



2017

• *Cluster evolution in molecular three-dimensional spin-crossover systems*

Laurentiu Stoleriu, Masamichi Nishino, Seiji Miyashita, Alexandru Stancu, Andreas Hauser, and Cristian Enachescu

Physical Review B **96** (6) (2017), p64115

DOI:10.1103/PhysRevB.96.064115

The nucleation and growth properties of domains of molecules of the same state in open boundary three-dimensional (3D) spin-crossover systems of various shapes are discussed within the framework of the mechanoelastic model. The molecules are situated on face-centered-cubic lattices and are linked by springs through which they interact. Monte Carlo simulations imply that clusters nucleate from corners in the case of systems having well-developed faces and from kinks in the case of spherical samples, in accordance with available experimental data. In addition, a method to characterize the cooperativity in these systems is proposed, which by scanning the fluctuations in the 3D samples can be related directly to powder x-ray-diffraction experiments.

• *Controlling Lanthanide Exchange in Triple-Stranded Helicates: A Way to Optimize Molecular Light-Upconversion*

Claude Piguet, Davood Zare, Yan Suffren, Homayoun Nozary and Andreas Hauser

Angewandte Chemie International Edition **56** (46) (2017), p14612-14617

DOI:10.1002/anie.201709156

Keywords: helicate • kinetics • keystone mechanism • heterometallic • molecular upconversion

The kinetic lability of hexadentate gallium-based tripods is sufficient to ensure thermodynamic self-assembly of luminescent heterodimetallic $[\text{GaLn}(\text{L}3)]^{3+}$ helicates on the hour time scale, where Ln is a trivalent 4f-block cation. The inertness is however large enough for preserving the triple-helical structure when $[\text{GaLn}(\text{L}3)]^{3+}$ is exposed to lanthanide exchange. The connection of a second gallium-based tripod further slows down the exchange processes to such an extent that spectroscopically active $[\text{CrErCr}(\text{L}4)]^{3+}$ can be diluted into closed-shell $[\text{GaYGa}(\text{L}4)]^{3+}$ matrices without metal scrambling. This feature is exploited for pushing molecular-based energy transfer upconversion (ETU) at room temperature.

• *Triplet state CPL active helicene-dithiolene platinum bipyridine complexes*

Thomas Biet, Thomas Cauchy, Qinchao Sun, Jie Ding, Andreas Hauser, Patric Oulevey, Thomas Bürgi, Denis Jacquemin, Nicolas Vanthuyne, Jeanne Crassous and Narcis Avarvari

Chemical Communications **53** (66) (2017), p9210-9213

DOI:10.1039/C7CC05198K

Chiral metal dithiolene complexes represent a family of chiral precursors, which can give rise to molecular materials with properties resulting from the interplay of chirality with conductivity, magnetism, and photophysics. We describe herein the first examples of chiral metal diimine dithiolene complexes, by the use of a platinum(II) centre coordinated by 2,2'-bipyridine and helicene-dithiolene ligands. Straightforward synthesis of racemic and enantiopure complexes allows the preparation of luminescent Pt(bipy) [4] and [6]helicene compounds for which the solid-state structure was determined as well. TD-DFT calculations support the assignment of the low energy bands observed in the UV-vis absorption spectra as mixed metal-ligand-to-ligand charge transfer transitions and confirm that the emission band results from the T1 excited state. Interestingly the enantiopure [6]helicene complexes show CPL activity at room temperature in acetonitrile solutions with anisotropy factors of $3\text{Å}^{-10^{-4}}$.

• *Cr^{III} as an alternative to Ru^{II} in metallo-supramolecular chemistry*

Davood Zare, Benjamin Doistau, Homayoun Nozary, Céline Besnard, Laure Guénée, Yan Suffren, Anne-Laure Pelé, Andreas Hauser and Claude Piguet

Dalton Transactions **46** (2017), p8992-9009

DOI:10.1039/c7dt01747b

Compared with divalent ruthenium coordination complexes, which are widely exploited as parts of multi-component photonic devices, optically active trivalent chromium complexes are under-represented in multi-metallic supramolecular architectures performing energy conversion because of the tricky preparation of stable heteroleptic Cr^{III} building blocks. We herein propose a kind of remedy with the synthesis of a novel family of kinetically inert heteroleptic bis-terdentate mononuclear complexes, which can be incorporated into dinuclear rod-like diads as a proof-of-concept. The mechanism and magnitude of intermetallic Cr-Cr communications have been unraveled by a combination of magnetic, photophysical and thermodynamic investigations. Alternated aromatic/alkyne connectors provided by Sonogashira coupling reactions emerge as the most efficient wires for long-distance communication between two chromium centres bridged by Janus-type back-to-back bis-terdentate receptors.

• *Search for Electron Delocalization from $[\text{Fe}(\text{CN})_6]^{3-}$ to the Dication of Viologen in $(\text{DNP})_3[\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$*

Ahmed S. Abouelwafa, Andreas Hauser, Valeriu Mereacre, Yanhua Lan, Gary J. Long, Fernande Grandjean, Gernot Buth, Christopher E. Anson and Annie K. Powell

Inorganic Chemistry **56** (11) (2017), p6477-6488

DOI:10.1021/acs.inorgchem.7b00540

$\text{K}_3\text{Fe}(\text{CN})_6$ reacts with the viologen 1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dication, $(\text{DNP})_2^{2+}$, to form a supramolecular complex, $(\text{DNP})_3[\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$ (**1**). The crystal structure of **1** reveals that there are two $[\text{Fe}(\text{CN})_6]^{3-}$ anions within an organic framework of three $(\text{DNP})_2^{2+}$ cations with the shortest Fe(III)-N-Fe(III) distances of ca. 9.8 Å..., distances that minimize extensive long-range magnetic exchange coupling interactions between the $[\text{Fe}(\text{CN})_6]^{3-}$ anions, and, thus, **1** is paramagnetic above ca. 17 K and exhibits weak ferromagnetic coupling between 17 and 3 K and antiferromagnetic coupling between 3 and 1.8 K. The long Fe(III)-N-Fe(III) distances permit slow spin-lattice relaxation and slow spin-lattice paramagnetic relaxation, relative to the iron-57 Larmor precession frequency, as is evidenced by the Mössbauer spectra measured between 3 and 60 K; between 85 and 295 K, rapid paramagnetic relaxation is observed. Both the slow spin-lattice relaxation and slow spin-lattice relaxation are mediated by the organic, π -conjugated viologen cations. The Fe-N distances, the Mössbauer isomer shifts, the temperature dependence of the magnetic susceptibility, and the 3 K magnetization results all indicate the presence of low-spin Fe(III) ions in the $[\text{Fe}(\text{CN})_6]^{3-}$ anions in **1**. There is no unequivocal indication of the presence of any formal electron delocalization or transfer from the $[\text{Fe}(\text{CN})_6]^{3-}$ anion to the $(\text{DNP})_2^{2+}$ cations in the results obtained from X-ray crystallography, magnetic measurements, and Mössbauer spectra. Because of enhancement of the spin-orbit coupling by the heavy-atom or -ion effect, the Fe(III) ions in the $[\text{Fe}(\text{CN})_6]^{3-}$ anions interact with the $(\text{DNP})_2^{2+}$ cations, causing them to fluoresce with increasing intensity upon cooling from 90 to 25 K when excited at 300 nm. The resulting luminescence of the viologen $(\text{DNP})_2^{2+}$ cation induced by the $[\text{Fe}(\text{CN})_6]^{3-}$ anions indicates the presence of significant mixing of the molecular orbitals derived from the $[\text{Fe}(\text{CN})_6]^{3-}$ anions and the molecular orbitals associated with the $(\text{DNP})_2^{2+}$ cations to yield bonding supramolecular orbitals in **1**, a mixing that is also observed between 50 and 3 K in the temperature dependence of the isomer shift of **1**.

• *A Simple Approach for Predicting the Spin State of Homoleptic Fe(II) Tris-diimine Complexes*

Hoa Phan, Jeremy J. Hrudka, Dilyara Igimbayeva, Latévi M. Lawson Daku and Michael Shatruk

Journal of the American Chemical Society **139** (18) (2017), p6437-6447

DOI:10.1021/jacs.7b02098

We propose a simple method for predicting the spin state of homoleptic complexes of the Fe(II) d⁶ ion with chelating diimine ligands. The approach is based on the analysis of a single metric parameter within a free (noncoordinated) ligand: the interatomic separation between the N-donor metal-binding sites. An extensive analysis of existing complexes allows the determination of critical N-A-N

distances that dictate the regions of stability for the high-spin and low-spin complexes, as well as the intermediate range in which the magnetic bistability (spin crossover) can be observed. The prediction has been tested on several complexes that demonstrate the validity of our method.

- *Triggering the emission by the helical turn in thiadiazole-helicenes*

Thomas Biet, Kévin Martin, Jihane Hankache, Nora Hellou, Andreas Hauser, Thomas Bürgi, Nicolas Vanthuyne, Tal Aharon, Marco Caricato, Jeanne Crassous and Narcis Avarvari

Chemistry - A European Journal **23** (2) (2017), p437-446 DOI:10.1002/chem.201604471

Keywords: chirality • circular dichroism • density functional calculations • helicenes • heterocycles

Introduction of heterocycles in the helical skeleton of helicenes allows modulation of their redox, chiroptical and photophysical properties. Herein, we describe the straightforward preparation and structural characterization by single crystal X-ray diffraction of thiadiazole-[7]helicene, which has been resolved into (M) and (P) enantiomers by chiral HPLC, together with its S-shaped double [4]helicene isomer, as well as the smaller congeners thiadiazole-[5]helicene and benzothiadiazole-anthracene. A copper(II) complex with two thiadiazole-[5]helicene ligands has been structurally characterized and it shows the presence of both (M) and (P) isomers coordinated to the metal centre. The emission properties of the unprecedented heterohelicenes are highly dependent on the helical turn, as the [7]- and [5]helicene are poorly emissive, whereas their isomers, that is, the S-shaped double [4]helicene and thiadiazole-benzanthracene, are luminescent, with quantum efficiencies of 5.4% and 6.5%, respectively. DFT calculations suggest a quenching of the luminescence of enantiopure [7]helicenes through an intersystem crossing mechanism arising from the relaxed excited S1 state.

- *Ultrafast transient IR spectroscopy and DFT calculations of ruthenium(II) polypyridyl complexes*

Qinchao Sun, Bogdan Dereka, Eric Vauthey, Latevi Max Lawson Daku and Andreas Hauser

Chemical Science **8** (1) (2017), p223-230 DOI:10.1039/C6SC01220E

Ultrafast time-resolved infrared spectroscopy of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine), $[\text{Ru}(\text{mbpy})_3]^{2+}$ (mbpy = 6-methyl-2,2'-bipyridine), and $[\text{Ru}(\text{mphen})_3]^{2+}$ (mphen = 2-methyl-1,10-phenanthroline) in deuterated acetonitrile serves to elucidate the evolution of the system following pulsed excitation into the ¹MLCT band at 400 nm. Whereas for $[\text{Ru}(\text{bpy})_3]^{2+}$ no intermediate state can be evidenced for the relaxation of the corresponding ³MLCT state back to the ground state, for $[\text{Ru}(\text{mbpy})_3]^{2+}$ and $[\text{Ru}(\text{mphen})_3]^{2+}$ an intermediate state with a lifetime of about 400 ps is observed. The species associated IR difference spectra of this state are in good agreement with the calculated difference spectra of the lowest energy ³dd state using DFT. The calculated potential energy curves for all the complexes in the triplet manifold along the metal-ligand distance show that for $[\text{Ru}(\text{bpy})_3]^{2+}$ the ³dd state is at higher energy than the ³MLCT state and that there is a substantial barrier between the two minima. For $[\text{Ru}(\text{mbpy})_3]^{2+}$ and $[\text{Ru}(\text{mphen})_3]^{2+}$, the ³dd state is at lower energy than the ³MLCT state.

2016

- *Room Temperature Magnetic Switchability Assisted by Hysteretic Valence Tautomerism in a Layered Two Dimensional Manganese-Radical Coordination Framework*

Anthony Lannes, Yan Suffren, Jean Bernard Tommasino, Rodica Chiriac, François Toche, Lhoussain Khrouz, Florian Molton, Carole Duboc, Isabelle Kieffer, Jean-Louis Hazemann, Christian Reber, Andreas Hauser, and Dominique Luneau

Journal of the American Chemical Society **138** (50) (2016), p16493-16501 DOI:10.1021/jacs.6b10544

The manganese-nitronyl-nitroxide two dimensional coordination polymer $\{[\text{Mn}_2(\text{NITIm})_3\text{ClO}_4]_n\}$ ($\text{NITImH} = 2-(2\text{-imidazolyl})-4,4,5,5\text{-tetramethyl-4,5-dihydro-1H-3-oxide-1-oxyl}$) undergoes an unusual hysteretic thermally induced valence tautomeric transition near room temperature, during which the manganese(II) ions are oxidized to manganese(III) and two of the three deprotonated radicals (NITIm^-) are reduced to their diamagnetic aminoxyl form (denoted $\text{NITIm}_{\text{red}}^{2-}$). Upon cooling, the high-temperature species $\{[\text{Mn}_2(\text{NITIm})_3\text{ClO}_4]_n\}$ (NITIm^-) turns into the low-temperature species $\{[\text{Mn}_2(\text{NITIm}_{\text{red}})_2(\text{NITIm})\text{ClO}_4]_n\}$ (NITIm^-) around 274 K, while on heating the process is reversed at about 287 K. This valence tautomeric phenomenon is supported by temperature-dependent magnetic susceptibility measurements, differential scanning calorimetry (DSC), crystal structure determination, UV-vis absorption, X-ray absorption (XAS) and emission (XES) and Electron Paramagnetic Resonance (EPR) spectroscopies in the solid-state.

- *Study of switching in spin transition compounds within the mechanoelastic model with realistic parameters*

Cristian Enachescu and Andreas Hauser

Physical Chemistry Chemical Physics **18** (30) (2016), p20591-20599 DOI:10.1039/C6CP02806C

Here we reproduce the static and dynamical properties of spin-crossover complexes in the framework of the mechanoelastic model applied to triangular lattices. The switching processes between the high-spin and low-spin states are studied by combining the Monte Carlo method with the elastic lattice relaxation. The transition probabilities between the two states take into account intrinsic parameters, the values of which are approximated from experimental quantities (e.g., the energy gap, and the degeneracy ratio from the thermodynamic enthalpy and the entropy difference between the states), and the elastic force or elastic energy stored in the springs connecting the spin-changing centres. The value of the corresponding spring constant is estimated from the experimentally determined variation of the ligand-field strengths in the two spin states due to the cooperativity and the bulk modulus. Both simulated hysteresis loops and relaxation curves are in agreement with experimental data. Cooperativity related phenomena such as like-spin domain formation and the evolution of the interaction distribution with the HS fraction are also analysed.

- *Taming Lanthanide-Centered Upconversion at the Molecular Level*

Yan Suffren, Bahman Golezorkhi, Davood Zare, Laure Guénée, Homayoun Nozary, Svetlana V. Eliseeva, Stéphane Petoud, Andreas Hauser and Claude Piguet

Inorganic Chemistry **55** (20) (2016), p9964-9972 DOI:10.1021/acs.inorgchem.6b00700

Considered at the beginning of the 21st century as being incompatible with the presence of closely bound high-energy oscillators, lanthanide-centered superexcitation, which is the raising of an already excited electron to an even higher level by excited-state energy absorption, is therefore a very active topic strictly limited to the statistical doping of low-phonon bulk solids and nanoparticles. We show here that molecular lanthanide-containing coordination complexes may be judiciously tuned to overcome these limitations and to induce near-infrared (NIR)-to-visible (VIS)-light upconversion via the successive absorption of two low-energy photons using linear-optical responses. Whereas single-ion-centered excited-state absorption mechanisms remain difficult to implement in lanthanide complexes, the skillful design of intramolecular intermetallic energy-transfer processes operating in multimetallic architectures is at the origin of the recent programming of erbium-centered molecular upconversion.

- *Spectroscopy and chemical bonding in transition metal complexes*

Andreas Hauser and Christian Reber

Structure and Bonding **172** (2016), p291-312 DOI:10.1007/430_2015_195

Keywords: transition metal complexes • spectroscopy • photophysics and photochemistry • high pressure • intersystem crossing • spin crossover • ultrafast methods

Optical spectroscopy of transition metal complexes plays an important role in establishing excited state electronic and nuclear structures and thus in the elucidation of the multitude of photophysical and photochemical relaxation processes. The most important advances in this area of research over the past decade are due to the development of new experimental techniques such as ultrafast spectroscopy

as well as structure determination in conjunction with other methods such as high pressure and variable temperature techniques. In this contribution, several paradigmatic systems, namely of complexes of chromium(III), iron(II), ruthenium(II), nickel(II), platinum(II) and palladium(II), are discussed with regard to their excited electronic and nuclear structures and photophysical relaxation processes.

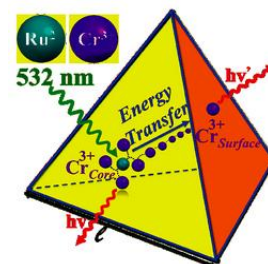
- **Directional Energy Transfer in Nanocrystals of $[\text{Ru}(2,2'\text{-bipyridine})_3][\text{NaCr}(\text{oxalate})_3]$**

E. Previtera, A. Tissot, A. Hauser

European Journal of Inorganic Chemistry **2016** (13-14) (2016), p1972-1979

DOI:10.1002/ejic.201501204

Keywords: energy transfer • nanoparticles • nanocrystals • ruthenium • chromium • luminescence



Size-controlled nanocrystals (140 nm and 670 nm) and microcrystals (2.5 mm) of the three-dimensional oxalate network $[\text{Ru}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$, ox = oxalate, bpy = 2,2'-bipyridine, were prepared by the reverse micelle technique. The photo-physical properties of the $[\text{Cr}(\text{ox})_3]^{3-}$ chromophores in the nanocrystals at low temperatures are significantly different from those of the same chromophore in 4 mm crystallites prepared by fast precipitation. For the latter, the absorption in the region of the R lines of the ${}^4\text{A}_2\text{g} \rightarrow {}^6\text{E}_g$ transition is characterized by a sharp doublet. For the nanocrystals the inhomogeneous broadening of the two lines is considerably larger with tails on the low-energy side. Whereas the 4 mm crystallites at low temperatures just show equally sharp emission from the R_1 line, the emission intensity from the nanocrystallites is shifted into the low-energy tail. Time resolved fluorescence line narrowing spectra and luminescence decay curves demonstrate that this is due to efficient directional energy migration from the center of the nanocrystals towards the surface.

2015

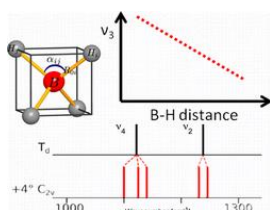
- **$\text{Pd}_2\text{Au}_{36}(\text{SR})_{24}$ cluster: structure studies**

Bei Zhang, Sameh Kaziz, Houhua Li, Dawid Wodka, Sami Malola, Olga V. Safonova, Maarten Nachtegaal, Clement Mazet, Igor Dolamic, Jordi Llorca, Elina Kalenius, Latevi Max Lawson Daku, Hannu Häkkinen, Thomas Buerger and Noelia Barrabes

Nanoscale **7** (40) (2015), p17012-17019

DOI:10.1039/C5NR04324G

The location of the Pd atoms in $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$, is studied both experimentally and theoretically. X-ray photoelectron spectroscopy (XPS) indicates oxidized Pd atoms. Palladium K-edge extended X-ray absorption fine-structure (EXAFS) data clearly show Pd-S bonds, which is supported by far infrared spectroscopy. By comparing theoretical EXAFS spectra in R space and circular dichroism spectra of the staple, surface and core doped structures with experimental spectra.



- **Quantitative Spectra-Structure Relations for Borohydrides**

Vincenza D'Anna, Latevi Max Lawson Daku and Hans Hagemann

The Journal of Physical Chemistry C **119** (38) (2015), p21868-21874

DOI:10.1021/acs.jpcc.5b06045

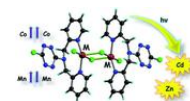
Among the different potential hydrogen storage materials, borohydrides have been largely investigated because of their high gravimetric and volumetric hydrogen content. In the analysis of borohydrides, vibrational spectroscopy plays an important role since it gives information on the local structure of the $\text{BH}_4^{\delta-}$ ion inside the solid. Here the GF method, developed by Wilson, is used in order to determine the local symmetry of $\text{BH}_4^{\delta-}$ in solid borohydrides starting from their vibrational spectra. Two different cases of deformations of $\text{BH}_4^{\delta-}$ are considered. In the first case, the effects of small angular variations on the vibrational spectra of borohydrides will be taken into account; starting from the splitting of the bands corresponding to the deformation modes, the angular deformations will be estimated. In the second one, the $\text{BH}_4^{\delta-}$ under chemical pressure (in different cubic alkali halides) is considered; in this case, the symmetry of the $\text{BH}_4^{\delta-}$ remains T_d , while the bond lengths change according to the pressure experienced. Different practical examples will be illustrated.

- **Structural, Photophysical and Magnetic Properties of Transition Metal Complexes Based on the Dipicolylamino-chloro-1,2,4,5-tetrazine Ligand**

Iuliia Nazarenko, Flavia Pop, Qinchao Sun, Andreas Hauser, Francesc Lloret, Miguel Julve, Abdelkrim El-Ghayoury and Narcis Avarvari

Dalton Transactions **44** (19) (2015), p8855-8866

DOI:10.1039/c5dt00550g



The ligand 3-chloro-6-dipicolylamino-1,2,4,5-tetrazine (Cl-TTZ-dipica)**1**, prepared by the direct reaction between 3,6-dichloro-1,2,4,5-tetrazine and di(2-picolyl)-amine, afforded a series of four neutral transition metal complexes formulated as $[\text{Cl-TTZ-dipica-MCl}_2]_2$, with $\text{M} = \text{Zn(II)}\textbf{2a}$, $\text{Cd(II)}\textbf{2b}$, $\text{Mn(II)}\textbf{2c}$ and $\text{Co(II)}\textbf{2d}$, when reacted with the corresponding metal chlorides. The dinuclear structure of the isostructural complexes was disclosed by single crystal X-ray analysis, clearly indicating the formation of $[\text{M}^{\text{II}}-(\text{m-Cl})_2\text{M}^{\text{II}}]$ motifs and the involvement of the amino nitrogen atom in semi-coordination with the metal centers, thus leading to distorted octahedral coordination geometries. Moreover, the chlorine atoms, either coordinated to the metal or as substituent on the tetrazine ring, engage respectively in specific anion- π intramolecular and intermolecular interactions with the electron poor tetrazine units in the solid state, thus controlling the supramolecular architecture. Modulation of the emission properties is observed in the case of the Zn(II) and Cd(II) complexes when compared to the free ligand. A striking difference is observed in the magnetic properties of the Mn(II) and Co(II) complexes. An antiferromagnetic coupling takes place in the dimanganese(II) compound ($J = -1.25 \text{ cm}^{-1}$) while the Co(II) centers are ferromagnetically coupled in the corresponding complex ($J = +0.55 \text{ cm}^{-1}$), the spin Hamiltonian being defined as $H = -J\textbf{S}_A\textbf{S}_B$.

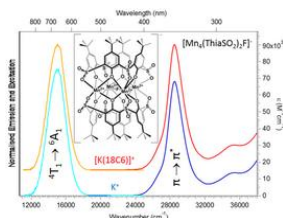
- **Analysis of first order reversal curves in the thermal hysteresis of spin-crossover nanoparticles within the mechanoelastic model**

Laurentiu Stoleriu, Alexandru Stancu, Pradip Chakraborty, Andreas Hauser and Cristian Enachescu

Journal of Applied Physics **117B** (2015), p307

DOI:10.1063/1.4914953

The recently obtained spin-crossover nanoparticles are possible candidates for applications in the recording media industry as materials for data storage, or as pressure and temperature sensors. For these applications, the intermolecular interactions and interactions between spin-crossover nanoparticles are extremely important, as they may be essential factors in triggering the transition between the two stable phases: the high-spin and low-spin ones. In order to find correlations between the distributions in size and interactions and the transition temperatures distribution, we apply the FORC (First Order Reversal Curves) method, using simulations based on a mechanoelastic model applied to 2D triangular lattices composed of molecules linked by springs and embedded in a surfactant. We consider two Gaussian distributions: one is the size of the nanoparticles and another is the elastic interactions between edge spin-crossover molecules and the surfactant molecules. In order to disentangle the kinetic and non-kinetic parts of the FORC distributions, we compare the results obtained for different temperature sweeping rates. We also show that the presence of few larger particles in a distribution centered around much smaller particles dramatically increases the hysteresis width.



- **Discrete polynuclear manganese(II) complexes with thiacalixarene ligands: synthesis, structures and photophysical properties**

Yan Suffren, Niall O'Toole, Andreas Hauser, Erwann Jeanneau, Arnaud Brioude and Cedric Desroches
Dalton Transactions **44** (17) (2015), p7991-8000 DOI:10.1039/C5DT00827A

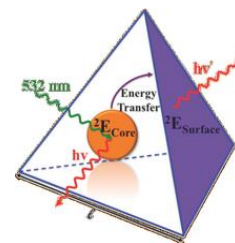
The synthesis, crystal structure and photophysical properties of the new compound $[\text{Mn}_4(\text{ThiaSO}_2)_2\text{F}][\text{K}(18\text{-crown-}6)]$, $\text{ThiaSO}_2 = p\text{-tert butylsulphonylcalix[4]arene}$, are presented and compared to the ones of $[\text{Mn}_4(\text{ThiaSO}_2)_2\text{F}]\text{K}$. The strong orange luminescence is attributed to the Mn^{2+} centred ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition. Its temperature and pressure dependence and quenching by molecular dioxygen are reported. The latter is attributed to energy transfer from the ${}^4\text{T}_1$ state exciting dioxygen to its ${}^1\text{E}_g$ state. In the solid state, the quenching is much more efficient in $[\text{Mn}_4(\text{ThiaSO}_2)_2\text{F}][\text{K}(18\text{-crown-}6)]$ than in $[\text{Mn}_4(\text{ThiaSO}_2)_2\text{F}]\text{K}$. This is attributed to the open pore structure of the former allowing fast diffusion of dioxygen into the crystal lattice.

- **Directional Energy Migration in Nanoparticles of Crystalline Metal Complexes**

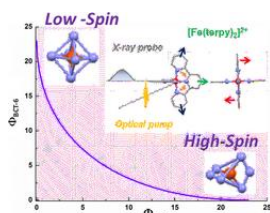
Elia Previtera, Antoine Tissot, Robert W. Johns and Andreas Hauser

Advanced Materials **27** (11) (2015), p1832-1836 DOI:10.1002/adma.201405179

Keywords: Cr(III) • energy migration • luminescence • nanocrystals • oxalate networks



Size-controlled micro- and nanocrystals of a $[\text{Ru}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$ coordination network are prepared using reverse micelles. Compared with the bulk reference, the 2E emission of the Cr(III) ions indicates an efficient directional energy migration toward the surface of the nanocrystals.



- **Mapping the Ultrafast Changes of Continuous Shape Measures in Photoexcited Spin Crossover Complexes without Long-Range Order**

S. E. Canton, X. Zhang, L. M. Lawson Daku, Y. Liu, J. Zhang and S. Alvarez

The Journal of Physical Chemistry C **119** (6) (2015), p3322-3330 DOI:10.1021/jp5117189

Establishing a tractable yet complete reaction coordinate for the spin-state interconversion in $d^4\text{d}^d$ transition metal complexes is an integral aspect of controlling the dynamics that govern their functionality. For spin crossover phenomena, the limitations of a single-mode approximation that solely accounts for an isotropic increase in the metal-ligand bond length have long been recognized for all but the simple octahedral monodentate Fe^{II} compounds. However, identifying the coupled deformations that also impact on the unimolecular rate constants remains experimentally and theoretically challenging, especially for samples that do not display long-range order or when crystallization profoundly alters the dynamics. Owing to the rapid progress in ultrafast X-ray absorption spectroscopy (XAS), it is now possible to obtain transient structural information in any physical phase with unprecedented details. Using picosecond XAS and DFT modeling, the structure adopted by the photoinduced high-spin state of solvated $[\text{Fe}(\text{terpy})_2]^{2+}$ (terpy: 2,2',6'-terpyridine) has been recently established. Based on these results, the methodology of the continuous shape measure is applied to classify and quantify the short-lived distortion of the first coordination shell. The reaction coordinate of the spin-state interconversion is clearly identified as a double axial bending. This finding sets a benchmark for gauging the influence of first-sphere and second-sphere interactions in the family of Fe^{II} complexes that incorporate terpy derivatives. Some implications for the optimization of related photoactive Fe^{II} complexes are also outlined.

- **Dynamic Jahn-Teller Effect in the Metastable High-Spin State of Solvated $[\text{Fe}(\text{terpy})_2]^{2+}$**

X. Zhang, L. M. Lawson Daku, J. Zhang, K. Suarez-Alcantara, G. Jennings, C. A. Kurtz and S. E. Canton

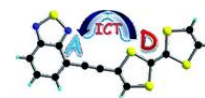
The Journal of Physical Chemistry C **119** (6) (2015), p3312-3321 DOI:10.1021/jp5117068

Characterizing structural distortions in the metastable spin states of $d^4\text{d}^d$ transition metal ion complexes is crucial to understand the nature of their bistability and eventually control their switching dynamics. In particular, the impact of the Jahn-Teller effect needs to be assessed for any electronic configuration that could be effectively degenerate, as in e.g. the high-spin (HS) manifold of highly symmetric homoleptic Fe^{II} complexes. However, capturing its manifestations remains challenging since crystallization generally alters the molecular conformations and their interconversion. With the rapid progress of ultrafast X-ray absorption spectroscopy, it is now possible to collect data with unprecedented signal-to-noise ratio, opening up for detailed structural characterization of transient species in the homogeneous solution phase. By combining the analysis of picosecond X-ray absorption spectra with DFT simulations, the structure of the photoinduced HS state is elucidated for solvated $[\text{Fe}(\text{terpy})_2]^{2+}$ (terpy = 2,2',6'-terpyridine). This species can be viewed as the average D_{2h} symmetry in D_{2h} symmetry that originates from a dynamic Jahn-Teller effect in the HS manifold. These results evidence the active role played by this particular instance of vibronic coupling in the formation of the HS state for this benchmark molecule. Ultimately, correlating the interplay between intramolecular and intermolecular degrees of freedom to conformational strain and distortions in real time should contribute to the development of advanced functionalities in transition metal ion complexes.

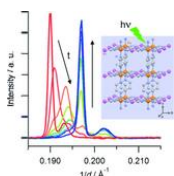
- **Modulation of the charge transfer and photophysical properties in non-fused tetrathiafulvalene-benzothiadiazole derivatives**

Flavia Pop, Sabine Seifert, Jihane Hankache, Jie Ding, Andreas Hauser and Narcis Avarvari

Organic & Biomolecular Chemistry **13** (2015), p1040-1047 DOI:10.1039/c4ob02100b



Bis(thiomethyl)- and bis(thiohexyl)-tetrathiafulvalene-bromo-benzothiadiazoles, containing electron donor tetrathiafulvalene (TTF) and electron acceptor benzothiadiazole (BTDA) units, have been prepared by Stille coupling reactions between the TTF-SnMe_3 precursors and BTDA-Br_2 . In another series of experiments, TTF-acetylene-BTD compounds have been synthesized by Sonogashira coupling between either TTF-acetylenes and BTDA-Br_2 in low yields, or TTF-iodine and BTDA-acetylene in moderate yields. In the compound $\text{TTF-C}_6\text{H}_4\text{-BTDA}$ the TTF and BTDA units are coplanar in the solid state, as shown by the single crystal X-ray structure, and there is segregation in the packing between the donor and acceptor units. All the derivatives have good electron donor properties, as determined by cyclic voltammetry measurements, and they can also be reversibly reduced thanks to the presence of the BTDA moiety. UV-visible spectroscopy and photophysical investigations show the presence of an intramolecular charge transfer (ICT) band and an emission band originating from the charge transfer. Both the absorption and the emission are modulated by the substitution scheme and the insertion of the acetylenic bridge.



- **Structural Investigation of the High Spin→Low Spin Relaxation Dynamics of the Porous Coordination Network [Fe(pz)Pt(CN)₄]·2.6 H₂O**

Teresa Delgado, Antoine Tissot, Céline Besnard, Laure Guénée, Philip Pattison and Andreas Hauser

Chemistry - A European Journal **21** (9) (2015), p3664-3670

DOI:10.1002/chem.201405405

Keywords: cooperative effects • LIESST • organic electronics • relaxation dynamics • spin crossover • X-ray diffraction studies

The Hoffman-type coordination compound [Fe(pz)Pt(CN)₄]·2.6H₂O (pz=pyrazine) shows a cooperative thermal spin transition at around 270 K. Synchrotron powder X-Ray diffraction studies reveal that a quantitative photoinduced conversion from the low-spin (LS) state into the high-spin (HS) state, based on the light-induced excited spin-state trapping effect, can be achieved at 10 K in a microcrystalline powder. Time-resolved measurements evidence that the HS→LS relaxation proceeds by a two-step mechanism: a random HS→LS conversion at the beginning of the relaxation is followed by a nucleation and growth process, which proceeds until a quantitative HS→LS transformation has been reached.

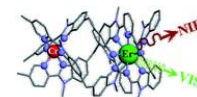
- **Smaller than a nanoparticle with the design of discrete polynuclear molecular complexes displaying near-infrared to visible upconversion**

Davood Zare, Yan Suffren, Laure Guénée, Svetlana V. Eliseeva, Homayoun Nozary, Lilit Aboshyan-Sorgho,

Stéphane Petoud, Andreas Hauser and Claude Piguet

Dalton Transactions **44** (6) (2015), p2529-2540

DOI:10.1039/C4DT02336F



This work shows that the operation of near-infrared to visible light-upconversion in a discrete molecule is not limited to non-linear optical processes, but may result from superexcitation processes using linear optics. The design of nine-coordinate metallic sites made up of neutral N-heterocyclic donor atoms in kinetically inert dinuclear [GaEr(L₁)₃]³⁺ and trinuclear [GaErGa(L₂)₃]³⁺ helicates leads to [ErN₉] chromophores displaying unprecedented dual visible nanosecond Er(⁴S_{3/2}→⁴I_{15/2}) and near-infrared microsecond Er(⁴I_{13/2}→⁴I_{15/2}) emissive components. Attempts to induce one ion excited-state absorption (ESA) upconversion upon near-infrared excitation of these complexes failed because of the too-faint Er-centred absorption cross sections. The replacement of the trivalent gallium cation with a photophysically-tailored pseudo-octahedral [CrN₆] chromophore working as a sensitizer for trivalent erbium in [CrEr(L₁)₃]³⁺ improves the near-infrared excitation efficiency, leading to the observation of a weak energy transfer upconversion (ETU). The connection of a second sensitizer in [CrErCr(L₂)₃]³⁺ generates a novel mechanism for upconversion, in which the superexcitation process is based on the Cr^{III}-sensitizers. Two successive Cr^{III}-Er energy transfer processes (concerted-ETU) compete with a standard Er-centred ETU, and a gain in upconverted luminescence by a factor larger than statistical values is predicted and observed.

- **On the Role of Ligand-Field States for the Photophysical Properties of Ruthenium(II) Polypyridyl Complexes**

Qinchao Sun, Sandra Mosquera-Vazquez, Yan Suffren, Jihane Hankache, N. Amstutz, Latévi Max Lawson Daku, Eric Vauthey and Andreas Hauser

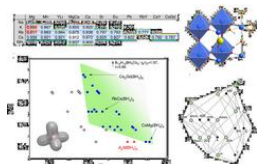
Coordination Chemistry Reviews **282-283** (2015), p87-99

DOI:10.1016/j.ccr.2014.07.004

Keywords: Ruthenium(II) polypyridyl complexes • ligand-field states • luminescence quenching • photophysical properties • high-pressure

The role of ligand-field states for the photophysical properties of d⁶ systems has been discussed in a large number of publications over the past decades. Since the seminal paper by Houten and Watts, for instance, the quenching of the ³MLCT luminescence in ruthenium(II) polypyridyl complexes is attributed to the presence of the first excited ligand-field state, namely a component of the ³T₁(²E_g) state, at similar energies. If this state lies above the ³MLCT state, the luminescence is quenched via thermal population at elevated temperatures only. If it lies well below, then the luminescence is quenched down to cryogenic temperatures. In this contribution we present transient absorption spectra on non-luminescent ruthenium polypyridyl complexes such as [Ru(m-bpy)₃]²⁺, m-bpy = 6-methyl-2,2'-bipyridine, in acetonitrile at room temperature, which reveal an ultra-rapid depopulation of the ³MLCT state but a much slower ground state recovery. We propose that in this and related complexes the methyl groups force longer metal-ligand bond lengths, thus resulting in a lowering of the ligand-field strength such that the ³dd state drops to below the ³MLCT state, and that furthermore the population of this state from the ³MLCT state occurs faster than its decay to the ground state. In addition we demonstrate that in this complex the luminescence can be switched on by external pressure, which we attribute to a destabilisation of the ligand-field state by the pressure due to its larger molecular volume compared to the ground state as well as the ³MLCT state.

2014



- **Structure and properties of complex hydride perovskite materials**

Pascal Schouwink, Morten B. Ley, Antoine Tissot, Hans Hagemann, Torben R. Jensen, Lubomír Smrcek and Radovan Cerný

Nature Communications **5** (2014), p5706

DOI:10.1038/ncomms6706

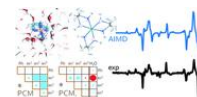
Perovskite materials host an incredible variety of functionalities. Although the lightest element, hydrogen, is rarely encountered in oxide perovskite lattices, it was recently observed as the hydride anion H⁻, substituting for the oxide anion in BaTiO₃. Here we present a series of 30 new complex hydride perovskite-type materials, based on the non-spherical tetrahydroborate anion BH₄⁻ and new synthesis protocols involving rare-earth elements. Photophysical, electronic and hydrogen storage properties are discussed, along with counterintuitive trends in structural behaviour. The electronic structure is investigated theoretically with density functional theory solid-state calculations. BH₄⁻-specific anion dynamics are introduced to perovskites, mediating mechanisms that freeze lattice instabilities and generate supercells of up to 16 Å—the unit cell volume in AB(BH₄)₃. In this view, homopolar hydridic di-hydrogen contacts arise as a potential tool with which to tailor crystal symmetries, thus merging concepts of molecular chemistry with ceramic-like host lattices. Furthermore, anion mixing BH₄⁻→X⁻ (X⁻=C⁻, Br⁻, I⁻) provides a link to the known ABX₃ halides.

- **Where does the Raman optical activity of [Rh(en)₃]³⁺ come from? Insight from a combined experimental and theoretical approach**

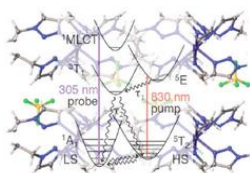
Marie Humbert-Droz, Patric Oulevey, Latévi Max Lawson Daku, Sandra Lubner and Hans Hagemann and Thomas Bürgi

Phys. Chem. Chem. Phys. **16** (42) (2014), p23260-23273

DOI:10.1039/C4CP02145B



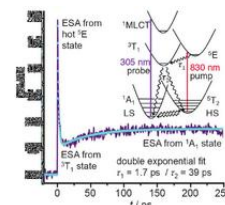
Backscattered Raman optical activity (ROA) spectra are measured for $\bar{1}$ - and $\bar{1}$ -tris-(ethylenediamine)rhodium(III) chloride in aqueous solution. In addition, the spectra of the four possible conformers in the $\bar{1}$ configuration are investigated by *ab initio* calculations. The $\bar{1}$ ($\bar{1}\bar{1}\bar{1}$) conformer is in best agreement with experimental spectra and examined in more details. The two most stable conformers according to the calculations are not compatible with the experimental ROA spectrum. Insights into the origin of observed band intensities are obtained by means of group coupling matrices. The influence of the first solvation shell is explored via *ab initio* molecular dynamics simulation. Taking explicit solvent molecules into account further improves the agreement between calculation and experiment. Analysis of selected normal modes using group coupling matrices shows that solvent molecules lead to normal mode rotation and thus contribute to the ROA intensity, whereas the contribution of the Rh can be neglected.



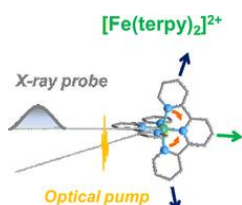
- **Light-induced spin-state switching in the mixed crystal series of the 2D coordination network $\{[Zn_{1-x}Fe_x(bbtr)_3](BF_4)_2\}$: optical spectroscopy and cooperative effects**
Pradip Chakraborty, Cristian Enachescu, Arnaud Humair, Leo Egger, Teresa Delgado, Antoine Tissot, Laure Guénée, Céline Besnard, Robert Bronisz and Andreas Hauser
Dalton Transactions **43** (47) (2014), p17786-17796 DOI:10.1039/C4DT01728E

Depending on the iron(II) concentration, the mixed crystals of $\{[Zn_{1-x}Fe_x(bbtr)_3](BF_4)_2\}$, $bbtr = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{butane}$, $0.01 \leq x \leq 1$, show macroscopic light-induced bistability between the high-spin and the low-spin state. In the highly diluted system with $x = 0.01$ and up to $x = 0.31$, the photoinduced low-spin state always relaxes back to the high-spin state independent of the initial light-induced low-spin fraction. In the highly concentrated mixed crystals with $x = 0.67, 0.87$ and 1 , the strong cooperative effects coupled to a crystallographic phase transition result in light-induced bistability with decreasing critical light-induced low-spin fraction and increasing hysteresis width for increasing iron(II) concentrations. The lower limit for the light-induced bistability is estimated at $x \approx 0.5$.

- **The role of ligand-field states in the ultrafast photophysical cycle of the prototypical iron(II) spin-crossover compound $[Fe(ptz)_6](BF_4)_2$**
Andrea Marino, Pradip Chakraborty, Marina Servol, Maciej Lorenc, Eric Collet, and Andreas Hauser
Angewandte Chemie International Edition **53** (15) (2014), p3863-3867 DOI:10.1002/anie.201310884
Keywords: intersystem crossing • LIESST • ligand-field states • spin crossover • ultrafast spectroscopy



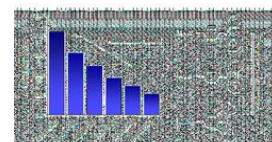
Light-induced excited spin state trapping (LIESST) in iron(II) spin-crossover compounds, i.e., the light-induced population of the high-spin ($S=2$) state below the thermal transition temperature, was discovered thirty years ago. For irradiation into metal-ligand charge transfer (MLCT) bands of the low-spin ($S=0$) species the acknowledged sequence takes the system from the initially excited MLCT to the high-spin state via the 1MLCT state within ~ 150 fs, thereby bypassing low-lying ligand-field (LF) states. Nevertheless, these play a role, as borne out by the observation of LIESST and reverse-LIESST on irradiation directly into the LF bands for systems with only high-energy MLCT states. Herein we elucidate the ultrafast reverse-LIESST pathway by identifying the lowest energy $S=1$ LF state as intermediate state with a lifetime of 39 ps for the light-induced high-spin to low-spin conversion on irradiation into the spin-allowed LF transition of the high-spin species in the NIR.



- **Probing the Anisotropic Distortion of Photoexcited Spin Crossover Complexes with Picosecond X-ray Absorption Spectroscopy**
Sophie E. Canton, Xiaoyi Zhang, Latévi M. Lawson Daku, Amanda L. Smeigh, Jianxin Zhang, Yizhu Liu, Carl-Johan Wallentin, Klaus Attenkofer, Guy Jennings, Charles A. Kurtz, David Gosztola, Kenneth Wärnmark, Andreas Hauser and Villy Sundström
Journal of Physical Chemistry C **118** (8) (2014), p4536-4545 DOI:10.1021/jp5003963

For numerous spin crossover complexes, the anisotropic distortion of the first coordination shell around the transition metal center governs the dynamics of the high-spin/lowspin interconversion. However, this structural parameter remains elusive for samples that cannot be investigated with crystallography. The present work demonstrates how picosecond X-ray absorption spectroscopy is able to capture this specific deformation in the photoinduced high-spin state of solvated $[Fe(terpy)_2]^{2+}$, a complex which belongs to the prominent family of spin crossover building blocks with nonequivalent metal π ligand bonds. The correlated changes in $Fe\pi^*N_{distal}$, $Fe\pi^*N_{axial}$, and bite angle $N_{distal}Fe\pi^*N_{axial}$ extracted from the measurements are in very good agreement with those predicted by DFT calculations in D_{2d} symmetry. The outlined methodology is generally applicable to the characterization of ultrafast nuclear rearrangements around metal centers in photoactive molecular complexes and nanomaterials, including those that do not display long-range order.

- **Oxadiazole based bipolar host materials employing planarized triarylamine donors for RGB PHOLEDs with low efficiency roll-off**
Paul Kautny, Daniel Lumpi, Yanping Wang, Antoine Tissot, Johannes Binterger, Ernst Horkel, Berthold Stoeger, Christian Hametner, Hans Hagemann, Dongge Ma and Johannes Fröhlich
Journal of Materials Chemistry C **2** (11) (2014), p2069-2081 DOI:10.1039/c3tc32338b



A series of 6 novel triarylamine-containing oxadiazole compounds (*o*-PCzPOXD, *o*-ICzPOXD, *o*-TPATOXD, *o*-PCzTOXD, *o*-ICzTOXD, *o*-CzTOXD) have been designed, synthesized and characterized concerning applications as host materials in PHOLED devices. To further improve the ortho-linkage concept, the impact of incorporating planarized electron-donating triarylamine (TAA) structures on intramolecular charge transfer was examined. The effect was evaluated for two series of electron-accepting oxadiazole scaffolds, realizing *ortho*-linkage on the benzene (POXD) and the thiophene (TOXD) core. Thermal analysis shows increased glass-transition temperatures for planarized structures indicating an improved morphological stability. A higher degree of planarization also results in significantly increased singlet and triplet energy values, revealing the impact on the intramolecular charge transfer. Employing the developed materials, red (*o*-TPATOXD: CE_{max} : 28.8 cd A $^{-1}$, EQE_{max} : 16.9%), green (*o*-PCzPOXD: CE_{max} : 62.9 cd A $^{-1}$, EQE_{max} : 17.1%) and blue (*o*-PCzPOXD: CE_{max} : 29.8 cd A $^{-1}$, EQE_{max} : 13.4%) devices were achieved showing remarkably low efficiency roll-off for planarized donors. Hence, this is the first report of efficient blue devices for this specific class of host materials. It is proposed that the results correlate with an increasing *ortho*-linkage effect and decreasing donor strength of the TAA moiety by planarization and, thus, tackling one of the major challenges in PHOLED research: improving both triplet energy and compound stability.

- **Large π -Conjugated Chromophores Derived from Tetrathiafulvalene**
Hongpeng Jia, Jie Ding, Andreas Hauser, Silvio Decurtins and Shi-Xia Liu
Asian Journal of Organic Chemistry **3** (2) (2014), p198-202 DOI:10.1002/ajoc.201300144
Keywords: dipyrro[3,2-a:2',3'-c]phenazines • photophysics • redox chemistry • ruthenium • tetrathiafulvalenes

A large π -conjugated chromophore composed of two dipyrro[3,2-a:2',3'-c]phenazine (dppz) units directly fused to the central tetrathiafulvalene (TTF) core, has been prepared as a bridging ligand, and its strong binding ability to Ru^{2+} forming a new dinuclear complex is presented. The electronic absorption and luminescence and the electrochemical behaviour of the free ligand as well as the Ru^{2+} complex have been investigated in detail. The free ligand shows a very strong band in the UV region consistent with ligand centred $\pi-\pi^*$ transitions and an intense broad band in the visible region corresponding to an intramolecular charge transfer (ILCT) transition. Upon coordination, a metal-to-ligand charge transfer (MLCT) appears at 22520 cm $^{-1}$ while the ILCT band is bathochromically shifted by 1620 cm $^{-1}$. These electrochemically amphoteric chromophores have also been characterized by spectroelectrochemical methods. The oxidized radical species of the free ligand show a strong tendency to undergo aggregation, in which long-distance attractive interactions overcome the electrostatic repulsion. Moreover, these two new chromophores reveal an ILCT fluorescence with large solvent-dependent Stokes shifts and quantum efficiencies of 0.052 for the free ligand and 0.016 for its dinuclear Ru^{2+} complex in CH_2Cl_2 .

- **Modeling Transition Metal Complexes in the Framework of the Spin-Crossover Phenomenon: a DFT Perspective**

Latevi Max Lawson Daku

Current Inorganic Chemistry **3** (3) (2013), p242-259

DOI:10.2174/1877944103666140110231029

Keywords: density functional theory • spin crossover • transition metal complexes

Using the study of the low-spin complex $[\text{Fe}(\text{bpy})_3]^{2+}$ in the gas phase and in condensed phases as a guideline, we examine different aspects of the application of DFT to the study of transition metal complexes in the framework of spin crossover or related phenomena.

- **Crystal structure solution of an elusive polymorph of Dibenzylsquaramide**

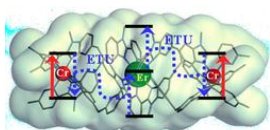
Anna Portell, Xavier Alcobé, Latévi M. Lawson Daku and Radovan Cerny and Rafel Prohens

Powder Diffraction **28** (S2) (2013), p470-480

DOI:10.1017/S0885715613000821

Keywords: dibenzylsquaramide • crystal structure • X-ray powder diffraction

The crystal structure of the third polymorph of dibenzylsquaramide (Portell, A.À *et al.*, 2009), (fig. 1) has been determined from laboratory X-ray powder diffraction data by means of direct space methods using the computing program FOX. (Favre-Nicolin and AËernÀ½, 2002) The structure resolution has not been straightforward due to several difficulties on the indexing process and in the space group assignment. The asymmetric unit contains two different conformers, which has implied an additional difficulty during the Rietveld (Rietveld, 1969) refinement. All these issues together with particular structural features of disquaramides are discussed.



- **Near-Infrared to Visible Light-Upconversion in Molecules: From Dream to Reality**

Yan Suffren, Davood Zare, Svetlana V. Eliseeva, Laure Guénée, Homayoun Nozary, Timothée Lathion, Lilit

Aboshyan-Sorgho, Stéphane Petoud, Andreas Hauser and Claude Piguet

Journal of Physical Chemistry C **117** (51) (2013), p26957-26963

DOI:10.1021/jp4107519

Light-upconversion via stepwise energy transfer from a sensitizer to an activator exploits linear optics for converting low-energy infrared or near-infrared incident photons to higher energy emission occurring in the part of the electromagnetic spectrum ranging from visible to ultraviolet. Stepwise excitation is restricted to activators possessing intermediate long-lived excited states such as those found for trivalent lanthanide cations dispersed in solid-state matrices. When the activator is embedded in a molecular complex, efficient non-radiative relaxation processes usually reduce excited state lifetimes to such an extent that upconversion becomes too inefficient to be detected under practical excitation intensities. Theoretical considerations suggest that the combination of millisecond timescale sensitizers with a central lanthanide activator located in supramolecular complexes circumvents this bottleneck by creating a novel pathway reminiscent of the energy transfer upconversion mechanism observed in doped solids. Application of this novel concept to chromium/erbium pairs in discrete triple-stranded helicates demonstrates that strong-field trivalent chromium chromophores irradiated with near-infrared photons produce upconverted green erbium-centered emission both in the solid state and in solution.

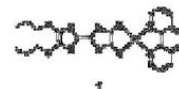
- **A Pt(II) complex with both a phenanthroline and a tetrathiafulvalene-extended dithiolate ligand: Synthesis, crystal structure, electro-chemical and spectroscopic properties**

Chunyang Jia, Jie Ding, Shi-Xia Liu, Gaël Labat, Antonia Neels, Andreas Hauser and Silvio Decurtins

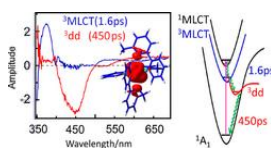
Polyhedron **55** (2013), p87-91

DOI:10.1016/j.poly.2013.02.064

Keywords: tetrathiafulvalene • intramolecular charge-transfer • spectroelectrochemistry



The reaction of 4,5-bis(2'-cyano-ethylsulfanyl)-4',5'-dipropylthiotetrathiafulvalene with $[\text{Pt}(\text{phen})\text{Cl}_2]$ (phen = 1,10-phenanthroline) with CsOH as base in $\text{CH}_3\text{OH}/\text{THF}$ affords the target complex **1** in 44% yield. This complex crystallizes in the monoclinic space group $P2_1/c$, $M = 790.01$, $a = 12.1732(12)$, $b = 15.851(2)$, $c = 14.5371(16)$ Å, $\alpha = 90^\circ$, $\beta = 107.693(12)^\circ$, $\gamma = 90^\circ$, $V = 2672.4(5)$ Å³ and $Z = 4$. It undergoes two reversible single-electron oxidation and two irreversible reduction processes. An intense electronic absorption band at 15200 cm^{-1} (658 nm) in CH_2Cl_2 is assigned to the intramolecular mixed metal/ligand-to-ligand charge transfer (LLCT) from a tetrathiafulvalene-extended dithiolate-based HOMO to a phenanthroline-based LUMO. This band shifts hypsochromically with increasing solvent polarity. Systematic changes in the optical spectra upon oxidation allow precise tuning of the oxidation states of **1** and reversible control over its optical properties. Irradiation of **1** at 15625 cm^{-1} (640 nm) in glassy solution below 150 K results in emission from the ³LLCT excited state.



- **Experimental Evidence of Ultrafast Quenching of the ³MLCT Luminescence in Ruthenium(II) Tris-bipyridyl Complexes via a ³dd State**

Qinchao Sun, Sandra Mosquera-Vazquez, Latevi Max Lawson Daku, Laure Guénée, Harold A. Goodwin, Eric Vauthey and Andreas Hauser

Journal of the American Chemical Society **135** (37) (2013), p13660-13663

DOI:10.1021/ja407225t

Ultrafast transient absorption spectroscopy serves to identify the ³dd state as intermediate quencher state of the ³MLCT luminescence in the non-luminescent ruthenium complexes $[\text{Ru}(\text{m-bpy})_3]^{2+}$ (m-bpy = 6-methyl-2,2'-bipyridine) and $[\text{Ru}(\text{tm-bpy})_3]^{2+}$ (tm-bpy = 4,4'-bis(6-methyl-2-thienyl)-2,2'-bipyridine). For $[\text{Ru}(\text{m-bpy})_3]^{2+}$, the population of the ³dd state occurs within 1.6 ps, while the return to the ground state takes 450 ps. For $[\text{Ru}(\text{tm-bpy})_3]^{2+}$, the corresponding values are 0.16 and 7.5 ps, respectively. According to DFT calculations, methyl groups added in the 6 and 6' positions of bipyridine stabilize the ³dd state by $\sim 4000\text{ cm}^{-1}$ each, compared to $[\text{Ru}(\text{bpy})_3]^{2+}$.

- **Book review: Spin-Crossover Materials. Properties and Applications. Edited by Malcolm A. Halcrow.**

Andreas Hauser

Angewandte Chemie International Edition **52** (2) (2013)

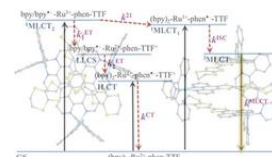
DOI:10.1002/anie.201306160

- **Complexes with Redox-Active Ligands: Synthesis, Structure, and Electrochemical and Photophysical Behavior of the Ru(II) Complex with TTF-Annulated Phenanthroline**

Lawrence K. Keniley, Nathalie Dupont, Lipika Ray, Jie Ding, Kirill Kovnir, Jordan M. Hoyt and Andreas Hauser and Michael Shatruk

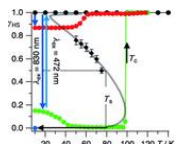
Inorganic Chemistry **52** (14) (2013), p8040-8052

DOI:10.1021/ic4006949



Ru(II) complexes with chelating ligands, 4,4'-bis(5,5'-ethylenedithiotetrathiafulvenyl)[4,5- π][1,10]phenanthroline (**L1**), 1,3-dithiole-2-thione[4,5- π][1,10]phenanthroline (**L2**), and 1,3-dithiole-2-one[4,5- π][1,10]phenanthroline (**L3**), have been prepared and their structural, electrochemical, and photophysical properties investigated. Density functional theory (DFT) calculations indicate that the highest occupied molecular orbital of $[\text{Ru}(\text{bpy})_2(\text{L1})](\text{PF}_6)_2$ (**1**) is located on the tetrathiafulvalene (TTF) subunit and appears $\sim 0.6\text{ eV}$ above the three Ru-centered d orbitals. In agreement with this finding, **1** exhibits three reversible oxidations: the two at lower potentials take place on the TTF subunit, and the one at higher potential is due to the $\text{Ru}^{3+}/\text{Ru}^{2+}$ redox couple. Complexes $[\text{Ru}(\text{bpy})_2(\text{L2})](\text{PF}_6)_2$ (**2**) and $[\text{Ru}(\text{bpy})_2(\text{L3})](\text{PF}_6)_2$ (**3**) exhibit only the $\text{Ru}^{3+}/\text{Ru}^{2+}$ -related oxidation. The optical absorption spectra of all complexes reveal a characteristic metal-to-ligand charge transfer (MLCT) band centered around 450 nm. In addition, in the spectrum of **1** the MLCT band is augmented by a low-energy tail that extends beyond 500 nm and is attributed to the intraligand charge transfer (ILCT) transition of **L1**.

according to time-dependent DFT calculations. The substantial decrease in the luminescence quantum yield of **1** compared to those of **2** and **3** is attributed to the reductive quenching of the emissive state via electron transfer from the TTF subunit to the Ru³⁺ center, thus allowing nonradiative relaxation to the ground state through the lower-lying ILCT state. In the presence of O₂, complex **1** undergoes a photoinduced oxidative cleavage of the central C≡C bond of the TTF fragment, resulting in complete transformation to **3**. This photodegradation process was studied with ¹³C NMR and optical absorption spectroscopy.



- **Light Induced Bistability in the 2D Coordination Network {[Fe(bbtr)₃](BF₄)₂]_n}: Wavelength-Selective Addressing of Molecular Spin States**

Pradip Chakraborty, Sébastien Pillet, El-Eulmi Bendeif, Cristian Enachescu, Robert Bronisz and Andreas Hauser
Chemistry - A European Journal **19** (34) (2013), p11418-11428 DOI:10.1002/chem.201301257

Keywords: cooperative effects • iron • photoinduced bistability • photoswitching • spin crossover

Whereas the neat polymeric Fe(II) compound {[Fe(bbtr)₃](ClO₄)₂]_n (bbtr=1,4-di(1,2,3-triazol-1-yl)butane) shows an abrupt spin transition centered at 107 K facilitated by a crystallographic symmetry breaking, in the covalently linked 2D coordination network of {[Fe(bbtr)₃](BF₄)₂]_n, Fe(II) stays in the high-spin state down to 10 K. However, strong cooperative effects of elastic origin result in reversible, persistent and wavelength-selective photoswitching between the low-spin and high-spin manifolds. This compound thus shows true light-induced bistability below 100 K. The persistent bidirectional optical switching behavior is discussed as a function of temperature, irradiation time and intensity. Crystallographic studies reveal a photo-induced symmetry breaking and serve to establish the correlation between structure and cooperative effects. The static and kinetic behavior is explicated within the framework of the mean-field approximation.

- **Determination of the molecular structure of the short-lived light-induced high-spin state in the spin-crossover compound [Fe(6-mepy)₃tren](PF₆)₂**

Pradip Chakraborty, Antoine Tissot, Lisa Peterhans, Laure Guénée, Céline Besnard, Philip Pattison and Andreas Hauser
Physical Review B **87** (21) (2013), p214306 DOI:10.1103/PhysRevB.87.214306

In the spin-crossover compound [Fe(6-mepy)₃tren](PF₆)₂, (6-mepy)₃tren = tris(4-[(6-methyl)-2-pyridyl]-3-aza-butenyl)amine, the high-spin state can be populated as metastable state below the thermal transition temperature via irradiation into the metal to ligand charge transfer absorption band of the low-spin species. At 10 K, the lifetime of this metastable state is only 1 s. Despite this, it is possible to determine an accurate excited state structure by following the evolution of relevant structural parameters by synchrotron X-ray diffraction under continuous irradiation with increasing intensity. The difference in metal-ligand bond length between the high-spin and the low-spin state is found to be 0.192 Å... obtained from an analysis of the experimental data using the mean-field approximation to model cooperative effects.

- **A modified cyclen azaxanthone ligand as a new fluorescent probe for Zn²⁺**

Hela Nouri, Cyril Cadiou, Latevi Max Lawson Daku, Andreas Hauser, Sylviane Chevreux, Isabelle Déchamps-Olivier, Fabien Lachaud, Riadh Ternane, Malika Trabelsi-Ayadi, Françoise Chuburu and Gilles Lemerrier
Dalton Transactions **42** (2013), p12157-12164 DOI:10.1039/c3dt51216a

A new cyclen derivative **L**, bearing a methyl-chromeno-pyridinylidene hydrazone moiety, was synthesized and studied in MeOH, as potential fluorescent "OFF-on-ON" sensors for Zn(II). Photophysical properties of this ligand being PET regulated, **L** was only weakly emissive in the absence of metal ions (OFF). **L** fluorescence was increased modestly upon addition of one equivalent of Zn(II), and further increased upon addition of a second equivalent. Therefore, Zn:**L** behaved as a highly sensitive ON sensor for zinc. This efficiency was correlated to Zn(II) coordination via the hydrazone moiety of the fluorophore, producing an efficient Chelation-Enhanced Fluorescence (CHEF) effect. A complementary theoretical study carried out with DFT calculations further elucidated of the optical properties.

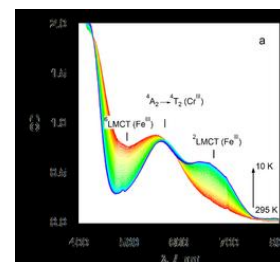
- **Photoinduced Relaxation Dynamics in Iron(II) Spin-Crossover Nanoparticles: The Significance of Crystallinity**

Pradip Chakraborty, Marie-Laure Boillot, Antoine Tissot and Andreas Hauser
Angewandte Chemie International Edition **52** (28) (2013), p7139-7142 DOI:10.1002/anie.201301562
Keywords: crystallinity • nanoparticles • optical spectroscopy • spin crossover • spin relaxation

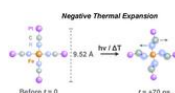
A switch in time: A fast precipitation technique was used to prepare 75 nm Fe^{II} spin-crossover nanocrystals. Their photoswitching dynamics, based on the light-induced excited spin-state trapping effect, has been investigated by means of optical spectroscopy. A significant variation of the switching properties is observed compared to similar but amorphous nanoparticles.

- **Stimuli Responsive Hybrid Magnets: Tuning the Photoinduced Spin-Crossover in Fe(III) Complexes Inserted into Layered Magnets**

Miguel Clemente-León, Eugenio Coronado, Maurici López-Jordà, João C. Waerenborgh, Cédric Desplanches, Hongfeng Wang, Jean-François Létard, Andreas Hauser and Antoine Tissot
Journal of the American Chemical Society **135** (23) (2013), p8655-8667 DOI:10.1021/ja402674x



The insertion of a [Fe(sal₂-trien)]⁺ complex cation into a 2D oxalate network in the presence of different solvents results in a family of hybrid magnets with coexistence of magnetic ordering and photoinduced spin-crossover (LIESST effect) in compounds [Fe^{III}(sal₂-trien)]_n[Mn^{II}Cr^{III}(ox)₃]_n·CHCl₃ (**1A-CHCl₃**), [Fe^{III}(sal₂-trien)]_n[Mn^{II}Cr^{III}(ox)₃]_n·CHBr₃ (**1A-CHBr₃**), and [Fe^{III}(sal₂-trien)]_n[Mn^{II}Cr^{III}(ox)₃]_n·CH₂Br₂ (**1A-CH₂Br₂**). The three compounds crystallize in a 2D honeycomb anionic layer formed by Mn^{II} and Cr^{III} ions linked through oxalate ligands and a layer of [Fe(sal₂-trien)]⁺ complexes and solvent molecules (CHCl₃, CHBr₃, or CH₂Br₂) intercalated between the 2D oxalate network. The magnetic properties and Mössbauer spectroscopy indicate that they undergo long-range ferromagnetic ordering at 5.6 K and a spin crossover of the intercalated [Fe(sal₂-trien)]⁺ complexes at different temperatures T_{1/2}. The three compounds present a LIESST effect with a relaxation temperature T_{LIESST} inversely proportional to T_{1/2}. The isostructural paramagnetic compound, [Fe^{III}(sal₂-trien)]_n[Zn^{II}Cr^{III}(ox)₃]_n·CH₂Cl₂ (**2A-CH₂Cl₂**) was also prepared. This compound presents a partial spin crossover of the inserted Fe^{III} complex as well as a LIESST effect. Finally, spectroscopic characterization of the Fe^{III} doped compound [Ga_{0.99}Fe_{0.01}(sal₂-trien)]_n[Mn^{II}Cr^{III}(ox)₃]_n·CH₂Cl₂ (**3A-CH₂Cl₂**) shows a gradual and complete thermal spin crossover and a LIESST effect on the isolated Fe^{III} complexes. This result confirms that cooperativity is not a necessary condition to observe the LIESST effect in an Fe^{III} compound.

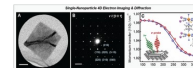


- **Unusual molecular material formed through irreversible transformation and revealed by 4D electron microscopy**

Renske M. van der Veen, Antoine Tissot and Andreas Hauser and Ahmed H. Zewail
Physical Chemistry Chemical Physics **15** (20) (2013), p7831 DOI:10.1039/c3cp51011e

Four-dimensional (4D) electron microscopy (EM) uniquely combines the high spatial resolution to pinpoint individual nano-objects, with the high temporal resolution necessary to address the dynamics of their laser-induced transformation. Here, using 4D-EM, we demonstrate the *in situ* irreversible transformation of individual nanoparticles of the molecular framework Fe(pyrazine)Pt(CN)₄. The newly formed material exhibits an unusually large negative thermal expansion (*i.e.* contraction), which is revealed by time-resolved imaging and diffraction. Negative thermal expansion is a unique property exhibited by only few materials. Here we show that the

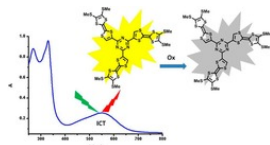
increased flexibility of the metalâ€cyanide framework after the removal of the bridging pyrazine ligands is responsible for the negative thermal expansion behavior of the new material. This *in situ* visualization of single nanostructures during reactions should be extendable to other classes of reactive systems.



• **Single-nanoparticle phase transitions visualized by four-dimensional electron microscopy**

Renske M. van der Veen, Oh-Hoon Kwon, Antoine Tissot, Andreas Hauser and Ahmed H. Zewail
Nature Chemistry **5** (5) (2013), p395-402 DOI:10.1038/NCHEM.1622

The advancement of techniques that can probe the behaviour of individual nanoscopic objects is of paramount importance in various disciplines, including photonics and electronics. As it provides images with a spatiotemporal resolution, a four-dimensional electron microscopy, in principle, should enable the visualization of single-nanoparticle structural dynamics in real and reciprocal space. Here, we demonstrate the selectivity and sensitivity of the technique by visualizing the spin crossover dynamics of single, isolated metalâ€organic framework nanocrystals. By introducing a small aperture in the microscope, it was possible to follow the phase transition and the associated structural dynamics within a single particle. Its behaviour was observed to be distinct from that imaged by averaging over ensembles of heterogeneous nanoparticles. The approach reported here has potential applications in other nanosystems and those that undergo (bio)chemical transformations.



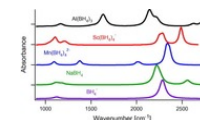
• **Tetrathiafulvalene-1,3,5-triazines as (Multi)Donor-Acceptor Systems with Tunable Charge Transfer: Structural, Photophysical, and Theoretical Investigations**

Flavia Pop, François Riobé, Sabine Seifert, Thomas Cauchy, Jie Ding, Nathalie Dupont, Andreas Hauser and Marius Koch and Narcis Avarvari
Inorganic Chemistry **52** (9) (2013), p5023-5034 DOI:10.1021/ic3027336

Palladium-catalyzed cross-coupling reactions between chlorinated 1,3,5-triazines (TZ) and tetrathiafulvalene (TTF) trimethyltin derivatives afford mono- and C_3 -symmetric tris(TTF)-triazines as donorâ€acceptor compounds in which the intramolecular charge transfer (ICT) is modulated by the substitution scheme on TTF and TZ and by chemical or electrochemical oxidation. The TTF-TZ- Cl_2 and (SMe) $_2$ TTF-TZ- Cl_2 derivatives show fully planar structures in the solid state as a consequence of the conjugation between the two units. Electrochemical and photophysical investigations, supported by theoretical calculations, clearly demonstrate that the lowest excited state can be ascribed to the intramolecular charge transfer (ICT) $I\dot{E}(TTF)\dot{A}^+I\dot{E}^*(TZ)$ transition. The tris(TTF) compound [(SMe) $_2$ TTF] $_3$ -TZ shows fluorescence when excited in the ICT band, and the emission is quenched upon oxidation. The radical cations $TTF^{+\dot{A}E}$ are easily observed in all of the cases through chemical and electrochemical oxidation by steady-state absorption experiments. In the case of [(SMe) $_2$ TTF] $_3$ -TZ, a low energy band at 5000 cm^{-1} , corresponding to a coupling between $TTF^{+\dot{A}E}$ and TTF units, is observed. A crystalline radical cation salt with the TTF-TZ- Cl_2 donor and PF_6^- anion, prepared by electrocrystallization, is described.

• **Vibrational spectra and structure of borohydrides**

Vincenza D'Anna and Latévi Max Lawson Daku and Hans Hagemann
Journal of Alloys and Compounds **580** (S1) (2013) DOI:10.1016/j.jallcom.2013.01.112
Keywords: hydrogen storage • vibrational spectra • borohydrides • FG method

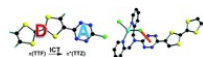


A comparison of the vibrational spectra of many inorganic borohydrides allows us to distinguish compounds with isolated BH_4^- ions and compounds containing complex ions such as $Sc(BH_4)_4^-$. The characteristic spectral features of both types of compounds are identified, showing that the Bâ€H bonding is quite different in both cases. A detailed analysis of the vibrations of the isolated BH_4^- ions provides new information about their local structure. Angular deformations of individual borohydride ion are analyzed quantitatively. It appears that the compounds containing isolated BH_4^- ions belong to those with the most electropositive cations and the highest decomposition temperature, while the complex borohydrides show significantly lower decomposition temperatures and possible diborane formation.

• **Synthesis and Redox and Photophysical Properties of Benzodifuran-Spiropyran Ensembles**

Hui Li, Jie Ding, Songjie Chen, Christoph Beyer, Shi-Xia Liu, Hans-Achim Wagenknecht, Andreas Hauser and Silvio Decurtins
Chemistry - A European Journal **19** (20) (2013), p6459-6466 DOI:10.1002/chem.201204043
Keywords: asymmetric synthesis • click chemistry • electron transfer • photochromism • redox chemistry • spiro compounds

Two benzodifuran (BDF)-coupled spiropyran (SP) systems and their BDF reference compounds were obtained in good yields through Huisgenâ€Meldalâ€Sharpless click chemistry and then subjected to investigation of their electrochemical and photophysical properties. In both SP and merocyanine (MC) forms of the coupled molecules, the BDF-based emission is quenched to around 1â€% of the quantum yield of emission from the BDF reference compounds. Based on electrochemical data, this quenching is attributed to oxidative electron-transfer quenching. Irradiation at 366â€nm results in ring opening to the MC forms of the BDF-coupled SP compounds and the SP reference compound with a quantum efficiency of about 50â€%. The rate constants for the thermal ring closing are approximately $3.4 \times 10^{-3} s^{-1}$. However, in the photostationary states the MC fractions of the coupled molecules are substantially lower than that of the reference SP compound, attributed to the observed acceleration of the ring-closing reaction upon irradiation. As irradiation at 366â€nm invariably also excites higher-energy transitions of the BDF units in the coupled compounds, the ring-opening reaction is accelerated relative to the SP reference, which results in lower MC fractions in the photostationary state. Reversible photochromism of these BDF-coupled SP compounds renders them promising in the field of molecular switches.



• **Tetrathiafulvalene-s-tetrazine: versatile platform for donor-acceptor systems and multifunctional ligands**

Flavia Pop, Jie Ding, Latévi Max Lawson Daku, Andreas Hauser and Narcis Avarvari
RSC Advances **3** (2013), p3218-3221 DOI:10.1039/c3ra21702g

The structurally characterized tetrathiafulvalene-1,2,4,5-tetrazine donorâ€acceptor system shows redox tuneable intramolecular charge transfer, solvatochromic and electrochromic behaviour. Attachment of a dipicolyl-amine chelating unit affords a multifunctional ligand, which allows the preparation of the $ZnCl_2$ complex in which an anionâ€ interaction is seen.

• **Electron Transfer between Hydrogen-Bonded Pyridylphenols and a Photoexcited Rhenium(I) Complex**

William Herzog, Catherine Bronner, Susanne Löffler, Bice He, Daniel Kratzert, Dietmar Stalke, Andreas Hauser and Oliver S. Wenger
ChemPhysChem **14** (6) (2013), p1168-1176 DOI:10.1002/cphc.201201069
Keywords: electron transfer • luminescence • photochemistry • proton transfer • transient absorption

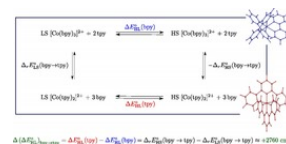
Two pyridylphenols with intramolecular hydrogen bonds between the phenol and pyridine units have been synthesized, characterized crystallographically, and investigated by cyclic voltammetry and UV/vis spectroscopy. Reductive quenching of the triplet metal-to-ligand charge-transfer excited state of the $[Re(CO)_3(phen)(py)]^+$ complex (phen=1,10-phenanthroline, py=pyridine) by the two pyridylphenols and two reference phenol molecules is investigated by steady-state and time-resolved luminescence spectroscopy, as well as by transient absorption spectroscopy. Sternâ€Volmer analysis of the luminescence quenching data provides rate constants for the bimolecular excited-state quenching reactions. H/D kinetic isotope effects for the pyridylphenols are on the order of 2.0, and the bimolecular quenching reactions are up to 100â€times faster with the pyridylphenols than with the reference phenols. This observation is attributed to the markedly less positive oxidation potentials of the pyridylphenols with respect to the reference phenols (â€0.5â€V), which in turn is caused by proton coupling of the phenol oxidation process. Transient absorption spectroscopy provides unambiguous evidence for the photogeneration of phenoxyl radicals, that is, the overall photoreaction is clearly a proton-coupled electron-transfer process.

- **Towards accurate estimates of the spin-state energetics of spin-crossover complexes within density functional theory: a comparative case study of cobalt(II) complexes**

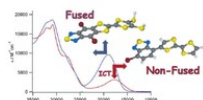
Alfredo Vargas, Itana Krivokapic, Andreas Hauser and Latévi Max Lawson Daku

Physical Chemistry Chemical Physics **15** (11) (2013), p3752-3763

DOI:10.1039/c3cp44336a



We report a detailed DFT study of the energetic and structural properties of the spin-crossover Co(II) complex $[\text{Co}(\text{tpy})_2]^{2+}$ ($\text{tpy} = 2,2',6',6''\text{-tetrakis}(\pi\text{-phenyl})-4,4''\text{-bipyridine}$) in the low-spin (LS) and the high-spin (HS) states, using several generalized gradient approximation and hybrid functionals. In either spin-state, the results obtained with the functionals are consistent with one another and in good agreement with available experimental data. Although the different functionals correctly predict the LS state as the electronic ground state of $[\text{Co}(\text{tpy})_2]^{2+}$, they give estimates of the HS \leftrightarrow LS zero-point energy difference $E_{\text{HS}}^{\text{ZPE}} - E_{\text{LS}}^{\text{ZPE}}$ (tpy) \AA which strongly depend on the functional used. This dependency on the functional was also reported for the DFT estimates of the zero-point energy difference $E_{\text{HS}}^{\text{ZPE}} - E_{\text{LS}}^{\text{ZPE}}$ (bpy) \AA in the HS complex $[\text{Co}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'\text{-bipyridine}$) [A. Vargas, A. Hauser and L. M. Lawson Daku, *J. Chem. Theory Comput.*, 2009, **5**, 97]. The comparison of the $E_{\text{HS}}^{\text{ZPE}} - E_{\text{LS}}^{\text{ZPE}}$ (tpy) \AA and $E_{\text{HS}}^{\text{ZPE}} - E_{\text{LS}}^{\text{ZPE}}$ (bpy) \AA estimates showed that all functionals correctly predict an increase of the zero-point energy difference upon the bpy \rightarrow tpy ligand substitution, which furthermore weakly depends on the functionals, amounting to $(E_{\text{HS}}^{\text{ZPE}} - E_{\text{LS}}^{\text{ZPE}})_{\text{bpy} \rightarrow \text{tpy}} \text{\AA} \approx +2670 \text{ cm}^{-1} \text{\AA}$. From these results and basic thermodynamic considerations, we establish that, despite their limitations, current DFT methods can be applied to the accurate determination of the spin-state energetics of complexes of a transition metal ion, or of these complexes in different environments, provided that the spin-state energetics is accurately known in one case. Thus, making use of the availability of a highly accurate *ab initio* estimate of the HS \leftrightarrow LS energy difference in the complex $[\text{Co}(\text{NCH})_3]^{2+}$ [L. M. Lawson Daku, F. Aquilante, T. W. Robinson and A. Hauser, *J. Chem. Theory Comput.*, 2012, **8**, 4216], we obtain for $[\text{Co}(\text{tpy})_2]^{2+}$ \AA and $[\text{Co}(\text{bpy})_3]^{2+}$ best estimates of $E_{\text{HS}}^{\text{ZPE}} - E_{\text{LS}}^{\text{ZPE}}$ (bpy) $\text{\AA} \approx -2800 \text{ cm}^{-1} \text{\AA}$ and $E_{\text{HS}}^{\text{ZPE}} - E_{\text{LS}}^{\text{ZPE}}$ (tpy) $\text{\AA} \approx 0 \text{ cm}^{-1} \text{\AA}$, in good agreement with the known magnetic behaviour of the two complexes.



- **Tetrathiafulvalene-Benzothiadiazoles as Redox-Tunable Donor-Acceptor Systems: Synthesis and Photophysical Study**

Flavia Pop, Anneliese Amacher, Narcis Avarvari, Jie Ding, Latevi Max Lawson Daku, Andreas Hauser, Marius Koch, Jürg Hauser and Shi-Xia Liu and Silvio Decurtins

Chemistry - A European Journal **19** (7) (2013), p2504-2514

DOI:10.1002/chem.201202742

Keywords: charge transfer • donor-acceptor systems • fluorescence • photophysics • redox chemistry

Electrochemical and photophysical analysis of new donor \rightarrow acceptor systems **2A** and **3**, in which a benzothiadiazole (BTD) unit is covalently linked to a tetrathiafulvalene (TTF) core, have verified that the lowest excited state can be ascribed to an intramolecular charge-transfer (ICT) $[(\text{TTF})^{\text{+}}(\text{BTD})^{\text{-}}]$ transition. Owing to better overlap of the HOMO and LUMO in the fused scaffold of compound **3**, the intensity of the ^1ICT band is substantially higher compared to that in compound **2**. The corresponding CT fluorescence is also observed in both cases. The radical cation $\text{TTF}^{\text{+}}$ is easily observed through chemical and electrochemical oxidation by performing steady-state absorption experiments. Interestingly, compound **2A** is photo-oxidized under aerobic conditions.

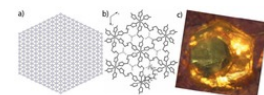
- **Analysis of the Experimental Data for Pure and Diluted $[\text{Fe}_x\text{Zn}_{1-x}(\text{bbtr})_3](\text{ClO}_4)_2$ Spin-Crossover Solids in the Framework of a Mechanoelastic Model**

Pradip Chakraborty and Cristian Enachescu and Andreas Hauser

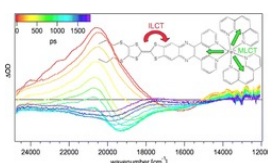
European Journal of Inorganic Chemistry **2013** (5-6) (2013), p770-780

DOI:10.1002/ejic.201201193

Keywords: spin crossover • mechanoelastic model • doping • iron • zinc



The mechanoelastic model is applied to reproduce the experimental relaxation and thermal transition curves as determined for crystals of pure and diluted $[\text{Fe}_x\text{Zn}_{1-x}(\text{bbtr})_3](\text{ClO}_4)_2$ ($\text{bbtr} = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{butane}$) spin-crossover systems. In the mechanoelastic model, the spin-crossover complexes are situated in a hexagonal planar lattice, which is similar to the 2D coordination polymer with (3,6) network topology of $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$. These complexes are linked by springs, which simulate the elastic interactions between them. Owing to the change in volume of the complexes during the spin transition, an elastic force accompanies the switch of every complex. This force propagates through the entire lattice and causes a shift of all molecules in the system and thus results in a new nuclear configuration. First, the ability of the model to reproduce various shapes of thermal transition and relaxation curves in pure compounds is analyzed; these range from gradual to very steep and include hysteresis behavior for the former and from single exponential to sigmoidal or with several steps for the latter. A structural phase transition can also be accounted for by changing the shape of the sample at a fixed temperature from a regular to an elongated hexagon. Furthermore, the effect of adding Zn as a dopant in a mixed crystal series is discussed. The role of dopants on the cluster evolution is also analyzed directly and by using the correlation factor.



- **A Donor-Acceptor Tetrathiafulvalene Ligand Complexed to Iron(II): Synthesis, Electrochemistry, and Spectroscopy of $[\text{Fe}(\text{phen})_2(\text{TTF-dppz})](\text{PF}_6)_2$**

Nathalie Dupont, Ying-Fen Ran, Shi-Xia Liu, Jakob Grilj, Eric Vauthey, Silvio Decurtins and Andreas Hauser

Inorganic Chemistry **52** (1) (2013), p306-312

DOI:10.1021/ic3019277

The synthesis and photophysical properties of the complex $[\text{Fe}(\text{phen})_2(\text{TTF-dppz})]^{2+}$ ($\text{TTF-dppz} = 4,4'\text{-bis}(\text{propylthio})\text{tetrathiafulvalene-1,1'-di}(\text{pyridino}[3,2\text{-}a:2'\text{-}a']\text{phenazine}$, phen = 1,10-phenanthroline) are described. In this complex, excitation into the metal \rightarrow ligand charge transfer bands results in the population of a high-spin state of iron(II), with a decay lifetime of approximately 1.5 ns, in dichloromethane, at room temperature. An intraligand charge transfer state can also be obtained and has a lifetime of 38 ps. A mechanism for the different states reached is proposed based on transient absorption spectroscopy.

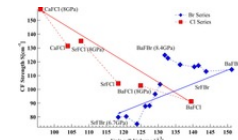
- **Effect of Pressure on the Free Ion and Crystal Field Parameters of Sm^{2+} in BaFBr and SrFBr Hosts**

Prodipta Pal, Tiphaine Penhouët and Vincenza D'Anna and Hans Hagemann

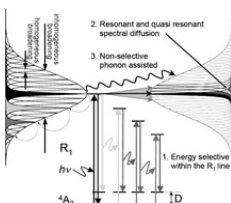
Journal of Luminescence **134** (2013), p678-685

DOI:10.1016/j.jlumin.2012.07.010

Keywords: Sm^{2+} • high pressure luminescence • crystal field • BaFBr • SrFBr



The emission spectra of Sm^{2+} doped in BaFBr and SrFBr hosts were measured at 10 \AA K from ambient pressure to 8 \AA GPa. The crystal field energy levels determined from the emission spectra were used to extract the free ion parameters (F_2^0 and F_4^0) and crystal field parameters (B_2^0). The variation of F_2^0 and F_4^0 as a function of pressure was studied systematically and was discussed in relation to the central field and symmetry restricted covalency models. The change of the spin orbit coupling parameter (ζ) with pressure for SrFBr: Sm^{2+} showed very different behavior than in other matlockite hosts. Moreover the variation of B_2^0 under pressure was studied. The pressure dependence of the B_2^0 was described quantitatively using the Superposition Model (SM) with the help of structural parameters as a function of pressure, obtained from periodic DFT calculations. The validity of the SM was tested for Sm^{2+} in BaFBr and SrFBr. It is shown that this model does not apply to SrFBr, in contrast to other matlockite host materials.



- **Chromium(III)-trisoxalate, a versatile building block for luminescent materials**

Mia Milos, Andreas Hauser

Journal of Luminescence **133** (2013), p15-20

DOI:10.1016/j.jlumin.2011.12.053

Keywords: chromium(III)-tris-oxalate • energy migration • fluorescence line narrowing • spectral diffusion • persistent spectral hole burning

Chromium(III)-trisoxalate, $[\text{Cr}(\text{ox})_3]^{3-}$ ($\text{ox} = \text{C}_2\text{O}_4^{2-}$), incorporated into polymeric networks of composition $[\text{NaCr}(\text{ox})_3][\text{M}^{\text{II}}(\text{bpy})_3] \cdot n\text{H}_2\text{O}$ and $[\text{NaCr}(\text{ox})_3][\text{M}^{\text{II}}(\text{bpy})_3]\text{ClO}_4$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{M}^{\text{II}} = \text{Zn, Fe, Ru}$; $\text{M}^{\text{II}} = \text{Rh, Cr}$), results in interesting features ranging from phonon-assisted and resonant energy migration within the R1 line the e^2E state to persistent spectral side-hole burning via the latter, and manifestations of specific nearest-neighbour H-bonding interactions between bipyridine and oxalate.

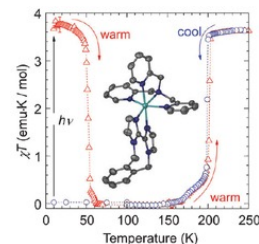
2012

- Heteroleptic FeII Complexes of 2,2'-Biimidazole and Its Alkylated Derivatives: Spin-Crossover and Photomagnetic Behavior**

Hoa V. Phan, Pradip Chakraborty, Meimei Chen, Yitzi M. Calm, Kirill Kovnir, Lawrence K. Keniley, Jordan M. Hoyt, Elisabeth S. Knowles, Céline Besnard, Mark W. Meisel, Andreas Hauser, Catalina Achim and Michael Shatruk

Chemistry - A European Journal **18** (49) (2012), p15805-15815 DOI:10.1002/chem.201202045

Keywords: iron complexes • LIESST effect • N ligands • photomagnetism • spin crossover



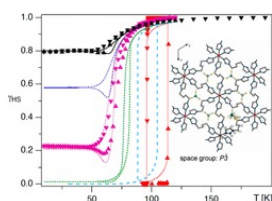
Three iron(II) complexes, $[\text{Fe}(\text{TPMA})(\text{BIM})](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (**1**), $[\text{Fe}(\text{TPMA})(\text{XBIM})](\text{ClO}_4)_2$ (**2**), and $[\text{Fe}(\text{TPMA})(\text{XBBIM})](\text{ClO}_4)_2$ (**3**), were prepared by reactions of Fe^{2+} perchlorate and the corresponding ligands (TPMA=tris(2-pyridylmethyl)amine, BIM=2,2'-biimidazole, XBIM=1,1'-bis(2,2'-biimidazol-5-yl)-2,2'-bipyridine, XBBIM=1,1'-bis(2,2'-biimidazol-5-yl)-2,2'-bibenzimidazole). The compounds were investigated by a combination of X-ray crystallography, magnetic and photomagnetic measurements, and Mössbauer and optical absorption spectroscopy. Complex **1** exhibits a gradual spin crossover (SCO) with a $T_{1/2} = 190 \text{ K}$, whereas **2** exhibits an abrupt SCO with approximately 7 K thermal hysteresis ($T_{1/2} = 196 \text{ K}$ on cooling and 203 K on heating). Complex **3** is in the high-spin state in the $200\text{--}300 \text{ K}$ range. The difference in the magnetic behavior was traced to differences between the inter- and intramolecular interactions in **1** and **2**. The crystal packing of **2** features a hierarchy of intermolecular interactions that result in increased cooperativity and abruptness of the spin transition. In **3**, steric repulsion between H atoms of one of the pyridyl substituents of TPMA and one of the benzene rings of XBBIM results in a strong distortion of the Fe^{2+} coordination environment, which stabilizes the high-spin state of the complex. Both **1** and **2** exhibit a photoinduced low-spin to high-spin transition (LIESST effect) at 50 K . The difference in the character of intermolecular interactions of **1** and **2** also manifests in the kinetics of the decay of the photoinduced high-spin state. For **1**, the decay rate constant follows the single-exponential law, whereas for **2** it is a stretched exponential, reflecting the hierarchical nature of intermolecular contacts. The structural parameters of the photoinduced high-spin state at 50 K are similar to those determined for the high-spin state at 295 K . This study shows that *N*-alkylation of BIM has a negligible effect on the ligand field strength. Therefore, the combination of TPMA and BIM offers a promising ligand platform for the design of functionalized SCO complexes.

- Accurate Spin-State Energetics of Transition Metal Complexes: I. CCSD(T), CASPT2 and DFT Study of $[\text{M}(\text{NCH})_6]^{2+}$ ($\text{M} = \text{Fe, Co}$)**

Latevi Max Lawson Daku, Francesco Aquilante, Timothy William Robinson and Andreas Hauser

Journal of Chemical Theory and Computation **8** (11) (2012), p4216-4231 DOI:10.1021/ct300592w

Highly accurate estimates of the high-spin/low-spin energy difference $\Delta E_{\text{H-L}}$ in the high-spin complexes $[\text{Fe}(\text{NCH})_6]^{2+}$ and $[\text{Co}(\text{NCH})_6]^{2+}$ have been obtained from the results of CCSD(T) calculations extrapolated to the complete basis set limit. These estimates are shown to be strongly influenced by scalar relativistic effects. They have been used to assess the performances of the CASPT2 method and of 30 density functionals of the GGA, meta-GGA, global hybrid, RSH and double-hybrid types. For the CASPT2 method, the results of the assessment support the proposal (Kepenekian, M.; Robert, V.; Le Guennic, B. *J. Chem. Phys.* **2009**, *131*, 114702) that the ionization potential/electron affinity (IPEA) shift defining the zeroth-order Hamiltonian be raised from its standard value of 0.25 au to 0.50 au . For the determination of $\Delta E_{\text{H-L}}$ in Fe(II) complexes with a $[\text{FeN}_6]^{2+}$ core. At the DFT level, some of the assessed functionals proved to perform within chemical accuracy ($\pm 350 \text{ cm}^{-1}$) for the spin-state energetics of $[\text{Fe}(\text{NCH})_6]^{2+}$, others for that of $[\text{Co}(\text{NCH})_6]^{2+}$, but none of them simultaneously for both complexes. As demonstrated through a reparametrization of the CAM-PBE0 range-separated hybrid, which led to a functional that performs within chemical accuracy for the spin-state energetics of both complexes, performing density functionals of broad applicability may be devised by including in their training sets highly accurate data like those reported here for $[\text{Fe}(\text{NCH})_6]^{2+}$ and $[\text{Co}(\text{NCH})_6]^{2+}$.



- Thermal and Light-Induced Spin Switching Dynamics in the 2D Coordination Network of $[\text{Zn}_{1-x}\text{Fe}_x(\text{bbtr})_3](\text{ClO}_4)_2$: The Role of Cooperative Effects**

Pradip Chakraborty, Cristian Enachescu, Christophe Walder, Robert Bronisz and Andreas Hauser
Inorganic Chemistry **51** (18) (2012), p9714-9722 DOI:10.1021/ic301006c

The thermal spin transition, the photoexcitation, and the subsequent spin relaxation in the mixed crystal series of the covalently linked two-dimensional network $[\text{Zn}_{1-x}\text{Fe}_x(\text{bbtr})_3](\text{ClO}_4)_2$ ($x = 0.02\text{--}1$, $\text{bbtr} = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{-butane}$) are discussed. In the neat compound, the thermal spin transition with a hysteresis of 13 K is accompanied by a crystallographic phase transition (Kusz, J.; Bronisz, R.; Zubko, M.; Bednarek, H. *J. Chem. Eur. J.* **2011**, *17*, 6807). In contrast, the diluted crystals with $x \approx 0.1$ stay essentially in the high-spin state down to low temperatures and show typical first order relaxation kinetics upon photoexcitation, and the structural phase transition is well separated from the spin transition. With increasing Fe(II) concentration, steeper thermal transitions and sigmoidal relaxation curves indicate increasingly important cooperative effects. Already at $x = 0.38$, the spin relaxation is governed by cooperative interactions between Fe(II) centers, and the crystallographic phase transition begins to influence the spin transition. The kinetic behavior of the thermal spin transition is reproduced within the framework of a dynamic mean-field model.

- A Synthetic and Mechanistic Investigation of the Chromium Tricarbonyl-Mediated Masamune-Bergman Cyclization. Direct Observation of a Ground-State Triplet *p*-Benzyne Biradical**

Kai E. O. Yljoki, Séverine Lavy, Angelika Fretzen, E. Peter Kündig, Théo Berclaz and Gérald Bernardinelli and Céline Besnard
Organometallics **31** (15) (2012), p5396-5404 DOI:10.1021/om300427j

A new room-temperature chromium tricarbonyl-mediated cycloaromatization of enediynes is reported. The reaction occurs with both cyclic and acyclic enediynes in the presence of $[\text{Cr}(\text{CO})_3(\text{I}^{\text{R}}\text{-naphthalene})]$ and both a coordinating solvent and a hydrogen atom source, providing chromium-arene complexes in reasonable yield and good diastereocontrol. The mechanism of the reaction has been probed through DFT computational and spectroscopic methods. These studies suggest that direct C1--C6 bond formation from an I^{R} -enediynes complex is the lowest-energy path, forming a metal-bound *p*-benzyne biradical. NMR spectroscopy suggests that enediyne alkene coordination occurs in preference to alkyne coordination, forming a THF-stabilized olefin intermediate; subsequent alkyne coordination leads to cyclization. While biradical quenching occurs rapidly and primarily via the singlet biradical, the triplet state biradical is detectable by EPR spectroscopy, suggesting intersystem crossing to a triplet ground state.

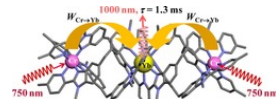
- Optimizing Millisecond Time Scale Near-Infrared Emission in Polynuclear Chrome(III)-Lanthanide(III) Complexes**

Lilit Aboshyan-Sorgho, Homayoun Nozary, Annina Aebischer, Jean-Claude G. Bünzli, Pierre-Yves Morgantini, Kevin R. Kittilstved, Andreas Hauser, Svetlana V. Eliseeva and Stéphane Petoud and Claude Piguet

Journal of the American Chemical Society **134** (30) (2012), p12675-12684

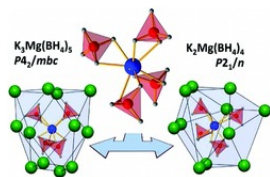
DOI:10.1021/ja304009b

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This work illustrates a simple approach for optimizing long-lived near-infrared lanthanide-centered luminescence using trivalent chromium chromophores as sensitizers. Reactions of the segmental ligand **L2A** with stoichiometric amounts of $M(\text{CF}_3\text{SO}_3)_2\text{A}$ ($M = \text{Cr}, \text{Zn}$) and $\text{Ln}(\text{CF}_3\text{SO}_3)_3\text{A}$ ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$) under aerobic conditions quantitatively yield the D_3 -symmetrical trinuclear $[\text{MLnM}(\text{L2})_3](\text{CF}_3\text{SO}_3)_6$ complexes ($M = \text{Zn}, \text{A} = 7; M = \text{Cr}, \text{A} = 9$), in which the central lanthanide activator is sandwiched between the two transition metal cations. Visible or NIR irradiation of the peripheral Cr(III) chromophores in $[\text{CrLnCr}(\text{L2})_3]\text{A}$ induces rate-limiting intramolecular intermetallic $\text{Cr}^{\text{IV}}\text{Ln}$ energy transfer processes ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$), which eventually produces lanthanide-centered near-infrared (NIR) or IR emission with apparent lifetimes within the millisecond range. As compared to the parent dinuclear complexes $[\text{CrLn}(\text{L1})_3]^{6+}$, the connection of a second strong-field $[\text{CrLn}(\text{L2})_3]^{9+}$ significantly enhances the emission intensity without perturbing the kinetic regime. This work opens novel exciting photophysical perspectives via the buildup of non-negligible population densities for the long-lived doubly excited state $[\text{Cr}^*\text{LnCr}^*(\text{L2})_3]^{9+}\text{A}$ under reasonable pumping powers.

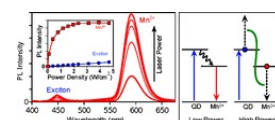


- **Bimetallic Borohydrides in the System $M(\text{BH}_4)_2\text{-KBH}_4$ ($M = \text{Mg}, \text{Mn}$): On the Structural Diversity**
Pascal Schouwink, Vincenza D'Anna, Morten Brix Ley, Latévi Max Lawson Daku, Bo Richter, Torben R. Jensen and Hans Hagemann and Radovan Cerný
The Journal of Physical Chemistry C **116** (20) (2012), p10829-10840 DOI:10.1021/jp212318s

Four novel bimetallic borohydrides have been discovered, $\text{K}_2\text{M}(\text{BH}_4)_4\text{A}$ ($\text{MA} = \text{Mg}$ or Mn), $\text{K}_3\text{Mg}(\text{BH}_4)_5$, and $\text{KMn}(\text{BH}_4)_3$, and are carefully investigated structurally as well as regarding their decomposition reaction mechanism by means of in situ synchrotron radiation powder X-ray diffraction (SR-PXD), vibrational spectroscopies (Raman and IR), thermal analysis (TGA and DTA), and ab initio density functional theory (DFT) calculations. Mechano-chemical synthesis (ball-milling) using the reactants KBH_4 , $1\pm\text{-Mg}(\text{BH}_4)_2$, and $1\pm\text{-Mn}(\text{BH}_4)_2\text{A}$ ensures chlorine-free reaction products. A detailed structural analysis reveals significant similarities as well as surprising differences among the two isomorphs $\text{K}_2\text{M}(\text{BH}_4)_4$, most importantly concerning the extent to which the complex anion $[\text{M}(\text{BH}_4)_4]^{2-}\text{A}$ is isolated in the structure. Anisotropic thermal expansion and an increase in symmetry at high temperatures in $\text{K}_3\text{Mg}(\text{BH}_4)_5\text{A}$ is ascribed to the motion of BH_4 groups inducing hydrogen repulsive effects, and the dynamics of $\text{K}_3\text{Mg}(\text{BH}_4)_5\text{A}$ are investigated. Decomposition in the manganese system proceeds via the formation of $\text{KMn}(\text{BH}_4)_3$, the first perovskite type borohydride reported to date.

- **Luminescence Saturation via Mn^{2+} -Exciton Cross Relaxation in Colloidal Doped Semiconductor Nanocrystals**

Liam R. Bradshaw, Andreas Hauser and Emily J. McLaurin and Daniel R. Gamelin
The Journal of Physical Chemistry C **116** (16) (2012), p9300-9310 DOI:10.1021/jp300765y



Colloidal Mn^{2+} -doped semiconductor nanocrystals such as $\text{Mn}^{2+}\text{:ZnSe}$ have attracted broad attention for potential applications in phosphor and imaging technologies. Here, we report saturation of the sensitized Mn^{2+} photoluminescence intensity at very low continuous-wave (CW) and quasi-CW photoexcitation powers under conditions that are relevant to many of the proposed applications. Time-resolved photoluminescence measurements and kinetic modeling indicate that this saturation arises from an Auger-type nonradiative cross relaxation between an excited Mn^{2+} ion and an exciton within the same nanocrystal. A lower limit of $k = 2 \text{ A}^{-1} \times 10^{10} \text{ s}^{-1}\text{A}^{-1}$ is established for the fundamental rate constant of the $\text{Mn}^{2+}({}^4\text{T}_1)$ -exciton cross relaxation.

- **Lanthanide-mediated triangular cationic assemblies: structural and physico-chemical properties**

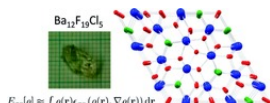
Soumaila Zebret, Nathalie Dupont, Céline Besnard, Gérald Bernardinelli and Josef Hamacek
Dalton Transactions **41** (16) (2012), p4817-4824 DOI:10.1039/c2dt12227h

This contribution investigates Ln^{III} complexes formed with a small ditopic ligand, L1, and their structural, thermodynamic and photophysical properties. The spectrophotometric and NMR titrations evidence the triangular assemblies $[\text{Ln}_3(\text{L1-H})_3]^{6+}$ at stoichiometric conditions and their properties are discussed in relation to L2-containing analogues. In addition, the dinuclear species, $[\text{Ln}_2(\text{L1-H})]^{5+}$, is observed with an excess of metal.

- **Optical sensitization and upconversion in discrete polynuclear chromium-lanthanide complexes**

Lilit Aboshyan-Sorgho, Martine Cantuel, Stephane Petoud and Andreas Hauser and Claude Piguet
Coordination Chemistry Reviews **256** (15-16) (2012), p1644-1663 DOI:10.1016/j.ccr.2011.12.013

Due to its extreme kinetic inertness, trivalent chromium, Cr(III), has been rarely combined with labile trivalent lanthanides, Ln(III), to give discrete self-assembled (supra)molecular polynuclear complexes. However, the plethora of accessible metal-centered excited states possessing variable lifetimes and emissive properties, combined with the design of efficient intramolecular $\text{Cr}(\text{III})\text{A}^{\text{III}}\text{Ln}(\text{III})$ energy transfer processes open attractive perspectives for programming directional light-conversion within these heterometallic molecules. Efforts made to address this exciting challenge for both light-sensitization and light-upconversion are discussed in this article.

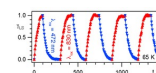


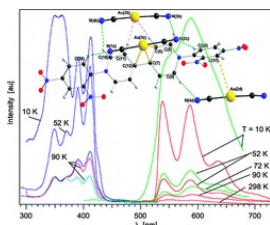
- **Crystal chemistry in the barium fluoride chloride system**
Hans Hagemann, Vincenza D'Anna and Latevi Max Lawson Daku and Frank Kubel
Crystal Growth & Design **12** (3) (2012), p1124-1131 DOI:10.1021/cg201588s

The crystal chemistry of the barium fluoride chloride system is studied both experimentally and theoretically. Different synthetic approaches yield nanocrystalline materials as well as large single crystals. The crystalline phases identified so far are BaFCl , $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$ and $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ (in two modifications) and compared with analogous compounds. It is demonstrated that the compound $\text{Ba}_2\text{F}_3\text{Cl}$ reported by Fessenden and Lewin 50 years ago corresponds to $\text{Ba}_7\text{F}_{12}\text{Cl}_2$. The phase diagram of the $\text{BaCl}_2\text{-BaF}_2$ system is reinvestigated for fluoride mole fractions between 0.5 and 1. The peritectic formation of $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$ is observed. Periodic DFT calculations are performed for all structures in this system, including a hypothetical structure for $\text{Ba}_2\text{F}_3\text{Cl}$, based on the experimental structure of $\text{Ba}_2\text{H}_3\text{Cl}$. The energy of formation of the different barium fluoride chloride compounds from BaCl_2 and BaF_2 (normalized for one barium atom per formula unit), as calculated by DFT at 0K, is within only about $\pm 15 \text{ kJ/mol}$. Comparison with recent experimental results on calcium and strontium hydride chloride (bromide) compounds, suggest the possibility of a mutual exclusion between the $\text{M}_2\text{X}_3\text{Y}$ and $\text{M}_7\text{X}_{12}\text{Y}_2$ ($M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{X} = \text{H}, \text{F}, \text{Y} = \text{Cl}, \text{Br}$) structures. The single crystal structure of PbFBr is also reported.

- **Persistent Bidirectional Optical Switching in the 2D High-Spin Polymer $\{[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2\}_\infty$**
Pradipt Chakraborty, Robert Bronisz, Céline Besnard, Laure Guénée, Phil Pattison and Andreas Hauser
Journal of the American Chemical Society **134** (2012), p4049-4052 DOI:10.1021/ja211897t

In the covalently linked 2D coordination network $\{[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2\}_\infty$, $\text{bbtr} = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{butane}$, the iron(II) centers stay in the high-spin (HS) state down to 10 K. They can, however, be quantitatively converted to the low-spin (LS) state by irradiating into the near-IR spin allowed $d\text{-d}$ band and back again by irradiating into the visible $d\text{-d}$ band. The compound shows true light-induced bistability below 100 K, thus, having the potential for persistent bidirectional optical switching at elevated temperatures.





• *Photophysical Properties of $[Au(CN)_2]_2$ Dimers Trapped in a Supramolecular Electron-Acceptor Organic Framework*

Ahmed S. Abouelwafa, Christopher E. Anson, Andreas Hauser, Howard H. Patterson, François Baril-Robert and Xiaobo Li and Annie K. Powell

Inorganic Chemistry **51** (3) (2012), p1294-1301

DOI:10.1021/ic201109u

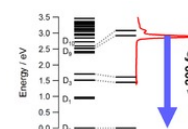
Dicyanoaurate reacts with the organic acceptor molecule, 1,1'-bis-(2,4-dinitrophenyl)-4,4'-bipyridinium **DNP**⁺, to form a supramolecular complex with the general formula $[Au(CN)_2]_2DNP^+ \cdot 4H_2O$. The complex was characterized by X-ray crystallography, and its photophysical properties were investigated in the solid-state. Although the initial $(DNP)Cl_2$ compound does not show photoluminescence behavior and the dicyanoaurate shows photoluminescence only in the UV range, the resulting supramolecular complex displays two simultaneous, essentially independent, photoluminescence bands in the visible range originating from individual contributions of the **DNP**⁺ unit and the dicyanoaurate dimers. This unusual simultaneous photoluminescence behavior displayed by both the dicyanoaurate donor units and the redox-active 4,4'-bipyridinium acceptor have lifetimes of 0.5 ns and several hundred ns, respectively.

• *Photophysics of Galvinoxyl Free Radical Revisited*

Jakob Grifl, Cedric Zonca and Latevi Max Lawson Daku and Eric Vauthey

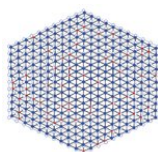
Physical Chemistry Chemical Physics **14** (2012), p6351-6358

DOI:10.1039/c2cp23577c



The photophysical properties of the free neutral radical galvinoxyl were studied by a combination of femtosecond time-resolved spectroscopy and quantum chemical calculations. The electronic absorption spectrum is dominated by an intense band at 430 nm that is ascribed to the $D_{9,10} \rightarrow D_0$ transitions. Upon photoexcitation at 400 nm, the population of the $D_{9,10}$ states decays within less than 200 fs to the electronic ground state. This ultrafast internal conversion does not involve intramolecular modes with large amplitude motion as the measured dynamics does not show any significant dependence on the environment, but is most probably facilitated by a high density of electronic states of different character. Depending on the solvent, a weak transient band due to the galvinoxylate anion is also observed. This closed-shell species, which is fluorescent although its deactivation is also dominated by non-radiative decay, is generated upon biphotonic ionization of the solvent and electron capture. The ultrashort excited-state lifetime of the galvinoxyl radical precludes photoinduced disproportionation previously claimed to be at the origin of the formation of both anion and cation.

2011



• *Thermal hysteresis in spin-crossover compounds studied within the mechanoelastic model and its potential application to nanoparticles*

C. Enachescu, P. Chakraborty, L. Stoleriu, A. Stancu, A. Hauser

Physical Review B **84** (13) (2011), p134102

DOI:10.1103/PhysRevB.84.134102

The recently developed mechanoelastic model is applied to characterize the thermal transition in spin-crossover complexes, with special attention given to the case of spin-crossover nanoparticles. In a two-dimensional system, hexagonal-shaped samples with open boundary conditions are composed of individual molecules that are linked by springs and can switch between two states, namely, the high-spin (HS) and the low-spin (LS) states. The switching of an individual molecule during the spin transition is decided by way of a Monte Carlo standard procedure, using transition probabilities depending on the temperature, the energy gap between the two states, the enthalpy difference, the degeneracy ratio, and the local pressure determined by the elongation or compression of its closest springs. The influence of external parameters, such as temperature sweeping rate and pressure, or intrinsic features of the system, such as the value of its spring constant, on the width of the thermal hysteresis, its shape, and its position are discussed. The particular case of spin-crossover nanoparticles is treated by considering them embedded into a polymer environment, which essentially affects the molecules situated at the edges and faces by decreasing their transition probabilities from HS to LS. Finally, the pressure hysteresis, obtained by varying the external pressure at constant temperature is discussed.

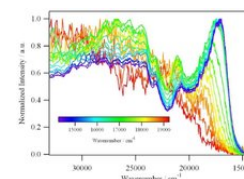
• *Targeting π -Conjugated Multiple Donor-Acceptor Motifs Exemplified by Tetrathiafulvalene-Linked Quinoxalines and Tetrabenz[bc,ef,hi,uv]ovalenes: Synthesis, Spectroscopic, Electrochemical, and Theoretical Characterization*

Hong-Peng Jia, Jie Ding, Ying-Fen Ran, Shi-Xia Liu, Carmen Blum, Irina Petkova, Andreas Hauser and Silvio Decurtins

Chemistry - An Asian Journal **6** (12) (2011), p3312-3321

DOI:10.1002/asia.201100515

Keywords: charge transfer • donor-acceptor systems • nanographene • redox chemistry • tetrathiafulvalene



An efficient synthetic approach to a symmetrically functionalized tetrathiafulvalene (TTF) derivative with two diamine moieties, 2-[5,6-diamino-4,7-bis(4-pentylphenoxy)-1,3-benzodithiol-2-ylidene]-4,7-bis(4-pentylphenoxy)-1,3-benzodithiole-5,6-diamine (**2**), is reported. The subsequent Schiff-base reactions of **2** afford large π -conjugated multiple $D_{\pi A}$ arrays, for example the triad 2-[4,9-bis(4-pentylphenoxy)-1,3-dithiol[4,5-g]quinoxaline-2-ylidene]-4,9-bis(4-pentylphenoxy)-1,3-dithiol[4,5-g]quinoxaline (**8**) and the corresponding tetrabenz[bc,ef,hi,uv]ovalene-fused pentad **1**, in good yields and high purity. The novel redox-active nanographene **1** is so far the largest known TTF-functionalized polycyclic aromatic hydrocarbon with a well-resolved 1H NMR spectrum. The electrochemically highly amphoteric pentad **1** and triad **8** exhibit various electronically excited charge-transfer states in different oxidation states leading to intense optical intramolecular charge transfer (ICT) absorbances over a wide spectral range. The chemical and electrochemical oxidations of **1** result in an unprecedented $TTF^{+} radical cation$ dimerization, leading to the formation of $[1^{+}]_2$ at room temperature in solution due to the stabilizing effect arising from strong π - π interactions. Moreover, ICT fluorescence is observed with large solvent-dependent Stokes shifts and quantum efficiencies of 0.05 for **1** and 0.035 for **8** in CH_2Cl_2 .

• *Study of the relaxation in diluted spin crossover molecular magnets in the framework of the mechano-elastic model*

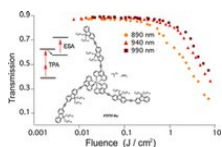
Cristian Enachescu, Laurentiu Stoleriu, Alexandru Stancu and Andreas Hauser

Journal of Applied Physics **109** (7) (2011), p711

DOI:10.1063/1.3556702

Keywords: magnetic impurities • metastable states • molecular magnetism • Monte Carlo methods • spin dynamics

We model here the behavior of spin transition compounds, considering molecules arranged in a 2D hexagonal lattice and interacting via springs. The role of impurities in the clustering and nucleation phenomena is analyzed, as well as the manner in which the impurities affect the relaxation curves. The switching of the individual molecules is checked using a Monte Carlo procedure. When a molecule changes its state, it also modifies its volume, and the new equilibrium positions of all the molecules are calculated. As in previously reported experiments, it is found here that bigger impurities slow down the relaxation from the metastable high-spin state to the low-spin state, while smaller impurities act in an opposite way. It is shown that if the concentration of the impurities is higher than a certain threshold, then they act as a barrier, trammeling the fast evolution of domains developing from the edges.



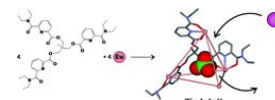
- **A novel ruthenium(III) complex for two-photon absorption-based optical power limiting in the near-IR range**
Mickaël Four, Didier Riehl, Olivier Mongin, Mireille Blanchard-Desce, Latévi Max Lawson Daku, Juliette Moreau, Jérôme Chauvin and Jacques A. Delaire and Gilles Lemerrier
Physical Chemistry Chemical Physics **13** (38) (2011), p17304-17312 DOI:10.1039/c1cp21661a

In this article, the synthesis of a novel high-conjugated ligand and its corresponding Ru(II) complex PTTF:Ru is reported, along with the linear and nonlinear optical characterizations. Two-photon absorption based optical power limiting properties (OPL), especially in the near infrared, are described and compared to those of the analogous complexes previously published. Combined with a preliminary theoretical approach, this allows us to highlight several key parameters for OPL optimization in such molecular systems and more particularly the spectral overlap between TPA and excited-state absorption.

- **Thermodynamics, Structure and Properties of Polynuclear Lanthanide Complexes with a Tripodal Ligand: Insight into their Self-Assembly**
Josef Hamacek, Céline Besnard, Tiphaine Penhouet, and Pierre-Yves Morgantini
Chemistry - A European Journal **17** (24) (2011), p6753-6764 DOI:10.1002/chem.201100173
Keywords: helical structures • lanthanides • polynuclear complexes • thermodynamics • tripodal ligands

Self-assembly processes between a tripodal ligand and Ln^{III} cations have been investigated by means of supramolecular analytical methods. At an equimolar ratio of components, tetranuclear tetrahedral complexes are readily formed in acetonitrile. The structural analysis of the crystallographic data shows a helical wrapping of binding strands around metallic cations. The properties of this series of highly charged 3D compounds were examined by using NMR spectroscopy and optical methods in solution and in the solid state. In the presence of excess metal, a new trinuclear complex was identified. The X-ray crystal structure elucidated the coordination of metallic cations with two ligands of different conformations. By varying the metal/ligand ratio, a global speciation of this supramolecular system has been evidenced with different spectroscopic methods. In addition, these rather complicated equilibria were successfully characterised with the thermodynamic stability constants. A rational analysis of the self-assembly processes was attempted by using the thermodynamic free energy model and the impact of the ligand structure on the effective concentration is discussed.

- **Lanthanide-Mediated Supramolecular Cages and Host-Guest Interactions**
Badr El Aroussi, Laure Guénée, Prodipta Pal, and Josef Hamacek
Inorganic Chemistry **50** (17) (2011), p8588-8597 DOI:10.1021/ic201156q



The structure and thermodynamic properties of lanthanide complexes with a new tripodal ligand **L2** have been elucidated using different physicochemical methods. At stoichiometric ratios, the tetrahedral three-dimensional complexes with lanthanide cations are formed in acetonitrile with good stabilities. Despite minor structural changes comparing to previously investigated tripodal ligands, the resulting assembly exhibits different features revealed with the crystal structure of $[\text{Eu}_4\text{L}_2](\text{OH})(\text{ClO}_4)_{11}$ (orthorhombic, $Pbcn$). Interestingly, the highly charged edifice contains an inner cage encapsulating a perchlorate anion. Such lanthanide mediated cage-like assemblies are rare, and may be of interest for different sensing applications. Indeed, the anionic guest can be exchanged with different anions. The related host-guest equilibria were investigated with NMR techniques. Various aspects of these reactions are qualitatively discussed.



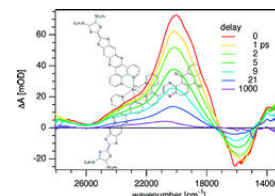
- **Near-Infrared to Visible Light Upconversion in a Trinuclear d-f-d Complex**
Lilit Aboshyan-Sorgho, Céline Besnard, Phil Pattison, Kevin R. Kittilstved, Annina Aebischer, Jean-Claude G. Bünzli, Andreas Hauser, Claude Piguet
Angewandte Chemie International Edition **50** (2011), p4108-4112 DOI:10.1002/anie.201100095
Keywords: helical structures • lanthanides • photochemistry • self-assembly • upconversion

The connection of two Cr^{III} sensitizers around a central Er^{III} acceptor in a self-assembled cation provides high local metal concentrations that favor efficient nonlinear energy transfer upconversion luminescence (see picture). Upon selective low-energy near-infrared irradiation of Cr^{III} -centered transitions, **1** displays an unprecedented molecular two-photon upconverted green Er^{III} -centered emission.

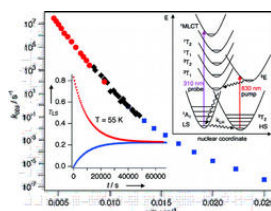
- **The kinetics features of a thermal spin transition characterized by optical microscopy on the example of $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$ single crystals: Size effect and mechanical instability**
Christian Chong, Ahmed Slimani, François Varret, Kamel Boukheddaden, Eric Collet, Jean-Claude Ameline, Robert Bronisz and Andreas Hauser
Chemical Physics Letters **504** (1-3) (2011), p29-33 DOI:10.1016/j.cplett.2011.01.041

We investigated by optical microscopy the thermal spin transition in single crystals of $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$ ($\text{bbtr} = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{butane}$). The growth of the low-spin phase was observed for different crystal orientations and sizes. The process always started from a corner of the crystal but its further development depended on the size, shape and thermal history of the crystal. In crystals of smaller size, under isothermal conditions, the low-spin phase developed in a continuous way, through the propagation of a rather well defined transformation front, with a higher propagation velocity inside the planes perpendicular to the c axis. In larger crystals the spontaneous occurrence of inhomogeneous stresses led to a stepwise propagation process.

- **Effect of the Addition of a Fused Donor-Acceptor Ligand on a Ru(II) Complex: Synthesis, Characterization, and Photoinduced Electron Transfer Reactions of $[\text{Ru}(\text{TTF-dppz})_2(\text{Aqphen})]^{2+}$**
Nathalie Dupont, Ying-Fen Ran, Hong-Peng Jia, Jakob Grilj, Jie Ding, Shi-Xia Liu and Silvio Decurtins and Andreas Hauser
Inorganic Chemistry **50** (8) (2011), p3295-3303 DOI:10.1021/ic101951n



The synthesis and the photophysical properties of the complex $[\text{Ru}(\text{TTF-dppz})_2(\text{Aqphen})]^{2+}$ (TTF = tetrathiafulvalene, dppz = dipyrro[3,2-a:2'a'-3'a''-c]phenazine, Aqphen = anthraquinone fused to phenanthroline via a pyrazine bridge) are described. In this molecular triad excitation into the metal-ligand charge transfer bands results in the creation of a long-lived charge separated state with TTF acting as electron donor and anthraquinone as terminal acceptor. The lifetime of the charge-separated state is 400 ns in dichloromethane at room temperature. A mechanism for the charge separation involving an intermediate charge-separated state is proposed based on transient absorption spectroscopy.



- **Low-Spin→High-Spin Relaxation Dynamics in the Highly Diluted Spin-Crossover System $[\text{Fe}_{0.98}\text{Zn}_{0.02}(\text{bbtr})_3](\text{ClO}_4)_2$**
Itana Krivokapic, Pradip Chakraborty, Cristian Enachescu, Robert Bronisz, and Andreas Hauser
Inorganic Chemistry **50** (5) (2011), p1856-1861 DOI:10.1021/ic102269y

Whereas the neat polymeric iron(II) compound $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$, $\text{bbtr} = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{butane}$, shows a quantitative spin transition triggered by a crystallographic phase transition centered at 107 K with a 13 K wide hysteresis, the iron(II) complexes in the diluted mixed crystals $[\text{Fe}_{1-x}\text{Zn}_x(\text{bbtr})_3](\text{ClO}_4)_2$, $x = 0.02$ and 0.1 , stay predominantly in the $^5\text{T}_2$ high-spin state down to cryogenic temperatures. However, the $^5\text{T}_2$ low-spin state can be populated as a metastable state via irradiation into the spin-allowed $^5\text{T}_2 \rightarrow ^5\text{E}_g$ ligand-field transition of the high-spin species in the near-infrared. The quantum efficiency of the light-induced conversion is approximately 10% at low temperatures and decreases rapidly above 160 K. The lifetime of the light-induced low-spin state decreases from 15 days at 40 K to 30 ns at 220 K, that is, by 14 orders of magnitude. In the high-temperature regime the activation energy for the low-spin \rightarrow high-spin relaxation is $1840(20) \text{ cm}^{-1}$.

- **Structural and vibrational properties of Ca_2FeH_6 and Sr_2RuH_6**

H. Hagemann, V. D'Anna, L.M. Lawson Daku, S. Gomes, G. Renaudin, and K. Yvon

Journal of Physics and Chemistry of Solids **72** (2011), p286-289

DOI:10.1016/j.jpcs.2011.01.001

Keywords: hydrogen storage materials • DFT calculations • lattice vibrations

The structural and vibrational properties of the isostructural compounds Ca_2FeH_6 and Sr_2RuH_6 are determined by periodic DFT calculations and compared with their previously published experimental crystal structures as well as new experimental vibrational data. The analysis of the vibrational data is extended to the whole series of alkaline-earth iron and ruthenium hydrides A_2TH_6 ($\text{A} = \text{Mg, Ca, Sr}$; $\text{T} = \text{Fe, Ru}$) in order to identify correlations between selected frequencies and the T-H bond length. The bulk moduli of Ca_2FeH_6 and Sr_2RuH_6 have also been determined within DFT. Their calculated values prove to compare well with the experimental values reported for Mg_2FeH_6 and several other compounds of this structure.

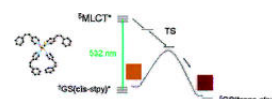
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- **Unidirectional Photoisomerization of Styrylpyridine for Switching the Magnetic Behavior of an Iron(II) Complex: A MLCT Pathway in Crystalline Solids**

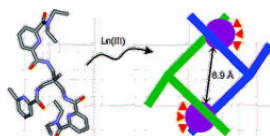
Antoine Tissot, Marie-Laure Boillot, Sébastien Pillet, Epiphane Codjovi, Kamel Boukheddaden, and Latévi Max Lawson Daku

Journal of Physical Chemistry C **114** (49) (2010), p21715-21722

DOI:10.1021/jp106583f



The photoreactivity of two iron(II)-styrylpyridine frameworks $\text{Fe}(\text{stpy})_2(\text{NCS})_2$ ($\text{stpy} = 4\text{-styrylpyridine}$) has been investigated for the very first time in a crystalline solid. A quantitative cis-to-trans isomerization of stilbenoids is shown to occur in the confined environment of the inorganic solid. The photochromic reaction was driven by a visible excitation into the metal-to-ligand charge transfer absorption of the high-spin all-cis complex. The solid-state transformation is accompanied by a unit-cell volume increase and an amorphization. Interestingly, the photoproduct formed by irradiating the high-spin all-cis reactant undergoes a spin conversion when the temperature is decreased. This observation is related to the ligand-driven light-induced spin change effect in a constrained environment.



- **Unsymmetrical Tripodal Ligand for Lanthanide Complexation: Structural, Thermodynamic, and Photophysical Studies**

Badr El Aroussi, Nathalie Dupont, Gérald Bernardinelli and Josef Hamacek

Inorganic Chemistry **49** (2) (2010), p606-615

DOI:10.1021/ic901757u

Two tridentate and one bidentate binding strands have been anchored on a carbon atom to provide a new unsymmetrical tripodal ligand **L** for Ln(III) coordination. The ligand itself adopts a single conformation in solution stabilized by intramolecular hydrogen bonds evidenced in the solid state. The reaction of **L** with trivalent lanthanides provides different coordination complexes depending on the metal/ligand ratio. The speciation studies with selected lanthanides were performed in solution by means of NMR, ESMS, and spectrophotometric titrations. Differences in coordination properties along the lanthanide series were evidenced and may be associated with the changes in the ionic size. However, thermodynamic stability constants for the species of the same stoichiometry do not significantly vary. In addition, the structure of the dinuclear complex $[\text{Eu}_2\text{L}_2]^{6+}$ has been elucidated in the solid state, where the complex crystallizes predominantly as an M-isomer. The crystal structure shows the coordination of two different ligands to each europium cation through tridentate strands, and the europium nine-coordinate sphere is completed with three solvent molecules. Finally, the results of photophysical investigations of $[\text{Eu}_2\text{L}_2]^{6+}$ are in close agreement with the structural parameters determined by crystallography.

- **Significant variation of the singlet-quintet intersystem crossing rate constant in an iron(II) high-spin complex as a function of temperature**

Itana Krivokapic, Pradip Chakraborty, Robert Bronisz, Cristian Enachescu and Andreas Hauser

Angewandte Chemie **49** (45) (2010), p8509-8512

DOI:10.1002/anie.201004500

In the dilute mixed-crystal system $[\text{Zn}_{1-x}\text{Fe}_x(\text{bbtr})_3](\text{ClO}_4)_2$, $x = 2\%$ ($\text{bbtr} = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{butane}$), the iron(II) centers are predominantly in the high-spin state. The low-spin state can be populated as a metastable state by irradiation with near-IR light; the rate constant of the low-spin \rightarrow high-spin relaxation spans 14 orders of magnitude between 40 and 220 K

- **Competition Between Photo-Excitation and Relaxation in Spin Crossover Complexes in The Frame of a Mechano-Elastic Model**

C. Enachescu, L. Stoleriu, A. Stancu, A. Hauser

Physical Review B **82** (2010), p104114

DOI:10.1103/PhysRevB.82.104114

In this paper we use a recently proposed elastic model in order to study the competition between linear photoexcitation and cooperative relaxation in spin-crossover molecular magnets. The difference in molecular size between the two possible spin states, that is, the high-spin and the low-spin states, respectively, induces distortions of the crystal lattice. These determine the elastic interactions between molecules, treated here as connecting springs that are either compressed or extended from their equilibrium length, thus modulating the local probability for the high-spin \rightarrow low-spin relaxation. The crossover of individual molecules within the lattice is checked by a standard Monte Carlo procedure. Using very simple assumptions and a minimum number of parameters, photoexcitation curves and hysteresis loops under continuous irradiation below the thermal transition temperature can thus be simulated. The formation of clusters is analyzed and the presence of inhomogeneities in the system is investigated.

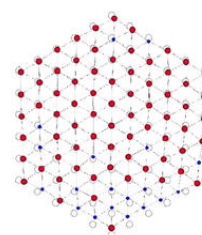
- **Cluster evolution in spin crossover systems observed in the frame of a mechano-elastic model**

C. Enachescu, M. Nishino, S. Miyashita, L. Stoleriu, A. Stancu, A. Hauser

Europhysics Letters **91** (2) (2010), p27003

DOI:10.1209/0295-5075/91/27003

Keywords: Spin crossover • general studies of phase transitions • domain effects • magnetization curves • hysteresis

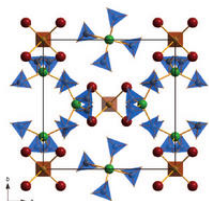


In this paper we study the cluster formation and evolution in spin crossover systems during the thermal transition in the frame of a mechano-elastic model applied to open boundary hexagonal lattices. The switching processes between the high-spin (HS) and low-spin

(LS) state are studied by a method combining a Monte Carlo standard procedure on the spin state and the lattice relaxation. In the present study, we adopt the transition probabilities of the spin state taking into account the energy gap between the two states, the degeneracy ratio and the local pressure determined by the elongations of the closest springs. It is found that clusters of molecules in the same state tend to grow starting from corners, as in available experimental data. Some qualitative differences between the processes of cluster formation for the two hysteresis branches, i.e., HS to LS and LS to HS are pointed out. Moreover, we have studied the dependence of cluster formation on the strength of the elastic interactions, and also on the system size. The size dependence of the ratio between the system size and the maximum cluster length is very weak, which indicates the appearance of macroscopic domains.

- **Effect of External Pressure on the Excitation Energy Transfer from $[\text{Cr}(\text{ox})_3]^{3+}$ to $[\text{Cr}(\text{bpy})_3]^{3+}$ in $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$**
Mia Milos, Prodipta Pal, and Andreas Hauser
ChemPhysChem **11** (14) (2010), p3161-3166 DOI:10.1002/cphc.201000324
Keywords: $[\text{Cr}(\text{bpy})_3]^{3+}$ • $[\text{Cr}(\text{ox})_3]^{3+}$ • 3D oxalate networks • excitation energy transfer • high pressures

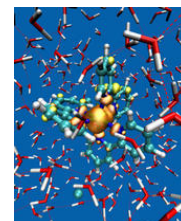
Resonant excitation energy transfer from $[\text{Cr}(\text{ox})_3]^{3+}$ to $[\text{Cr}(\text{bpy})_3]^{3+}$ in the doped 3D oxalate networks $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}^{III}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$ ($\text{ox}=\text{C}_2\text{O}_4$, $\text{bpy}=2,2'\text{-bipyridine}$, $\text{M}=\text{Al}, \text{Rh}$) is due to two types of interaction, namely super exchange coupling and electric dipole-dipole interaction. The energy transfer probability for both mechanisms is proportional to the spectral overlap of the ${}^4\text{E}_g \leftarrow {}^6\text{A}_1$ emission of the $[\text{Cr}(\text{ox})_3]^{3+}$ donor and the ${}^4\text{A}_g \leftarrow {}^2\text{T}_1$ absorption of the $[\text{Cr}(\text{bpy})_3]^{3+}$ acceptor. The spin-flip transitions of (pseudo-)octahedral Cr^{3+} are known to shift to lower energy with increasing pressure. Because the shift rates of the two transitions in question differ, the spectral overlap between the donor emission and the acceptor absorption is a function of applied pressure. For $[\text{Rh}_{1-x}\text{Cr}_x(\text{bpy})_3][\text{NaM}_{1-y}\text{Cr}_y(\text{ox})_3]\text{ClO}_4$ the spectral overlap is thus substantially reduced on increasing pressure from 0 to 2.5 GPa. As a result, the energy transfer probability decreases with increasing pressure as evidenced by a decrease in the relative emission intensity from the $[\text{Cr}(\text{bpy})_3]^{3+}$ acceptor.



- **$\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$: A Complex Double-Cation Borohydride with a New Structure**
Inge Lindemann, Roger Domènech Ferrer, Lothar Dunsch, Yaroslav Filinchuk, Radovan Cerný, Hans Hagemann, Vincenza D'Anna, Latévi Max Lawson Daku, Ludwig Schultz, Oliver Gutfleisch
Chemistry - A European Journal **16** (2010), p8707-8712 DOI:10.1002/chem.201000831
Keywords: borohydrides • density functional calculations • hydrogen storage • metathesis • X-ray diffraction

The new double-cation Al-Li-borohydride is an attractive candidate material for hydrogen storage due to a very low hydrogen desorption temperature ($\sim 70^\circ\text{C}$) combined with a high hydrogen density (17.2 wt %). It was synthesised by high-energy ball milling of AlCl_3 and LiBH_4 . The structure of the compound was determined from image-plate synchrotron powder diffraction supported by DFT calculations. The material shows a unique 3D framework structure within the borohydrides (space group = $P-43n$, $a = 11.3640(3) \text{ \AA}$). The unexpected composition $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$ can be rationalized on the basis of a complex cation $[\text{BH}_4\text{Li}_4]^{3+}$ and a complex anion $[\text{Al}(\text{BH}_4)_4]^-$. The refinements from synchrotron powder diffraction of different samples revealed the presence of limited amounts of chloride ions replacing the borohydride on one site. In situ Raman spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TG) and thermal desorption measurements were used to study the decomposition pathway of the compound. Al-Li-borohydride decomposes at $\sim 70^\circ\text{C}$, forming LiBH_4 . The high mass loss of about 20% during the decomposition indicates the release of not only hydrogen but also diborane.

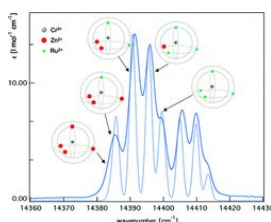
- **Ab Initio Molecular Dynamics Study of an Aqueous Solution of $[\text{Fe}(\text{bpy})_3]^{2+}$ in the Low-Spin and in the High-Spin States**
Latévi Max Lawson Daku and Andreas Hauser
Journal of Physical Chemistry Letters **1** (2010), p1830-1835 DOI:10.1021/jz100548m



The mechanism of the photoinduced low-spin \rightarrow high-spin spin crossover is actively being investigated in Fe(II) complexes in solution using ultrafast spectroscopies. These studies accurately inform on the reaction coordinate of the Fe(II) chromophore upon photoexcitation. However, they leave open questions regarding the role of the solvent. Here, we report the description from a fully ab initio molecular dynamics study of the structure of $[\text{Fe}(\text{bpy})_3]^{2+}$ in water and of the organization of its solvation shell in the low-spin and the high-spin states. In particular, the low-spin \rightarrow high-spin change of states is shown to be accompanied (i) by a 0.191 \AA lengthening of the $\text{Fe}\cdots\text{N}$ bond, in agreement with experiment, and (ii) by an increased thermal fluctuation of the molecular edifice, which both result from the weakening of the $\text{Fe}\cdots\text{N}$ bond. Furthermore, our results suggest that about two water molecules are expelled from the first solvation shell of $[\text{Fe}(\text{bpy})_3]^{2+}$, which consists of water molecules intercalated between the bpy ligands.

- **Persistent Spectral Hole-Burning in the R_1 Line of Cr^{3+} -Doped $\text{NaMg}[\text{Al}(\text{oxalate})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$ Induced by Resonant Energy Transfer**
Mia Milos, Andreas Hauser
Journal of Physical Chemistry A **114** (12) (2010), p4169-4172 DOI:10.1021/jp9120832

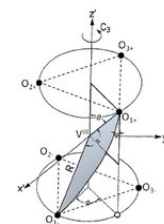
In the 3D network $[\text{Rh}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]\text{ClO}_4$ ($\text{ox} = \text{oxalate}$, $\text{bpy} = 2,2'\text{-bipyridine}$) phonon-assisted as well as resonant energy migration within the R_1 line of the ${}^4\text{A}_g \leftarrow {}^2\text{E}$ transition of Cr^{3+} has been identified. The latter is dominant below 4.2 K, and in a fluorescence line narrowing spectrum, it manifests itself in a multiline pattern across the inhomogeneous line width with spacings corresponding to the zero-field splitting of the ${}^4\text{A}_g$ ground state (Milos, M.; Kairouani, S.; Rabaste, S.; Hauser, A. *Coord. Chem. Rev.* **2008**, 252, 2540). H. Riesen demonstrated efficient spectral hole burning within the R_1 line of Cr^{3+} doped at low concentrations into partially deuterated $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$ (Riesen, H. *Coord. Chem. Rev.* **2006**, 250, 1737). Here we show that at higher Cr^{3+} concentrations in the same host, both phenomena can be observed simultaneously, the resonant energy migration thus creating an additional series of persistent side holes.



- **Structural Study of Mixed Crystals of $[\text{Zn}_{1-x}\text{Ru}_x(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$ Probed by High-Resolution Absorption Spectroscopy and High-Pressure Experiments**
Mia Milos, Tiphaine Penhouet, Prodipta Pal, Andreas Hauser
Inorganic Chemistry **49** (7) (2010), p3402-3408 DOI:10.1021/ic902514w

In the mixed crystal series of the cubic three-dimensional networks of composition $[\text{Zn}_{1-x}\text{Ru}_x(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$ ($0 \leq x \leq 1$, $\text{ox} = \text{C}_2\text{O}_4^{2-}$, $\text{bpy} = 2,2'\text{-bipyridine}$), high-resolution absorption spectroscopy in the region of the ${}^4\text{A}_g \leftarrow {}^2\text{E}$ transition (R-lines) reveals the creation of five specific spectroscopic sites for the $[\text{Cr}(\text{ox})_3]^{3+}$ complex. The concentration of these spectroscopic sites follows a binomial distribution of $[\text{Zn}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ among the four nearest neighbors of a given $[\text{Cr}(\text{ox})_3]^{3+}$ complex within the network. The tris-bipyridine complexes occupying those positions have an optimal $\text{Fe}\cdots\text{F}$ interaction with the oxalate ligands of the tris-oxalate chromophore. The energy of each spectroscopic $[\text{Cr}(\text{ox})_3]^{3+}$ site depends on the total concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the mixed crystal and on its specific

distribution among the four nearest neighbors. Single crystal X-ray diffraction indicates a reduction of the unit cell volume when $[\text{Zn}(\text{bpy})_3]^{2+}$ ($a = 15.6365(18) \text{ \AA}$) is substituted by $[\text{Ru}(\text{bpy})_3]^{2+}$ ($a = 15.5098(6) \text{ \AA}$). This alone would lead to a red-shift of the R lines in analogy to the red-shift of $25.2 \text{ cm}^{-1}/\text{GPa}$ due to the decrease of the metal ligand $\text{Cr} \cdots \text{O}$ bond length as observed in high-pressure luminescence experiments. However, specific $\text{I} \cdots \text{I}$ interactions with the nearest neighbors have the opposite effect and shift the transition in discrete jumps to higher energies with increasing $[\text{Ru}(\text{bpy})_3]^{2+}$ mole fraction.



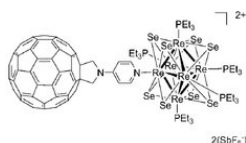
• *Electronic Structure and Photophysics of Pseudo-Octahedral Vanadium(III) Oxo Complexes*

Kevin R. Kittilstved and Andreas Hauser

Coordination Chemistry Reviews **254** (21-22) (2010), p2663-2676

DOI:10.1016/j.ccr.2010.02.021

The electronic structure and the photophysical properties of the vanadium(III) ion in pseudo-octahedral oxygen coordination is reviewed. V^{3+} has received much interest from spectroscopists in recent years due to the advancement of state-of-the-art experimental techniques such as inelastic neutron scattering and high-field electron paramagnetic resonance spectroscopy that directly interrogate its large ground state zero-field splittings (ZFSs) and to rational parameterization of the ligand field parameters using the angular overlap model. However, for V^{3+} these ZFSs can be large enough to also be probed directly by high-resolution electronic absorption spectroscopy of intra-configurational ($t_{2g}^2 \rightarrow t_{2g}^1 e_g^1$) spin-forbidden transitions in the near-IR and visible regions. The luminescent properties of V^{3+} with hexa-oxo and tris-bidentate di-oxo-coordination are quite disappointing compared to its neighbor in the periodic table, Cr^{3+} , in similar environments. The efficient non-radiative pathways in these compounds are reviewed and compared to recent work on V^{3+} doped into $\text{NaMgAl}(\text{ox})_3 \cdot 9\text{H}_2\text{O}$. The poor luminescence quantum efficiencies of V^{3+} oxo complexes is explained by strong coupling of multi-phonon processes with a dynamic Jahn-Teller distortion originating from the 3E trigonal component of the $^3T_{1g}$ ground state.



• *An Electrochemical and Photophysical Study of a Covalently Linked Inorganic-Organic Dyad*

Axel Kahnt, Leo-Philipp Heiniger, Shi-Xia Liu, Xiaoyan Tu, Zhiping Zheng, Andreas Hauser, Silvio Decurtins, Dirk M. Guldi

ChemPhysChem **11** (2010), p651-658

DOI:10.1002/cphc.200900728

Keywords: cluster compounds • cyclic voltammetry • energy transfer • fullerenes • radiation chemistry

A molecular donor-acceptor dyad comprising a hexarhenium cluster core, $[\text{Re}_6(\text{I}_{1/2}\text{Se})_6]^{2+}$, and a fullerene moiety which are covalently linked through a pyridine ligand was synthesized and fully characterized. The electrochemical and photophysical properties are reported. The detailed study includes cyclic voltammetry, steady-state absorption and fluorescence spectroscopy, radiation chemistry and transient absorption spectroscopy. A light-induced electron transfer between the inorganic cluster moiety and the fullerene can be excluded. However, a light-induced energy transfer from the rhenium cluster to the fullerene is proposed.

2009

• *Time-resolved x-ray absorption spectroscopy: Watching atoms dance*

Chris J Milne, Van-Thai Pham, Wojciech Gawelda, Renske M van der Veen, Amal El Nahhas, Steven L Johnson, Paul Beaud, Gerhard Ingold, Frederico Lima, Dimali A Vithanage, Maurizio Benfatto, Daniel Grolimund, Camelia Borca, Maik Kaiser, Andreas Hauser, Rafael Abela, Christian Bressler and Majed Chergui

Journal of Physics: Conference Series **190** (2009), p12052

DOI:10.1088/1742-6596/190/1/012052

The introduction of pump-probe techniques to the field of x-ray absorption spectroscopy (XAS) has allowed the monitoring of both structural and electronic dynamics of disordered systems in the condensed phase with unprecedented accuracy, both in time and in space. We present results on the electronically excited high-spin state structure of an $\text{Fe}(\text{II})$ molecular species, $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$, in aqueous solution, resolving the Fe-N bond distance elongation as 0.2 \AA . In addition an analysis technique using the reduced χ^2 goodness of fit between FEFF EXAFS simulations and the experimental transient absorption signal in energy space has been successfully tested as a function of excited state population and chemical shift, demonstrating its applicability in situations where the fractional excited state population cannot be determined through other measurements. Finally by using a novel ultrafast hard x-ray 'slicing' source the question of how the molecule relaxes after optical excitation has been successfully resolved using femtosecond XANES.

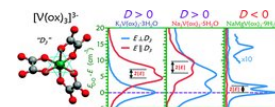
• *Ground-State Electronic Structure of Vanadium(III) Trisoxalate in Hydrated Compounds*

Kevin R. Kittilstved, Lilit Aboshyan Sorgho, Nahid Amstutz, Philip L.W. Tregenna-Piggott and Andreas Hauser

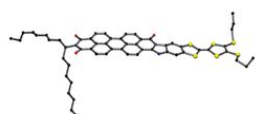
Inorganic Chemistry **48** (16) (2009), p7750-7764

DOI:10.1021/ic900613p

Keywords: high-resolution spectroscopy • zero-field splittings • anisotropic ligand fields • hydrogen bonding



The ground-state electronic structures of $\text{K}_3\text{V}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$, $\text{Na}_3\text{V}(\text{ox})_3 \cdot 5\text{H}_2\text{O}$, and $\text{NaMgAl}_{1-x}\text{V}_x(\text{ox})_3 \cdot 9\text{H}_2\text{O}$ ($0 < x \leq 1$, $\text{ox} = \text{C}_2\text{O}_4^{2-}$) have been studied by Fourier transform electronic absorption and inelastic neutron scattering spectroscopies. High-resolution absorption spectra of the $^3T_1(t_{2g}^2) \rightarrow ^3T_2(t_{2g}^2)$ spin-forbidden electronic origins and inelastic neutron scattering measurements of the pseudo-octahedral $[\text{V}(\text{ox})_3]^{3-}$ complex anion below 30 K exhibit both axial and rhombic components to the zero-field-splittings (ZFSs). Analysis of the ground-state ZFS using the conventional $S = 1$ spin Hamiltonian reveals that the axial ZFS component changes sign from positive values for $\text{K}_3\text{V}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$ ($D_{\text{ax}} = +5.3 \text{ cm}^{-1}$) and $\text{Na}_3\text{V}(\text{ox})_3 \cdot 5\text{H}_2\text{O}$ ($D_{\text{ax}} = +7.2 \text{ cm}^{-1}$) to negative values for $\text{NaMgAl}_{1-x}\text{V}_x(\text{ox})_3 \cdot 9\text{H}_2\text{O}$ ($D_{\text{ax}} = -9.8 \text{ cm}^{-1}$ for $x = 0.013$, and $D_{\text{ax}} = -12.7 \text{ cm}^{-1}$ for $x = 1$) with an additional rhombic component, $|E|$, that varies between 0.8 and 2 cm^{-1} . On the basis of existing crystallographic data, this phenomenon can be identified as due to variations in the axial and rhombic ligand fields resulting from outer-sphere H-bonding between crystalline water molecules and the oxalate ligands. Spectroscopic evidence of a crystallographic phase change is also observed for $\text{K}_3\text{V}(\text{ox})_3 \cdot 3\text{Y}_2\text{O}$ ($\text{Y} = \text{H or D}$) with three distinct lattice sites below 30 K, each with a unique ground-state electronic structure.



• *A Compactly Fused π -Conjugated Tetrathiafulvalene-Perylene diimide Donor-Acceptor Dyad*

Michael Jaggi, Carmen Blum, Nathalie Dupont, Jakob Grilj, Shi-Xia Liu, Jürg Hauser, Andreas Hauser and Silvio Decurtins

Organic Letters **11** (14) (2009), p3096-3099

DOI:10.1021/ol901186n

The synthesis and structural characterization of a tetrathiafulvalene-fused perylene diimide molecular dyad is presented. Its largely extended π -conjugation provides intense optical absorption bands over a wide spectral range. The planar functional molecule exhibits a short-lived nonluminescent excited state attributed to intramolecular charge separation.

- **Model for Elastic Relaxation Phenomena in Finite 2D Hexagonal Molecular Lattices**

Cristian Enachescu, Laurentiu Stoleriu, Alexandru Stancu and Andreas Hauser

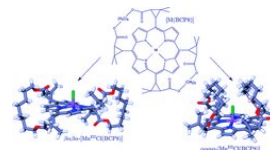
Physical Review Letters **102** (25) (2009), p257204 DOI:10.1103/PhysRevLett.102.257204

The relaxation in a spin transition compound is modeled on the basis of molecules interacting by the way of connecting springs and situated in a bidimensional open boundary hexagonal lattice. The switch of individual molecules is randomly checked using a standard Monte Carlo procedure. The switching probability depends on the energy gap between the two states in the absence of interactions and on the elongations of the nearest springs. The main characteristics of the experimental relaxation curves are reproduced and clustering and nucleation phenomena are detected.

- **Density-Functional Theory Study of the Stereochemistry of Chloroiron(III) and Chloromanganese(III) Complexes of a Bridled Chirophyrin**

Latévi Max Lawson Daku, Anna Castaings and Jean-Claude Marchon

Inorganic Chemistry **48** (12) (2009), p5164-5176 DOI:10.1021/ic900031c



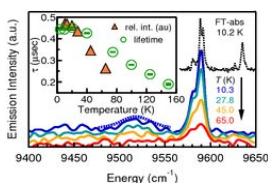
Transition metal complexes of chirophyrins, in which two adjacent meso substituents are linked by a strap of eight methylene groups, [M(BCP8)], can exist as either an $\pm\pm\pm\pm\pm\pm$ or $\pm\pm\pm\pm\pm^2$ atropisomer depending on the nature of the coordinated metal cation. This remarkable conformational versatility was investigated by density-functional theory calculations for the d^5 chloroiron(III) complex in the low-spin and high-spin states and for the d^4 high-spin chloromanganese(III) complex. The lowest-lying electronic state of all of the conformers of the chloroiron(III) bridled chirophyrin is found to be the high-spin state. For the chloroiron(III) complex in the low-spin or the high-spin state and for the high-spin chloromanganese(III) complex, the most stable form is predicted to be the $\pm\pm\pm\pm\pm\pm$ conformer in which the chloride axial ligand is located within the cavity provided by the bridles. The predicted stereochemistries are compared with those similarly obtained (i) for the chloroiron(III) and chloromanganese(III) complexes of tetramethylchirophyrin, which is devoid of straps, and (ii) for the d^{10} zinc(II) and low-spin d^8 nickel(II) BCP8 complexes, on the basis of the effects tied to the occupancy of the stereochemically active $d_{x^2-y^2}$ -type antibonding orbital level, to the restraints imposed by the straps, and to the presence of the axial chloride ligand.

- **A model for spectral diffusion induced by resonant energy migration applied to the $^4A_2 \rightarrow ^2E$ transition of Cr^{3+} in $[Cr(ox)_3]^{3-}$ ($ox = C_2O_4^{2-}$)**

Mia Milos, Andreas Hauser

Journal of Luminescence **129** (12) (2009), p1901-1904 DOI:10.1016/j.jlumin.2009.04.093

In the 3D oxalate networks $[NaCr(ox)_3][Rh(bpy)_3]ClO_4$ and $[NaCr(ox)_3][Ru(bpy)_3]$ ($ox = oxalate$, $bpy = 2,2'$ -bipyridine) three different types of energy migration within the $^4A_2 \rightarrow ^2E$ transition can be identified. One is a resonant process between spectral members spaced by the ground-state zero-field splitting (ZFS). This leads to the sequential appearance of additional sharp lines spaced by the ground-state ZFS in the fluorescence line narrowing spectrum across the inhomogeneous line. The second one is a quasi-resonant process between spectral neighbours and manifests itself by rapid spectral diffusion. The third one is the well-known phonon-assisted process setting in at higher temperature.



- **Electronic structure of V^{3+} in $NaMgAl(ox)_3 \cdot 9H_2O$ probed by Fourier transform spectroscopy**

Kevin R. Kittilstved and Andreas Hauser

Journal of Luminescence **129** (12) (2009), p1493-1496 DOI:10.1016/j.jlumin.2009.02.021

Keywords: Vanadium trisoxalate • V^{3+} electronic structure • Fourier transform spectroscopy • Near-IR luminescence

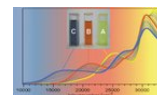
High-resolution Fourier transform absorption and luminescence spectroscopy reveal axial and rhombic zero-field splittings of the spin-forbidden electronic origins of V^{3+} in $NaMgAl(ox)_3 \cdot 9H_2O$ ($ox = oxalate$) single crystals below 25 K. The temperature dependence of the integrated absorption of the split features display behavior consistent with a Boltzmann distribution within the zero-field split 3A_2 ground state of V^{3+} . Weak luminescence is observed in the near-IR from the lowest energy spin-forbidden transition with a luminescence lifetime of less than 0.5 ns at 11 K and an estimated quantum efficiency of the order of 10^{-5} .

- **Imidazole-Annulated Tetrathiafulvalenes exhibiting pH-Tuneable Intramolecular Charge Transfer and Redox Properties**

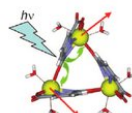
Jincai Wu, Nathalie Dupont, Shi-Xia Liu, Antonia Neels, Andreas Hauser, Silvio Decurtins

Chemistry - An Asian Journal **4** (3) (2009), p392-399 DOI:10.1002/asia.200800322

Keywords: charge transfer • donor-acceptor systems



In order to study the electronic interactions in donor-acceptor ensembles as a function of pH, an efficient synthetic route to three imidazole-annulated tetrathiafulvalene (TTF) derivatives 1-3 is reported. Their electronic absorption spectra, in view of photoinduced intramolecular charge transfer, and their electrochemical behavior were investigated, and pKa values for the two protonation processes on the acceptor unit were determined in organic solvents by photometric titration. The influence of the TTF moiety on these values is discussed.



- **Self-Assembly of a Trinuclear Luminescent Europium Complex**

Soumaila Zebret, Nathalie Dupont, Gérald Bernardinelli, Josef Hamacek

Chemistry - A European Journal **15** (14) (2009), p3355-3358 DOI:10.1002/chem.200802676

Keywords: europium • luminescence • self-assembly • supramolecular chemistry • trinuclear complexes

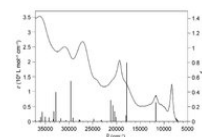
Triangular luminescent box: Self-assembly of a new multidentate receptor with europium cations results in the formation of trinuclear discrete complexes. X-ray crystallography shows that nine-coordinate cations are linked by ligands to provide a triangular complex in the solid state and in solution. Despite the coordinated solvent molecules, this topologically unusual complex exhibits remarkable luminescent properties.

- **Pronounced Electrochemical Amphoterism of a Fused Donor-Acceptor Compound: A Planar Merge of TTF with a TCNQ-Type Bithienoquinoxaline**

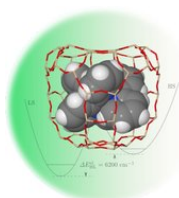
Xavier Guégano, Alexander L. Kanibolotsky, Carmen Blum, Stijn F. L. Mertens, Shi-Xia Liu, Antonia Neels, Hans

Hagemann, Peter J. Skabara, Samuel Leutwyler, Thomas Wandlowski, Andreas Hauser and Silvio Decurtins

Chemistry - A European Journal **15** (1) (2009), p63-66 DOI:10.1002/chem.200802011



Electronic absorption spectrum of 1 in DMF solution at room temperature, together with the calculated oscillator strengths.



- **Influence of Guest-Host Interactions on the Structural, Energetic, and Mössbauer Spectroscopy Properties of Iron(II)tris(2,2'-bipyridine) in the Low-Spin and High-Spin States: A Density-Functional Theory Study of the Zeolite-Y Embedded Complex**

Alfredo Vargas, Andreas Hauser and Latévi Max Lawson Daku

Journal of Chemical Theory and Computation **5** (1) (2009), p97-115

DOI:10.1021/ct800284g

Density functional theory is applied within a supramolecular approach to the study of the guest-host interactions in $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$ and their influence on the structural, energetic, and ^{57}Fe Mössbauer spectroscopy properties of the encapsulated $[\text{Fe}(\text{bpy})_3]^{2+}$ complex in the low- and high-spin states. The structures of the isolated complex and the supramolecular model used for $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$ were optimized in both spin-states using different generalized gradient approximation (PBE, HCTH, OLYP) and hybrid (B3LYP*, O3LYP) functionals. The results obtained are consistent with one another and show that, in either spin-state, the structure of $[\text{Fe}(\text{bpy})_3]^{2+}$ shrinks and distorts upon encapsulation. Still, the structural changes experienced by the complex in a given spin-state remain limited, especially in that they do not lead to a substantial variation of the ^{57}Fe quadrupole splitting, whose calculated values are in very good agreement with available experimental data. The decomposition of the guest-host interaction energy into its electrostatic, Pauli and orbital contributions shows that the bonding between the complex and the supercage is more electrostatic than covalent. The ability of modern functionals to accurately describe the interactions explains the remarkable consistency of the results obtained with the various functionals. In particular, although the functionals perform very differently for the determination of the high-spin/low-spin energy difference $^1E_{\text{H-L}}$ in $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$, they consistently predict that the encapsulation entails a destabilization of the high-spin state with regard to the low-spin state of $^1E_{\text{H-L}} = 2500 \text{ cm}^{-1}$. Using for $[\text{Fe}(\text{bpy})_3]^{2+}$ the CASPT2 value of $^1E_{\text{H-L}} = 3700 \text{ cm}^{-1}$ [Pierloot, K.; Vancoillie, S.J. Chem. Phys. 2006, 125, 124303; Pierloot, K.; Vancoillie, S.J. Chem. Phys. 2008, 128, 034104], we obtain for the high-spin/low-spin energy difference in $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$, a best ab initio estimate of $^1E_{\text{H-L}} = 6200 \text{ cm}^{-1}$.

- **Spin-transition in nearly cubic site in $[\text{Fe}^{\text{II}}(\text{L})_3][\text{PF}_6]_2$**

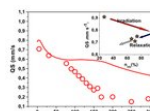
Vibha Mishra, Rabindranath Mukherjee, Jorge Linares, Epiphane Codjovi, François Varret and Latévi Max Lawson Daku

Hyperfine Interactions **188** (1-3) (2009), p71-78

DOI:10.1007/s10751-008-9891-6

Keywords: spin-transition • ^{57}Fe Mössbauer spectroscopy • iron(II) complex • ligand-field • density functional theory

The spin-transition ($^1A_1 \rightarrow ^5T_2$) behaviour of a new mononuclear iron(II) compound $[\text{Fe}^{\text{II}}(\text{L})_3][\text{PF}_6]_2$ ($\text{L} = 2\text{-[3-(2\text{-}\pi\text{-pyridyl})\text{pyrazole-1-ylmethyl}]\text{pyridine}}$) has been investigated by ^{57}Fe Mössbauer spectroscopy. Analysis of the Mössbauer spectra revealed low value of the quadrupole splitting of the high-spin state which reflects iron(II) to be in nearly cubic lattice site. Mössbauer spectra under light show the light-induced excited spin state trapping effect and the observed quadrupole splitting of the metastable high-spin state is found little sensitive to the high-spin fraction value. DFT calculations are in progress to document the almost cubic nature of the ligand-field acting on the iron atom.



2008

- **What governs nitrogen configuration in substituted aminophosphines?**

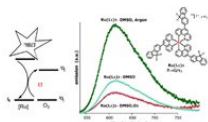
Matthew D. Wodrich, Alfredo Vargas, Pierre-Yves Morgantini, Gabriel Merino, Clémence Corminboeuf

Journal of Physical Organic Chemistry **22** (2) (2008), p101-109

DOI:10.1002/poc.1431

Keywords: stereoelectronic effects • electron delocalization • hyperconjugation • density functional theory

The trigonal planar geometry of the nitrogen atom in commonly used phosphoramidite ligands is not in line with the traditional valence shell electron pair repulsion (VSEPR) model. In this work, the effects governing nitrogen configuration in several substituted aminophosphines, A_2PNB_2 ($\text{A} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{Me}, \text{OMe}, \text{BINOP}$), are examined using modern computational analytic tools. The electron delocalization descriptions provided by both electron localization function (ELF) and block localized wavefunction analysis support the proposed relationships between conformation and negative hyperconjugative interactions. In the parent H_2PNH_2 , the pyramidal nitrogen configuration results from nitrogen lone pair electron donation into the $\sigma^*_{\text{P-H}}$ orbital. While enhanced effects are seen for F_2PNMe_2 , placing highly electronegative fluorine substituents on nitrogen (i.e., Me_2PNF_2) eliminates delocalization of the nitrogen lone pair. Understanding and quantifying these effects can lead to greater flexibility in designing new catalysts.



- **$^3\text{MLCT}$ excited states in Ru(II) complexes: Reactivity and related two-photon absorption applications in the near-infrared spectral range**

Gilles Lemerrier, Adeline Bonne, Mickaël Four and Latévi M. Lawson Daku

Comptes Rendus Chimie **11** (6-7) (2008), p709-715

DOI:10.1016/j.crci.2007.11.012

Keywords: Ruthenium(II) complexes • Polypyridyl ligands • Two-photon absorption • $^3\text{MLCT}$ • Dioxygen sensors • Photodynamic therapy

The synthesis and characterization of new 1,10-phenanthroline-based chromophores LT1, LT2 and LD1 featuring fluorene unit(s) are reported. Their absorption and emission as well as their two-photon absorption properties in the $450\text{--}650 \text{ nm}$ spectral range are discussed in comparison with the parent 1,10-phenanthroline and already described ligands L1 and L2.

- **Ruthenium(II) Coordination Chemistry of a Fused Donor-Acceptor Ligand: Synthesis, Characterization and Photoinduced Electron Transfer Reactions of $[\{\text{Ru}(\text{bpy})_2(\text{TTF-pbp})\}](\text{PF}_6)_2$ ($n = 1, 2$)**

Christine Goze, Nathalie Dupont, Elvira Beitler, Claudia Leiggner, Hongpeng Jia, Philippe Monbaron, Shi-Xia Liu,

Antonia Neels, Andreas Hauser and Silvio Decurtins

Inorganic Chemistry **47** (23) (2008), p11010-11017

DOI:10.1021/ic801252t

A π -extended, redox-active bridging ligand $4,4'$ -bis(propylthio)tetrathiafulvenyl[dipyrido[2,3- a :3',2'- c]phenazine (L) was prepared via direct Schiff-base condensation of the corresponding diamine-tetrathiafulvalene (TTF) precursor with 4,7-phenanthroline-5,6-dione. Reactions of L with $[\text{Ru}(\text{bpy})_3]^{2+}$ afforded its stable mono- and dinuclear ruthenium(II) complexes **1** and **2**. They have been fully characterized, and their photophysical and electrochemical properties are reported together with those of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{ppb})]^{2+}$ ($\text{ppb} = \text{dipyrido[2,3- a :3',2'- c]phenazine}$) for comparison. In all cases, the first excited state corresponds to an intramolecular TTF \rightarrow ppb charge-transfer state. Both ruthenium(II) complexes show two strong and well-separated metal-to-ligand charge-transfer (MLCT) absorption bands, whereas the $^3\text{MLCT}$ luminescence is strongly quenched via electron transfer from the TTF subunit. Clearly, the transient absorption spectra illustrate the role of the TTF fragment as an electron donor, which induces a triplet intraligand charge-transfer state ($^3\text{ILCT}$) with lifetimes of approximately 200 and 50 ns for mono- and dinuclear ruthenium(II) complexes, respectively.



- **Towards inert and pre-organized d-block-containing receptors for trivalent lanthanides: The synthesis and characterization of triple-helical monometallic OsII and bimetallic OsII-LnIII complexes**

Thomas Riis-Johannessen, Nathalie Dupont, Gabriel Canard, Gérald Bernardinelli, Andreas Hauser and Claude Piguet

Dalton Transactions **28** (2008), p3661-3677

DOI:10.1039/b718885d

The mononuclear Os^{II} complex [Os(L1)₃](PF₆)₂ (L1 = 5-methyl(1-methylbenzimidazol-2-yl)pyridine) is an obvious candidate for the design of an inert d-block-based tripodal receptor capable of binding and photosensitizing trivalent lanthanides (Ln^{III}). It has thus been prepared and its two enantiomeric meridional (*l*^{mer} and *l*^{mer}) and facial (*rac-fac*) isomers have been separated by ion-exchange chromatography. The optical isomers have been characterized by CD spectroscopy and assignments of absolute configuration confirmed by an X-ray crystallographic study of *l*^{mer}-[Os(L1)₃](PF₆)₂·1.5MeCN (monoclinic, *P*2₁, *Z* = 4). Comparison of the latter structure with that of *racemic-fac*-[Os(L1)₃](PF₆)₂ (monoclinic, *C*2/c, *Z* = 8) and [Os(bipy)₃](PF₆)₂ (where bipy = 2,2'-bipyridine) shows minimal structural variations, but differences are observed in the photophysical and electrochemical properties of the respective compounds. Luminescence emissions from Os^{II} complexes of L1 are typically lower in energy, with shorter lifetimes and lower quantum yields than their bipy analogues, whilst metal-centred oxidation processes are more facile due to the enhanced I⁺-donor ability of L1. The key relationships between these parameters are discussed. Finally, though challenged by (i) the low reactivity of many osmium precursors and (ii) the irreversible formation of competing side products, the synthesis and purification of the heterobimetallic triple-stranded helicate *HHH*-[OsLu(L2)₃](CF₃SO₃)₅ has been realised, in which L2 is a segmental ligand containing the same bidentate unit as that found in L1 further connected to a tridentate binding site adapted for complexing Ln^{III}. Its solid-state structure has been established by X-ray crystallography (triclinic, *P*1̄, *Z* = 2).

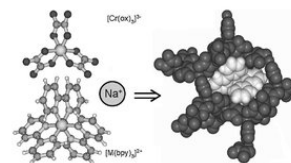
- **Energy migration within the ²E state of Cr³⁺**

Mia Milos, Sélim Kairouani, Sébastien Rabaste and Andreas Hauser

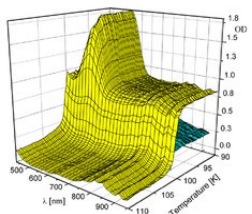
Coordination Chemistry Reviews **252** (23-24) (2008), p2540-2551

DOI:10.1016/j.ccr.2008.04.006

Keywords: resonant and phonon-assisted excitation energy migration • [Cr(ox)3]³⁻ • fluorescence line narrowing • spectral diffusion



Excitation energy migration is an important phenomenon at high concentration of luminescent chromophores. In crystalline solids it results in a quenching of the intrinsic luminescence of the chromophore as the excitation energy migrates to impurity centres or other forms of trap sites. As concluded from the extensively studied systems where Cr³⁺ is doped as the active chromophore into inert host lattices, energy migration in crystalline solids is usually a phonon-assisted process, in which the simultaneous creation or annihilation of phonons helps to bridge the energy mismatch in the energy levels of two neighbouring chromophores within an inhomogeneously broadened absorption band. However, in the three-dimensional network systems [Ru(bpy)₃][NaCr(ox)₃] and [Rh(bpy)₃][NaCr(ox)₃]ClO₄, it proved possible to unambiguously identify three different mechanisms for energy migration within the R₁ line of the ⁴A₂ → ²E transition of Cr³⁺. In addition to the common temperature dependant phonon-assisted process, a resonant process between the zero-field split components of the ⁴A₂ ground state leading to a multi-line pattern in a fluorescence line narrowing spectrum and a quasi-resonant process within the same component leading to fast spectral diffusion can be identified at very low temperature. The parameters governing these processes are discussed and the behaviour of the model systems is compared to more conventional doped oxides and related systems.



- **The interaction between the spin transition and a crystallographic phase transition in the spin-crossover compound [Fe(bbtr)₃](ClO₄)₂: Nucleation, formation of domains and fluctuations**

Itana Krivokapic, Cristian Enachescu, Robert Bronisz and Andreas Hauser

Inorganica Chimica Acta **361** (12-13) (2008), p3616-3622

DOI:10.1016/j.ica.2008.03.064

The thermal and the light-induced spin transition in [Fe(bbtr)₃](ClO₄)₂ (bbtr = 1,4-di(1,2,3-triazol-1-yl)) as well as the high-spin → low-spin relaxation following the light-induced population of the high-spin state below the thermal transition temperature are discussed in relation to the accompanying crystallographic phase transition. The experimental data have exclusively been obtained using optical single crystal absorption spectroscopy.

- **Spin transition and relaxation dynamics coupled to a crystallographic phase transition in a polymeric iron(II) spin-crossover system**

Itana Krivokapic, Cristian Enachescu, Robert Bronisz and Andreas Hauser

Chemical Physics Letters **455** (4-6) (2008), p192-196

DOI:10.1016/j.cplett.2008.02.088

The spin-crossover compound [Fe(bbtr)₃](ClO₄)₂ (bbtr = 1,4-di(1,2,3-triazol-1-yl)butane) forms a polymeric hexagonal sheet structure. It shows an abrupt thermal spin transition with 13 Å K wide hysteresis around 105 Å K, as evidenced by single crystal optical spectroscopy. The transition temperature for the thermal high-spin → low-spin transition on cooling as well as the relaxation kinetics just below T_c^{HT} depend upon the history of the sample. This is typical for a nucleation and growth mechanism and domain formation. In contrast, the high-spin → low-spin relaxation following the light-induced population of the high-spin state at low temperatures is governed by the intersystem crossing process.

- **Synthesis of new ethynylbipyridine-linked mono- and bis-tetrathiafulvalenes: electrochemical, spectroscopic, and Ru(II)-binding studies**

Christine Goze, Shi-Xia Liu, Claudia Leiggenger, Lionel Sanguinet, Eric Levillain, Andreas Hauser, Silvio Decurtins

Tetrahedron **64** (7) (2008), p1345-1350

DOI:10.1016/j.tet.2007.11.056

Keywords: Tetrathiafulvalene • Ruthenium(II) complex • Photophysical properties • Cyclic voltammetry • Donor-acceptor systems

Two new ethynylbipyridine-linked mono- and bis-tetrathiafulvalene (TTF) derivatives, together with a Ru(II) complex, were synthesized using Sonogashira coupling reactions and characterized by UV/vis spectroscopy and cyclic voltammetry. They display a clear electrochemically amphoteric behavior consisting of two reversible single-electron oxidation waves (typical for TTF derivatives) and one reversible single-electron reduction wave (bpy) and act as donor-acceptor (D-A) systems. Furthermore, for the Ru(II) complex, a quite intense fluorescence originating from the ³MLCT state is observed.

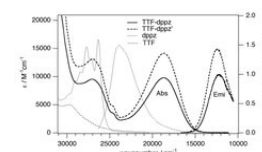
2007

- **Dual Luminescence and Long-lived Charge Separated states in Donor-Acceptor Assemblies based on Tetrathiafulvalene Fused Ruthenium(II)-Polypyridine Complexes**

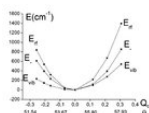
Leiggenger, Claudia; Dupont, Nathalie; Liu, Shi-Xia; Goze, Christine; Decurtins, Silvio; Breitler, Elvira; Hauser, Andreas

Chimia **61** (10) (2007), p621-625

DOI:10.2533/chimia.2007.621



The creation of long-lived charge-separated states in donor-acceptor assemblies has been the goal of many studies aimed at mimicking the primary processes in photosynthesis. Here we present such assemblies based on tetrathiafulvalene (TTF) as electron donor and a dipyrrophenazine (dppz) unit as electron acceptor in the form of a fused ligand (TTF-dppz) coordinated to ruthenium(II) via the dipyrro coordination site and with 2,2'-bipyridine (bpy) as auxiliary ligand, namely [Ru(bpy)₃(TTF-dppz)]²⁺ (x = 1-3). For x = 2, irradiation into the metal to dppz charge transfer transition results in electron transfer from TTF to ruthenium, thus creating a charge-separated state best described by [(TTF^{•+}-dppz)Ru(dppz^{•-}-TTF)(bpy)]²⁺ with a lifetime of 2.5 ns in dichloromethane.

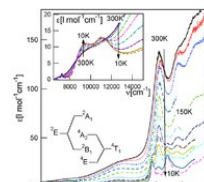


- **DFT-Based Studies on the Jahn-Teller Effect in 3d Hexacyanometalates with Orbitally Degenerate Ground States**
Mihail Atanasov, Peter Comba, Claude A. Daul and Andreas Hauser
Journal of Physical Chemistry A **111** (37) (2007), p9145-9163 DOI:10.1021/jp0731912

The topology of the ground-state potential energy surface of $M(CN)_6$ with orbitally degenerate $^2T_{2g}$ ($M = Ti^{III} (t_{2g}^1), Fe^{III}$ and Mn^{II} (both low-spin t_{2g}^5)) and $^3T_{1g}$ ground states ($M = V^{III} (t_{2g}^2), Mn^{III}$ and Cr^{II} (both low-spin t_{2g}^4)) has been studied with linear and quadratic Jahn-Teller coupling models in the five-dimensional space of the I_{μ_3} and I_{μ_2} octahedral vibrations ($T_g \hat{=} (I_{\mu_3} + I_{\mu_2})$). Jahn-Teller coupling problem ($T_g \hat{=} ^2T_{2g}, ^3T_{1g}$). A procedure is proposed to give access to all vibronic coupling parameters from geometry optimization with density functional theory (DFT) and the energies of a restricted number of Slater determinants, derived from electron replacements within the $t_{2g}^{1,5}$ or $t_{2g}^{2,4}$ ground-state electronic configurations. The results show that coupling to the I_{μ_2} bending mode is dominant and leads to a stabilization of D_{3d} structures (absolute minima on the ground-state potential energy surface) for all complexes considered, except for $[Ti(CN)_6]^{3-}$, where the minimum is of D_{4h} symmetry. The Jahn-Teller stabilization energies for the D_{3d} minima are found to increase in the order of increasing CN \rightarrow M π back-donation ($Ti^{III} < V^{III} < Mn^{III} < Fe^{III} < Mn^{II} < Cr^{II}$). With the angular overlap model and bonding parameters derived from angular distortions, which correspond to the stable D_{3d} minima, the effect of configuration interaction and spin-orbit coupling on the ground-state potential energy surface is explored. This approach is used to correlate Jahn-Teller distortion parameters with structures from X-ray diffraction data. Jahn-Teller coupling to trigonal modes is also used to reinterpret the anisotropy of magnetic susceptibilities and g tensors of $[Fe(CN)_6]^{3-}$, and the $^3T_{1g}$ ground-state splitting of $[Mn(CN)_6]^{3-}$, deduced from near-IR spectra. The implications of the pseudo Jahn-Teller coupling due to $t_{2g} \hat{=} e_g$ orbital mixing via the trigonal modes (I_{μ_2}) and the effect of the dynamic Jahn-Teller coupling on the magnetic susceptibilities and g tensors of $[Fe(CN)_6]^{3-}$ are also addressed.

- **Optical investigation of spin-crossover in cobalt(II) bis-terpy complexes**

Cristian Enachescu, Itana Krivokapic, Mohamed Zerara, Jose Antonio Real, Nahid Amstutz and Andreas Hauser
Inorganica Chimica Acta **360** (13) (2007), p3945-3950 DOI:10.1016/j.ica.2007.06.022



The spin transition of the $[Co(terpy)_2]^{2+}$ complex (terpy = 2,2',6'-terpyridine) is analysed based on experimental data from optical spectroscopy and magnetic susceptibility measurements. The single crystal absorption spectrum of $[Co(terpy)_2](ClO_4)_2$ shows an asymmetric absorption band at $14\,400\,cm^{-1}$ with an intensity typical for a spin-allowed $d \hat{=} d$ transition and a temperature behaviour typical for a thermal spin transition. The single crystal absorption spectra suggest that in this compound, the complex is essentially in the high-spin state at all temperatures. However, the increase in intensity observed in the region of the low-spin MLCT transition with increasing temperature implies an unusual partial thermal population of the low-spin state of up to about 10% at room temperature. Finally, high-spin \rightarrow low-spin relaxation curves following pulsed laser excitation for $[Co(terpy)_2](ClO_4)_2$ dispersed in KBr discs, and as a comparison for the closely related $[Co(4\text{-terpyridone})_2](ClO_4)_2$ spin-crossover compound are given.

- **Photoinduced Energy Transfer Processes within Dyads of Metallophthalocyanines Compactly Fused to a Ruthenium(II) Polypyridine Chromophore**

Marco Haas, Shi-Xia Liu, Axel Kahnt, Claudia Leiggenger, Dirk M. Guldi, Andreas Hauser, and Silvio Decurtins
Journal of Organic Chemistry **72** (20) (2007), p7533-7543 DOI:10.1021/jo0710477

An unsymmetric, peripherally octasubstituted phthalocyanine (Pc)1, which contains a combination of dipyrro[3,2-f2a $\hat{=}$ 3a $\hat{=}$ h] quinoxaline and 3,5-di-*tert*-butylphenoxy substituents, has been obtained via a statistical condensation reaction of two corresponding phthalonitriles. Synthetic procedures for the selective metalation of the macrocyclic cavity and the periphery of 1 were developed, leading to the preparation of the key precursor metallophthalocyanines 3a $\hat{=}$ 5 in good yields. Two different strategies were applied to the synthesis of compact dyads MPc $\hat{=}$ 8 ($M = Mg(II), Co(II), Zn(II)$). Intramolecular electronic interactions in these dyads were studied by absorption, emission, and transient absorption spectroscopy. Upon photoexcitation, these dyads exhibit efficient intramolecular energy transfer from the Ru(II) chromophore to the MPC moiety.

- **First-principles study of the pressure dependence of the structural and vibrational properties of the ternary metal hydride Ca_2RuH_6**

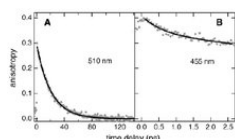
Latévi Max Lawson Daku and Hans Hagemann
Physical Review B **76** (1) (2007), p14118 DOI:10.1103/PhysRevB.76.014118

The influence of pressure on the structural and vibrational properties of a_2RuH_6 has been investigated using periodic density functional theory calculations performed at the local density approximation (LDA) and generalized gradient approximation (GGA) levels. At ambient pressure, the calculated structure and vibrational frequencies are in satisfactory agreement with experimental data. The calculated $\epsilon_m > P$ -curves could be fitted with the Vinet equation of state, yielding $\epsilon_m > B = 67.6$ and $\epsilon_m > B = 58.5$ GPa at the LDA and GGA levels, respectively, and $\epsilon_m > B^0 = 4.0$ at both theoretical levels. The unit cell parameter is found to decrease faster with increasing pressure than the Ru $\hat{=}$ H bond length. The calculated pressure dependence of the vibrational frequencies agrees well with experiment for $\epsilon_m > 1/2g(T_{2g})$ but not for $\epsilon_m > 1/2g(A_{1g})$.

- **Fused Donor-Acceptor Ligands in Ru^{II} Chemistry: Synthesis, Electrochemistry and Spectroscopy of $[Ru(bpy)_{3-n}(TTF\text{-}dppz)_n](PF_6)_2$**

Christine Goze, Claudia Leiggenger, Shi-Xia Liu, Lionel Sanguinet, Eric Levillain, Andreas Hauser, Silvio Decurtins
ChemPhysChem **8** (2007), p1504-1512 DOI:10.1002/cphc.200700066

Three ruthenium(II) polypyridine complexes of general formula $[Ru(bpy)_{3-n}(TTF\text{-}dppz)_n](PF_6)_2$ ($n = 1-3$, bpy = 2,2'-bipyridine), with one, two or three redox-active TTF-dppz (4',5'-bis(propylthio)tetrathiafulvenyl[dipyrro[3,2-a:2',3'-c]phenazine) ligands, were synthesised and fully characterised. Their electrochemical and photophysical properties are reported together with those of the reference compounds $[Ru(bpy)_3](PF_6)_2$, $[Ru(dppz)_3](PF_6)_2$ and $[Ru(bpy)_2(dppz)](PF_6)_2$ and the free TTF-dppz ligand. All three complexes show intraligand charge-transfer (ILCT) fluorescence of the TTF-dppz ligand. Remarkably, the complex with $n = 1$ exhibits luminescence from the Ru $^{2+}$ dppz metal-to-ligand charge-transfer (3MLCT) state, whereas for the other two complexes, a radiationless pathway via electron transfer from a second TTF-dppz ligand quenches the 3MLCT luminescence. The TTF fragments as electron donors thus induce a ligand-to-ligand charge-separated (LLCS) state of the form TTF-dppz $^{\cdot-}$ -Ru $^{2+}$ -dppz-TTF $^{\cdot+}$. The lifetime of this LLCS state is approximately 2.3 ns, which is four orders of magnitude longer than that of 0.4 ns for the ILCT state, because recombination of charges on two different ligands is substantially slower.



- **Investigation of the Influence of Solute-Solvent Interactions on the Vibrational Energy Relaxation Dynamics of Large Molecules in Liquids**

Anatolio Pigliucci, Guillaume Duvanel, Latévi Max Lawson Daku, Eric Vauthey
Journal of Physical Chemistry A **111** (28) (2007), p6135-6145 DOI:10.1021/jp069010y

The influence of solute-solvent interactions on the vibrational energy relaxation dynamics of perylene and substituted perylenes in the first singlet excited-state upon excitation with moderate (< 0.4 eV) excess energy has been investigated by monitoring the early narrowing of their fluorescence spectrum. This narrowing was found to occur on timescales ranging from a few hundreds of femtoseconds to a few picoseconds. Other processes, such as a partial decay of the fluorescence anisotropy and the damping of a low-frequency oscillation due to the propagation of a vibrational wavepacket, were found to take place on a very similar time scale. No significant relationship between the strength of nonspecific solute-solvent interactions and the vibrational energy relaxation dynamics of the solutes could be evidenced. On the other hand, in alcohols the spectral narrowing is faster with a solute having H-bonding sites, indicating that this specific interaction tends to favor vibrational energy relaxation. No relationship between the dynamics of spectral narrowing and macroscopic solvent properties, such as the thermal diffusivity, could be found. On the other hand, a correlation between this narrowing dynamics and the number of low-frequency modes of the solvent molecules was evidenced. All these observations cannot

be discussed with a model where vibrational energy relaxation occurs via two consecutive and dynamically well-separated steps, namely ultrafast intramolecular vibrational redistribution followed by slower vibrational cooling. On the contrary, the results indicate that both intra- and intermolecular vibrational energy redistribution processes are closely entangled and occur, at least partially, on similar timescales.

- **Capturing Transient Electronic and Molecular Structures in Liquids by Picosecond X-Ray Absorption Spectroscopy**

W. Gawelda, V. T. Pham, A. El Nahhas, M. Kaiser, Y. Zaushtsyn, S. L. Johnson, D. Grolimund, R. Abela, A. Hauser, C. Bressler, M. Chergui

American Institute of Physics Conference Proceedings **882** (2007), p31-36

DOI:10.1063/1.2644425

We describe an advanced setup for time-resolved x-ray absorption fine structure (XAFS) Spectroscopy with picosecond temporal resolution. It combines an intense femtosecond laser source synchronized to the x-ray pulses delivered into the microXAS beamline of the Swiss Light Source (SLS). The setup is applied to measure the short-lived high-spin geometric structure of photoexcited aqueous $\text{Fe}(\text{bpy})_3$ at room temperature.

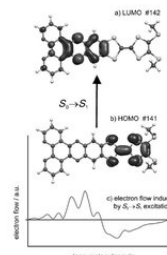
- **An Experimental and Computational Study on Intramolecular Charge Transfer: A Tetrathiafulvalene Fused Dipyridophenazine Molecule**

Chunyang Jia, Shi-Xia Liu, Christian Tanner, Claudia Leiggner, Antonia Neels, Lionel Sanguinet, Eric Levillain, Samuel Leutwyler, Andreas Hauser, Silvio Decurtins

Chemistry - A European Journal **13** (13) (2007), p3804-3812

DOI:10.1002/chem.200601561

Keywords: charge transfer • donor-acceptor systems • nitrogen heterocycles • photophysical properties • tetrathiafulvalene



To study the electronic interactions in donor-acceptor (D-A) ensembles, D and A fragments are coupled in a single molecule. Specifically, a tetrathiafulvalene (TTF)-fused dipyrido[3,2-a:2',3'-c]phenazine (dppz) compound having inherent redox centers has been synthesized and structurally characterized. Its electronic absorption, fluorescence emission, photoinduced intramolecular charge transfer, and electrochemical behavior have been investigated. The observed electronic properties are explained on the basis of density functional theory.

- **Ab initio static and molecular dynamics study of 4-styrylpyridine: Structure, energy and reactivity of the cis and trans isomers in the ground state**

Latévi Max Lawson Daku, Jorge Linares, Marie-Laure Boillot

ChemPhysChem **8** (9) (2007), p1402-1416

DOI:10.1002/cphc.200700117

Keywords: ab initio calculations • density functional calculations • isomerization • molecular dynamics • transition states

We report an in-depth theoretical study of 4-styrylpyridine in its singlet S ground state. The geometries and the relative stabilities of the *trans* and *cis* isomers were investigated within density functional theory (DFT) as well as within Hartree-Fock (HF), second-order Møller-Plesset (MP2), and coupled cluster (CC) theories. The DFT calculations were performed using the B3LYP and PBE functionals, with basis sets of different qualities, and gave results that are very consistent with each other. The molecular structure is thus predicted to be planar at the energy minimum, which is associated with the *trans* conformation, and to become markedly twisted at the minimum of higher energy, which is associated with the *cis* conformation. The results of the calculations performed with the post-HF methods approach those obtained with the DFT methods, provided that the level of treatment of the electronic correlation is high enough and that sufficiently flexible basis sets are used. Calculations carried out within DFT also allowed the determination of the geometry and the energy of the molecule at the biradicaloid transition state associated with the thermal *cis* \rightarrow *trans* isomerization and at the transition states associated with the enantiomerization of the *cis* isomer and with the rotations of the pyridinyl and phenyl groups in the *trans* and *cis* isomers. Car-Parrinello molecular dynamics simulations were also performed at 50, 150, and 300 K using the PBE functional. The studies allowed us to evidence the highly flexible nature of the molecule in both conformations. In particular, the *trans* isomer was found to exist mainly in a nonplanar form at finite temperatures, while the rotation of the pyridinyl ring in the *cis* isomer was incidentally observed to take place within ~ 1 ps during the simulation carried out at 150 K on this isomer.

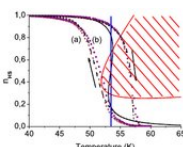
- **Structural Determination of a Short-lived Iron(II) Complex by Picosecond X-ray Absorption Spectroscopy**

Wojciech Gawelda, Van-Thai Pham, Maurizio Benfatto, Yuri Zaushtsyn, Maik Kaiser, Daniel Grolimund, Steven L. Johnson, Rafael Abela, Andreas Hauser, Christian Bressler, Majed Chergui

Physical Review Letters **98** (2007), p57401

DOI:10.1103/PhysRevLett.98.057401

Structural changes of the iron(II)-tris-bipyridine ($[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$) complex induced by ultrashort pulse excitation and population of its short-lived (~ 0.6 ps) quintet high spin state have been detected by picosecond x-ray absorption spectroscopy. The structural relaxation from the high spin to the low spin state was followed over the entire lifetime of the excited state. A combined analysis of the x-ray-absorption near-edge structure and extended x-ray-absorption fine structure spectroscopy features delivers an Fe-N bond elongation of 0.2 Å... in the quintet state compared to the singlet ground state.



- **Light-induced phase separation in the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ spin-crossover single crystal**

F. Varret, K. Boukheddaden, C. Chong, A. Goujon, B. Gillon, J. Jeftic, A. Hauser

Europhysics Letters **77** (3) (2007), p30007

DOI:10.1209/0295-5075/77/30007

We present novel insight on like-spin domains (LSD) in cooperative spin transition solids by following the photo-transformation and the subsequent relaxation of a $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ single crystal in the vicinity of the light-induced instability. Self-organization under light is observed, accompanied by Barkhausen-like noise and jumps which reveal the presence of elastic interactions between LSDs. The light-induced phase separation process is discussed in terms of a dynamic potential providing spinodal instability in the corresponding temperature range. This useful concept is applicable to all types of switchable molecular solids.

- **Spin-crossover in cobalt(II) imine complexes**

Itana Krivokapic, Mohamed Zerara, Latévi Max Lawson Daku, Alfredo Vargas, Cristian Enachescu, Christina Ambrus, Philip Tregenna-Piggott, Nahid Amstutz, Elmars Krausz and Andreas Hauser

Coordination Chemistry Reviews **251** (2007), p364-378

DOI:10.1016/j.ccr.2006.05.006

Whereas there are hundreds of known iron(II) spin-crossover compounds, only a handful of cobalt(II) spin-crossover compounds have been discovered to date, and hardly an in depth study on any of them exists. This review begins with an introduction into the theoretical aspects to be considered when discussing spin-crossover compounds in general and cobalt(II) systems in particular. It is followed by case studies on $[\text{Co}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{terpy})_2]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{terpy} = 2,2':6,6':2,2'$ -terpyridine) presenting and discussing results from magnetic susceptibility measurements, X-ray crystallography, optical spectroscopy, and EPR spectroscopy.

- *Chiroptical and Computational Studies of a Bridled Chiorporphyrin and of Its Nickel(II), Copper(II), and Zinc(II) Complexes*
Géraldine Maheut, Anna Castaings, Jacques Pécaut, Latévi Max Lawson Daku, Gennaro Pescitelli, Lorenzo Di Bari, and Jean-Claude Marchon

Journal of the American Chemical Society **128** (19) (2006), p6347-6356

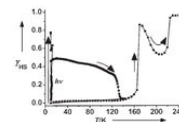
DOI:10.1021/ja054926o

Circular dichroism (CD) spectra and density functional theory (DFT) calculations are reported for a series of conformationally bistable chiorporphyrins with 8-methylene bridges MBP-8, which can display either an $1\pm1\pm1\pm1$ or an $1\pm1\pm1\pm2$ orientation of their meso substituents. From DFT geometry optimizations, the most stable form of ZnBCP-8 is found to be the $1\pm1\pm1\pm1$ conformer. By passing to NiBCP-8, there is a strong stabilization of the $1\pm1\pm1\pm2$ conformation with respect to the $1\pm1\pm1\pm1$ conformation, consistent with the X-ray structures of $1\pm1\pm1\pm1$ -ZnBCP-8 and $1\pm1\pm1\pm2$ -NiBCP-8. A correlation between the sign of the CD signal in the Soret region and the conformation of the BCP-8 compounds is reported: the $1\pm1\pm1\pm1$ conformers H₂BCP-8 and ZnBCP-8 show a positive CD signal, whereas the $1\pm1\pm1\pm2$ conformers NiBCP-8 and CuBCP-8 exhibit a negative signal. The possible contributions to the rotational strengths of $1\pm1\pm1\pm2$ -NiBCP-8 and $1\pm1\pm1\pm1$ -ZnBCP-8, calculated on the basis of their crystal structures, have been analyzed. The CD signals are found to result from a combination of both the inherent chirality of the porphyrin and of extrinsic contributions due to the chiral bridges. These results may have a broad significance for understanding the chiroptical properties of chiral porphyrins and hemoproteins and for monitoring stimuli-responsive, conformationally bistable chiorporphyrin compounds.

- *Photoswitching of the Dielectric Constant of the Spin-Crossover Complex [Fe(L)(CN)₂]₂H₂O*
Sébastien Bonhommeau, Thomas Guillon, Latévi Max Lawson Daku, Philippe Demont, José Sanchez Costa, Jean-François Létard, Gábor Molnár, Azzedine Bousseksou

Angewandte Chemie International Edition **45** (10) (2006), p1625-1629

DOI:10.1002/anie.200503252



Photoswitching of the dielectric constant has been observed for the first time in the spin-crossover complex [Fe(L)(CN)₂]₂·H₂O (L=2,13-dimethyl-6,9-dioxo-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, see picture). The electrical detection of a photoinduced change in spin state could allow the use of such complexes in optical information-storage devices.

- *Ab initio calculations of external-field shifts of the 661-nm quadrupole clock transition in neutral Ag atoms*
Suat Topcu, Jamil Nasser, Latévi Max Lawson Daku, and Stephan Fritzsche

Physical Review A **73** (4) (2006), p42503

DOI:10.1103/PhysRevA.73.042503

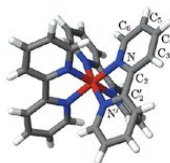
Frequency shifts of the Ag $\hat{A} \rightarrow \hat{A} 4d^{10}5s \hat{A}^2S_{1/2-1/2}(F=0, M_F=0)$ to $4d^95s^2 \hat{A}^2D_{3/2-3/2}(F^{3/2}=2, M_F=0)$ electric-quadrupole transition at 330.6 Å nm due to external fields are calculated using multiconfigurational self-consistent field methods. As this forbidden transition is free from first order Doppler and Zeeman effects, it is under investigation for the realization of an atomic optical clock. The calculated perturbations are the light shift, the blackbody frequency shift, and the quadratic Zeeman shift. Results show that a total uncertainty of 10^{-18} could be reached without confining the atoms in a Lamb-Dicke regime in an optical lattice.

- *Electronic Structure, Spectroscopic Properties, and Reactivity of Molybdenum and Tungsten Nitrido and Imido Complexes with Diphosphine Coligands: Influence of the trans Ligand*
Klaus Mersmann, Andreas Hauser, Nicolai Lehnert, and Felix Tuczek

Inorganic Chemistry **45** (2006), p5044-5056

DOI:10.1021/ic060141n

A series of molybdenum and tungsten nitrido, [M(N)(X)(diphos)₂], and imido complexes, [M(NH)(X)(diphos)₂]^Y, (M = Mo, W) with diphosphine coligands (diphos = dppe/depe), various trans ligands (X = N₃, Cl, NCCH₃) and different counterions (Y⁻ = Cl⁻, BPh₄⁻) is investigated. These compounds are studied by infrared and Raman spectroscopies; they are also studied with isotope-substitution and optical-absorption, as well as emission, spectroscopies. In the nitrido complexes with *trans*-azido and -chloro coligands, the metal-¹⁵N stretch is found at about 980 cm⁻¹; upon protonation, it is lowered to about 920 cm⁻¹. The $\hat{A}_1, \hat{A}_1^+E^- (n \hat{A}_1^+ E^-)$ electronic transition is observed for [Mo(N)(N₃)(dppe)₂] at 398 nm and shows a progression in the metal-¹⁵N stretch of 810 cm⁻¹. The corresponding $\hat{E} \hat{A}_1^+A^- (E^- \hat{A}_1^+ A^-)$ emission band is observed at 542 nm, exhibiting a progression in the metal-¹⁵N stretch of 980 cm⁻¹. In the imido system [Mo(NH)(N₃)(dppe)₂]BPh₄, the $n \hat{A}_1^+ E^-$ transition is shifted to lower energy (518 nm) and markedly decreases in intensity. In the *trans*-nitride complex [Mo(N)(NCCH₃)(dppe)₂]BPh₄, the metal-¹⁵N(nitrido) stretching frequency increases to 1016 cm⁻¹. The $n \hat{A}_1^+ E^-$ transition now is found at 450 nm, shifting to 525 nm upon protonation. Most importantly, the reduction of this nitrido-*trans*-nitride complex is drastically facilitated compared to its counterparts with anionic *trans*-ligands ($E_{red}^0 = \hat{A}_1^+1.5$ V vs Fc/Fc⁺). On the other hand, the basicity of the nitrido group is decreased (pK_a([Mo(NH)(NCCH₃)(dppe)₂]BPh₄)₂ = 5). The implications of these findings with respect to the Chatt cycle are discussed.



- *Density-functional theory investigation of the geometric, energetic and optical properties of the cobalt(II)tris(2,2'-bipyridine) complex in the high-spin and in the Jahn-Teller active low-spin state*
Alfredo Vargas, Mohamed Zerara, Elmars Krausz, Andreas Hauser, and Latévi Max Lawson Daku

Journal of Chemical Theory and Computation **2** (2006), p1342-1359

DOI:10.1021/ct6001384

State-of-the-art generalized gradient approximation (GGA) (PBE, OPBE, RPBE, OLYP, and HCTH), meta-GGA (VSXC and TPSS), and hybrid (B3LYP, B3LYP*, O3LYP, and PBE0) functionals are compared for the determination of the structure and the energetics of the D_3 [Co(bpy)₃]²⁺ complex in the \hat{A}_2 and \hat{E} trigonal components of the high-spin $\hat{T}_{1g}(t_{2g}^6 e_g^2)$ state and in the low-spin \hat{E} state of octahedral $\hat{E}_g(t_{2g}^6 e_g^2)$ parentage. Their comparison extends also to the investigation of the Jahn-Teller instability of the \hat{E}^- state through the characterization of the extrema of C_2 symmetry of this spin state's potential energy surface. The results obtained for [Co(bpy)₃]²⁺ in either spin manifold are very consistent among the functionals used and are in good agreement with available experimental data. The functionals, however, perform very differently with respect to the spin-state energetics because the calculated values of the high-spin/low-spin energy difference $\hat{I}^0 E_{HL}$ vary between \hat{A}_1^+3212 and 3919 cm⁻¹. Semilocal functionals tend to give too large $\hat{I}^0 E_{HL}$ values and thus fail to correctly predict the high-spin state as the ground state of the isolated complex, while hybrid functionals tend to overestimate the stability of the high-spin state with respect to the low-spin state. Reliable results are, however, obtained with the OLYP, HCTH, B3LYP*, and O3LYP functionals which perform best for the description of the isolated complex. The optical properties of [Co(bpy)₃]²⁺ in the two spin states are also analyzed on the basis of electronic excitation calculations performed within time-dependent density functional response theory. The calculated absorption and circular dichroism spectra agree well with experimental results.

- *Preparation and characterization of 3-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)naphthopyranone: a luminescent redox-active donor-acceptor compound*
Stefan Dolder, Shi-Xia Liu, Xavier Guégano, Mihail Atanasov, Claude A. Daul, Claudia Leiggener, Andreas Hauser, Antonia Neels and Silvio Decurtins

Tetrahedron **62** (48) (2006), p11106-11111

DOI:10.1016/j.tet.2006.09.032

Keywords: Naphthopyranone • TTF • Donor-acceptor compound • Cyclic voltammetry • TDDFT calculations • Luminescence

A new 1,3-dithiol-2-ylidene substituted naphthopyranone **2** has been synthesized and characterized. UV-vis spectroscopic and cyclic voltammetry results, interpreted on the basis of density functional theory, show that **2** displays an intramolecular charge-transfer transition and acts like a donor-acceptor (D-A) system. Furthermore, a weak fluorescence originating from the excited charge-

- Keywords:** charge transfer • iron • laser spectroscopy • photophysics • spin crossover

Coordination Chemistry Reviews **250** (13-14) (2006), p1642-1652 DOI:10.1016/j.ccr.2005.12.006

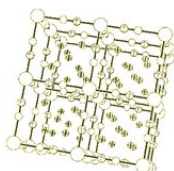
DOI:10.1039/b601173j

DOI:10.1002/adfm.200500329

DOI:10.1002/zaac.200500053

Applied Physics Letters **87** (25) (2005), p251904-251907 DOI:10.1063/1.2143409

Thu. 28 Mar 2024 20:18:01 +0100



• **DFT study of mixed-valent Mn(II/III) hexacyanide cluster**

Claude Daul, Cédric Rauzy, Silvio Decurtins, Patrick Franz, Andreas Hauser

International Journal of Quantum Chemistry **101** (6) (2005), p753-760

DOI:10.1002/qua.20333

Keywords: cluster • cyanide bridging ligand • DFT • manganese complexes • Prussian blue analogue

The cubic Prussian blue analogue $\text{Mn}_3[\text{Mn}(\text{CN})_6]_2 \cdot 15 \text{H}_2\text{O}$, which has the advantage of being transparent and magnetic ($T_N = 35 \text{ K}$) at the same time, has been investigated by density functional theory (DFT) calculations. The three-dimensional structure is built of Mn^{II} ions linked to Mn^{III} ions by $1/4$ -bridging cyanides, to form a crystal structure, which is related to the NaCl type. In a first step, the relative stabilities of the mononuclear complexes $[\text{Mn}(\text{CN})_6]^{z-}$ ($z = 2$ to 4) have been studied as a function of the oxidation state, spin configuration, and the linkage isomerism of the cyanide ligand. The results we have obtained by this investigation are in good agreement with our chemical expertise. In addition, the calculations have been extended to the dinuclear $[\text{Mn}_2(\text{CN})_{11}]^{z-}$ ($z = 5$ and 6) clusters. Furthermore, we used DFT to model the magnetic properties as well as the ${}^3T_1 \rightarrow {}^1A_1$ transition, which has been observed by single-crystal near-IR spectra of $\text{Mn}_3[\text{Mn}(\text{CN})_6]_2 \cdot 15 \text{H}_2\text{O}$.

• **Thermal- and Photoinduced Spin-State Switching in an Unprecedented Three-Dimensional Bimetallic Coordination Polymer**

Virginie Niel, Amber L. Thompson, Andrés E. Goeta, Cristian Enachescu, Andreas Hauser, Ana Galet, M. Carmen Muñoz, José A. Real

Chemistry - A European Journal **11** (7) (2005), p2047-2060

DOI:10.1002/chem.200400930

Keywords: argentophilic interactions • coordination modes • polymers • spin crossover

The compound $(\text{Fe}(\text{pmd})[\text{Ag}(\text{CN})_2][\text{Ag}_2(\text{CN})_3])$ (pmd=pyrimidine) was synthesized and characterized. Magnetic, calorimetric and single crystal visible spectroscopic studies demonstrate the occurrence of a two-step high-spin (HS) \rightarrow low-spin (LS) transition. The critical temperatures are $T_{C1}=185$ and $T_{C2}=148 \text{ K}$. Each step involves $\sim 50\%$ of the iron centers, with the low-temperature step showing a hysteresis of 2.5 K . The enthalpy and entropy variations associated with the two steps are $\Delta H_1=3.6 \pm 0.4 \text{ kJ mol}^{-1}$ and $\Delta S_1=19.5 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta H_2=4.8 \pm 0.4 \text{ kJ mol}^{-1}$ and $\Delta S_2=33.5 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$. Photomagnetic and visible spectroscopy experiments show that below 50 K , where the LS state is the thermodynamically stable state, the compound can be switched quantitatively to the HS state using green-red light ($550\text{--}650 \text{ nm}$). HS-to-LS relaxation experiments in the dark at temperatures between 15 and 55 K show that the relaxation takes place via a two-step cooperative process, which was analyzed in the context of the mean field theory. The crystal structure has been studied at 290 , 220 , 170 , 90 and 30 K together with 30 K after irradiation. The compound adopts monoclinic symmetry ($P2_1/c, Z=16$) at all temperatures. There are five $[\text{FeN}_6]$ pseudo-octahedral sites linked by pmc, $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Ag}_2(\text{CN})_3]^-$ bridging ligands to form an unprecedented three-dimensional (6,6) topology. The structural analysis allows for an understanding of the microscopic mechanism of the two-step behavior of the thermally induced spin transition as well as the corresponding relaxation of the photoexcited compound based on the individual changes of the five sites. Synergy between metalphilic interactions and the spin transition is also shown by the variation of the $\text{Ag}^{\text{I}}\text{Ag}$ distances. Correlations between the variation of the unit-cell volume and the change of $\text{Ag}^{\text{I}}\text{Ag}$ interactions within each step with the asymmetric change of the anomalous heat capacity have also been inferred.

• **Comparison of density functionals for energy and structural differences between the high- $[\text{Fe}T_{2g}(t_{2g})^4(e_g)^2]$ and low- $[\text{Fe}A_{1g}(t_{2g})^6(e_g)]$ spin states of iron(II) coordination compounds. II. More functionals and the hexaminoferrous cation, $[\text{Fe}(\text{NH}_3)_6]^{2+}$**

Antony Fouqueau, Mark E. Casida, Latévi Max Lawson Daku, Andreas Hauser, and Frank Neese

Journal of Chemical Physics **122** (4) (2005), p44110

DOI:10.1063/1.1839854

The ability of different density functionals to describe the structural and energy differences between the high- $[\text{Fe}T_{2g}(t_{2g})^4(e_g)^2]$ and low- $[\text{Fe}A_{1g}(t_{2g})^6(e_g)]$ spin states of small octahedral ferrous compounds is studied. This work is an extension of our previous study of the hexaquoferrous cation, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, [J. Chem. Phys. **120**, 9473 (2004)] to include a second compound, namely, the hexaminoferrous cation, $[\text{Fe}(\text{NH}_3)_6]^{2+}$ and several additional functionals. In particular, the present study includes the highly parametrized generalized gradient approximations (GGAs) known as HCTH and the meta-GGA VSXC [which together we refer to as highly parametrized density functionals (HPDFs)], now readily available in the GAUSSIAN03 program, as well as the hybrid functional PBE0. Since there are very few experimental results for these molecules with which to compare, comparison is made with best estimates obtained from second-order perturbation theory-corrected complete active space self-consistent field (CASPT2) calculations, with spectroscopy oriented configuration interaction (SORCI) calculations, and with ligand field theory (LFT) estimations. While CASPT2 and SORCI are among the most reliable *ab initio* methods available for this type of problem, LFT embodies many decades of empirical experience. These three methods are found to give coherent results and provide best estimates of the adiabatic low-spin \rightarrow high-spin energy difference, ΔE_{LH} adia, of $12 \pm 0.5 \text{ eV}$ for $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $9 \pm 0.5 \text{ eV}$ for $[\text{Fe}(\text{NH}_3)_6]^{2+}$. All functionals beyond the purely local approximation produce reasonably good geometries, so long as adequate basis sets are used. In contrast, the energy splitting, ΔE_{LH} adia, is much more sensitive to the choice of functional. The local density approximation severely over stabilizes the low-spin state with respect to the high-spin state. This ΔE_{LH} adia density functional theory (DFT) spin pairing-energy problem persists, but is reduced, for traditional GGAs. In contrast the hybrid functional B3LYP underestimates ΔE_{LH} adia by a few thousands of wave numbers. The RPBE GGA of Hammer, Hansen, and Nørskov gives good results for ΔE_{LH} adia as do the HPDFs, especially the VSXC functional. Surprisingly the HCTH functionals actually over correct the DFT spin pairing-energy problem, destabilizing the low-spin state relative to the high-spin state. Best agreement is found for the hybrid functional PBE0.

• **Tuning the Decay Time of Lanthanide-Based Near Infrared Luminescence from Micro- to Milliseconds through d- \rightarrow f Energy Transfer in Discrete Heterobimetallic Complexes**

Stéphane Torelli, Daniel Imbert, Martine Cantuel, Gérald Bernardinelli, Sandra Delahaye, Andreas Hauser, Jean-Claude G. Bünzli, Claude Piguet

Chemistry - A European Journal **11** (11) (2005), p3228-3242

DOI:10.1002/chem.200401158

Keywords: energy transfer • helicates • heterobimetallic complexes • lanthanides • near infrared luminescence

Inert and optically active pseudo-octahedral $\text{Cr}^{\text{III}}\text{N}_6$ and $\text{Ru}^{\text{II}}\text{N}_6$ chromophores have been incorporated by self-assembly into heterobimetallic triple-stranded helicates $\text{HHH}[\text{Cr}(\text{Ln})_3]^{6+}$ and $\text{HHH}[\text{Ru}(\text{Ln})_3]^{5+}$. The crystal structures of $[\text{Cr}(\text{Ln})_3](\text{CF}_3\text{SO}_3)_6$ ($\text{Ln}=\text{Nd}, \text{Eu}, \text{Yb}, \text{Lu}$) and $[\text{Ru}(\text{Ln})_3](\text{CF}_3\text{SO}_3)_5$ ($\text{Ln}=\text{Eu}, \text{Lu}$) demonstrate that the helical structure can accommodate metal ions of different sizes, without sizeable change in the intermetallic $\text{M}^{\text{II}}\text{Ln}$ distances. These systems are ideally suited for unravelling the molecular factors affecting the intermetallic $d \rightarrow f$ communication. Visible irradiation of the $\text{Cr}^{\text{III}}\text{N}_6$ and $\text{Ru}^{\text{II}}\text{N}_6$ chromophores in $\text{HHH}[\text{M}(\text{Ln})_3]^{5/6+}$ ($\text{Ln}=\text{Nd}, \text{Yb}, \text{Er}, \text{M}=\text{Cr}, \text{Ru}$) eventually produces lanthanide-based near infrared (NIR) emission, after directional energy migration within the complexes. Depending on the kinetic regime associated with each specific d-f pair, the NIR luminescence decay times can be tuned from micro- to milliseconds. The origin of this effect, together with its rational control for programming optical functions in discrete heterobimetallic entities, are discussed.

• **Assessment of Density Functionals for the High-Spin/Low-Spin Energy Difference in the Low-Spin Iron(II) Tris(2,2'-bipyridine) Complex**

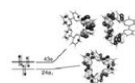
Latévi Max Lawson Daku, Alfredo Vargas, Andreas Hauser, Antony Fouqueau, Mark Earl Casida

ChemPhysChem **6** (7) (2005), p1393-1410

DOI:10.1002/cphc.200400584

Keywords: density functional calculations • iron(II) complexes • time-resolved spectroscopy • high-spin \rightarrow low-spin relaxation • spin crossover

In the iron(II) low-spin complex $[\text{Fe}(\text{bpy})_3]^{2+}$, the zero-point energy difference between the ${}^5T_{2g}(t_{2g}^2e_g^2)$ high-spin and the ${}^1A_{1g}(t_{2g}^6)$ low-spin states, ΔE_{HL} , is estimated to lie in the range of $2500\text{--}5000 \text{ cm}^{-1}$. This estimate is based on the low-temperature dynamics of the high-spin \rightarrow low-spin relaxation following the light-induced population of the high-spin state and on the assumption that the bond-length difference between the two states Δr_{HL} is equal to the average value of $\Delta r_{\text{HL}} \approx 0.2 \text{ Å}$, as found experimentally for the spin-crossover system. Calculations based on density functional theory (DFT) validate the structural assumption insofar as the low-spin-state optimized geometries are found to be in very good agreement with the experimental X-ray structure of the complex and the predicted high-spin geometries are all very close to one another for a whole series of common GGA (PB86, PW91, PBE, RPBE) and hybrid (B3LYP, B3LYP*, PBE1PBE) functionals. This confirmation of the structural assumption underlying the estimation of ΔE_{HL} from experimental



relaxation rate constants permits us to use this value to assess the ability of the density functionals for the calculation of the energy difference between the HS and LS states. Since the different functionals give values from -1000 to 12000 cm⁻¹, the comparison of the calculated values with the experimental estimate thus provides a stringent criterion for the performance of a given functional. Based on this comparison the RPBE and B3LYP* functionals give the best agreement with experiment.

- *Synthesis and Electrochemical and Photophysical Studies of Tetrathiafulvalene-Annulated Phthalocyanines*

Claudia Loosli, Chunyang Jia, Shi-Xia Liu, Marco Haas, Marylène Dias, Eric Levillain, Antonia Neels, Gael Labat, Andreas Hauser, and Silvio Decurtins

Journal of Organic Chemistry **70** (13) (2005), p4988-4992

DOI:10.1021/jo0501801

The synthesis of tetrakis(tetrathiafulvalene)-annulated metal-free and metallophthalocyanines **5a~8** via the tetramerization of the phthalonitrile derivative **4** is reported. All of them have been fully characterized by electronic absorption spectroscopy, thin-layer cyclic voltammetry, mass spectrometry, and elemental analysis. Their solution electrochemical data show two reversible four-electron oxidation waves, indicating that these fused systems are strong π -electron donors, which give rise to tetra- or octaradical cation species. For the metal-free phthalocyanine **5**, additionally a reversible one-electron wave was found in the negative direction arising from the reduction of the macrocycle. Moreover, the tetrathiafulvalene unit acts as an efficient reductive electron-transfer quencher for the phthalocyanine emission, but upon its oxidation, an intense luminescence is switched on.

- *Time-Resolved Spectroscopy of the Metal-to-Metal Charge Transfer Excited State in Dinuclear Cyano-Bridged Mixed-Valence Complexes*

Brendan P. Macpherson, Paul V. Bernhardt, Andreas Hauser, Stéphane Pagès, and Eric Vauthey

Inorganic Chemistry **44** (15) (2005), p5530-5536

DOI:10.1021/ic0506512

Visible pump-probe spectroscopy has been used to identify and characterize short-lived metal-to-metal charge transfer (MMCT) excited states in a group of cyano-bridged mixed-valence complexes of the formula $[LCo^{II}NCM^{III}(CN)_5]_2$, where L is a pentadentate macrocyclic pentaamine (L¹⁴) or triamine-dithiaether (L^{14S}) and M is Fe or Ru. Nanosecond pump-probe spectroscopy on frozen solutions of $[L^{14}Co^{II}NCFe^{III}(CN)_5]_2$ and $[L^{14S}Co^{II}NCFe^{III}(CN)_5]_2$ at 11 K enabled the construction of difference transient absorption spectra that featured a rise in absorbance in the region of 350–400 nm consistent with the generation of the ferricyanide chromophore of the photoexcited complex. The MMCT excited state of the Ru analogue $[L^{14}Co^{II}NCRu^{III}(CN)_5]_2$ was too short-lived to allow its detection. Femtosecond pump-probe spectroscopy on aqueous solutions of $[L^{14}Co^{II}NCFe^{III}(CN)_5]_2$ and $[L^{14S}Co^{II}NCFe^{III}(CN)_5]_2$ at room temperature enabled the lifetimes of their Co^{II}→Fe^{III} MMCT excited states to be determined as 0.8 and 1.3 ps, respectively.

2004

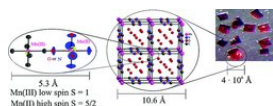
- *Photophysical properties of three-dimensional transition metal tris-oxalate network structures*

Andreas Hauser, Marianne E. von Arx, Vaughan S. Langford, Sélim Kairouani, Ueli Oetliker, Anne Pillonnet

Topics in Current Chemistry, Transition Metal and Rare Earth Compounds. Excited States, Transitions, and Interactions, Vol III **241** (2004) DOI:10.1007/b96860

Keywords: oxalate networks • $[Cr(ox)_3]^{3-}$ • $[Cr(bpy)_3]^{3+}$ • 2E state • resonant energy transfer • phonon-assisted energy transfer • Förster transfer • Exchange interaction

Excitation energy transfer processes play an important role in many areas of physics, chemistry and biology. The three-dimensional oxalate networks of composition $[M(III)(bpy)_3][M(III)(ox)_3]ClO_4$ (bpy=2,2-bipyridine, ox=oxalate, M=alkali ion) allow for a variety of combinations of different transition metal ions. The combination with chromium(III) on both the tris-bipyridine as well as the tris-oxalate site constitutes a model system in which it is possible to differentiate unambiguously between energy transfer from $[Cr(ox)_3]^{3-}$ to $[Cr(bpy)_3]^{3+}$ due to dipole-dipole interaction on the one hand and exchange interaction on the other hand. Furthermore it is possible to just as unambiguously differentiate between the common temperature dependent phonon-assisted energy migration within the 2E state of $[Cr(ox)_3]^{3-}$, and a unique resonant process.



- *Crystalline, Mixed-Valence Manganese Analogue of Prussian Blue: Magnetic, Spectroscopic, X-ray and Neutron Diffraction Studies*

Patrick Franz, Christina Ambrus, Andreas Hauser, Dmitry Chernyshov, Marc Hostettler, Jürg Hauser, Lukas Keller, Karl Krämer, Helen Stoeckli-Evans, Philip Pattison, Hans-Beat Bürgi, and Silvio Decurtins

Journal of the American Chemical Society **126** (50) (2004), p16472-16477

DOI:10.1021/ja0465451

The compound of stoichiometry $Mn(II)_3[Mn(III)(CN)_6]_2 \cdot zH_2O$ ($z = 12 \pm 16$) (**1**) forms air-stable, transparent red crystals. Low-temperature single crystal optical spectroscopy and single crystal X-ray diffraction provide compelling evidence for N-bonded high-spin manganese(II), and C-bonded low-spin manganese(III) ions arranged in a disordered, face-centered cubic lattice analogous to that of Prussian Blue. X-ray and neutron diffraction show structured diffuse scattering indicative of partially correlated (rather than random) substitutions of $[Mn(II)(CN)_6]$ ions by $(H_2O)_6$ clusters. Magnetic susceptibility measurements and elastic neutron scattering experiments indicate a ferrimagnetic structure below the critical temperature $T_c = 35.5$ K.

- *Ligand-field theoretical considerations*

Andreas Hauser

Topics in Current Chemistry, Spin-crossover in Transition Metal Compounds, Vol I **233** (2004), p49-58

DOI:10.1007/b40394-9

Keywords: spin crossover • ligand field theory • optical properties • vibronic structure • configurational coordinate

The phenomenon of the thermal spin transition, as observed for octahedral transition metal complexes having a d 4 to d 7 electronic configuration, can be fully rationalised on the basis of ligand field theory. In order to arrive at a self-consistent description of the vibronic structure of spin crossover compounds, it is essential to take into account the fact that the population of anti-bonding orbitals in the high-spin state results in a substantially larger metal-ligand bond length than for the low-spin state. Whereas the electron-electron repulsion is not affected to any great extent by such a bond length difference, the ligand field strength for iron(II) spin crossover compounds can be estimated to be almost twice as large in the low-spin state as compared to the one for the high-spin state. In fact, the dependence of the ligand field strength on the metal-ligand distance may be considered the quantum mechanical driving force for the spin crossover phenomenon.

- *Light-induced spin-crossover and the high-spin -> low-spin relaxation*

Andreas Hauser

Topics in Current Chemistry, Spin-crossover in Transition Metal Compounds, Vol II **234** (2004), p155-198

DOI:10.1007/b95416

Keywords: thermal and light-induced spin crossover • high-spin->low-spin relaxation • Intersystem crossing • external pressure • chemical pressure • cooperative effects • Iron(II) complexes

The discovery of a light-induced spin transition at cryogenic temperatures in a series of iron(II) spin-crossover compounds in 1984 has had an enormous impact on spin-crossover research. Apart from being an interesting photophysical phenomenon in its own right, it provided the means of studying the dynamics of the intersystem crossing process between the high-spin and the low-spin state in a series of compounds and over a large temperature range. It could thus be firmly established that intersystem crossing in spin-crossover compounds is a tunnelling process, with a limiting low-temperature lifetime below 50 K and a thermally activated region above 100 K. This review begins with an elucidation of the mechanism of the light-induced spin transition, followed by an in depth discussion of the

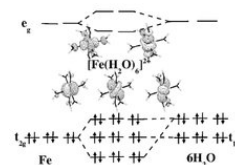
- **Comparison of density functionals for energy and structural differences between the high- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and low- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ spin states of the hexaquoferrous cation $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$**

Antony Fouqueau, Sébastien Mer, Mark E. Casida, Latevi Max Lawson Daku, Andreas Hauser, Tsonka

Mineva, and Frank Neese

Journal of Chemical Physics **120** (20) (2004), p9473-9486

DOI:10.1063/1.1710046



A comparison of density functionals is made for the calculation of energy and geometry differences for the high- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and low- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ spin states of the hexaquoferrous cation $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. Since very little experimental results are available (except for crystal structures involving the cation in its high-spin state), the primary comparison is with our own complete active-space self-consistent field (CASSCF), second-order perturbation theory-corrected complete active-space self-consistent field (CASPT2), and spectroscopy-oriented configuration interaction (SORCI) calculations. We find that generalized gradient approximations (GGAs) and the B3LYP hybrid functional provide geometries in good agreement with experiment and with our CASSCF calculations provided sufficiently extended basis sets are used (i.e., polarization functions on the iron and polarization and diffuse functions on the water molecules). In contrast, CASPT2 calculations of the low-spin \rightarrow high-spin energy difference $E_{\text{LH}} = E_{\text{L}} - E_{\text{H}}$ appear to be significantly overestimated due to basis set limitations in the sense that the energy difference of the atomic asymptotes ($5d^6 \rightarrow 6s^1$ excitation of Fe^{2+}) are overestimated by about 3000 cm^{-1} . An empirical shift of the molecular E_{LH} based upon atomic calculations provides a best estimate of $12\text{ae} \pm 3000 \text{ae} \pm 13\text{ae} \pm 3000 \text{cm}^{-1}$. Our unshifted SORCI result is $13\text{ae} \pm 300 \text{cm}^{-1}$, consistent with previous comparisons between SORCI and experimental excitation energies which suggest that no such empirical shift is needed in conjunction with this method. In contrast, after estimation of incomplete basis set effects, GGAs with one exception underestimate this value by $3000\text{ae} \pm 4000 \text{cm}^{-1}$ while the B3LYP functional underestimates it by only about 1000 cm^{-1} . The exception is the GGA functional RPBE which appears to perform as well as or better than the B3LYP functional for the properties studied here. In order to obtain a best estimate of the molecular E_{LH} within the context of density functional theory (DFT) calculations we have also performed atomic excitation energy calculations using the multiplet sum method. These atomic DFT calculations suggest that no empirical correction is needed for the DFT calculations.

- **Cobalt(II)-tris-2,2'-bipyridine as a Spin-Crossover Complex: Evidence for Cooperative Effects in Three-Dimensional Oxalate Networks**

Mohamed Zerara, Andreas Hauser

ChemPhysChem **5** (3) (2004), p395-399

DOI:10.1002/cphc.200301044

Keywords: cooperative effects • host-guest systems • magnetic properties • spin crossover • X-ray diffraction

In the three-dimensional oxalate network structures of composition $[\text{Co}(\text{M}^{1+}(\text{bpy})_3)[\text{M}'(\text{ox})_3]$, the spin state of the $[\text{Co}(\text{bpy})_3]^{2+}$ complex can be tuned by means of chemical pressure. With $\text{M}' = \text{Na}$ it is a classic high-spin complex. Substitution of Na by Li stabilises the complex and it becomes a spin-crossover complex. Dilution with $\text{M}^{1+} = \text{Fe}$ reinforces this effect, and $\text{M}^{1+} = \text{Zn}$ reverses it.

- **Ruthenium(II) as a Novel "Labile" Partner in Thermodynamic Self-Assembly of Heterobimetallic d-f Triple-Stranded Helicates**

Stéphane Torelli, Sandra Delahaye, Andreas Hauser, Gérald Bernardinelli, Claude Piguet

Chemistry - A European Journal **10** (14) (2004), p3503-3516

DOI:10.1002/chem.200400092

Keywords: helical structures • isomerization • lanthanides • ruthenium • self-assembly

Unsymmetrical substituted bidentate benzimidazol-2-ylpyridine ligands L2 and L3 react with $[\text{Ru}(\text{dmsO})_4\text{Cl}_2]$ in ethanol to give statistical 1:3 mixtures of *fac*- $[\text{Ru}(\text{L})_3]^{2+}$ and *mer*- $[\text{Ru}(\text{L})_3]^{2+}$ ($i = 2, 3$; $\Delta G^\circ_{\text{isomerisation}} = -2.7 \text{ kJ mol}^{-1}$). In more polar solvents (acetonitrile, methanol), the free energy of the *fac*/*mer* meridional isomerisation process favours *mer*- $[\text{Ru}(\text{L})_3]^{2+}$, which is the only isomer observed in solution at the equilibrium ($\Delta G^\circ_{\text{isomerisation}} = 11.4 \text{ kJ mol}^{-1}$). Since the latter process takes several days for $[\text{Ru}(\text{L}_2)_3]^{2+}$, *fac*- $[\text{Ru}(\text{L}_2)_3]^{2+}$ and *mer*- $[\text{Ru}(\text{L}_2)_3]^{2+}$ have been separated by chromatography, but the 28-fold increase in velocity observed for $[\text{Ru}(\text{L}_3)_3]^{2+}$ provides only *mer*- $[\text{Ru}(\text{L}_3)_3]^{2+}$ after chromatography ($\text{RuCl}_2 \cdot \text{H}_2\text{O} \cdot \text{N}_3\text{O}_8\text{Cl}_2$, monoclinic, $P2_1/n$, $Z=4$). The *fac* isomer can be stabilised when an appended tridentate binding unit, connected at the 5-position of the benzimidazol-2-ylpyridine unit in ligand L1, interacts with nine-coordinate lanthanides(III). The free energy of the *fac*/*mer* meridional isomerisation is reversed ($\Delta G^\circ_{\text{isomerisation}} = 11.4 \text{ kJ mol}^{-1}$), and the $\text{Ru} \text{ae} \text{N}$ bonds are labile enough to allow the quantitative thermodynamic self-assembly of $HHH\text{-}[\text{RuLu}(\text{L}_1)_3]^{5+}$ within hours ($[\text{RuLu}(\text{L}_1)_3](\text{CF}_3\text{SO}_3)_{4.5}$, $\text{Cl}_{0.5}(\text{CH}_3\text{OH})_{2.5}$; $\text{RuLuCl}_{0.6}\text{H}_{1.09}\text{Cl}_{0.5}\text{N}_{2.1}\text{O}_{19}\text{S}_{4.5}\text{F}_{13.5}$, triclinic, P_2 , $Z=2$). Electrochemical and photophysical studies show that the benzimidazol-2-ylpyridine units in L1-L3 display similar I^{e} -acceptor properties to, but stronger I^{e} -donor properties than, those found in 2,2'-bipyridine. This shifts the intraligand $\text{I}^{\text{e}} \rightarrow \text{I}^{\text{e}}$ and the MLCT transitions toward lower energies in the pseudo-octahedral $[\text{Ru}(\text{L})_3]^{2+}$ ($i = 2, 3$) chromophores. The concomitant short lifetime of the $^3\text{MLCT}$ excited state points to efficient, thermally activated quenching via low-energy Ru-centred d-d states, a limitation which is partially overcome by mechanical coupling in $HHH\text{-}[\text{RuLu}(\text{L}_1)_3]^{5+}$.

2003

- **Investigation of the Reduced High-Potential Iron-Sulfur Protein from Chromatium vinosum and Relevant Model Compounds: A Unified Picture of the Electronic Structure of $[\text{Fe}_4\text{S}_4]^{2+}$ Systems through Magnetic and Optical Studies**

Latévi M. Lawson Daku, Jacques Pécaut, Alix Lenormand-Foucaut, Béatrice Vieux-Melchior, Peter Iveson, and Jeanne Jordanov

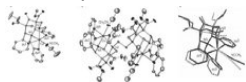
Inorganic Chemistry **42** (21) (2003), p6824-6850

DOI:10.1021/ic034494n

Magnetization measurements and variable temperature optical spectroscopy have been used to investigate, within the $4\text{ae} \sim 300 \text{ K}$ temperature range, the electronic structure of the reduced high-potential iron protein (HiPIP) from *Chromatium vinosum* and the model compounds $(\text{Cat})_2[\text{Fe}_4\text{S}_4(\text{SR})_4]$, where $\text{SR} = 2,4,6\text{-triisopropylphenylthiolate}$ (1), 2,6-diphenylphenylthiolate (2), diphenylmethylthiolate (3), 2,4,6-triisopropylbenzylthiolate (4, 4ae), 2,4,6-triphenylbenzylthiolate (5, 5ae), 2,4,6-tri-*tert*-butylbenzylthiolate (6), and $\text{Cat}^+ = \text{NEt}_4$ (1, 2, 3, 4ae , 5ae , 6), PPh_4 (4, 5). The newly synthesized $2^{\cdot-}$, $3^{\cdot-}$, $5^{\cdot-}$, and $6^{\cdot-}$ complexes are, as $1^{\cdot-}$ and $4^{\cdot-}$, excellent models of the reduced HiPIPs: they exhibit the $[\text{Fe}_4\text{S}_4]^{3+/2+}$ redox couple, because of the presence of bulky ligands which stabilize the $[\text{Fe}_4\text{S}_4]^{3+}$ oxidized core. Moreover, the presence of SCH_2 groups in $4^{\cdot-}$, $5^{\cdot-}$, and $6^{\cdot-}$, as in the $[\text{Fe}_4\text{S}_4]$ protein cores, makes them good biomimetic models of the HiPIPs. The X-ray structure of 2 is reported: it crystallizes in the orthorhombic space group $Pcca$ with no imposed symmetry and a d_{2d} -distorted geometry of the $[\text{Fe}_4\text{S}_4]^{2+}$ core. Fit of the magnetization data of the reduced HiPIP and of the 1, 2, 3, 4, 5, and 6 compounds within the exchange and double exchange theoretical framework leads to exchange coupling parameters $J = 261\text{ae} \sim 397 \text{cm}^{-1}$. A firm determination of the double exchange parameters B or, equivalently, the transfer integrals $t^2 = 5B$ could not be achieved that way. The obtained $|B|$ values remain however high, attesting thus to the strength of the spin-dependent electronic delocalization which is responsible for lowest lying electronic states being characterized by delocalized mixed-valence pairs of maximum $\text{spin}^{\cdot}/2$. Electronic properties of these systems are then accounted for by the population of a diamagnetic ground level and excited paramagnetic triplet and quintet levels, which are respectively J and $3J$ above the ground level. Optical studies of 1, 2, 4ae , 5ae , and 6 but also of $(\text{NEt}_4)_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{C}_6\text{H}_5)_4]$ and the isomorph $(\text{NEt}_4)_2[\text{Fe}_4\text{S}_4(\text{S}-t\text{Bu})_4]$ and $(\text{NEt}_4)_2[\text{Fe}_4\text{S}_4(\text{S}-t\text{Bu})_4]$ compounds reveal two absorption bands in the near infrared region, at $705\text{ae} \sim 760 \text{ nm}$ and $1270\text{ae} \sim 1430 \text{ nm}$, which appear to be characteristic of valence-delocalized and ferromagnetically coupled $[\text{Fe}_2\text{S}_2]^{2+}$ ($X = \text{S}, \text{Se}$) units. The $|B|$ and $|t^2|$ values can be directly determined from the location at $10|B|$ of the low-energy band, and are respectively $699\text{ae} \sim 787$ and $3497\text{ae} \sim 3937 \text{cm}^{-1}$. Both absorption bands are also present in the 77 K spectrum of the reduced HiPIP, at 700 and 1040 nm (Cordonio, M.; Wang, R.-H.; Rawlings, J.; Gray, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 6534 \sim 6535). The blue shift of the low-energy band is attributed to the inequivalent environments of the Fe sites in the protein, rather than to an increase of $|t^2|$ when going from the models to the HiPIP. The small differences observed in known geometries of $[\text{Fe}_4\text{S}_4]^{2+}$ clusters, especially in the $\text{Fe} \sim \text{Fe}$ distances, cannot probably lead to drastic changes in the direct $\text{Fe} \sim \text{Fe}$ interactions (parameter t^2) responsible for the delocalization phenomenon. These differences are however magnetostatically significant as shown by the $261\text{ae} \sim 397 \text{cm}^{-1}$ range spanned by J . The cluster's geometry, hence the efficiency of the $\text{Fe} \sim \text{Fe}$ superexchange pathways, is proposed to be controlled by the more or less tight fit of the cluster within the cavity provided by its environment.

- *Fine tuning the electronic properties of $[M(bpy)_3]^{2+}$ complexes by chemical pressure ($M = Fe^{2+}, Ru^{2+}, Co^{2+}$, $bpy = 2,2'$ -bipyridine)*
Andreas Hauser, Nahid Amstutz, Sandra Delahaye, Sabine Schenker, Aasma Sadki, Regula Sieber, Mohamed Zerara
Structure and Bonding **106** (2003), p81

- *Excited Spin State Trapping (LIESST, NIESST)*
Andreas Hauser, Philipp Gütlich
Comprehensive Coordination Chemistry II **2** (2003), p427



- *Bond-Stretch Isomerism: Trapped Isomeric Structures of Hexacoordinate Copper(II) Bispidine Chromophores along a Jahn-Teller Active Vibrational Coordinate*
Peter Comba, Andreas Hauser, Marion Kerscher, Hans Pritzkow
Angewandte Chemie International Edition **42** (37) (2003), p4536-4540 DOI:10.1002/anie.200351900
Keywords: coordination chemistry • copper • Jahn-Teller effects • N ligands

Copper(II) complexes of the pentadentate bispidine ligands exist in two isomeric forms (see structure) with bond-length differences up to 0.5 Å.... The stabilization of either isomer may be achieved by a variation of the substituent at N7.

- *The quantum efficiency of the photo-excitation in a Fe(II) spin-crossover compound*
Enachescu, Cristian; Oetliker, Ueli; Hauser, Andreas;
Journal of Optoelectronics and Advanced Materials **5** (1) (2003), p267-272

In this paper we discuss on the quantum efficiency in spin crossover compounds. Spin crossover solids are text-book examples of photo switchable materials that present a thermal spin transition from the diamagnetic low-spin state, thermodynamically stable at low temperatures, to the paramagnetic high-spin state becoming the thermodynamically stable state at elevated temperature. By irradiating them with an appropriate wavelength, they can pass from the stable low spin state to the metastable high spin state at temperatures below the thermal transition temperature. For the compound $[Fe(pic)_3]Cl_2 \cdot EtOH$, the question regarding the quantum efficiency of the photo-conversion process that is the number of molecules converted by one single photon and its possible dependency on irradiation intensity gave rise to a controversy. The experimental results presented in this paper demonstrate that the quantum efficiency of the photo-conversion at 11 K is on the order of unity, with no noticeable dependency of the quantum efficiency on light intensity. It does, however, depend to a small extent on the fraction of complexes already converted to the high-spin state.

- *External pressure and light influence on internal pressure in a spin-crossover solid $[Zn : Fe(ptz)_6](BF_4)_2$*
Jeftic, Jelena; Ecolivet, Claude; Hauser, Andreas;
High Pressure Research **23** (3) (2003), p359-363 DOI:10.1080/0895795031000139127

The relation between the internal pressure during spin-crossover is compared to the chemical pressure induced by dilution with zinc. Further, the light of a specific LIESST (Light Induced Excited Spin State Trapping) wavelength is used to induce partial stabilisation of high-spin state and thus shift temperature of the spin-crossover towards lower values. The de-coupling of the spin-crossover and structural phase transition is discussed.

2002

- *Ruthenium(II) complex of bis(2,2'-bipyridine)(6,7-dicyano-dipyrido[3,2-a:2',3'-c]phenazine): synthesis, structure, electrochemical and luminescence studies*

Julia Rusanova, Silvio Decurtins, Eduard Rusanov, Helen Stoeckli-Evans, Sandra Delahaye and Andreas Hauser
Dalton Transactions (23) (2002), p4318-4320 DOI:10.1039/b210440g

A novel ruthenium complex with a 6,7-dicyanosubstituted dpz ligand has been synthesised: its crystal structure and physico-chemical studies are reported.

- *Chemical pressure*

Hauser, Andreas; Amstutz, Nahid; Delahaye, Sandra; Sadki, Asmaâ; Schenker, Sabine; Sieber, Regula; Zerara, Mohamed
Chimia **56** (12) (2002), p685-689 DOI:10.2533/00094290277679858

Keywords: chemical pressure • $[Co(bpy)_3]^{2+}$ • $[Fe(bpy)_3]^{2+}$ • guest host interaction • intersystem crossing • luminescence • radiationless deactivation • $[Ru(bpy)_3]^{2+}$ • spin-crossover

The physical and photophysical properties of three classic transition metal complexes, namely $[Fe(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$, and $[Co(bpy)_3]^{2+}$, can be tuned by doping them into a variety of inert crystalline host lattices. The underlying guest-host interactions are discussed in terms of a chemical pressure.

- *Resonant and Phonon-Assisted Excitation Energy Transfer within the R_1 Lines of $[Cr(Ox)_3]^{3-}$ in a System with Two Crystallographically Non-equivalent Lattice Sites*

Marianne E. von Arx and Andreas Hauser

Journal of Physical Chemistry A **106** (31) (2002), p7106-7112 DOI:10.1021/jp020174y

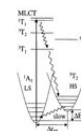
The $[Ru(bpy)_3][LiCr(ox)_3]$ system ($bpy = 2,2'$ -bipyridine, $ox =$ oxalate) has two crystallographically non-equivalent $[Cr(ox)_3]^{3-}$ sites. In steady-state resonant and nonresonant fluorescence line narrowing (FLN) experiments on the R_1 lines of the two non-equivalent $[Cr(ox)_3]^{3-}$ chromophores, multiline spectra are observed at 1.6 K. Such multiline spectra are clear evidence for resonant energy transfer processes within the inhomogeneously broadened R_1 lines. In addition, time-resolved experiments show that also site-to-site energy transfer occurs, which turns out to be resonant, too, however with a non-negligible phonon-assisted contribution even at 1.5 K.

- *Resonant Energy Transfer in the Mixed Crystal Series $[Rh(bpy)_3][NaAl_{1-x}Cr_x(ox)_3]ClO_4$ ($bpy = 2,2'$ -bipyridine, $ox =$ Oxalate, $x = 0.05-1$)*

Marianne E. von Arx, Vaughan S. Langford, Ueli Oetliker, and Andreas Hauser

Journal of Physical Chemistry A **106** (31) (2002), p7099-7105 DOI:10.1021/jp0201736

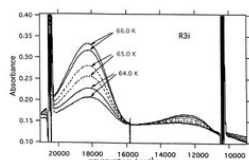
Efficient resonant energy transfer occurs within the R_1 line of the $^4A_2 \rightarrow ^4E$ transition of the $[Cr(ox)_3]^{3-}$ chromophore in mixed crystal $[Rh(bpy)_3][NaAl_{1-x}Cr_x(ox)_3]ClO_4$ ($x = 0.05-1$, $ox =$ oxalate, $bpy = 2,2'$ -bipyridine). This manifests itself in the form of multiline patterns in resonant fluorescence line narrowing (FLN) experiments at 1.5 K. The conditions for such a resonant process to occur are that the inhomogeneous line width of the R_1 line is larger than the zero-field splitting of the ground state, which, in turn, is larger than the homogeneous line width of the transition. The number of lines and their relative intensities depend critically upon the $[Cr(ox)_3]^{3-}$ concentration and the excitation wavelength within the inhomogeneous distribution. The basic model for resonant energy transfer as presented by von Arx et al. (*Phys. Rev B* **1996**, **54**, 15800) is extended to include the effects of diluting the chromophores in an inert host lattice and of nonresonant R_2 excitation. In addition, Monte Carlo simulations serve to explain the temporal evolution of the multiline pattern following pulsed excitation.



- **Photoexcitation in the Spin-Crossover Compound $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ ($\text{pic} = 2\text{-Picolyamine}$)**
Enachescu, C.; Oetliker, U.; Hauser, A.
Journal of Physical Chemistry B **106** (37) (2002), p9540-9545 DOI:10.1021/jp020765o

$[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ ($\text{pic} = 2\text{-picolyamine}$) is a spin-crossover compound that can be converted from the low-spin state to the high-spin state at temperatures below the thermal transition temperature by way of light irradiation in the visible part of the electromagnetic spectrum. For this compound, the question regarding the quantum efficiency of this photoconversion process and its possible dependence on irradiation intensity gave rise to some controversy. The experimental results presented in this paper demonstrate that the quantum efficiency of the photoconversion at 11 K is on the order of unity, with no noticeable dependence on irradiation intensity. It does, however, depend to some extent on the fraction of complexes already converted to the high-spin state.

2001



- **Quasi-static nature of the light induced thermal hysteresis in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ spin-transition solid**
Jefic, J.; Matsarski, M.; Hauser, A.; Goujon, A.; Codjovi, E.; Linares, J.; Varret, F.;
Polyhedron **20** (11-14) (2001), p1599-1606 DOI:10.1016/S0277-5387(01)00660-X
Keywords: light induced thermal hysteresis • $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ • spin-transition solid

The quasi-static nature of a light induced thermal hysteresis was studied on the spin-transition compound $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, by means of optical spectroscopy and magnetic measurements in the temperature interval between 10 and 80 K. Various experimental procedures are discussed in relation to the competition between the two processes considered, namely the photoexcitation and the high-spin \rightarrow low-spin relaxation. A detailed discussion of the experimental parameters, which should be considered in order to avoid erroneous interpretations of LITH, is given.

- **Biphasic Behaviour in the High-Spin \rightarrow Low-Spin Relaxation of $[\text{Fe}(\text{btpa})](\text{PF}_6)_2$ in solution ($\text{btpa} = \text{N}, \text{N}, \text{N}', \text{N}'$ -Tetrakis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-bipyridine)**
S. Schenker, P. C. Stein, J. A. Wolny, C. Brady, J. J. McGarvey, H. Toftlund, A. Hauser
Inorganic Chemistry **40** (1) (2001), p134-139 DOI:10.1021/ic000656t

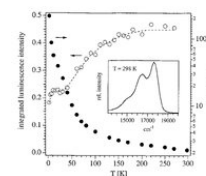
The light-induced high-spin \rightarrow low-spin relaxation for the $\text{Fe}(\text{II})$ spin-crossover compounds $[\text{Fe}(\text{btpa})](\text{PF}_6)_2$ and $[\text{Fe}(\text{b(bdpa)})](\text{PF}_6)_2$ in solution, where btpa is the potentially octadentate ligand $\text{N}, \text{N}, \text{N}', \text{N}'$ -tetrakis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-bipyridine and b(bdpa) is the analogous hexadentate ligand $\text{N}, \text{N}, \text{N}', \text{N}'$ -bis(benzyl)- $\text{N}, \text{N}, \text{N}', \text{N}'$ -bis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-bipyridine, respectively, has been studied by temperature-dependent laser flash photolysis. $[\text{Fe}(\text{b(bdpa)})](\text{PF}_6)_2$ shows single-exponential $^5\text{T}_2 \rightarrow ^5\text{A}_1$ relaxation kinetics, whereas $[\text{Fe}(\text{btpa})](\text{PF}_6)_2$ exhibits solvent-independent biphasic relaxation kinetics. The fast process of $[\text{Fe}(\text{btpa})](\text{PF}_6)_2$ with a rate constant, k_{HL} , of $2.5 \times 10^7 \text{ s}^{-1}$ at 295 K and an activation energy, E_a , of $1294(26) \text{ cm}^{-1}$ in methanol can be assigned to the $^5\text{T}_2 \rightarrow ^5\text{A}_1$ relaxation as well. The slow process with a k_{HL} (295 K) of $3.7 \times 10^5 \text{ s}^{-1}$ and a E_a of $2297(32) \text{ cm}^{-1}$ in methanol is assigned to a coupling of the $^5\text{T}_2 \rightarrow ^5\text{A}_1$ relaxation process to a geometrical rearrangement within the pendent pyridyl arms.

2000

- **Pressure, temperature and light influence on spin transition solids**
Jelena Jefic, Andreas Hauser, François Varret, Claude Ecolivet
High Pressure Research **18** (1-6) (2000), p195-201 DOI:10.1080/08957950008200968

Present paper is an overview of our efforts during the past few years to understand complicated correlations of physical phenomena related to pressure in $\text{Fe}(\text{II})$ solid state spin transition systems. Some principal results concerning p , T , λ -experiments are extracted. In the context of correlation of the crystallographic phase transition with simultaneous HS \rightarrow LS relaxation and LS \rightarrow HS photopopulation, we show the latest results: Brillouin and magnetic measurements on the crystal $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$.

- **Luminescence and Energy Transfer of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Cr}(\text{ox})_3]^{3-}$, and $[\text{Os}(\text{bpy})_3]^{2+}$ in Three-Dimensional Oxalato-Networks**
von Arx, M. E.; Burattini, E.; Hauser, A.; van Pieterse, L.; Pellaux, R.; Decurtins, S.
Journal of Physical Chemistry A **104** (5) (2000), p883-893 DOI:10.1021/jp993368v



Luminescence and energy transfer in $[\text{Zn}_{1-x}\text{Ru}_x(\text{bpy})_3][\text{NaAl}_x\text{Cr}_y(\text{ox})_3]$ ($x \approx 0.01$, $y \approx 0.006$ to 0.22 ; $\text{bpy} = 2,2'$ -bipyridine, $\text{ox} = \text{C}_2\text{O}_4^{2-}$) and $[\text{Zn}_{1-x}\text{Ru}_x\text{Os}_y(\text{bpy})_3][\text{NaAl}(\text{ox})_3]$ ($x \approx 0.01$, $y \approx 0.012$) are presented and discussed. Surprisingly, the luminescence of the isolated luminophores $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3][\text{NaAl}(\text{ox})_3]$ is hardly quenched at room temperature. Steady-state luminescence spectra and decay curves show that energy transfer occurs between $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Cr}(\text{ox})_3]^{3-}$ and between $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ in $[\text{Zn}_{1-x}\text{Ru}_x\text{Os}_y(\text{bpy})_3][\text{NaAl}_x\text{Cr}_y(\text{ox})_3]$ and $[\text{Zn}_{1-x}\text{Ru}_x\text{Os}_y(\text{bpy})_3][\text{NaAl}(\text{ox})_3]$, respectively. For a quantitative investigation of the energy transfer, a shell type model is developed, using a Monte Carlo procedure and the structural parameters of the systems. A good description of the experimental data is obtained assuming electric dipole \rightarrow electric dipole interaction between donors and acceptors, with a critical distance R_c for $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Cr}(\text{ox})_3]^{3-}$ energy transfer of 15 \AA ... and for $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Os}(\text{bpy})_3]^{2+}$ energy transfer of 33 \AA These values are in good agreement with those derived using the Förster-Dexter theory.

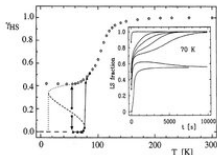
- **A thermal spin transition in $[\text{Co}(\text{bpy})_3][\text{LiCr}(\text{ox})_3]$ ($\text{ox} = \text{C}_2\text{O}_4^{2-}$; $\text{bpy} = 2,2'$ -bipyridine)**
Regula Sieber, Silvio Decurtins, Helen Stoeckli-Evans, Claire Wilson, Dima Yufit, Judith A. K. Howard, Silvia C. Capelli, Andreas Hauser
Chemistry - A European Journal **6** (2) (2000), p361-368
DOI:10.1002/(SICI)1521-3765(20000117)6:2<361::AID-CHEM361>3.0.CO;2-Y
Keywords: cobalt • magnetic properties • N ligands • optical properties • oxalate networks • spin crossover

Incorporation of $[\text{Co}(\text{bpy})_3]^{2+}$ into the cavities of the three-dimensional oxalate network structure in $[\text{Co}(\text{bpy})_3][\text{LiCr}(\text{ox})_3]$ produces chemical pressure that destabilises the normal high-spin ground state $^4\text{T}_1$ to such an extent that the $[\text{Co}(\text{bpy})_3]^{2+}$ complex becomes a spin-crossover complex. It shows a temperature-dependent equilibrium between the ^2E low-spin and the $^4\text{T}_1$ high-spin states.

- Spiering, H.; Kohlhaas, T.; Romstedt, H.; Hauser, A.; Bruns-Yilmaz, C.; Kusz, J.; Gütlich, P.; Coordination Chemistry Reviews **190-192** (1999), p629-647 DOI:10.1016/S0010-8545(99)00109-5
Keywords: phase transition • spin crossover • correlation

- Jelena Jetic, François Varret, Andreas Hauser, Olivier Roubeau, Marie Matsarski, Jean-Pierre Rivera
Molecular Crystals and Liquid Crystals **335** (1999), p511-520 DOI:10.1080/10587259908028892
Keywords: spin transition • photography • laser photoexcitation • instability

- Vaughan S. Langford, Marianne E. von Arx, and Andreas Hauser
Journal of Physical Chemistry A **103** (36) (1999), p7161-7169 DOI:10.1021/jp9911301



- Keywords: iron(II) coordination compounds • spin-crossover • cooperative effects • high-spin \leftrightarrow low-spin relaxation • bistability

- P. Gülich, A. Hauser, H. Spiering
Inorganic Electronic Structure and Spectroscopy Vol 2 (1999), p575

- Schenker, A. Hauser, W. Wang, I. Y. Chan
Chemical Physics Letters **297** (3-4) (1998), p281-286 DOI:10.1016/S0009-2614(98)01136-1

- *High-spin -> low-spin relaxation in $[Zn_{1-x}Fe_x(6\text{-mepy})_3(py)_y\text{tren}](PF_6)_2$*

S. Schenker, A. Hauser, W. Wang, I. Y. Chan

Journal of Chemical Physics **109** (22) (1998), p9870-9878

DOI:10.1063/1.477681

The thermal spin transition in the diluted mixed crystal $[Zn_{1-x}Fe_x(6\text{-mepy})_3\text{tren}](PF_6)_2$ ($x = 0.00025$, $6\text{-mepy} = 4\text{-methyl-2-pyridyl-3-aza-3-butenylamine}$) is studied at 1 bar and 1 kbar by temperature-dependent absorption spectroscopy. From thermodynamic analysis of the high-spin (HS) fractions, values for ΔH_{HS} and ΔS_{HS} of $1551(50) \text{ cm}^3 \text{ mol}^{-1}$ and $7.5(5) \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ and a molecular volume of reaction ΔV_{HS} of $22(2) \text{ Å}^3$ result. Reconsideration of the cooperative effects in the neat $[Fe(6\text{-mepy})_3\text{tren}](PF_6)_2$ from Adler et al. [Hyperfine Interact. **47**, 343 (1989)] result in a lattice shift, ΔV_{HS} of $208(15) \text{ cm}^3 \text{ mol}^{-1}$ and an interaction constant, I^{a} , of $109(15) \text{ cm}^3 \text{ mol}^{-1}$. Temperature-dependent laser flash photolysis experiments in the spin-crossover system $[Zn_{1-x}Fe_x(6\text{-mepy})_3\text{tren}](PF_6)_2$ and the LS system $[Zn_{1-x}Fe_x(py)_3\text{tren}](PF_6)_2$ in the pressure range between 1 bar and 1 kbar are presented. Above $\approx 100 \text{ K}$ the HS \rightarrow LS (low-spin) relaxations behave classically, whereas they become almost temperature independent below 50 K. At ambient pressure, the low-temperature tunneling rate constant in $[Zn_{1-x}Fe_x(py)_3\text{tren}](PF_6)_2$ is more than three orders of magnitude larger than the one in $[Zn_{1-x}Fe_x(6\text{-mepy})_3\text{tren}](PF_6)_2$. An external pressure of 27 kbar accelerates the low-temperature tunneling process by almost nine orders of magnitude. The kinetic results are discussed within the theory of nonadiabatic multiphonon relaxation.

- *High-spin \rightarrow low-spin relaxation in the two-step spin-crossover compound $[Fe(pic)_3]Cl_2 \cdot EtOH$ ($pic = 2\text{-picolylamine}$)*

H. Romstedt, A. Hauser, H. Spiering

Journal of Physics and Chemistry of Solids **59** (2) (1998), p265-275

DOI:10.1016/S0022-3697(97)00142-X

Keywords: Fe(II) compounds • high spin-low spin relaxation • two-step spin transition

The spin-crossover compound $[Fe(pic)_3]Cl_2 \cdot EtOH$ ($pic = 2\text{-picolylamine}$) shows an unusual two-step spin transition. This is thought to be caused by specific nearest-neighbour interactions and short-range correlations and requires a theoretical treatment of the elastic interactions between the spin-changing molecules beyond the mean-field approximation. Such short-range correlations also influence the high-spin \rightarrow low-spin relaxation following the light-induced population of the high-spin state at cryogenic temperatures, leading to characteristic deviations from the predictions of a mean-field treatment. These deviations are directly observable by comparison of the full and unperturbed relaxation curves with curves for which the short-range correlations were destroyed using an appropriate irradiation technique. Monte Carlo simulations including both nearest-neighbour and long-range interactions give a description of the observed relaxation curves which is consistent with the thermal spin equilibrium.

1997

- *Crystal structures, magnetic structures and photophysics in supra-molecular transition-metal oxalate compounds*

Silvio Decurtins, Helmut W. Schmalte, René Pellaux, Peter Fischer, Andreas Hauser

Molecular Crystals and Liquid Crystals **305** (1997), p227-237

DOI:10.1080/10587259708045060

Polymeric two- and three-dimensional, homo- and heterometallic oxalate-bridged coordination compounds offer exciting opportunities, mainly in the fields of molecular magnetism and photophysics. Given that a large variety of magnetic phenomena have been reported so far from these molecular magnets, very limited experience is gained from elastic neutron scattering experiments. Therefore, with two examples, we will address the topic of the elucidation of magnetic structures by means of the neutron scattering technique. In addition, due to the possibility of the variation of different metal ions in varying oxidation states, interesting photophysical processes can be observed within the extended three-dimensional host/guest systems.

- *Helium gas pressure cell for pressures up to 1 kbar (0.1 GPa) in conjunction with the cold head of a closed-cycle He refrigerator*

Jelena Jetic, Ueli Kindler, Hartmut Spiering and Andreas Hauser

Measurement science and technology **8** (5) (1997), p479-483

DOI:10.1088/0957-0233/8/5/003

A helium gas pressure cell for pressures up to 1 kbar (0.1 GPa) has been developed in conjunction with a closed-cycle He refrigerator allowing variable temperatures between 15 and 300 K. Both cell and refrigerator are equipped with optical windows suitable for photophysical measurements, such as temperature- and pressure-dependent absorption spectroscopy or laser flash photolysis. Examples of measurements on iron(II) spin-crossover systems are given. In these compounds, comparatively small external pressures induce significant changes in the thermodynamic equilibrium as well as in the relaxation dynamics.

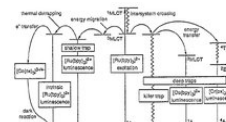
- *Magnetism and photophysics in supramolecular transition-metal compounds*

S. Decurtins, H.W. Schmalte, R. Pellaux, A. Hauser, M.E. von Arx and P. Fischer

Synthetic metals **85** (1-3) (1997), p1689-1694

DOI:10.1016/S0379-6779(97)80399-2

Keywords: self-organization in macromolecules • neutron diffraction • magnetic phase transition



Based on a synthetic strategy, extended anionic, homo and bimetallic oxalato-bridged transition-metal compounds with two (2D) and three-dimensional (3D) connectivities can be synthesized and crystallized. Thereby, the choice of the templating counterions will determine the crystal chemistry. Since the oxalato bridge is a mediator for both antiferro and ferromagnetic interactions between similar and dissimilar metal ions, long-range magnetic ordering will occur. Examples of the determination of magnetic structures in 2D and 3D compounds by means of elastic neutron scattering methods will be discussed. In addition, due to the possibility of the variation of different metal ions in varying oxidation states, interesting photophysical processes can be observed within the extended three-dimensional host/guest systems.

- *Pressure effects on the HS -> LS relaxation in $[Zn_{1-x}Fe_x(6\text{-mepy})_3\text{tren}](PF_6)_2$*

Wei Wang, I. Y. Chan, Sabine Schenker, and Andreas Hauser

Journal of Chemical Physics **106** (9) (1997), p3817-3820

DOI:10.1063/1.473436

Laser flash photolysis experiments were performed on the mixed crystal $[Zn_{1-x}Fe_x(6\text{-mepy})_3\text{tren}](PF_6)_2$ ($x = 0.00025$) at 10 K in the pressure range between 1 bar and 20 kbar. An external pressure of 20 kbar accelerates the low-temperature tunneling process by almost eight orders of magnitude.

- *Cooperativity in the Iron(II) Spin-Crossover Compound $[Fe(ptz)_6](PF_6)_2$ under the Influence of External Pressure ($ptz = 1\text{-}n\text{-Propyltetrazole}$)*

J. Jetic, R. Hinek, S.C. Capelli, A. Hauser

Inorganic Chemistry **36** (14) (1997), p3080-3087

DOI:10.1021/ic961404o

The iron(II) spin-crossover compound $[Fe(ptz)_6](PF_6)_2$ ($ptz = 1\text{-}n\text{-propyltetrazole}$) crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.6439(4) \text{ Å}$, $b = 10.8685(4) \text{ Å}$, $c = 11.7014(4) \text{ Å}$, $\alpha = 75.644(1)^\circ$, $\beta = 71.671(1)^\circ$, $\gamma = 60.815(1)^\circ$, and $Z = 1$. In $[Fe(ptz)_6](PF_6)_2$, the thermal spin transition is extremely steep because of cooperative effects of elastic origin. The transition temperature at ambient pressure is $74(1) \text{ K}$. An external pressure of 1 kbar shifts the transition temperature to $102(1) \text{ K}$, corresponding to a stabilization of the low-spin state, which is smaller in volume. The volume difference between the high-spin and the low-spin state, ΔV_{HS} , is $24(2) \text{ Å}^3$ /molecule. The interaction constant I^{a} , as a measure of cooperativity, is within experimental error independent of external pressure and has a value of $101(5) \text{ cm}^3 \text{ mol}^{-1}$. In contrast to the case of the related compound $[Fe(ptz)_6](BF_4)_2$ (Decurtins et al. *Inorg. Chem.* **1985**, **24**, 2174), there is no hysteresis due to a first-order crystallographic phase transition, nor is there a hysteresis induced by external pressure as in the mixed crystal $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$, $x = 0.1$ (Jetic et al. *J. Phys. Chem. Solids* **1996**, **57**, 1743). However, in $[Fe(ptz)_6](PF_6)_2$, the

interaction constant \hat{I}^c is found to be very close to the critical value above which a hysteresis solely due to the cooperative effects is expected. In addition, high-spin $\hat{\alpha}^+$ low-spin relaxation measurements were performed under external pressures of up to 1 kbar in the temperature interval between 50 and 60 K. An external pressure of 1 kbar accelerates the high-spin $\hat{\alpha}^+$ low-spin relaxation by 1 order of magnitude.

- *Pressure Study of the Thermal Spin Transition and the High-Spin \rightarrow Low-Spin Relaxation in the R3 and P1 Crystallographic Phases of $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ Single Crystals ($x = 0.1, 0.32, \text{ and } 1$; $\text{ptz} = 1\text{-}n\text{-propyltetrazole}$)*

J. Jętko, A. Hauser

Journal of Physical Chemistry B **101** (49) (1997), p10262-10270

DOI:10.1021/jp972083k

In the iron(II) spin-crossover compound $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, the thermal spin transition is accompanied by a crystallographic phase transition showing a hysteresis with $T_c^{\text{HT}} = 128 \text{ K}$ and $T_c^{\text{LT}} = 135 \text{ K}$ at ambient pressure [Franke, P. L.; Haasnot, J. G.; Zuur, A. P. *Inorg. Chim. Acta* **1982**, *59*, 5]. The hysteresis is due to an interplay between the spin-transition and the $R^3\hat{\alpha}^+P\hat{\alpha}^-$ crystallographic phase transition with a large low-spin fraction stabilizing the $P\hat{\alpha}^-$ phase at low temperatures. In the mixed crystal $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$, $x = 0.1$, with the iron complexes imbedded into the isomorphous zinc lattice, the crystallographic phase transition can be induced by an external pressure [Jętko, J.; Romstedt, H.; Hauser, A. *J. Phys. Chem. Solids* **1996**, *57*, 1743]. Thus the $P\hat{\alpha}^-$ phase is additionally stabilized by external pressure. The interaction constant \hat{I}^c , which describes cooperative effects between the spin-changing complexes, differs for the two crystallographic phases. Values for $\hat{I}^c(P\hat{\alpha}^-)$ of $144(8) \text{ cm}^3$ and the volume difference \hat{V}_{HL} of $29(4) \text{ \AA}^3$ are determined from a simultaneous fit to a series of transition curves for different pressures and iron content in the $P\hat{\alpha}^-$ phase. These values are compared to the corresponding values for the R^3 phase, viz. $\hat{I}^c(R^3)$ of $170(9) \text{ cm}^3$ and $\hat{V}_{\text{HL}}(R^3)$ of $26(3) \text{ \AA}^3$. Surprisingly $\hat{I}^c(R^3)$ is larger than $\hat{I}^c(P\hat{\alpha}^-)$ despite the fact that $\hat{V}_{\text{HL}}(R^3)$ is smaller than $\hat{V}_{\text{HL}}(P\hat{\alpha}^-)$. The high-spin $\hat{\alpha}^+$ low-spin relaxation at temperatures above $\sim 80 \text{ K}$ is thermally activated, while below $\sim 40 \text{ K}$ temperature independent tunnelling takes place. An external pressure of 1 kbar accelerates the high-spin $\hat{\alpha}^+$ low-spin relaxation exponentially by 1 order of magnitude in the tunnelling region in both crystallographic phases and regardless of x . In the concentrated material the high-spin $\hat{\alpha}^+$ low-spin relaxation is self-accelerating due to a buildup of an internal pressure [Hauser, A. *Chem. Phys. Lett.* **1992**, *192*, 65]. Both cooperative effects and external pressure result in a shift of the maximum of the $^1\text{A}_1\hat{\alpha}^+T_1$ absorption band.

1996

- *Role of π -Bonding for Trigonal Level Splittings in Chromium(III) Complexes. 4. Doublet States and Zeeman Level Splittings in $[\text{Cr}(\text{bpy})_3]^{3+}$*

Thomas Schönher, Michail Atanasov, and Andreas Hauser

Inorganic Chemistry **35** (7) (1996), p2077-2084

DOI:10.1021/ic950150o

A detailed analysis of Zeeman splittings of highly resolved spin-forbidden transitions in $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$ is presented. Assignments of vibronic bands are made based on low-temperature absorption, emission, and infrared spectra. The pattern of doublet states, obtained for $H = 0$ and $H = 5 \text{ T}$, is consistent with angular overlap model (AOM) calculations, which allow one to consider I_f - and I_e -interactions between the metal-d and relevant ligand orbitals and the particular angular geometry of the chromophore simultaneously. The observed level splittings are found to result from the combined effect of trigonal distortion and contributions of the symmetry adapted d_{ie} -orbitals involved due to coupling with corresponding counterparts from the bidentate ligand (*phase coupling*). The larger splitting of the lowest excited state $^2E_g(O_h)$ in the analogous CrO_4 salt is due to the more distorted geometry of the $[\text{CrN}_6]$ moiety. Related properties of the bipyridine ligand, which turn out to show donor behavior in the present compounds, and the acetylacetonate ligand are discussed, and AOM parameters for the metal-ligand I_e -interaction are correlated with results of MO calculations.

- *Resonant excitation energy transfer in $[\text{Rh}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]\text{ClO}_4$*

Andreas Hauser, Hans Riesen, René Pellaux and Silvio Decurtins

Chemical Physics Letters **261** (3) (1996), p313-317

DOI:10.1016/0009-2614(96)00969-4

Resonant fluorescence line narrowing of the R_1 line of the $[\text{Cr}(\text{ox})_3]^{3+}$ chromophore in $[\text{Rh}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]\text{ClO}_4$ at 1.6 K neither gives rise to the usual three-line pattern nor to spectral diffusion. Instead multi-line spectra with spacings equal to the zero-field splitting of the ground state are observed. This phenomenon is attributed to efficient non-radiative resonant energy transfer within the R_1 line.

- *Resonant and phonon-assisted excitation energy transfer in the R_1 line of $[\text{Cr}(\text{ox})_3]^{3+}$*

M. E. von Arx, A. Hauser, H. Riesen, R. Pellaux, S. Decurtins

Physical Review B **54** (22) (1996), p15800-15807

DOI:10.1103/PhysRevB.54.15800

In resonant fluorescence line narrowing (FLN) experiments in the R_1 transition of the $[\text{Cr}(\text{ox})_3]^{3+}$ chromophore in $[\text{Ru}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$ and $[\text{Rh}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]\text{ClO}_4$ multiline spectra are observed at 1.8 K , ($\text{ox} = \text{oxalate}$, $\text{bpy} = 2,2'$ -bipyridine). For $[\text{Rh}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]\text{ClO}_4$ the number of lines and their relative intensities depend critically upon the excitation wavelength within the inhomogeneous distribution, and in time-resolved FLN experiments additionally upon the delay. This behavior is clear evidence for a resonant energy-transfer process. At 4.2 K the more common phonon-assisted process becomes dominant, manifesting itself as spectral diffusion.

- *Photophysical and photochemical properties of three-dimensional metal-tris-oxalate network structures.*

A. Hauser, M. E. von Arx, R. Pellaux, S. Decurtins

Molecular Crystals and Liquid Crystals **286** (1996), p225-230

DOI:10.1080/10587259608042290

Chemical variation and combination of metal ions of different valencies in the oxalate backbone as well as in the tris-bpy cation of the three-dimensional network structures of the type $[\text{M}^{\text{II}}(\text{ox})_3][\text{M}^{\text{II}}(\text{bpy})_3]$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{ox} = \text{C}_2\text{O}_4^{2-}$), $[\text{M}^{\text{III}}(\text{ox})_3][\text{M}^{\text{II}}(\text{bpy})_3]$ and $[\text{M}^{\text{III}}(\text{ox})_3][\text{M}^{\text{III}}(\text{bpy})_3]\text{ClO}_4$ offer unique opportunities for studying a large variety of photophysical processes. Depending upon the relative energies of the excited states of the chromophores, excitation energy transfer either from the tris-bipyridine cation to the oxalate backbone or vice versa is observed, as for instance from $[\text{Ru}(\text{bpy})_3]^{2+}$ as photo-sensitizer to $[\text{Cr}(\text{ox})_3]^{3-}$ as energy acceptor in the combination $[\text{NaCr}(\text{ox})_3][\text{Ru}(\text{bpy})_3]$, or from $[\text{Cr}(\text{ox})_3]^{3-}$ to $[\text{Cr}(\text{bpy})_3]^{3+}$ in $[\text{NaCr}(\text{ox})_3][\text{Cr}(\text{bpy})_3]\text{ClO}_4$. In addition efficient energy migration within the oxalate backbone is observed. Furthermore, depending upon the excited state redox potentials, light-induced electron transfer processes may be envisaged.

- *Chiral three-dimensional supramolecular compounds: Homo and bimetallic oxalate and 1,2-dithiooxalate-bridged networks. A structural and photophysical study.*

S. Decurtins, H.W. Schmalle, R. Pellaux, P. Schneuwly, A. Hauser

Inorganic Chemistry **35** (6) (1996), p1451-1460

DOI:10.1021/ic950791j

In analogy to the $[\text{M}^{\text{II}}(\text{bpy})_3]^{2+}$ cations, where M^{II} is a divalent transition-metal and bpy is $2,2'$ -bipyridine, the tris-chelated $[\text{M}^{\text{II}}(\text{bpy})_3]^{3+}$ cations, where M^{II} is Cr^{II} or Co^{II} , induce the crystallization of chiral, anionic three-dimensional (3D) coordination polymers of oxalate-bridged ($1/4\text{-ox}$) metal complexes with stoichiometries $[\text{M}^{\text{II}}(\text{ox})_3]^{2-}$ or $[\text{M}^{\text{III}}(\text{ox})_3]^{2-}$. The tripositive charge is partially compensated by inclusion of additional complex anions like ClO_4^- , BF_4^- , or PF_6^- which are encapsulated in cubic shaped cavities formed by the bipyridine ligands of the cations. Thus, an elaborate structure of cationic and anionic species within a polymeric anionic network is realized. The compounds isolated and structurally characterized include $[\text{Cr}^{\text{II}}(\text{bpy})_3][\text{ClO}_4]_3$ (**1**), $[\text{Cr}^{\text{II}}(\text{bpy})_3][\text{ClO}_4][\text{Mn}^{\text{II}}_2(\text{ox})_3]$ (**2**), $[\text{Cr}^{\text{II}}(\text{bpy})_3][\text{BF}_4][\text{Mn}^{\text{II}}_2(\text{ox})_3]$ (**3**), $[\text{Co}^{\text{II}}(\text{bpy})_3][\text{PF}_6][\text{NaCr}^{\text{III}}(\text{ox})_3]$ (**4**). Crystal data: **1**, cubic, $P2_13$, $a = 15.523(4) \text{ \AA}$, $Z = 4$; **2**, cubic, $P4_32$, $a = 15.564(3) \text{ \AA}$, $Z = 4$; **3**, cubic, $P4_32$, $a = 15.553(3) \text{ \AA}$, $Z = 4$; **4**, cubic, $P2_13$, $a = 15.515(3) \text{ \AA}$, $Z = 4$. Furthermore, it seemed likely that 1,2-dithiooxalate (dto) could act as an alternative to the oxalate bridging ligand, and as a result the compound $[\text{Ni}^{\text{II}}(\text{phen})_3][\text{NaCo}^{\text{III}}(\text{dto})_3]\text{C}_3\text{H}_5\text{O}$ (**5**) has successfully been isolated and structurally characterized. Crystal data: **5**, orthorhombic, $P2_12_12_1$, $a = 16.238(4) \text{ \AA}$, $b = 16.225(4) \text{ \AA}$, $c = 18.371(5) \text{ \AA}$, $Z = 4$. In addition, the

photophysical properties of compound **1** have been investigated in detail. In single crystal absorption spectra of $[\text{Cr}^{\text{III}}(\text{bpy})_3][\text{ClO}_4][\text{NaCr}^{\text{III}}(\text{ox})_3]$ (**1**), the spin-flip transitions of both the $[\text{Cr}(\text{bpy})_3]^{3+}$ and the $[\text{Cr}(\text{ox})_3]^{3-}$ chromophores are observed and can be clearly distinguished. Irradiating into the spin-allowed $^4A_g \rightarrow ^4T_2$ absorption band of $[\text{Cr}(\text{ox})_3]^{3-}$ results in intense luminescence from the 2E state of $[\text{Cr}(\text{bpy})_3]^{3+}$ as a result of rapid energy transfer processes.

- *Intersystem Crossing Dynamics in the Iron(III) Spin-Crossover Compounds $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ and $[\text{Fe}(\text{Sal}_2\text{tr})]\text{PF}_6$*

S. Schenker, A. Hauser, R. M. Dyson

Inorganic Chemistry **35** (16) (1996), p4676-4682

DOI:10.1021/ic960010u

The high-spin \rightarrow low-spin relaxation dynamics of the Fe(III) spin-crossover complexes $[\text{Fe}(\text{Sal}_2\text{tr})]\text{PF}_6$ ($\text{H}_2\text{Sal}_2\text{tr}$ = Bis(salicylaldimino)triethylenetetramine) and $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ (Hacpa = *N*-(1-acetyl-2-propylidene)-2-pyridylmethylamine) are discussed within the theory of nonadiabatic multiphonon relaxation. A Huang-Rhys factor S of ~ 25 , estimated on the basis of average metal-ligand bond length differences Δr_{HL} of ~ 0.12 Å..., explains the observed low-temperature tunneling rate constants $k_{\text{HL}}(T \rightarrow 0)$ of $\sim 10^2$ s $^{-1}$ Å as well as the thermally activated process at $T > \sim 100$ K semiquantitatively. The results obtained for the Fe(III) compounds are compared to those for Fe(II) spin-crossover compounds.

- *The HS \rightarrow LS Relaxation under External Pressure in the Fe(II) Spin Crossover System $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ (ptz = 1-propyltetrazole, $x = 0.1$)*

J. Jętic, A. Hauser

Chemical Physics Letters **248** (5-6) (1996), p458-463

DOI:10.1016/0009-2614(95)01297-4

At low temperatures an external pressure of 1 kbar accelerates the high-spin \rightarrow low-spin relaxation in the $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ ($x = 0.1$, spin-crossover system by one order of magnitude. This is due to the large difference in volume between the high-spin and low-spin states of 26 Å 3 /molecule. The relative vertical and horizontal shifts of the potential wells of the two states as a function of pressure are estimated to be 130 cm $^{-1}$ /kbar and 10 $^{-3}$ Å/kbar, respectively.

- *Interplay between the spin transition and the crystallographic phase transition in the Fe(II) spin-crossover system $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ ($x = 0.1$; ptz = 1-propyltetrazole)*

J. Jętic, H. Romstedt, A. Hauser

Journal of Physics and Chemistry of Solids **57** (11) (1996), p1743-1750

DOI:10.1016/0022-3697(96)00033-9

Keywords: inorganic compounds • high pressure • phase transitions • thermodynamic properties

In the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (ptz = 1-propyltetrazole) spin-crossover system, the thermal spin transition is accompanied by a first order crystallographic phase transition ($T_c^{\text{HS}} = 128$ K and $T_c^{\text{LS}} = 135$ K) from $R\bar{3}c$ above T_c^{HS} to $P\bar{1}$ at low temperatures (Wiehl L., *Acta Cryst.* **B49**, 289 (1993)). The high-symmetry phase can be super-cooled, in which case the spin transition is still complete and quite steep ($T_{1/2} = 125 \pm 2$ K) but now without a hysteresis. The corresponding interaction constant $|J|$ is 170 cm $^{-1}$. In the diluted system $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ ($x = 0.1$), the spin transition is gradual with $T_{1/2} = 95 \pm 2$ K. From the shift of $T_{1/2}$ towards high temperatures with external pressure a value for $|J|$ of 26 Å 3 /molecule is obtained. Pressures above 250 bar induce a crystallographic phase transition even in the diluted system, as a result of which the spin transition is discontinuous. The interplay between the thermal spin transition and the crystallographic phase transition in the neat and the diluted system is discussed consistently.

- *The $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ Spin-Crossover System - Part Two: Hysteresis in the LIESST Regime*

R. Hinek, H. Spiering, P. Gütllich, A. Hauser

Chemistry - A European Journal **2** (11) (1996), p1435-1439

DOI:10.1002/chem.19960021116

Keywords: hysteresis • iron complexes • LIESST • spin crossover • tetrazoles

In the $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ spin-crossover system the iron(II) complexes occupy two nonequivalent lattice sites, sites A and B. Complexes on site A show a thermal high-spin (HS) \rightarrow low-spin (LS) transition at 105 K, whereas complexes on site B remain in the HS state down to 10 K. Complexes on both sites exhibit light-induced spin state conversions (LIESST) at 20 K: LS \rightarrow HS on site A with $\lambda = 514.5$ nm, and HS \rightarrow LS on site B with $\lambda = 820$ nm. The relaxation processes subsequent to the HS \rightarrow LS conversion on site B reveal a light-induced HS \rightarrow LS bistability for the complexes on site B at 70 K. The bistability as well as the absence of a thermal spin transition on site B are attributed to a thermal hysteresis for the B-site complexes with a critical temperature T^{HS} K on heating. This hysteresis can be interpreted in terms of strong cooperative effects of elastic origin, which, in addition, cause characteristic deviations of the relaxation on site B from first-order kinetics (self-acceleration). In contrast, the HS \rightarrow LS relaxation at 60 K on site A after irradiation with $\lambda = 514.5$ nm shows an unusual self-retardation.

- *The $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ Spin-Crossover System - Part One: HS-LS Transition on Two Lattice Sites*

R. Hinek, H. Spiering, D. Schollmeyer, P. Gütllich, A. Hauser

Chemistry - A European Journal **2** (11) (1996), p1427-1434

DOI:10.1002/chem.19960021115

Keywords: iron complexes • LIESST • spin crossover • tetrazoles

The $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ spin-cross-over system (etz = 1-ethyl-1H-tetrazole) crystallizes in space group $P\bar{1}$, with the following lattice constants at 298 K: $a = 10.419(3)$, $b = 15.709(1)$, $c = 18.890(2)$ Å..., $\beta = 71.223(9)^\circ$, $V = 77.986(10)$ Å 3 , and $\rho = 84.62(1)$ Å $^{-3}$. The population of the two sites $n_{\text{A}}:n_{\text{B}}$ is 2:1. Iron(II) on site A undergoes a thermal low-spin (LS) \rightarrow high-spin (HS) transition with $T_{1/2} = 105$ K, whereas that on site B remains in the high-spin state down to cryogenic temperatures. Application of external pressure of up to 1200 bar between 200 and 60 K does not cause formation of the low-spin state on site B. On site A the high-spin state can be populated as a metastable state at 20 K by irradiating the sample with $\lambda = 514.5$ nm; on site B a light-induced population of the low-spin state can be achieved with $\lambda = 820$ nm.

1995

- *Intersystem Crossing in Iron(II) Coordination Compounds: A Model Process between Classical and Quantum Mechanical Behaviour.*

Andreas Hauser

Comments on Inorganic Chemistry **17** (1) (1995), p17-40

DOI:10.1080/02603599508035780

Keywords: intersystem crossing • spin-crossover • iron(II) coordination compounds • nonadiabatic multiphonon relaxation • strong vibronic coupling limit • tunnelling

Intersystem crossing is the crucial first step determining the quantum efficiency of very many photochemical and photophysical processes. Spin-crossover compounds of first-row transition metal ions, in particular of Fe(II), provide model systems for studying it in detail. Because in these compounds there are no competing relaxation processes, intersystem crossing rate constants can be determined over a large temperature interval. The characteristic features are tunnelling at temperatures below ~ 480 K and a thermally activated process above ~ 100 K. This, as well as the twelve order of magnitude increase of the low-temperature tunnelling rate constant on going from a spin-crossover compound with a small zero-point energy difference to a low-spin compound with a substantially larger one, can be understood on the basis of a nonadiabatic multiphonon process in the strong vibronic coupling limit.

- *Absorption and luminescence spectroscopy of ferrate (VI) doped into crystals of K_2MO_4 ($M = S, Se, Cr, Mo$)*

Thomas C. Brunold, Andreas Hauser and Hans U. Güdel

Journal of Luminescence **59** (5) (1994), p321-332 DOI:10.1016/0022-2313(94)90059-0

The absorption spectra of the ferrate (VI) ion (FeO_4^{2-}) in K_2MO_4 ($M = S, Se, Cr, Mo$) host lattices consist of a series of relatively weak bands at low energy, which can be assigned to transitions within the partially filled 3d shell and some intense bands at higher energy, which are assigned to ligand-to-metal charge transfer transitions (LMCT). In the near-infrared (NIR) region sharp lines are observed belonging to the spin-forbidden spin-flip transitions $^3A_2 \rightarrow ^1E$ and $^3A_2 \rightarrow ^1A_1$. The lowest excited state is the 1E state, serving as initial state for a $^1E \rightarrow ^3A_2$ sharp-line luminescence at around 6200 cm^{-1} . Another luminescence is observed centered at 9000 cm^{-1} , which is assigned to the $^3T_2 \rightarrow ^3A_2$ transition. It is rather broad and three orders of magnitude weaker than the 1E luminescence at 30K as a result of efficient non-radiative relaxation processes to the 1E state. The temperature dependence of the total intensity and the lifetime of the $^1E \rightarrow ^3A_2$ luminescence is understood within a complex scheme of radiative and non-radiative processes.

- *Cooperative effects in the $[Fe(mtz)_6](BF_4)_2$ spin-crossover system: fine tuning the energy gap*

Roland Hinek, Philipp Gutlich, Andreas Hauser

Inorganic Chemistry **33** (3) (1994), p567-572 DOI:10.1021/ic00081a027

- *Kinetic Studies on the Photochemically Activated Solvation of $[(\eta^6\text{-arene})_1Ru(\eta^6\text{-arene})_2]^+$ Sandwich Compounds*

Thomas Karlen, Andreas Hauser, Andreas Ludi

Inorganic Chemistry **33** (10) (1994), p2213-2218 DOI:10.1021/ic00088a025

- *A polymeric two-dimensional mixed-metal network. Crystal structure and magnetic properties of $\{[P(Ph)_4][MnCr(ox)_3]\}_n$*

S. Decurtins, H.W. Schmalle, H.R. Oswald, A. Linden, J. Ensling, P. Gütlisch, A. Hauser

Inorganica Chimica Acta **216** (1-2) (1994), p65-73 DOI:10.1016/0020-1693(93)03711-1

Keywords: crystal structures • magnetism • manganese complexes • chromium complexes • dinuclear complexes

The mixed-metal ferromagnet $\{[P(Ph)_4][MnCr(ox)_3]\}_n$, where Ph is phenyl and ox is oxalate, has been prepared and a two-dimensional network structure, extended by Mn(II)-ox-Cr(III) bridges, has been determined from single crystal X-ray data. Crystal data: space group $R\bar{3}c$, $a=b=18.783(3)$, $c=57.283(24)$ Å, $V=1200$ Å³, $Z=24$ ($C_{30}H_{20}O_{12}P_4Mn$). The magnetic susceptibility data obey the Curie-Weiss law in the temperature range 260 ± 20 K with a positive Weiss constant of 10.5 K. The temperature dependence of the molar magnetization exhibits a magnetic phase transition at $T_c=5.9$ K. The structure is discussed in relation to the strategy for preparing molecular based ferromagnets and, in addition, it is a solution to the question of the dimensionality of the $[MM'(ox)_3]_n$ network, which in principle can extend two- or three-dimensionally to the crystal lattice. The optical absorption spectra of the single crystals are assigned to the $d \rightarrow e$ CrO_6 chromophores. Their polarization patterns reflect the electric dipole selection rules for D_3 symmetry. A strong site selective luminescence from the chromium(III) $2E$ states is observed at low temperature and the system may be suitable for studying energy transfer mechanisms.

- *Low-Temperature Tunneling in the Spin-State Relaxation Dynamics of Iron(III) Spin-Crossover Compounds*

Sabine Schenker, Andreas Hauser

Journal of the American Chemical Society **116** (12) (1994), p5497-5498 DOI:10.1021/ja00091a075

- *Thermal and Optical Switching of Iron(II) Complexes*

Philipp Gütlisch, Andreas Hauser, Hartmut Spiering

Angewandte Chemie International Edition **33** (20) (1994), p2024-2054 DOI:10.1002/anie.199420241

Transition metal chemistry contains a class of complex compounds for which the spin state of the central atom changes from high spin to low spin when the temperature is lowered. This is accompanied by changes of the magnetic and optical properties that make the thermally induced spin transition (also called spin crossover) easy to follow. The phenomenon is found in the solid state as well as in solution. Amongst this class, iron(II) spin crossover compounds are distinguished for their great variety of spin transition behavior; it can be anything from gradual to abrupt, stepwise, or with hysteresis effects. Many examples have been thoroughly studied by Mössbauer and optical spectroscopy, measurements of the magnetic susceptibilities and the heat capacities, as well as crystal structure analysis. Cooperative interactions between the complex molecules can be satisfactorily explained from changes in the elastic properties during the spin transition, that is, from changes in molecular structure and volume. Our investigations of iron(II) spin crossover compounds have shown that green light will switch the low spin state to the high spin state, which then can have a virtually unlimited lifetime at low temperatures (this phenomenon is termed light-induced excited spin state trapping - acronym: LIESST). Red light will switch the metastable high spin state back to the low spin state. We have elucidated the mechanism of the LIESST effect and studied the deactivation kinetics in detail. It is now well understood within the theoretical context of radiationless transitions. Applications of the LIESST effect in optical information technology can be envisaged.

- *Spin crossover und LIESST: thermisch und optisch schaltbare Eisen(II)-Komplexmoleküle*

P. Gütlisch, A. Hauser, H. Spiering

Angewandte Chemie **106** (20) (1994), p2109-2141 DOI:10.1002/ange.19941062006

In der Übergangsmetallchemie gibt es eine Klasse von Komplexverbindungen, bei denen eine Temperaturniedrigung einen Wechsel im Spinzustand des Zentralatoms vom High-Spin- in den Low-Spin-Zustand bewirkt. Dabei ändern sich die magnetischen und optischen Eigenschaften, über die der thermische Spinübergang (auch Spin crossover genannt) sehr gut verfolgt werden kann. Dieses Phänomen tritt sowohl in flüssiger Phase als auch im Festkörper auf. Eine herausragende Stellung nehmen Eisen(II) - Spin crossover - Verbindungen ein, in denen der Spinübergang im Festkörper auf sehr unterschiedliche Weise - graduell, abrupt, mit Hysterese oder stufenweise - verlaufen kann und mit Mössbauer- und optischer Spektroskopie, mit magnetischen Suszeptibilitäts- und Wärmekapazitätsmessungen sowie durch Kristallstrukturanalyse intensiv untersucht worden ist. Die kooperative Wechselwirkung zwischen den einzelnen Komplexmolekülen kann befriedigend durch elastische Eigenschaften und durch die Änderung von Gestalt und Volumen der Komplexmoleküle beim Spinübergang erklärt werden. Bei Untersuchungen an Eisen(II)-Spin crossover-Verbindungen konnte man beobachten, daß sich der Low-Spin-Zustand mit grünem Licht in den High-Spin-Zustand umschalten läßt, der bei tiefen Temperaturen eine nahezu unendlich lange Lebensdauer haben kann (LIESST = Light-Induced Excited Spin State Trapping). Mit rotem Licht läßt sich der metastabile High-Spin- wieder in den Low-Spin-Zustand zurückschalten. Der Mechanismus des LIESST-Effekts ist aufgeklärt, die Zerfallskinetik im Detail untersucht und im Rahmen der Theorie strahlungsloser Übergänge verstanden. Anwendungen des LIESST-Effekts in der optischen Informationstechnik sind denkbar.

- *Evidence for strong mixing between the LC and MLCT excited states in bis(2-phenylpyridinato-C2,N')(2,2'-bipyridine)iridium(III)*

Mirco G. Colombo, Andreas Hauser, Hans U. Guedel

Inorganic Chemistry **32** (14) (1993), p3088-3092 DOI:10.1021/ic00066a020

The well-resolved absorption, excitation, and luminescence spectra of $[Ir(ppy)_2(bpy)]^+$ ($ppyH = 2\text{-phenylpyridine}$, $bpy = 2,2'\text{-bipyridine}$) in different media at cryogenic temperatures are presented. In solutions and glasses at ambient temperature the lowest energy excited

state corresponds to an Ir - bpy charge-transfer excitation whereas in the crystalline host lattice [Rh(ppy)2bpy]PF₆ the lowest excited state at 21 450 cm⁻¹ is assigned to a 37r-r* excitation localized on the cyclometalating ppy- ligands. The next higher excited Ir - bpy charge-transfer state has shifted to 21 820 cm⁻¹, only 300 cm⁻¹ above the 3LC excited state. The close proximity of the 3LC and 3MLCT excited states and the large spin-orbit coupling constant of Ir³⁺ induce a strong mixing of charge-transfer character into the 3LC lowest excited states, resulting in increased oscillator strengths, reduced lifetimes, short axis polarized transitions, and a large zero-field splitting of 10-15 cm⁻¹.

- *Four-wave-mixing in the Fe (II) spin-crossover system [Zn_{1-x}Fe_x(ptz)₆](BF₄)₂ (ptz = 1-propyltetrazole)*

Andreas Hauser

Chemical Physics Letters **202** (1-2) (1993), p173-178

DOI:10.1016/0009-2614(93)85368-X

Making use of the phenomenon of light-induced spin-crossover in the [Zn_{1-x}Fe_x(ptz)₆](BF₄)₂ spin-crossover system, very high diffraction efficiencies I₁ can be achieved in non-degenerate four-wave-mixing. In the mixed crystal with x=0.1 and at 76 K, i.e. at a temperature where the system is predominantly in the low-spin state, a value for I₁ of 43% was obtained. This is attributed to a phase grating due to the large difference in metal--ligand bondlength between the low-spin ground state and the light-induced high-spin state. The rate constant for the decay of the laser-induced grating as a function of temperature is found to be exactly twice the one of the high-spin to low-spin relaxation, as expected for a dilute system in the absence of cooperative effects.

- *Exchange interactions in mixed Yb³⁺-Cr³⁺ and Yb³⁺-Ho³⁺ dimers: An inelastic-neutron-scattering investigation of Cs₃Yb_{1.8}Cr_{0.2}Br₉ and Cs₃Yb_{1.8}Ho_{0.2}Br₉*

M. A. Aebersold, H. U. Güdel, A. Hauser, A. Furrer, H. Blank, and R. Kahn

Physical Review B **48** (1993), p12723-12731

DOI:10.1103/PhysRevB.48.12723

The two title compounds were synthesized and investigated with the inelastic-neutron-scattering (INS) technique. They contain mixed YbMBr₉³⁻ (M=Cr³⁺, Ho³⁺) dimers as discrete units, and the magnetic excitations of mixed Yb³⁺-Cr³⁺ and Yb³⁺-Ho³⁺ dimers could thus be observed. The Yb³⁺-Cr³⁺ dimer has three INS transitions, for which anisotropic exchange, as well as zero-field splitting of Cr³⁺, has to be included in the exchange Hamiltonian. For the Yb³⁺-Ho³⁺ dimer the effect of the exchange interaction manifests itself as a broadening and a splitting of the crystal-electric-field levels of the isolated Ho³⁺ ion. Taking into account the full (2J_A + 1) ground-state multiplet of Ho³⁺, as well as anisotropic exchange, gives a satisfactory description of this dimer.

1992

- *Cooperative Effects on the HS -> LS Relaxation in the [Fe(ptz)₆](BF₄)₂ Spin-Crossover System*

A. Hauser

Chemical Physics Letters **192** (1) (1992), p65-70

DOI:10.1016/0009-2614(92)85429-E

The high-spin to low-spin (HS to LS) relaxation in the [Fe(ptz)₆](BF₄)₂ spin-crossover system deviates strongly from first-order kinetics because of cooperative effects of elastic origin. The shift in horizontal and vertical displacement of the potential wells of the initial and final state relative to each other due to the build-up of an "internal" pressure is estimated from spectroscopic measurements. The HS to LS relaxation as such is described by the theory of nonadiabatic multiphonon relaxation in the strong-coupling limit, with a Huang-Rhys factor S of 45 which is much larger than the reduced energy gap p. The sigmoidal relaxation curves in [Fe(ptz)₆](BF₄)₂ result when a change in S of 1 and in p of 1 during the relaxation is taken into account.

1991

- *Intersystem crossing dynamics in Fe(II) coordination compounds*

Andreas Hauser, Andreas Vef, and Peter Adler

Journal of Chemical Physics **91** (12) (1991), p8710-8717

DOI:10.1063/1.461255

The 5T₂(HS)1A₁(LS) intersystem crossing rates have been determined for a number of Fe(II) coordination compounds between 10 and 270 K using time-dependent optical spectroscopy. Strong deviations from Arrhenius kinetics with nearly temperature independent tunneling at low temperatures and a thermally activated behavior at elevated temperatures with apparent activation energies smaller than the classical energy barrier were found. The tunneling rates range from ~10⁶ s⁻¹ for the doped spin crossover system [Zn_{1-x}Fe_x(ptz)₆](BF₄)₂ to ~10⁶ s⁻¹ for the doped low-spin (LS) system [Zn_{1-x}Fe_x(bipy)₃](PF₆)₂. The large range of 12 orders of magnitude in the low temperature tunneling rates as well as the activated region can be understood in terms of nonadiabatic multiphonon relaxation. Values for the Huang-Rhys parameter S of 40-50 and for the reduced energy gap p of 1-12 are estimated for the present series of compounds. The validity of an inverse energy gap law in the strong vibronic coupling limit with S_p is borne out by experiment.

- *Intersystem crossing in Fe(II) coordination compounds*

A. Hauser

Coordination Chemistry Reviews **111** (1991), p275-290

DOI:10.1016/0010-8545(91)84034-3

Due to the fact that for d₆ systems there are a number of low-lying ligand field (LF) states the relaxation from excited states of Fe(II) coordination compounds is, in general, a very fast and radiationless process. In Fe(II) spin-crossover systems, however, the zero point energy difference between the two lowest states, namely the low-spin (LS) 1A₁ and the high-spin (HS) 5T₂ state, is of the order of kBT, and some systems can be converted quantitatively to the HS state well below the thermal transition temperature by irradiating either into MLCT or LF absorption bands of the LS species, with HS to LS relaxation rates as small as 10⁶ s⁻¹ at 10 K. It is also possible to achieve a light-induced transient population of a HS state in Fe(II) LS compounds, but in this case the HS to LS relaxation rates can be larger than 10⁶ s⁻¹ even at low temperatures. The HS to LS relaxation rates show strong deviations from Arrhenius kinetics with nearly temperature independent tunnelling below 70 K and a thermally activated behaviour above 100 K. The range of 12 orders of magnitude in the low temperature tunnelling rate can be understood in terms of nonadiabatic multiphonon relaxation, where in the strong coupling limit, with the Huang-Rhys parameter S much larger than the reduced energy gap p, an inverse energy gap law holds.

- *Intersystem Crossing in [Fe(ptz)₆](BF₄)₂ (ptz = 1-propyltetrazole)*

A. Hauser

Journal of Chemical Physics **94** (4) (1991), p2741-2748

DOI:10.1063/1.459851

[Fe(ptz)₆](BF₄)₂ (ptz=1-propyltetrazole) is an Fe(II) spin crossover system, which shows a light-induced low-spin (1A₁) to high-spin (5T₂) conversion below ~50 K by irradiating into the spin allowed 1A₁ to 1T₁ d-d absorption band. This phenomenon, known as light-induced excited spin state trapping (LIESST), is reversible, and a subsequent irradiation into the 5T₂ to 5E band results in a light-induced 5T₂ to 1A₁ conversion (reverse LIESST). Single crystal absorption spectra of the title compound in the region of d-d transitions are reported. In addition to the well-established spin allowed 1A₁ to 1T₁ and 1A₁ to 1T₂ transitions of the low-spin species and the 5T₂ to 5E transition of the high-spin species two weak bands in the NIR are assigned to the spin forbidden 1A₁ to 3T₁ and 1A₁ to 3T₂ transitions. Direct irradiation into the 1A₁ to 3T₁ absorption band at 20 K results in a quantitative 1A₁ to 5T₂ conversion, proving that this low lying triplet state plays an important role in the mechanism of LIESST. A full kinetic scheme for LIESST and reverse-LIESST with the 3T₁ state as intermediate state is developed, and the quantum efficiencies for the various intersystem crossing steps involved are given: they are of the order of unity for the first step from the initially excited 1T₁ and 5E states to the intermediate 3T₁ state, respectively. The

1990

- *Thermal and light-induced spin crossover in iron(II) complexes*

Philipp Güttlich and Andreas Hauser

Coordination Chemistry Reviews **97** (1990), p1-22

DOI:10.1016/0010-8545(90)80076-6

Recently, we have discovered a fascinating photophysical effect in spin crossover complexes of iron(II) : Light-Induced Excited Spin State Trapping (LIESST). At sufficiently low temperatures, the low spin state (1A1) can be converted quantitatively to the high spin state (5T2) by irradiating the sample into the 1A1 \rightarrow 1T1 d-d absorption band (λ = 540 nm). The resulting metastable HS state has a very long lifetime at low temperatures, in some cases it does not decay noticeably over a period of several days at 10 K. Only at temperature above some critical temperature does thermal relaxation back to the LS state set in. The sample can also be reconverted to the LS state by irradiating into the 5T2 \rightarrow 5E absorption band (λ \geq 50 nm). The system thus behaves like an optical switch. The relative positioning - horizontally and vertically - of the potential wells of the two spin states is crucial for the lifetime of the metastable HS state.

1988

- *Light-induced excited spin state trapping (LIESST) in [Fe(2-mephen)₃]²⁺ embedded in polymer matrices*

Andreas Hauser, Jürgen Adler, Philipp Güttlich

Chemical Physics Letters **152** (6) (1988), p468-472

DOI:10.1016/0009-2614(88)80443-3

It is known that [Fe(2-mephen)₃](ClO₄)₂ in the solid state is an iron(II) spin-crossover system which shows light-induced excited spin state trapping (LIESST). The thermal spin-crossover behaviour of the complex [Fe(2-mephen)₃]²⁺ embedded in various polymer matrices is similar to the solid-state behaviour, and a light-induced long-lived excited state is observed at temperatures below 50 K. Relaxation curves show that polymer matrices are not very homogeneous media.

1986

- *Reversibility of light-induced excited spin state trapping in the Fe(ptz)₆(BF₄)₂, and the Zn_{1-x}Fe_x(ptz)₆(BF₄)₂ spin-crossover systems*

A. Hauser

Chemical Physics Letters **124** (6) (1986), p543-548

DOI:10.1016/0009-2614(86)85073-4

Fe(ptz)₆(BF₄)₂ (ptz = 1-propyltetrazole) is an iron(II) spin-crossover system which shows light-induced excited spin state trapping. In this paper we show that (a) the same phenomenon can also be observed in Zn_{1-x}Fe_x(ptz)₆(BF₄)₂ (x \approx 0.1) and is therefore basically a single-ion property, and (b) that the phenomenon is reversible. The efficiency of the light-induced spin crossover is of the order of 0.5% in the forward direction and 0.1% in the reverse direction.

- *High-spin \rightarrow low-spin relaxation kinetics and cooperative effects in the hexakis(1-propyltetrazole)iron bis(tetrafluoroborate) and [Zn_{1-x}Fe_x(ptz)₆](BF₄)₂ (ptz = 1-propyltetrazole) spin-crossover systems*

Andreas Hauser, Philipp Güttlich, and Hartmut Spiering

Inorganic Chemistry **25** (23) (1986), p4245-4248

DOI:10.1021/ic00243a036

[Fe(ptz)₆](BF₄)₂ (ptz = 1-propyltetrazole) and the mixed crystals [Zn_{1-x}Fe_x(ptz)₆](BF₄)₂ are Fe(II) spin-crossover compounds that exhibit light-induced excited-spin-state trapping. It is shown that (a) for x \approx 0.1 a single-ion treatment of both the spin equilibrium (M_HL = 510 (12) cm⁻¹, ASHL = 5.1 (2) cm⁻¹/K at T = 100 K) and the relaxation from the excited high-spin state (τ = 810 (30) cm⁻¹, A = 105/s) is appropriate and (b) for 0.2 \leq x \leq 1 cooperative effects observed in the relaxation from the high-spin state are of long-range nature and therefore of elastic rather than of electronic origin.

1985

- *Luminescence and absorption properties of vanadium dichloride (VCl₂), magnesium vanadium chloride (Mg_{1-x}V_xCl₂) and cadmium vanadium chloride (Cd_{1-x}V_xCl₂) crystals*

Brigitte Gaelli, Andreas Hauser, Hans U. Gudel

Inorganic Chemistry **24** (14) (1985), p2271-2275

DOI:10.1021/ic00208a029

Low-temperature luminescence and absorption spectra were recorded of VCl₂ doped into MgCl₂ and CdCl₂, as well as of the pure compound. There is evidence for excitation energy transfer in VCl₂ down to 5 K. In the diluted materials the luminescence remains unquenched up to 200 K (Cd_{1-x}V_xCl₂) and 250 K (Mg_{1-x}V_xCl₂). The broad-band 4T₂ - 4A₂ luminescence transition is highly structured in the diluted samples. There is multiple evidence for a Jahn-Teller effect in the 4T₂ state with an estimated Jahn-Teller energy of the order of 200 cm⁻¹. Polarized absorption and Zeeman measurements were used to assign the 4A₂, \rightarrow E_g, \rightarrow T₁ transitions.