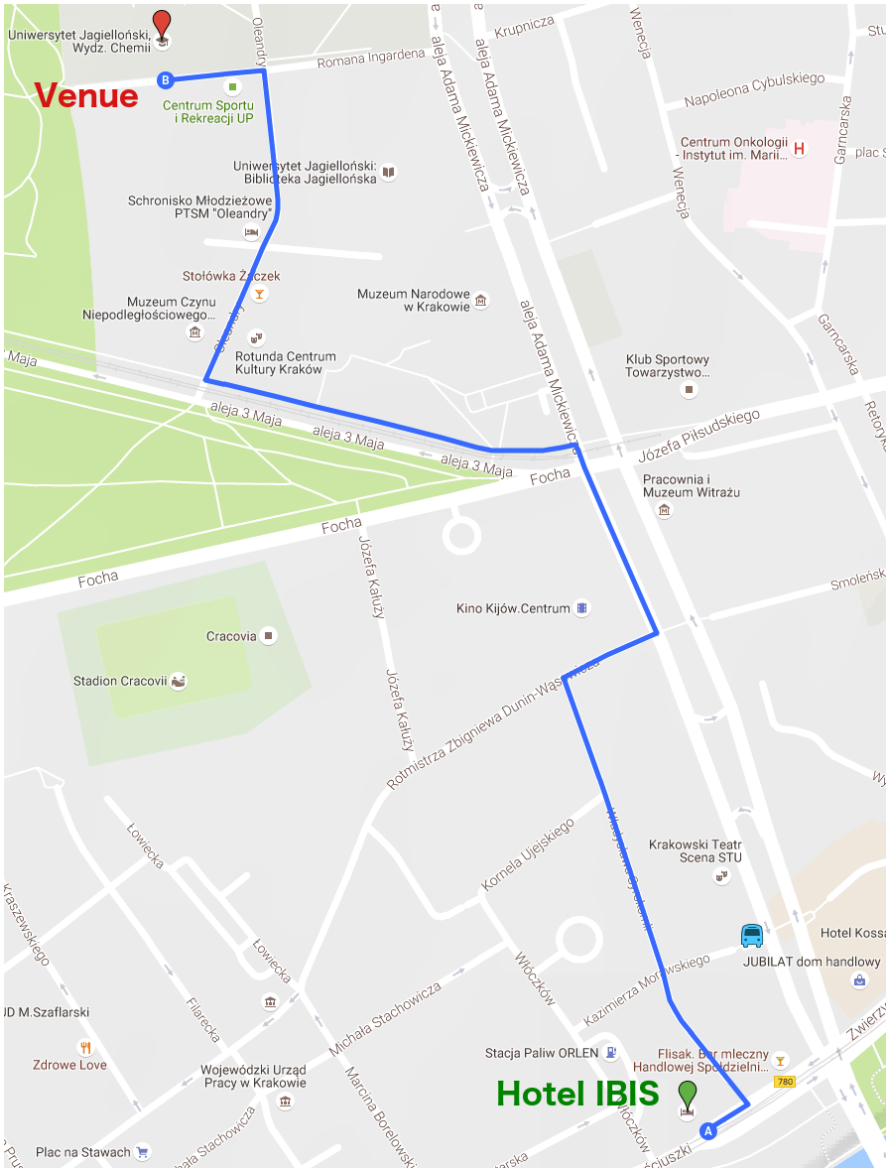
Walk first along Syrokomli Street and turn right into Dunin-Wąssowicza Street; then turn left and walk along Krasińskiego Avenue to reach the crossing with Focha Street (in front of you: the

main headquarters of the National Museum in Krakow, on the left: Błonia Park). Turn slightly left and walk along Trzeciego Maja Avenue parallel to the tram tracks. On the next crossing, turn right and continue along Oleandry Street (you are passing along the main library building of Jagiellonian University, to the right). Turn left into Ingardena Street, where the Faculty of Chemistry building is located.

On Thursday morning, someone of the organizers will be waiting at the Hotel IBIS to help you in getting to the venue. We can walk there together, starting from the hotel around 8:15 and 8:30 a.m.

Map

Interactive Google Map is available here (or click on the image below).



Program of Krakow meeting

Wednesday, September 7

16:00-21:00 ECOSTBio Registration (Hotel IBIS, lobby)

about 20 Informal dinner (restaurant Wanilia, Gołębia St. 6); *leave from IBIS at 19:40.*

Thursday, September 8

08:30-08:55 ECOSTBio Registration (Faculty of Chemistry, ground floor)

Session 1 (Lecture Hall, 2nd floor) – *jointly with CTTC VII*
Chair: Grace Morgan

09:00-09:40 **Marcel Swart**
Spinning around in transition-metal chemistry

09:40-10:00 Andrew Atkins
Assessment of functional and wave function method dependence on the intersystem crossing dynamics of CH_2S

10.00-10:20 Quan Phung
Density matrix renormalization group for transition metal complexes: does it work?

10:20-10.50 Coffee

Session 2 (Lecture Hall, 2nd floor) – *jointly with CTTC VII*
Chair: Rob Deeth

10.50-11:30 **Stefan Grimme**
Simplified quantum chemical methods for consistent structures, energies, and electronic spectra of large systems.

11.30-12:10 **Wesley Browne**
Connecting microscopic and macroscopic mechanisms – an experimentalists perspective on the role of theory in understanding reaction mechanisms

12:10-12.30 Balazs Pinter
Guiding principles for controlling the redox potential of ligand-centered electron transfer processes.

12:30-12:50 Panel discussion

12:50-13:00 Closing of CTTC7 conference

13.00-15.00 Lunch

Session 3 (Lecture Hall, 2nd floor)
Chair: Maja Gruden

15.00-15:20 Grace Morgan
Ordering Phenomena and Photophysical Properties of Manganese(III) and Iron(III) Spin State Switches.

15:20-15.50 **Roman Boca**
Solid state cooperativeness in spin crossover systems.

15.50-16:30 WG1: Database discussion

16:30-17.00 Coffee

17.00-18:30 Poster Session (+ pica-pica)

19:15-20.00 Walking to restaurant

20.00-23.00 Conference dinner (ZaKładka Food & Wine, Józefińska St. 2)

Friday, September 9

Session 4 (Lecture Hall, 2nd floor)
Chair: Jalila Simaan

09.00-09:30 **Rudi van Eldik**
Spin-state tuning of Fe(III) complexes in solution. Effect of non-innocent ligands and hydrostatic pressure.

09:30-09:50 Rubén Solorzano
Novel (coordination) polymer nanoparticles for advanced theranostics.

09.50-10:10 Paulo Martinho
Polymorphism in tridentate Fe(III) spin crossover compounds: transition temperatures and cooperativity.

10.10-10.30 Carlo Albero Gaggioli
Ligand effect on the oxidative addition of O_2 on Lau(I)-H complexes.

10:30-11.00 Panel discussion

11:00-11:30 Coffee

Session 5 (Computer Labs 114 & 114A, 1st floor)

11.30-13:00 Moisés Àlvarez, Davide Angelone, Marcel Swart
SPINSTATE Database – practical training iochem-bd

13.00-15.00 Lunch

Session 6 (Lecture Hall, 2nd floor)
Chair: John McGrady

15.00-15:30 **Piotr Pietrzyk**
Open-shell binding of small molecules to nickel sites in ZSM-5 zeolite – role of the spin density flow pathways

15:30-15.50 Leon Freitag
Novel multiconfigurational methods for large molecules: application to spin-crossover compounds.

15.50-16:10 Vera Krewald
Electronic structure analysis of transition metal dimers for dinitrogen photocleavage

16:10-16.40 Coffee

Session 7 (Lecture Hall, 2nd floor)
Chair: Jeremy Harvey

16.40-17:00 Danny Müller
Halogenated Propyltetrazoles – Substituent effects and chiral SCO complexes.

17.00-17:30 **Dimitrios Pantazis**
The mechanism of biological water oxidation: insights from spectroscopy-oriented quantum chemistry.

17.30-17:50 Panel discussion

17:50-18:00 Closing

about 20 Informal dinner

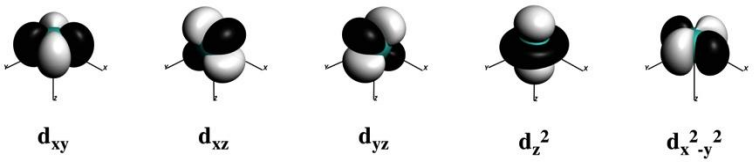
Invited and keynote lectures

SPINNING AROUND IN TRANSITION-METAL CHEMISTRY

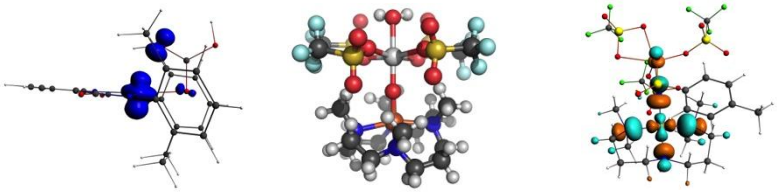
M. Swart,[ab*] A. Romero-Rivera,[b] K. Ray,[c] A. McDonald[d]

a) ICREA, Barcelona; b) IQCC & Dept. Química, Univ. Girona; c) Dept. Chemistry, Humboldt-Univ. Berlin; d) School of Chemistry, Trinity Coll. Dublin

The chemistry of the first-row transition-metals is highly diverse with a multitude of different reactivity and property patterns. This richness results from the partial occupation of the shell of d-orbitals, which leads to different oxidation and spin states.



Especially the spin states remain an enigmatic property that has triggered many studies, and recently the first text-book devoted entirely to it has appeared.[1] Of course, having a different number of unpaired electrons has a direct effect on the structure, magnetism, and reactivity of molecules. However, the assignment of spin states, and the role it plays in e.g. reactivity, is not unambiguous. Here I will present recent computational studies on iron(III/IV)-(hydro)(per)oxo species,[2,3] Mössbauer spectroscopy,[4] Sc^{3+}-capped iron-oxygen[2,3] and copper-nitrene[5,6] complexes, and terminal Ni(III)-oxygen adducts.[7]



Financial support from COST (H2020), GenCat and MINECO is greatly acknowledged.

[1] M. Swart, M. Costas (Eds.), Spin states in Biochemistry and inorganic chemistry: Influence on Structure and Reactivity, Wiley, Chichester UK, 2015.
[2] M. Swart, Chem. Commun. 49 (2013) 6650.
[3] J. Prakash, G.T. Rohde, K.K. Meier, A.J. Jasniewski, K.M. Van Heuvelen, E. Münck, L. Que Jr., J. Am. Chem. Soc. 137 (2015) 3478.
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SIMPLIFIED QUANTUM CHEMICAL METHODS FOR CONSISTENT STRUCTURES, ENERGIES, AND ELECTRONIC SPECTRA OF LARGE SYSTEMS

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Beringstrasse 4, D-53115 Bonn, Germany

Popular quantum chemical methods offer a good compromise between computational cost and accuracy but the search for improved approaches is still ongoing. The talk presents our efforts in this context to develop physically sound and numerically well behaved mean-field quantum chemical approximations which provide simultaneously accurate molecular and crystal structures as well as inter- and intra-molecular interaction and reaction energies. We apply Hartree-Fock or standard GGA components in global hybrid functionals with a relatively large amount of non-local Fock-exchange. In order to correct for the annoying basis set superposition error and to account for the important long-range London dispersion effects, our well-established D3 and gCP atom-pairwise schemes are used. Pre-defined Gaussian atomic-orbital basis sets of minimal or modified DZ Ahlrichs-type available for almost all elements are employed. The new composite schemes termed HF-3c (minimal basis set)[1] and PBEh-3c[2] (DZ level) together with e.g. double-hybrid functionals/"large AO basis set" for high accuracy form a hierarchy of accurate and robust general purpose electronic structure approaches. Very detailed benchmarks for the huge GMTKN30 energy database, supramolecular non-covalent interactions, molecular crystals (cell volumes and sublimation energies), as well as molecular structures are discussed. In a second part, the electronic absorption spectra (UV-vis or ECD) of molecules or molecular complexes with 500-1000 atoms are treated the simplified Tamm-Dancoff (sTDA)[3] and time-dependent (sTD)[4] methods. Extension to a newly developed tight-binding (TB) Hamiltonian expanded in an extended AO basis set (sTD(A)-xTB) is described as well.

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[2] S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, J. Chem. Phys. 143 (2015) 054107.
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CONNECTING MICROSCOPIC AND MACROSCOPIC MECHANSIMS – AN EXPERIMENTALISTS PERSPECTIVE ON THE ROLE OF THEORY IN UNDERSTANDING REACTION MECHANSIMS

W. R. Browne

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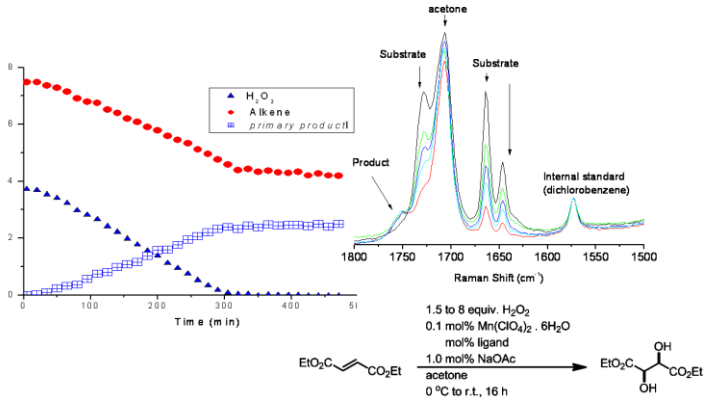
The search for new and better reactivity has driven the development of 1st row transition metal catalysis over the last several decades, not least in the field of oxidation catalysis. Our group has focused on manganese and iron based catalysts for both fine chemical and bulk applications, and more recently on Ni(II) based catalysts, employing environmentally benign oxidants. A key challenge faced in catalyst development and in optimisation is to move from catalyst discovery to catalysis design. However, design requires understanding of the fundamental mechanisms that underpin catalysis. In this contribution I will discuss our recent efforts in elucidation of reaction mechanisms and the consequences of a lack of mechanistic understanding at the system level (i.e. considering all reaction components and their interplay) for efforts to deploy theoretical methods. In particular, the synergy that can be achieved between theoretical and experimental methods to delve deep into understanding not just the catalytic cycle but also the broader context of the catalytic reaction. The choice of spectroscopic techniques used to study individual reactions will be emphasised.



Reaction monitoring with vibrational spectroscopy

SOLID STATE COOPERATIVENESS IN SPIN CROSSOVER SYSTEMS

R. Boča

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The conversion curve of the spin crossover, represented by the temperature dependence of the high-spin mole fraction $x = f(T)$, can be either gradual (close to the ideal Boltzmann behavior) or abrupt owing to the solid-state cooperativeness (abbr. Γ, γ, J, …). Appearance of the thermal hysteresis in spin crossover systems is conditioned by $T_c/k < \Gamma$. However, Γ appears as an internal parameter of the particular theory that accounts to the non-ideality (like activity) of the thermodynamic relationships owing to the intercentre interactions [1].

The interaction energy can be written in the form of a Taylor series $E = E_0 + \gamma_1 x + \gamma_2 x^2$ where the linear coefficient $\gamma_1 = \mu = -\chi$ relates to the chemical potential and/or electronegativity, and the quadratic one $\gamma_2 = \eta$ is nothing but the Pearson's hardness. These two parameters influence the transition temperature since $T_c = \Delta H/\Delta S + (\gamma_1 + \gamma_2)/\Delta S$ holds true [2].

By fitting the conversion curves (or directly the magnetic susceptibility) of spin crossover systems the values of T_c, ΔH, ΔS, and Γ have been extracted for 13 related mononuclear Fe(III) complexes of the $[FeL^5X]$ type, where L^5 stand for the pentadentate Schiff-base ligands. These parameters were subjected to a chemometric analysis by using the Pearson correlation, Cluster analysis, and Principal component analysis [3-5]. To this end, T_c closely correlates with ΔH (r = 0.92) unlike to the remaining parameters of the theory. While tuning of ΔH is rather straightforward on the basis of the crystal field strength, the understanding of ΔS is much more complex owing to manifold contributions, and the understanding and then a tuning of Γ is a challenge.

[1] R. Boča, W. Linert, Monatsh. Chem. 134 (2003) 199.
[2] R. Boča, R. Boča, M. Boča, H. Ehrenberg, H. Fuess, W. Linert, F. Renz, I. Svoboda, Chem. Phys. 293 (2003) 375.
[3] C. Krüger, P. Augustín, Ľ. Dlháň, J. Pavlik, J. Moncoľ, I. Nemec, R. Boča, F. Renz, Polyhedron 87 (2015) 194.
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[5] P. Augustin, R. Boča, Nova Biotechnol. Chim. 14 (2015) 96.

SPIN-STATE TUNING OF FE(III) COMPLEXES IN SOLUTION. EFFECT OF NON-INNOCENT LIGANDS AND HYDROSTATIC PRESSURE

R. van Eldik, M. Oszaja

Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg, 91058 Erlangen, Germany, and Faculty of Chemistry, Jagiellonian University, 30-060 Krakow, Poland
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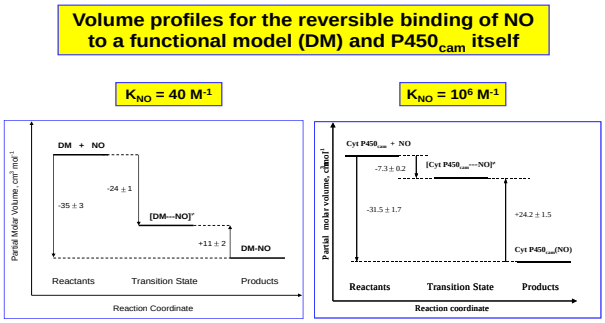
Non-innocent ligands such as nitric oxide ($^{\bullet}$NO) can affect the spin and formal oxidation state of Fe(III) complexes in solution. In general, such spin-state changes are coupled to large changes in partial molar volume of the transition and product states. This in turn causes kinetic and thermodynamic data for the reversible coordination of non-innocent ligands to depend significantly on hydrostatic pressure. Such data can be summarized in the form of volume profiles that represent the reaction in terms of volume changes along the reaction coordinate. A typical example is shown below.

The presentation will focus on a few examples selected from our own work that deal with the interaction of $^{\bullet}$NO with model Fe^{III}(porphyrin) complexes, functional model systems for Cytochrome P450 and the Cytochrome $P450_{cam}$ enzyme. In addition, more recent data on the interaction of $^{\bullet}$NO with microperoxidase 11 will be reported.



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[3] A. Franke, N. Hessenauer-Ilicheva, D. Meyer, G. Stochel, W.-D. Woggon and R. van Eldik, J. Am. Chem. Soc., 128 (2006) 13611.
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[5] A. Franke, E. Hartmann, I. Schlichting and R. van Eldik, J. Biol. Inorg. Chem., 17 (2012) 447.
[6] A. Franke and R. van Eldik, Microreview in Eur. J. Inorg. Chem., (2013) 460.
[6] A. Franke, M. Oszajca, M. Brindell, G. Stochel and R. van Eldik, Adv. Inorg. Chem., 67 (2015) 172.

OPEN-SHELL BINDING OF SMALL MOLECULES TO NICKEL SITES IN ZSM-5 ZEOLITE – ROLE OF THE SPIN DENSITY FLOW PATHWAYS

P. Pietrzyk,[1] T. Mazur,[1] K. Podolska-Serafin,[1] M. Radoń,[1] M. Chiesa,[2] Z. Sojka[1]

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[2]*Dipartimento di Chimica, Università di Torino, via P. Giuria 7, 10125, Torino, Italy*

Interaction of non-innocent and innocent small gas-phase molecules with transition-metal ions (TMI) is of central importance for understanding the chemistry of coordination systems. Depending on the electron configuration of TMI, nature of a small molecule, and stoichiometry of the interaction both paramagnetic and diamagnetic adducts are observed. In the case of paramagnetic adducts, EPR spectroscopy corroborated with relativistic quantum chemical calculations of the spin-Hamiltonian parameters has been widely used for studying their nature. Yet, molecular interpretation of the corresponding spectral parameters is not a trivial task, taking into account an intricate nature of the spin and electronic interactions within the metal-ligand units.

This contribution is focused on the interaction of NO, O_2 and CO with Ni(I)/Ni(II) ions dispersed inside the channels of ZSM-5 zeolite. Three types of adducts will be described: the side-on structure of nickel(II)-superoxo unit, monocarbonyl Ni(I)-CO and mononitrosyl Ni(II)-NO adducts, which were formed upon adsorption of the corresponding gas phase diatomics on nickel-exchanged ZSM-5 zeolite. Identification and spin-related properties were studied by mean of EPR/HYSCORE spectroscopy (continuous-wave and pulse modes), FTIR spectroscopy, DFT calculations based on the finite cluster models and CASSCF calculations of electronic structure.

In the case where small molecule is a non-innocent ligand, electronic structure of the adduct results from complicated and interlaced spin and charge flow along different channels (e.g. O_2) [1] or spin pairing due to antiferromagnetic coupling as in the case of NO. Interaction with CO leads to a strong electronic relaxation within 3d manifold of nickel [2]. The mechanism of the formation of CO and O_2 adducts was accounted for by ETS-NOCV population analysis. With this tool three distinct orbital channels (associated with σ, π, and δ overlap) of congruent and incongruent charge and spin density flows within the metal site and the ligand were identified. Whereas in the case of Ni(II)-NO, CAS calculations and a valence bond type analysis [3] unraveled that the $|(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^{\uparrow}(d_{x^2-y^2})^{\uparrow}(\pi_x^*)^0(\pi_y^*)^{\downarrow}|$ state represents dominant contribution to the electronic wave function. This result indicates that the magnetic properties originate from antiferromagnetic coupling between two open-shell subsystems (Ni(II)/zeolite site and NO) resulting in vanishing spin density at nitrogen atom and leaving one unpaired electron at the nickel center, which remains in agreement with the HYSCORE results.

THE MECHANISM OF BIOLOGICAL WATER OXIDATION: INSIGHTS FROM SPECTROSCOPY-ORIENTED QUANTUM CHEMISTRY

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The tetramanganese Mn_4CaO_5 cluster in the oxygen-evolving complex of Photosystem II is a prime example of a complex bioinorganic system that adopts different electronic and geometric forms as it goes through the water-oxidizing catalytic cycle [1]. X-ray crystallography and EXAFS offer several structural constraints but can neither provide unique models of the various catalytic states nor probe all of them. On the other hand, spectroscopic techniques that report on the local and global electronic structure of the metal ions (e.g. electron paramagnetic resonance and X-ray spectroscopies) are powerful and information-rich, but it is impossible to directly translate such data into precise structural models. The link between spectroscopy and atomistic structure can only be established through quantum chemical simulations that focus precisely on the prediction of such spectroscopic observables [2–4].

The application of spectroscopy-oriented quantum chemistry in biological photosynthesis has revolutionized our understanding of the oxygen evolving complex and its structure in the various catalytic states, in all of their complexity. It has pointed to previously unsuspected forms, uncovered functional principles and provided atomistic models that explain, rationalize and interconnect disparate experimental observations amassed over decades of experimental work, enabling their coherent structural interpretation [5,6]. Using this approach, we have recently achieved a greatly improved understanding, firmly grounded on both experiment and high-level theory, of regulatory aspects and mechanistic details in biological water oxidation, including substrate delivery to the active site [7] and the mechanism of O–O bond formation.

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Scientific talks

ASSESSMENT OF FUNCTIONAL AND WAVE FUNCTION METHOD DEPENDENCE ON THE INTERSYSTEM CROSSING DYNAMICS OF CH_2S

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We report unexpected large differences in the intersystem crossing (ISC) dynamics using both different wave function methods and different density functionals for the simple model system CH_2S. To simulate ISC dynamics in molecular complexes we have used SHARC [1], which is a code capable of performing surface hopping *ab initio molecular* dynamics including simultaneously non-adiabatic and spin-orbit couplings. To extend the capabilities of SHARC to larger systems and cheaper methods we have implemented the possibility to utilize linear response time-dependent density functional theory (TD-DFT) from the ADF program package [2]. Consequently, we have tested TD-DFT with SHARC for CH_2S using the functionals BP86, PBE, B3LYP, and BHandHLYP. The results have been compared to higher-level wavefunction methods such as MS-CASPT2 and SA-CASSCF from MOLCAS, and ADC(2) from Turbomole.

Remarkably, small differences (<0.2 eV) in the potential energy surfaces cause dramatic differences in the dynamics regarding ISC in this molecule. Specifically, SA-CASSCF shows a total triplet population of 4.5% after 500 fs, whereas MS-CASPT2 and ADC(2) have 0% in the triplet states, albeit for different reasons. The DFT GGA functionals compare well with the MS-CASPT2 calculations, showing no ISC. However, the hybrid functionals, particularly BHandHLYP, show ISC (25% triplet population after 500 fs). The presence or absence of ISC can be correlated to the variation of the C-S bond length during the dynamics.

An important conclusion is that the comparison of energies only at the Franck-Condon (FC) region is not enough to guarantee the correct dynamical behavior of a given method. Moreover, this is not restricted to only leading to erroneous conclusions from dynamics, but will also affect the results of any problems where one leaves the FC region, e.g., reaction pathways.

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DENSITY MATRIX RENORMALIZATION GROUP FOR TRANSITION METAL COMPLEXES: DOES IT WORK?

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The density matrix renormalization group (DMRG) [1] is one of the most promising novel methods to study strongly correlated molecular systems. With a polynomial scaling, DMRG can handle a much larger active space as compared to the conventional CASSCF method, allowing one to study large transition metal (TM) systems with 30-50 active orbitals. To account for dynamic correlation, so-called DMRG-cu(4)-CASPT2 or DMRG-PT2 has been recently developed [2]. In this work, we aim at answering a question "Does DMRG-PT2 work?" for TM systems, by studying the spin state energetics of two TM models (iron porphyrin FeP and manganese-oxo porphyrin $MnOP^+$). Encouraging results were obtained: DMRG-PT2 can reproduce the CASPT2 results to within 0.1-0.2 kcal/mol in calculations a small active space CAS(8,11) in FeP, and less than 2 kcal/mol for a medium-sized active space CAS(14,18) in $MnOP^+$. In calculations with a large active space of about 30 orbitals in, the performance of DMRG-PT2 is less impressive with an error up to 4 kcal/mol due to the errors introduced by two sources: the finite number of renormalized states *m*, and an approximation in the 4-particle reduced density matrix. The answer for the question "Does DMRG-PT2 works?" from our perspective is "Yes!". However, a lot of work must be done to make this novel method user-friendly for 'informed' users.

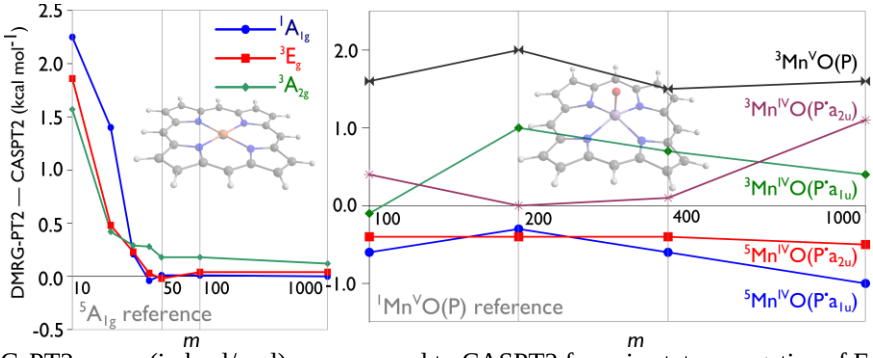

Figure 1. DMRG-PT2 errors (in kcal/mol) as compared to CASPT2 for spin state energetics of FeP and $MnOP^+$.

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GUIDING PRINCIPLES FOR CONTROLING THE REDOX POTENTIAL OF LIGAND-CENTERED ELECTRON TRANSFER PROCESSES

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The great potential in the cooperation of redox active ligands with abundant 1st row transition metals has mostly been recognized in the ongoing intense efforts to achieve sustainable chemical energy conversion covering fields of inert molecule activation, artificial photosynthesis, multi-electron reactivity and so on [1]. Also, conceptually it is the most intuitive strategy of cooperative catalysis: use redox non-innocent ligands as electron reservoirs for metals that cannot store enough electrons for the required multi-electron transformations, e.g. oxidative addition.

This systematic large-scale computational and conceptual investigation [2, 3] aims at rational redox-leveling, i.e. moderating redox potentials, of ligand-centered electron transfer processes potentially leading to cooperative catalysts with low overpotential in multielectron activation processes. To this end, metal and ligand-based reductions have been modeled in octahedral ruthenium complexes revealing metal-ligand interactions as one of the profound driving forces for the redox-active behavior of quinoine ligands, one of the most effective redox active and noninnocent ligand scaffolds. Through an extensive investigation of redox-active ligand derivatives we revealed the most critical factors that facilitate or suppress redox activity of ligands in metal complexes, from which basic rules for designing noninnocent/redox-active ligands are put forward and discussed.

We also 'designed' a hitherto unknown benzodipyrrole ligand (bdp), which contains three nonaromatic rings that synchronously become aromatic upon two-electron reduction. We find that the reduction of this new ligand is indeed very feasible taking place at about 1 V more positive potential than the parent benzoquinonediimine ligand indicating that non-aromatic-to-aromatic transitions indeed significantly ease ligand-centered reductions.

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ORDERING PHENOMENA AND PHOTOPHYSICAL PROPERTIES OF MANGANESE(III) AND IRON(III) SPIN STATE SWITCHES

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In recent years spin state ordering has emerged as an important effect in many molecular solids which show a multi-step thermal spin crossover (SCO). Detailed theoretical models to describe the microscopic origin of spin state ordering have recently been proposed[1],[2] and in all cases the high spin:low spin (HS:LS) ratio in the ordered state offers important information about the nature of the underlying frustration and/or the existence of sublattices. While the LS-HS size difference is regularly factored into theoretical treatments, significant differences in molecular shape between the two states are not included in these models. The recent surge in reports of SCO which is accompanied by a crystallographic phase transition[3],[4] includes several examples where there is also a change in point group symmetry. We are interested to further investigate the relationship between the conformational changes which may accompany SCO at the molecular level, particularly in Mn^{3+} SCO complexes. We present here recent results on several Mn^{3+}[5],[6] and Fe^{3+}[7],[8] complexes which show a variety of ordering types.

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NOVEL (COORDINATION) POLYMER NANOPARTICLES FOR ADVANCED THERANOSTICS

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Recently, nanoscale coordination polymer particles (CPPs) have emerged as an alternative platform to provide new opportunities for engineering multifunctional systems with applications in drug delivery and/or biomedical imaging. In general, CPPs exhibit high metal ion payloads content, high biocompatibility, low toxicity and offer the possibility to harbor additional functions. The pre-synthetic design strategies like judicious choice of metal ions and ligands can address the challenges of synthesizing such functional materials. Moreover, the ability to incorporate diverse metals useful for MRI allows constructing novel contrast agents for biomedical imaging. In this communication we will revise some of the applications developed in the group concerning this topic. [1-7]

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POLYMORPHISM IN TRIDENTATE FE(III) SPIN CROSSOVER COMPOUNDS: TRANSITION TEMPERATURES AND COOPERATIVITY

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The phenomenon of spin crossover (SCO) observed for d^4-d^7 first row transition metal ions is normally accompanied by drastic changes in the magnetic, optical and structural properties of molecules and materials,[1] making them very attractive for potential applications in data storage, molecular switching, molecular sensing and other molecular electronic devices.[2] Molecules exhibiting SCO may also present polymorphism which can affect dramatically their magnetic profile and their function.[3]

Here we discuss polymorphism in tridentate Fe(III) Schiff-base complexes with salEen (salEen = N-ethyl-N-(2-aminoethyl)salicylaldiminate) derived ligands. We have found that the temperature of both synthesis and crystallization highly influences the magnetic profile and transition temperatures for their perchlorate and tetrafluoroborate salts. Interesting is that very small changes in the packing of the compounds result in either abrupt spin transitions or exotic spin crossovers with stepped transition and hysteresis (Figure 1).

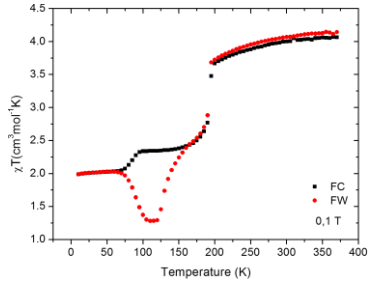

Figure 1 Magnetic profile for one of the Fe(III) polymorphs.

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LIGAND EFFECT ON THE OXIDATIVE ADDITION OF O_2 ON LAu(I)-H COMPLEXES

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Controlled activation of molecular oxygen is one of the biggest challenges in catalysis, since O_2 is kinetically quite stable, but it is highly desirable, in order to obtain a green, and easily accessible chemical oxidant. Recently, the reaction of O_2 with a gold(I) hydride complex was shown to form a hydroperoxide.[1] The overall spin state of the reactants is triplet (triplet O_2 and singlet Au(I) hydride), while the product has a singlet ground state, so the reaction is a spin-forbidden one. In a previous study,[2] we have computationally investigated the mechanism of the reaction shown in Fig. 1 (left), by means of analyzing three feasible mechanisms. We found that the oxidative addition of molecular oxygen is the kinetically favoured one (the corresponding energy profile together with the structures are shown in Fig. 1 right). Oxidative addition was until recently considered to be very unfavourable, if not impossible, with gold, while ubiquitous for palladium, because of the high redox potential of the Au(I)/Au(III) pair compared to that of the isoelectronic Pd(0)/Pd(II) one. This surprising result has led us to study the oxidative addition of O_2 into gold(I) hydride bond by changing the ligand, in order to get insights into the kinetic and thermodynamic of this important reaction. To achieve this goal, we studied the reaction profiles as in Fig.1 (right) for all the ligands analyzed, computing therefore structures 1 (LAuH), MECPs and structures 3 (the product of the oxidative addition). We then linked this mechanistic study with a bond-analysis investigation, in order to understand how the ligand modifies the activation barriers and the thermodynamic outcomes. This bond analysis has been carried out using the Charge-Displacement analysis [3] via NOCV framework.[4]

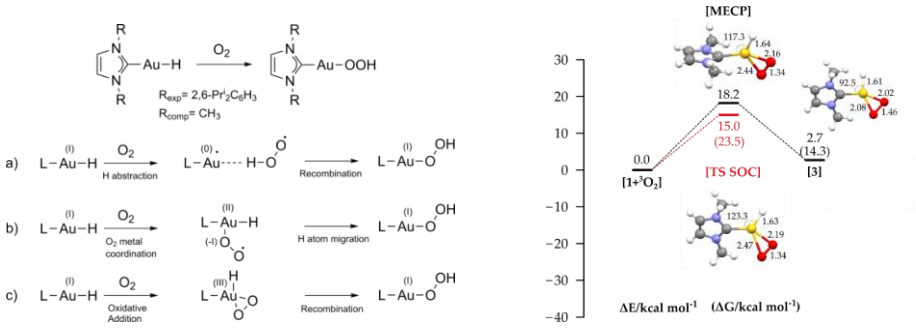

Figure 1: (Left) Reaction and analyzed mechanisms; Right) Energy profile for the oxidative addition.[2]

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NOVEL MULTICONFIGURATIONAL METHODS FOR LARGE MOLECULES: APPLICATION TO SPIN-CROSSOVER COMPOUNDS

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Density functional theory (DFT) has become a preferred computational method in bioinorganic chemistry[1], not least due to its computational affordability. However for many applications, especially those involving systems with close-lying electronic states such as spin crossover compounds[2], the accuracy of the DFT depends heavily on the density functional employed.

While ab-initio multiconfigurational methods are able to handle close-lying electronic states, they are often computationally unfeasible for large systems. Owing to recent developments such as density matrix renormalisation group (DMRG)[3, 4] and Cholesky decomposition of two-electron integrals[5], applications of multiconfigurational methods on increasingly larger systems are becoming feasible.

In this work, we present how novel multiconfigurational methods such as the density matrix renormalisation group (DMRG) together with dynamic correlation theories such as second-order complete active space perturbation theory (CASPT2)[6] and n-electron valence state perturbation theory (NEVPT2)[7] can aid in obtaining insights into the electronic structure, energies and properties of spin states of spin crossover complexes. Moreover, we present a NEVPT2 implementation employing a DMRG reference wavefunction and the Cholesky decomposition of the two-electron integrals, and its application to spin-state energetics of several iron and cobalt spin crossover complexes.

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ELECTRONIC STRUCTURE ANALYSIS OF TRANSITION METAL DIMERS FOR DINITROGEN PHOTOCLEAVAGE

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Cleaving the dinitrogen molecule efficiently and cheaply is a key research target towards sustainable chemical processes. As an alternative to thermal dinitrogen activation, a novel route is the photochemical N-N bond cleavage. Upon solar irradiation of specific inorganic complexes with linear M-N-N-M cores, two metal-nitrido complexes result. However, in some synthetic examples for this type of reactivity, the dominant reaction pathway is the cleavage of the metal-nitrogen bonds, yielding back the starting materials. The catalytic efficiency of the six known N_2 photoactivation catalysts is generally low, so that an electronic structure analysis with computational methods will help in designing improved catalysts.

The theoretical description of bond cleavage processes in systems with several transition metal ions poses several challenges: single-reference methods may have difficulties describing the bond-breaking process adequately, and although multi-reference methods are capable of that they might prove too expensive. While ultimately dynamical studies of the relaxation processes after light excitation are required to understand the two competing reaction pathways, a static quantum chemical analysis of the electronic structure can already provide insight into the origin of the observed bifurcated reactivity.[1, 2]

Herein, we present accurate electronic structure descriptions at the DFT and CASSCF/CASPT2 level for the ground and excited states of two selected synthetic examples, evaluating the adequacy of the chosen electronic structure methods by comparison with spectroscopic data. The two selected complexes, the osmium dimer $[Os_2(\mu\text{-}N_2)(NH_3)_{10}]^{5+}$ [3] and the molybdenum dimer $[Mo_2(\mu\text{-}N_2)(N^tBuPh)_6]$ [4], have different metal coordination environments and different degrees of chemical activation prior to light irradiation and are thus representative examples of the six synthetically established N_2 photocleavage catalysts. We evaluate similarities and differences in the electronic structures of the dimeric reactants and the monomeric metal-nitrido products, and discuss the implications for dinitrogen photocleavage with these complexes.

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HALOGENATED PROPYLTETRAZOLES – SUBSTITUENT EFFECTS AND CHIRAL SCO COMPLEXES

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Since the discovery of the spin crossover (SCO) effect a major reason for the continuous research was the aim for applicability. Actual ideas towards a technological use of SCO compounds range from multifunctional materials for sensing and switching up to optoelectronic devices and data storage.

So far, a technological application is still hampered by several challenges, a major one being the non-destructive read-out process of the actual spin state. Although, using the LIESST-effect, within femtoseconds the spin state may be changed, no comparable method is available for its determination. The "classical" laboratory methods (like magnetic measurements, spectroscopic methods, …) are inadequate when talking about miniaturization for technology.

During our current research we focused on a series of Fe(II) SCO complexes with halogenated N1-propyltetrazoles.

These compounds were used for a detailed study of the substituents effect on the SCO behaviour. First, we focussed on the influences exhibited by the type and position of the substituent on the spin transition, then extending the emphasis on solvent and anion effects. Additionally to this complete picture obtained so far, we concentrated on the issue of optical activity.

The substitution in the 2-position led to optically active ligands, those enantiomerically pure forms were prepared used for the preparation of the corresponding Fe(II)-SCO complexes. Thereby, we obtained the so far first chiral, enantiomerically pure, homoleptic monodentate Fe(II) SCO complexes. These were used for further investigations correlating the spin-state and the optical activity of the complex. We found, that spectroscopic characterization of the chiroptical properties allowed for a conclusion of the actual spin state.

Within this contribution we will present our results pointing towards a possible non-destructive read-out of the spin state via measurement of the chiroptical properties.

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Poster presentations

No.	Presenting author	Title
P1	Andjelković, Ljubica	COMPUTATIONAL STUDY OF THE SPIN-STATE ENERGETICS IN MANGANESE PHTHALOCYANINE
P2	Angelone, Davide	ELUCIDATION OF THE MECHANISM OF ACTIVATION OF OXYGEN BY IRON(II)POLYPYRIDYLAMINE COMPLEXES IN WATER
P3	Atkins, Andrew	UNVEILING THE MECHANISM OF ULTRAFAST INTERSYSTEM CROSSING OF THE ARCHETYPAL PHOTOSENSITIZER $[RU(BPY)_3]^{2+}$
P4	Borowski, Tomasz	OXIDATIVE C-C BOND CLEAVAGE BY TWO METALLOENZYMES AND ONE SYNTHETIC COMPLEX – COMPUTATIONAL STUDIES
P5	Brocławik, Ewa	HIGH-LEVEL SMALL-SCALE OR PERIODIC DFT MODELING FOR TM CENTERS IN ZEOLITES?
P6	Drabik, Gabriela	SPIN STATES AND H_2O/OH^- LIGAND BINDING PROPERTIES OF FERRIC CENTER IN A MICROPEROXIDASE MODEL: A DFT-D STUDY
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COMPUTATIONAL STUDY OF THE SPIN-STATE ENERGETICS IN MANGANESE PHTHALOCYANINE

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Since 3d transition metal ion complexes in different spin states usually display quite different structural, spectral and magnetic properties, and also reactivity, it is important to correctly determine the spin ground state of the system. Mn^{II} in MnPc has five d-electrons that can be distributed in a square-planar environment in three different ways: with a maximum number of unpaired electrons – the high spin state, with maximally paired electrons – the low spin state, or intermediate spin. The intermediate spin is the ground state,[1] however, different ground electronic states within this spin multiplicity are still a subject of debate in the literature.[2-6] In order to clarify these issues we performed Density Functional Theory (DFT) calculations with various Density Functional Approximations (DFAs) reliable for the spin state energetics. Moreover, lowest-lying states, ^4E_g, is the subject to the Jahn-Teller (JT) distortion.[7]

Our calculations revealed that ^4E_g is the ground state in MnPc, irrespective of level of theory employed. Intrinsic Distortion Path (IDP) model is successfully employed in the analysis of the JT distortion in MnPc.

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ELUCIDATION OF THE MECHANISM OF ACTIVATION OF OXYGEN BY IRON(II)POLYPYRIDYLAMINE COMPLEXES IN WATER

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A wide range of important enzyme-catalyzed reactions including the biosynthesis of natural products and metabolism of xenobiotics involve the generation of high valent iron species (i.e. Fe^{III}-OOH, Fe^{III}-(OO) and Fe^{IV}=O etc.) formed primarily by direct reaction of iron(II) and iron(III) based enzymes with oxygen. The transient nature of these intermediates, in particular those involving non-heme enzymes, frustrates efforts to observe them and elucidate mechanistic details. It is in this aspect that functional models for biological systems are essential. In recent years we have explored the activation of oxygen by Fe(II) polypyridylamine complexes, in particular to understand the factors that determine their activity in achieving substrate oxidation (such as the oxidative cleavage of double strand DNA).[1] In this contribution, we explore, in a combined experimental and theoretical study, the reaction of these complexes with oxygen and the pathways which are involved in achieving substrate oxidation. The major focus will be on the generation of superoxide radical from the reaction of Fe(II) polypyridylamine based complexes and oxygen and in particular the enhancement in reaction rates observed by irradiation with visible and UV light.[2] This will be complemented by state-of-the-art density functional studies using methods[3] that have been proven[4,5] to work well for spin-state properties that play a major role here.

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UNVEILING THE MECHANISM OF ULTRAFAST INTERSYSTEM CROSSING OF THE ARCHETYPAL PHOTOSENSITIZER $[RU(BPY)_3]^{2+}$

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Herein, I will first present a new theoretical tool for studying intersystem crossing (ISC) in transition metal complexes. We have implemented the capability of using linear response time-dependent density functional theory (TD-DFT) from the ADF program package [1] in combination with surface hopping molecular dynamics within the SHARC code[2]. Subsequently, the first application of the TD-DFT dynamics with SHARC will be presented, which is to calculate the excited state dynamics of the archetypal complex $[Ru(bpy)_3]^{2+}$ for transition metal containing photosensitizers.

In the excited state dynamics we see the onset of ISC immediately after excitation (within 0.5 fs) and the triplet population tails off to *ca.* 65% at 30 fs. Firstly, the timescales seen here agree with experimental observations for $[Ru(bpy)_3]^{2+}$ of ISC occurring in <30 fs [3]. Moreover, the speed of ISC predicted is much faster than is currently possible to measure with experimental methods.

Based on normal mode analysis and essential dynamics and considering the extremely short timescale of ISC in $[Ru(bpy)_3]^{2+}$ a mechanism due to vibrational motion must be excluded from consideration (shortest vibrational period is *ca.* 10 fs). Thus, the speed of ISC in $[Ru(bpy)_3]^{2+}$ has to be attributed to its high density of excited states (*ca.* 30 states within *ca.* 1 eV) and the size of spin orbit coupling. This is contrary to what is observed in organic systems where a specific motion activates ISC.

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OXIDATIVE C-C BOND CLEAVAGE BY TWO METALLOENZYMES AND ONE SYNTHETIC COMPLEX – COMPUTATIONAL STUDIES

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Cleavage of aliphatic C-C bonds takes place in many natural methabolic pathways, but it is also of relevance for converting chemical feedstocks into useful products. Recently we have studied with DFT method mechanisms of oxidative C-C bond cleavage reactions catalysed by two metalloenzymes, i.e. Fe(II)-dependent acireductone dioxygenase and Mn(II)-dependent quercetin dioxygenase [1] and one Cu(II) synthetic complex [2]. In all of these systems the organic substrate contains a reactive $C=C-O^-$ fragment, whereas the oxidant is either triplet dioxygen or singlet HNO, the latter is isoelectronic with singlet O_2. In this contribution we present the key results obtained for the three systems and compare them to highlight similarities (and important differences) between them.

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HIGH-LEVEL SMALL-SCALE OR PERIODIC DFT MODELING FOR TM CENTERS IN ZEOLITES?

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The two quandaries while modeling catalytically relevant systems concern: i) QC suitable to solve the problem, and ii) the type and the size of selected models. Points i) and ii) are critically interdependent and reasonable balance must be obeyed between the model size and the level of QC. We discuss this issue based on selected examples taken from our studies on the performance of ammonia-modified Co(II) sites in zeolites with respect to the activation of NO.

Zeolites are periodic structures built of Si- or Al-O_4 tetrahedrons (T). Exchanged TM cations (active sites for deNOx and fine chemistry) are usually diluted, linked to one or two T blocks. Working models may range from local clusters to periodic models of a real framework while QC from correlated wave function methods (WF) to DFT/BO-MD. Here we will illustrate which properties, and what credible insights into catalytic activity may be provided by modeling (Table 1).

Model	Method	Properties
Cluster (S)	CASPT2, CC	spin state energetics, wave function analysis
Cluster (S,M)	DFT	geometries, frequencies, electron density analysis
Periodic	DFT	Co siting (static), geometries, frequencies (harmonic)
	B-O MD	Co siting (dynamic), relative populations, frequencies

Table 1: Models (S-small, M-medium) and QC methods versus accessible properties

Co(II) sites with bound NO pose serious challenge for QC as they are non-innocent, showing many close-lying spin states, distinctly varying in properties. Their electronic structure and charge transfer properties require exact correlated WF methods, applicable only for very small models.

On the other hand, the speciation of Co(II) siting for centers modified by ammonia and NO sorption calls either for extremely large clusters or periodic modeling (including MD runs) to asses stable structures and their relative populations.

We are discussing the issue on the example of interpreting the experimental IR spectra taken for Co/MOR, CoFER and CoBEA zeolites after designed pre-treatment by NH_3 and NO. Our modeling [1,2] significantly aided the understanding of spectra: experiment pointed to two peaks due to three or five NH_3 co-ligands. QC revealed new, unforeseen features due to the spin change: 3 donor co-ligands after spin-flip imposed larger red-shift of NO than 5 co-ligands. MD studies may still enrich band assignment for various zeolite types and Co siting.

Acknowledgements: Support from NCN grant No. 2015/17/B/ST5/00023 and COST funds from STSM-CM1305-151114-051084 and STSM-CM1305-150215-051085 are kindly acknowledged.

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SPIN STATES AND H_2O/OH^- LIGAND BINDING PROPERTIES OF FERRIC CENTER IN A MICROPEROXIDASE MODEL: A DFT-D STUDY

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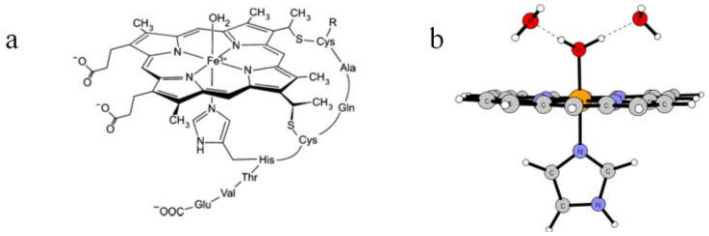
Dispersion-corrected DFT (B3LYP-D3) calculations are performed for a simple model of Fe(III) center in microperoxidase, considering its three protonation states: axial ligands H_2O/HHis , OH^-/HHis and OH^-/His^-. The computational model consists of iron-porphyrin without side chains, axially ligated by imidazole and water (or hydroxide, depending on the pH conditions)[1].

Relative spin-state energetics are analyzed, indicating an energetic proximity of the LS (S=1/2) and the HS (S=5/2) state for models with H_2O/HHis , OH^-/HHis axial ligands, in agreement with the thermal equilibrium behavior data. Also, accordingly with experiment, the OH^-/His^- form has a stronger preference for the LS state than the other two forms [2]. However, we observe a tendency of B3LYP functional to incorrectly overstabilize the IS (S=3/2) state, which should rather be placed slightly above the HS state to account for the EPR data due to mixed-spin (S=5/2, 3/2) state.

Binding energies of H_2O and OH^- ligands are determined with and without accounting for interaction with second-shell water molecules. The latter interaction is found to be crucial for the binding properties. Our calculations also indicate a significant *trans* effect of histidine on the geometry and energy of the Fe-O_{ax} bond. Upon deprotonation of the histidine, this bond elongates by 0.027Å and the bond energy drops down by 9.1 kcal/mol. For the model properly solvated with explicit second-shell water molecules, our calculations indicate that the effective binding energies of H_2O (to the form with HisH) and OH^- (to the form with His^-) may become comparable. This result may rationalize recent experimental observations that under certain conditions these ligands may be exchanged by NO at comparable rates [3].



(a) fragment of a microperoxidase structure [2];
(b) structure of the model with second-shell water molecules; both structures in the protonation state HisH/H_2O.

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A THEORETICAL APPROACH FOR THE ELASTIC STEP IN SPIN CROSSOVER COMPOUNDS

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It is well known that at low temperatures, spin crossover compounds can be switched from the ground low spin (LS) state to the long-lifetime metastable high-spin (HS) state using irradiation with appropriate wavelengths, the so called Light Induced Excited Spin State Trapping – LIESST effect. Recent experiments [1,2] using femtosecond laser for photoexcitation and the detailed analysis of the subsequent evolution of the system allowed the study of very fast dynamical phenomena. In solids, the photoexcitation process triggers a further change of the electronic states of the molecules after switching off the light and which takes place due to the propagation of the elastic waves, even before the increase of the crystal volume. This process was called elastic step and takes place on the acoustic time scale.

Here we use an elastic model in order to simulate the experimental elastic step. The difference in molecular size between LS and HS states induces elastic waves which propagates throughout the whole sample. After reproducing the experimental dependence of the elastic step of the photoexcitation percentage and temperature, we predict the behavior of the system in the case of the variation of some parameters, such as the elastic constant, the size of the system or the homogeneity of the photoexcitation. The delay in the evolution of the surface (see figure) and the contribution of the 40eorganization of the molecular states during elastic steps, leading to clusters of HS molecules towards edge or corners is also revealed.

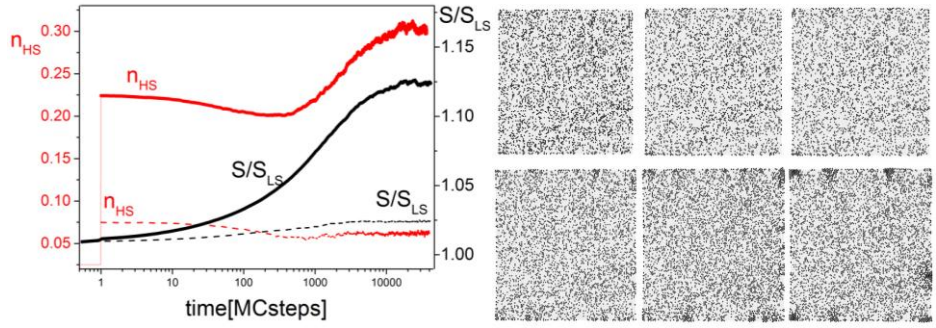

Figure: Variation of the fraction of HS molecules, n_{HS}, and of the area during elastic step for two photoexcitation rates (left) Evolution of molecular states during the elastic step: grey circles: LS, black circles: HS.(right)

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PHOTOSWITCHABLE $Cu^{II}_4Mo^{IV}$ AND $Cu^{II}_2Mo^{IV}$ CYANIDO-BRIDGED MOLECULES

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The molecular systems based on octacyanidometallates have attracted great attention over last years, mainly due to the formation of many interesting magnetic systems [1]. Due to the redox bistability of the $[Mo^{IV}(CN)_8]^{4-/3-}$ ion, it has been successfully used in design of the molecular systems switchable by light [2]. The most intensively studied group of photomagnetic cyanido-bridged assemblies is based on copper(II) complexes and octacyanidomolybdate(IV) ions.

Here we present two new cyanido-bridged molecules: $[Cu(L1)(py)]_4[Mo^{IV}(CN)_8]\cdot 14H_2O$ (1), **Cu_4Mo** and trimetallic $[(Cu(L2)]_2[Mo^{IV}(CN)_8]\cdot 9H_2O$ (2), **Cu_2Mo.** Both molecules reveal photomagnetic effect of different origin.

In the case of (1) the irradiation with 470 nm light induces the charge transfer between Mo and Cu metal centers, leading to the $Cu^{I}Cu^{II}_3Mo^{V}$ photoinduced system, which displays the ferromagnetic intramolecular interaction. The coupling constant J_2 has been calculated using the following Hamiltonian: $\hat{H}_2 = -J_2\hat{S}_{Mo}\cdot(\hat{S}_{Cu1}+\hat{S}_{Cu2}+\hat{S}_{Cu3}) + g_{Cu}\mu_B(\hat{S}_{Cu1}+\hat{S}_{Cu2}+\hat{S}_{Cu3})\cdot\vec{H} + g_{Mo}\mu_B\hat{S}_{Mo}\cdot\vec{H}$

The value of J_2 equals 104(3) cm^{-1}, which corresponds well with the values reported for this class of systems.

The trimetallic molecule Cu_2Mo^{IV} undergoes the singlet-triplet transition within the Mo^{IV} center upon the irradiation with 436 nm light. The photogenerated $Cu_2Mo^{IV}_{HS}$ magnetic system reveals the ferromagnetic interaction within the trimetallic molecule characterized by the value of coupling constant J_4=20.2(7) cm^{-1} calculated with the use of the Hamiltonian:

$\hat{H}_4 = -J_4\hat{S}_{Mo}\cdot(\hat{S}_{Cu1}+\hat{S}_{Cu2}) + g\mu_B(\hat{S}_{Cu1}+\hat{S}_{Cu2}+\hat{S}_{Mo})\cdot\vec{H}$

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STRUCTURAL, SPECTROSCOPIC, DNA-BINDING AND CYTOTOXIC PROPERTIES OF [Cu{$Ph_2P(O)NP(O)Ph_2$-*O*}$_2$(2,2′-bipy)(H_2O)]

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Only a handful of Cu^{II} complexes bearing chalcogenated imidodiphosphinato type of ligands $[Ph_2P(E)NP(E)Ph_2]^-$, E = O, S,[1] have been reported up to now [2-3].

In this work, the synthesis, as well as the structural and spectroscopic characterization of [Cu{$Ph_2P(O)NP(O)Ph_2$-*O*}$_2$(2,2′-bipy)(H_2O)] (**1**), will be presented.

X-ray crystallographic studies of **1** revealed a trigonal bipyramidal $Cu^{II}O_3N_2$ first coordination sphere. The structure is stabilized by intramolecular pi-pi stacking, as well as by hydrogen bonds involving the coordinated H_2O and the two $[Ph_2P(O)NP(O)Ph_2]^-$ ligands, which, unexpectedly, are coordinated in a monodentate fashion.

UV-vis and cw EPR spectroscopy studies provided evidence that in solution complex **1** exhibits a tetragonal structure. Ligand hyperfine interactions of the unpaired electron of **1** were investigated by pulsed ENDOR and HYSCORE spectroscopies.

DNA-binding experiments showed that complex **1** induces conformational changes to DNA. Moreover, complex **1** was shown to be cytotoxic towards the breast cancer cell line MCF-7 and to inhibit the G_2/M cycle transition.

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QM/MM STUDY OF ESTROGEN METABOLISM BY CYPS TO TOXIC AGENTS

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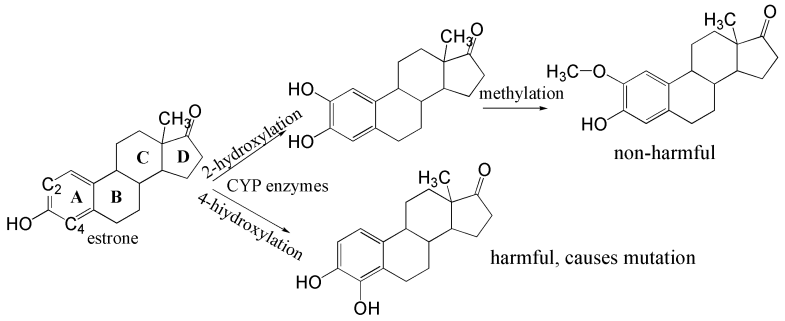
Estrogens are essential for the proper functioning of the human body, their primary role is the regulation of the reproductive system of animals and humans. Low levels of estrogens are responsible for increased bone loss and hot flashes in postmenopausal women, which have been treated by hormone replacement therapy (HRT) for the past 70 years. However, recent large-scale studies found a well-established connection between long exposure to estrogen and the risk of developing cancer. The carcinogenic activity of estrogens have been linked to their cytochrome P450 enzyme (CYPs) dependent metabolism, and two major pathways have been identified. 2-hydroxylation is usually regarded as a benign pathway, while 4-hydroxylation is supposed to lead to the toxic product. [1] However, the prevalence of the 2 or 4-hydroxylation pathways depends on various factors. (1) Increased unsaturation of ring B increases the ratio of 4-hydroxylated product.[2] (2) Isoform selectivity may also influence the product ratios in humans CYP1A1, CYP1A2, CYP1B1 and CYP3A4 have been implicated in estrogen-metabolism.[3]



In the present work we set out to identify the most important factors responsible for the regioselectivity of estrogen-metabolism. Our gas-phase calculations show that the unsaturation of ring B increases the electron density at C4 making it more susceptible to oxidation, which leads to decreased energies of activation for the aromatic carbon oxidation reaction catalyzed by CYPs. To address the regioselectivity of the various CYP isoforms, docking studies and molecular dynamics simulations have been performed. Now QM/MM calculations are underway to determine the energy of activation of the 2- and 4-hydroxylation reactions in the four CYP isoforms which could be used to assess the role of the various isoforms in estrogen-toxicity.

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THE SPIN CROSSOVER PROFILE IN IRON(III) SCHIFF-BASE COMPOUNDS: HALOGEN INFLUENCE

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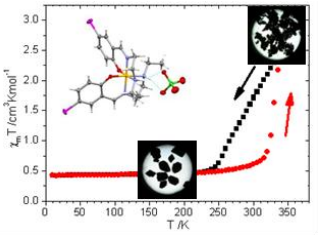
Technological advances have been pushing the limits of chemistry for the last few years towards creating more efficient and multifunctional molecules and materials. A phenomenon that shows great promise in molecular electronics is spin crossover (SCO).[1] This switching can be harnessed to develop materials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

Here we report the synthesis and characterization of halogen derivatized SCO compounds with an Fe(III) metallic center coordinated to tridentate (N2O) Schiff-base ligands. We have found that all compounds exhibit SCO with profiles ranging from gradual to abrupt with hysteresis and a detailed studies on the halogen influence on these and DFT calculations are also being carried out.



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SPIN-CROSSOVER IN A PSEUDO-TETRAHEDRAL BIS(FORMAZANATE) IRON COMPLEX

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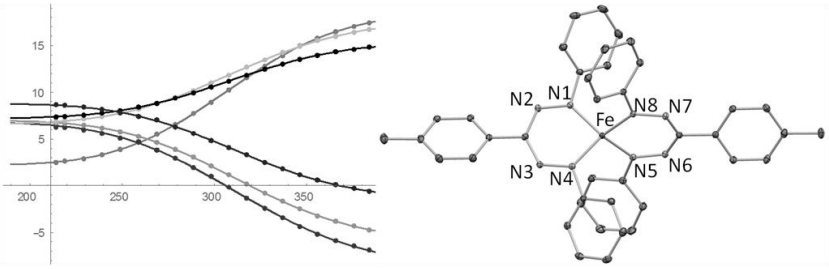
Coordination compounds that show electronic bistability are of interest for applications such as molecule-based data-storage, switches and sensors [1]. Complexes that show spin-crossover are well-known for 6-coordinate, octahedral geometries for which the ligand field strength is such that two spin states are close in energy and may be reversibly addressed. Due to a much weaker ligand field in 4-coordinate complexes, these (with very few exceptions) [2] lead to high spin-states only.

Here, we report a bis(formazanate)iron complex (L_2Fe) and present X-ray crystallographic, magnetic and spectroscopic evidence for spin cross-over behavior that allows thermal switching between S=0 and S=2 states [3]. Fitting of variable-temperature NMR solution data (see Figure below) suggests that the transition is driven by entropy changes and takes place with $T_{½}$ = 345 K. DFT calculations indicate that the unusual S=0 spin state is due to the π-acceptor properties of the formazanate ligands. As a result, one of the d-orbtials that is metal-ligand antibonding (t_2 in a tetrahedral geometry) gains bonding character and is significantly stabilized. This results in an orbital splitting diagram that is similar to that in octahedral complexes. The observation of spin cross-over in a (pseudo)tetrahedral iron compound presents a new design principle for materials with electronic bistability.



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SYNTHESIS AND CHARACTERIZATION OF POLY(DICYCLOPENTADIENE) GELS OBTAINED USING A NOVEL DITUNGSTEN VERSUS W AND RU MONONUCLEAR CATALYSTS

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The ring opening metathesis polymerization (ROMP) reaction yields polymeric materials with unique mechanical, optical, electrical and chemical properties. ROMP can be catalyzed by a broad range of metal-based catalytic systems, with forerunners being those of ruthenium, molybdenum and tungsten [1]. Bimetallic complexes with metal-metal bonds have been scarcely employed [2,3], although they provide more precise control over the stereoselectivity, since both metal centers can be involved in the reaction. Among those, $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**W_2**) turns out as an efficient yet inexpensive initiator for ROMP of a range of cycloolefins [4,5].

In this study, we implement **W_2** and commercially available WCl_6 for the synthesis of poly(dicyclopentadiene) (**PDCPD**) gels via ROMP of dicyclopentadiene (**DCPD**). Both catalysts require activation by small amounts of phenylacetylene. Dry-gels were compared with **PDCPD** aerogels synthesized using the well-established first and second generation Ru-based Grubbs' catalysts [6]. Data revealed that Ru-based catalysts favor the *trans*-, while W-based catalysts favor the *cis*-configuration. Most importantly, it is also shown that the configuration of the polymeric chain plays a key role in the swelling behavior of those **PDCPD** dry-gels in organic solvents.

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CONCEPTUAL INSIGHTS INTO DFT SPIN STATE ENERGETICS OF OCTAHEDRAL TRANSITION METAL COMPLEXES THROUGH A DENSITY DIFFERENCE ANALYSIS

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Computing consistent spin state energetics, especially when weak metal-ligand interactions influence the stability of corresponding states, is still challenging [1]. Particularly complicated are 1st row transition metals, as they can adopt various spin states that are difficult to model reliably. While Density Functional Theory has been extensively used for modeling large organometallic and bioinorganic systems and their reactions, it has also been recognized to provide unreliable relative spin state energetics in general [2, 3].

In this study we aim to understand how exact exchange admixture of hybrid DFT functionals influences the electron density and computed relative energy of spin states of various octahedral transition metal complexes. Using a straightforward density difference approach we identified the footprints of well-defined electron correlation effects in the electron density of simple reference systems as well as in that of representative iron(II) complexes.

An extension of this analysis convincingly supports the recently proposed concept that low-spin states are affected to a greater extent by the exact exchange admixture than high-spin states. We could also separate the change of molecular energy with exact exchange admixture to electron density and functional related contributions. These findings are discussed and put into context with the relative spin-state energy of 52 experimentally described octahedral transition metal complexes and their dependence on the extent of admixture of exact exchange in the B3LYP functional.

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A SUPRAMOLECULAR MIMIC OF THE REGULATION STEP OF FE-MONOOXYGENASES: ALLOSTERIC MODULATION OF FE(III)OOH AND FE(IV)-OXO FORMATION BY GUEST BINDING IN A HETERODINUCLEAR ZN(II)-FE(II) CALIX[6]ARENE-BASED FUNNEL COMPLEX.

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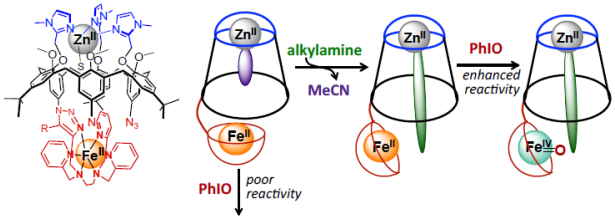
The performances of metalloenzymes as catalysts derive from years of evolution that allowed nature to optimize the arrangement of the enzyme/substrate assembly by a fine tuning of the coordination and supramolecular environment of the active site. In particular, a widespread supramolecular feature of oxidative metalloenzymes (iron and copper enzymes) is a remarkable *substrate-triggered activation of the metal site reactivity*: substrate binding induces an allosteric coordination change at the metal center that turns on O_2 activation.[1] To the best of our knowledge, the molecular system we report here is the first one where such a behavior is observed. A heterodinuclear Fe^{II}/Zn^{II} complex based on a calix[6]arene cavity scaffold was synthesized. Each of the metal centers exhibits one labile position allowing the coordination inside the cavity of a guest alkylamine at Zn^{II},[2] and the generation of reaction intermediates (Fe^{III}(OOH) and Fe^{IV}O) at the large rim.[3] A dependence between the chain length of the encapsulated alkylamine and the conversion in Fe^{III}(OOH) intermediate is observed. In addition, it is shown that the generation of the Fe^{IV}O intermediate is enhanced by addition of the alkylamine guest. Hence, this supramolecular system allows us to generate reactive species in the presence of a bound guest under the allosteric control of the guest.



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MECHANISTIC STUDIES ON CPD(II) OXIDATION OF ALCOHOLS

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The most active enzymes for oxidation reactions are those containing a heme moiety in their active sites. Although the active species in the catalytic cycle of various heme enzymes are analogous, they strongly differ in their function. It is believed that the ability to catalyze different types of reactions is connected with the structural differences in the prosthetic group and its environment, in particular with the nature of an amino acid coordinated in proximal position to the iron center in the active site (i.e. tyrosine for catalases, histidine for peroxidases, and cysteine for P-450). In the catalytic cycles of heme enzymes it is assumed that high-valent iron(IV)-oxo species (so called compound I, Cpd I), due to its very high reactivity, are key intermediates in oxygenation reactions of organic substrates. Only recently, iron(IV)-oxo porphyrin (compound II, Cpd II) has began to be perceived as an effective oxidant playing a complementary role to Cpd I in oxygenation reactions.

Therefore, the aim of our study was to perform a mechanistic study of the oxidation reaction of Cpd II model, in the catalytic oxidation of 4-methoxybenzyl alcohol (4-MB-alc) and 4-methoxybenzaldehyde (4-MB-ald).

The results were obtained within Density Functional Theory (DFT), as implemented in Turbomole v. 6.3 with B3LYP functional and def-TZVP basis set and compared with experimental stopped-flow kinetic measurements.

First, the active species taking part in the catalytic reaction were identified and the stability of various possible coordinative forms of the catalyst in solution was considered. Next, the molecular mechanism of oxidation of 4-MB-alc and 4-MB-ald was considered. We proposed the mechanism analogous to the oxygen-rebound mechanism of oxidation of hydrocarbons by porphyrins, and demonstrated that it could be broadened for aldehyde group as well. The presented mechanistic studies demonstrate that there is a pronounced impact of ligation as such on catalytic performance of the systems examined thus far. This includes two-state reactivity mechanism, which comes into play in un-ligated systems where the change between triplet and quintet multiplicity surfaces is observed. The changes in the type of axial ligand, nevertheless, have only subtle, if any, effect on their reactivity.

ROLE OF SOLVENT DEPENDENCE ON THE FORMATION OF REACTIVE NON-HEME IRON INTERMEDIATES WITH H_2O_2

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Understanding the formation and reactivity of non-heme Fe (III)-OOH and Fe (IV)=O is of central importance to the study of non-heme iron dependent enzymes such as Tau-D and metallodrugs such as bleomycin. 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_2O_2.[2,3,4,5] The complex $[(MeN3Py)Fe(II)(CH_3CN)_2](ClO_4)_2$ (**1**) is a biomimetic of such non-heme iron enzymes, and can catalyze the oxidation of alkenes to 1,2-diols, and epoxides.[1,2] However, oxidation of cyclooctene with H_2O_2 in presence of **1** provides the cis-diol product in acetonitrile, but the trans-diol product in acetone. This effect of solvent on the selectivity of the catalyst was rationalized by the differences in the stability of iron peroxy intermediates, which were proposed to form $Fe(III)OOH.CH_3CN$ and Fe(V)=O in acetonitrile. However, in acetone, the CH_3CN ligands were proposed to exchange with water present in the solvent, and addition of H_2O_2 leads to formation of an $Fe(III)\text{-}OO(CH_3)_2COH$ species, which undergoes homolysis to form an Fe(IV)=O species and a radical intermediate $\bullet O(CH_3)_2COH$, which subsequently reacts with alkenes to form the trans product. In this presentation the role of solvent and especially water content in the formation of Fe(III)-OOH species is discussed. The formation and reactivity of these species was investigated by a combination of UV/vis absorption, EPR and resonance Raman spectroscopies and spectroelectrochemistry. Finally, the formation of a thermodynamically stable Fe(III)-O-Fe(III) species is shown, which is highly dependent on the concentration of water present.

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CONTROLING ELECTON AND PROTON TRANSFER PROCESSES FOR FACILE GENERATION OF REACTIVE OXYGEN SPECIES UPON H_2O_2 INTERACTION WITH AMORPHOUS ZrO_2

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H_2O_2 decomposition is commonly catalysed by transition-metal-based systems that exhibit redox properties and show typical Fenton-like reactivity. However, also less conventional materials of non-redox nature, such as hardly reducible amorphous oxides, can be active in generation of reactive oxygen species (ROS) from H_2O_2. For the non-redox oxides mechanism of ROS formation is not trivial and involves interfacial electroprotic reactions combined with formation of open-shell products such as $O_2^{-\bullet}$, $HO_2^{\bullet}$, and $^{\bullet}OH$. The aim of this contribution is to examine the activity of amorphous ZrO_2 in ROS formation via H_2O_2 decomposition with special emphasis on spin-adducts detection with EPR spectroscopy.

Formation of the paramagnetic superoxo groups and hydroxyl radicals was confirmed by EPR spectroscopy. The EPR spectra recorded after treatment with H_2O_2 solution at various pH values represent a signal characteristic of surface-stabilized $O_2^{-\bullet}$ species. Temperature behavior of the observed signal (10 K – 77 K) and additional HYSCORE measurements showed that $O_2^{-\bullet}$ species were stabilized via H-bonding with surface hydroxyls, on the contrary to a reference material of amorphous Nb_2O_5 (also active in ROS generation) for which the presence of hyperfine splitting due to ^{93}Nb (I = 9/2) nuclei indicated direct attachment to the metal core. In the case of $^{\bullet}OH$ radicals, DMPO spin trapping and test reaction with OPD substrate monitored with UV-Vis spectroscopy were used.

The signal intensities of the particular ROS change strongly with pH of the reaction mixture. This observation indicated that the processes leading to ROS generation shall involve a proton transfer apart from electron transfer and the observed spin transformations. Spectroscopic measurements have shown that $^{\bullet}OH$ and $O_2^{-\bullet}$ radicals are formed simultaneously following an electroprotic mechanism ($H_2O_2 + HO_2^- = {}^{\bullet}OH + O_2^{-\bullet} + H_2O$). As a result, the nature of ROS produced upon H_2O_2 interaction with amorphous ZrO_2 can be controlled by varying pH of the reaction medium. At pH > 5.5 the main decomposition product of H_2O_2 was O_2 (catalase-like activity), while below this value peroxidase-like activity was observed resulting in concerted production of $^{\bullet}OH$ and $O_2^{-\bullet}$.

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THE ROLE OF SPIN STATES IN CATALYTIC MECHANISM OF THE INTRA- AND EXTRADIOL CLEAVAGE OF CATECHOLS BY O_2

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The microbial aerobic degradation of aromatic pollutants, which are widespread contaminants in soils and groundwaters, represents the intensive research area in the scientific community. A key step in the biodegradation of aromatic compounds is an oxidative cleavage of catechol derivatives and is facilitated by a class of enzymes known as catechol dioxygenase. Two different groups of enzymes play an essential role in the ring cleavage of catechol derivatives: the extradiol- and intradiol-cleaving dioxygenases. These two enzyme groups have different active sites, and thus catalyze different metabolic transformations. The ring cleavage of very inert, aromatic catechols can be catalyzed not only by the catechol dioxygenases, but also by biomimetic iron complexes. Using DFT we have elucidated the mechanism of the catalytic cycle for two biomimetic iron complexes with 2,11-diaza[3.3](2,6)pyridinophane and N,N′-dimethyl-2,11-diaza[3.3](2,6)pyridinophane ligands. It is shown that, although the sextet state is the ground state of both iron complexes at the beginning and at the very end of the catalytic cycle, the quartet state governs the reaction and determinates the product distribution.

NEW CHALLENGES FOR ELASTIC MODELS IN SPIN CROSSOVER COMPOUNDS

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Spin crossover solids are a class of materials with many potential applications due to their multi-hysteretic response to a wide range of perturbations, from temperature to pressure and electromagnetic radiation. In recent contributions [1, 2] we were able to show how this apparently complicated behavior can be explained by a rather simple physical model that takes into considerations the interplay of the molecular volume change during switching, and the local pressure intermediated by elastic interactions. Our mechano-elastic model is able to give insights on relaxation mechanisms [1], cluster formation and propagation [2], as well as quasistatic switching curves.

In this paper we discuss how the mechano-elastic model can also explain elastically driven cooperativity [3], triggered by femtosecond laser excitations.

Spin crossover crystals have been excited with a short (femtosecond) laser pulse and, afterwards, the fraction of the high spin state molecules (n_{HS}) has been monitored. Depending on the laser pulse power, which dictates the initial n_{HS} value, the time evolution shows either a normal relaxation behavior for small excitations, or an increase above initial n_{HS} value, followed saturation and relaxation, when the laser power is above a certain threshold.

We have used our model to explain this behavior, showing that there are two different types of local conditions:

(i) In the low excitation case, the high spin molecules are most probable isolated, surrounded by low spin neighbors and are subject to compressive stress due to the volume differences between the two states.

(ii) In the higher excitation case, the probability of having low spin molecules with two or more high spin close neighbors increases, leading to a negative pressure acting on some low spin molecules which will switch to high spin state without being photoexcited, an avalanche-type cooperative phenomenon.

We shall also discuss size effects in terms of both the 2D and the 3D model, underlying the differences between the two cases and the effects that could explain crystal cracks development.

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DENSITY FUNCTIONAL APPROXIMATION APPROACH FOR DETERMINATION OF OXIDATION STATES AND SPIN STATES OF OXOIRON COMPLEXES

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We report here a Density functional theory (DFT) computational study of a series of Fe^{III} and Fe^{IV} oxoiron complexes with a broad palette of ligands. Besides obtaining good structures, we are interested in obtaining an accurate prediction and description of spin states of the examined oxoiron complexes. For investigating the spin state energetics we have used different density functional approximations (S12g, BP86-D_3, OPBE, SSB-D, B3LYP, S12h and MVS), in order to test their performance. One of the main observations of this detailed study is the remarkable performance of BP86-D_3 for geometry optimization, and S12g for both, accurate geometry and determination of the ground spin state. Our results show that the density functionals can be used as a reliable computational tool for predicting and reproducing good geometries, determining the oxidation state, and providing accurate description of spin state energetics.

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