

Computational Chemistry

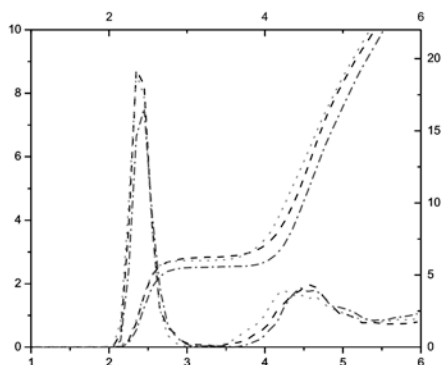
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Molecular Dynamics Simulations of CaCl₂ Aqueous Solutions

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Car-Parrinello Molecular Dynamics simulations have been used to investigate structural and energetic properties of CaCl₂ aqueous solutions. Results of 1 M CaCl₂ solutions are consistent with a previous study of a single Ca ion in a periodic box of 54 water molecules [1] and show no effect of the chlorine at low concentrations.



2 M CaCl₂ water solutions have been studied in terms of radial distribution functions and coordination numbers (figure). Contact and solvent separated Ca-Cl ion pairs formation have been observed, as in XRD experiments.

[1] I. Bakó, J. Hutter, G. Pálkás *J. Chem. Phys.* **2002**, *117*, 9838.

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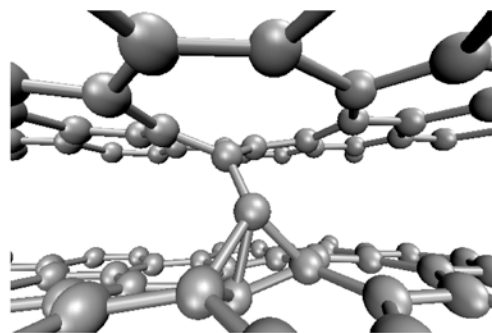
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First principles molecular dynamics study of radiation damage of graphite and carbon nanostructures

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Understanding the mechanisms of radiation-induced defect formation in carbon materials is crucial in nuclear technology [1] and for the manufacturing of nanostructures with desired properties [2]. Using first principles molecular dynamics we performed a systematic study of the non-equilibrium processes of radiation damage in graphite on the picosecond timescale. Our study reveals a rich variety of defect structures (Frenkel pairs, in-plane topological defects) with formation energies of 5-15 eV. In addition, the study clarifies the mechanisms underlying their creation and predicts unexpected preferences towards certain structures.



[1] J. H. W. Simmons, *Radiation Damage in Graphite* (Pergamon, London, 1965).

[2] F. Banhart, *Rep. Prog. Phys.* **1999**, *62*, 1181.

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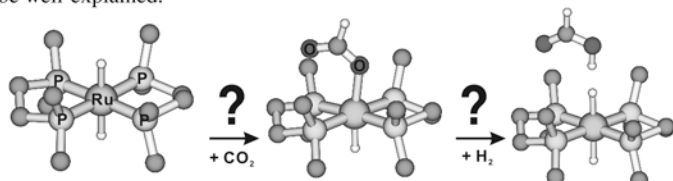
Towards Rational Design of Ruthenium CO₂-Hydrogenation Catalysts: Elucidation of Reaction Pathways

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Complete reaction pathways relevant in homogeneous CO₂ hydrogenation by a Ru dihydride catalyst (Ru(dmpe)₂H₂, dmpe = Me₂PCH₂CH₂PMe₂) are investigated by *ab initio* metadynamics [1]. We are able to reproduce the main steps of the processes, identify the reaction intermediates, and evaluate the corresponding free energy profiles. Our simulations indicate that the CO₂ insertion for the formation of formate complex proceeds via a concerted-insertion mechanism. It is a rapid and direct process, throughout a relatively small activation barrier, which is in agreement with what observed experimentally. The H₂ insertion to the formate-Ru complex and the formation of formic acid, instead, occurs via an intermediate Ru(η²-H₂) complex, where the molecular hydrogen interacts with the Ru center. This step has been identified as the rate-limiting step of the reaction. Hence, we propose a simple measure of the catalytic activity based on the analysis of the electronic structure of the corresponding transition-state. Taking this measure, the relation between different ligands and the experimental catalytic activities can be well-explained.



[1] M. Iannuzzi, A. Laio, and M. Parrinello, *Phys.Rev.Let.* **2003**, *90*, 238302.

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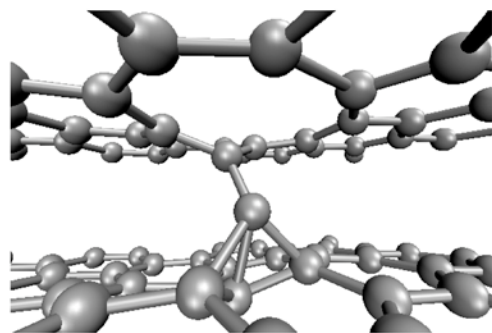
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[1] J. H. W. Simmons, *Radiation Damage in Graphite* (Pergamon, London, 1965).

[2] F. Banhart, *Rep. Prog. Phys.* **1999**, *62*, 1181.

Minisymposium Inorganic and Coordination Chemistry

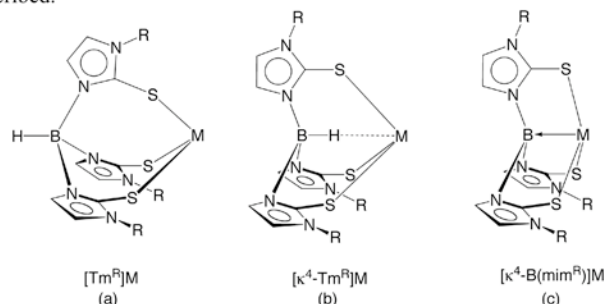
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Applications of Tris(mercaptoimidazolyl)hydroborato Ligands for Modeling Sulfur Rich Active Sites and For the Synthesis of Metallaboratranes

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The *tris*(2-mercapto-1-R-imidazolyl)hydroborato ligand, [Tm^R], is a versatile tripodal ligand that provides an [S₃] coordination mode that has diverse applications which range from modeling the active sites of zinc enzymes to the synthesis of olefin polymerization catalysts. In the vast majority of cases, the [Tm^R] ligand coordinates in a tridentate manner via the three sulfur atoms (Figure a), but more complex coordination modes have also been observed. For example, one of [Tm^{Ph}] ligands of the lead complex [Tm^{Ph}]₂Pb coordinates with an “inverted” ⁴-configuration (Figure b). An important recent development in the application of [Tm^R] ligands, as observed by several research groups, is concerned with the discovery that the B-H entity is reactive and may be cleaved by a metal center to generate “metallaboratranes” (Figure c) which feature a M→B dative bond. The bonding and reactivity of these novel compounds will be described.



Coordination Chemistry for the Design of Therapeutic Metal Complexes

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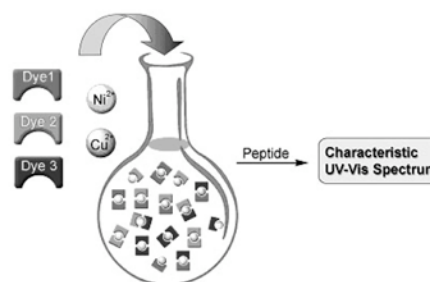
The roles of both the metal ion and its ligands can be crucial in the mechanism of action of therapeutic metal complexes: to achieve targeting to biological sites, and allow specific activation. I will discuss 3 examples from our recent research. Photoactivatable *cis* and *trans* platinum(IV) diazide complexes are relatively non-toxic to cells in the dark, but kill cancer cells by unusual mechanisms when irradiated. For organometallic ruthenium(II) arene anticancer complexes, chemical reactivity, anticancer activity and cellular processing are highly dependent on the nature of the arene and the other ligands, and the contrasting biological behavior of osmium(II) analogues is understandable from studies of their aqueous coordination chemistry under biologically-relevant conditions. Finally binding of antiviral and stem-cell-mobilizing metallomacrocycles to target membrane receptors appears to involve coordination of the metal to specific amino acid side-chains, H-bonding, hydrophobic interactions, and restraint of the configuration of the macrocycle.

Dynamic combinatorial libraries of dye complexes as flexible sensors for peptides

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Dynamic combinatorial libraries (DCLs) are adaptive chemical networks formed by combinatorial assembly of molecular building blocks under thermodynamic control. We have constructed a DCL of metal-dye complexes in which the library members have a different color. Any re-equilibration will therefore result in the variation of the UV-Vis spectrum of the mixture. We have shown that such a library can be used to identify dipeptides in aqueous solution with high selectivity.^[1] Furthermore we have found that the composition of a library can be optimized in combinatorial fashion for a specific sensing purpose.^[2]



[1] A. Buryak, K. Severin, *Angew. Chem. Int. Ed.* **2005**, *44*, 7935-7938.

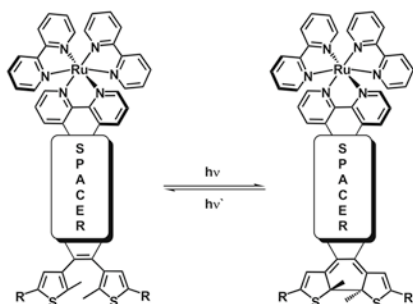
[2] A. Buryak, K. Severin, *J. Comb. Chem.* **2006** accepted.

Photochromic Dithienylethene Switches Connected at a Ruthenium(II) Center: Spacer, the Key of Success?

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Organic dithienylethene derivatives, commonly called Irie switches, have been extensively studied in recent time [1]. On the other hand, such derivatives involving metal complexes are not often described in literature. By introduction of a metal complex, electronic absorption properties are drastically changed by the appearance of the MLCT transition. It allows the use of visible light to close the switch photochemically by an energy transfer process from the excited metal centre to the switching unit [2].



We will discuss the crucial influence of the spacer on photochromic properties, thermal stability and fatigue resistance.

[1] M. Irie, *Chem. Rev.* **2000**, *100*, 1685.

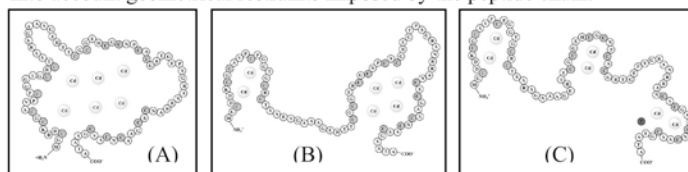
[2] J. Kühni, V. Adamo, and P. Belser, *Chimia.* **2006**, *60*, 207.

The cluster structure of a wheat metallothionein

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Wheat metallothionein (MT) is a seed specific plant metallothionein. Like the mammalian isoforms, wheat MT is a cysteine-rich protein with low molecular weight and the ability to bind d^{10} metal ions in form of metal-thiolate clusters. Naturally, it is found as a Zn^{II} containing species. As we found the metal-to-protein ratio to be 6:1, it is obvious that only sub-stoichiometrically metal-loaded forms have been described in the literature so far. Still unaddressed remains the nature of the metal-thiolate clusters formed. All three arrangements depicted below can be explained purely based on geometrical considerations or even known cluster structures: A "super-cluster" combining all three cysteine-rich regions (A), a two-domain structure consisting of a smaller two- as well as a larger four-metal ion cluster (B), or even a structure consisting of three clusters, each formed by one cysteine-rich segment of the protein (C). An alternative arrangement to (B) featuring two separate clusters of equal size seems less likely solely taking into account geometrical restraints imposed by the peptide chain.



We will present strong experimental support for the nature of the metal-thiolate cluster formed in wheat MT based on spectroscopical methods supplemented by ESI-MS data and results from (bio-) chemical reactions.

Financial support for this project comes from the SNF (200021-105269/1 to EF) and the Research Fund of the University of Zürich (57010101 to EF).

[1] Y. Kojima, P. Binz, J. H. R. Kägi, *Metallothionein IV*, ed. C. Klaassen, **1999**, 3-6.

[2] E. Peroza, E. Freisinger, *submitted*.