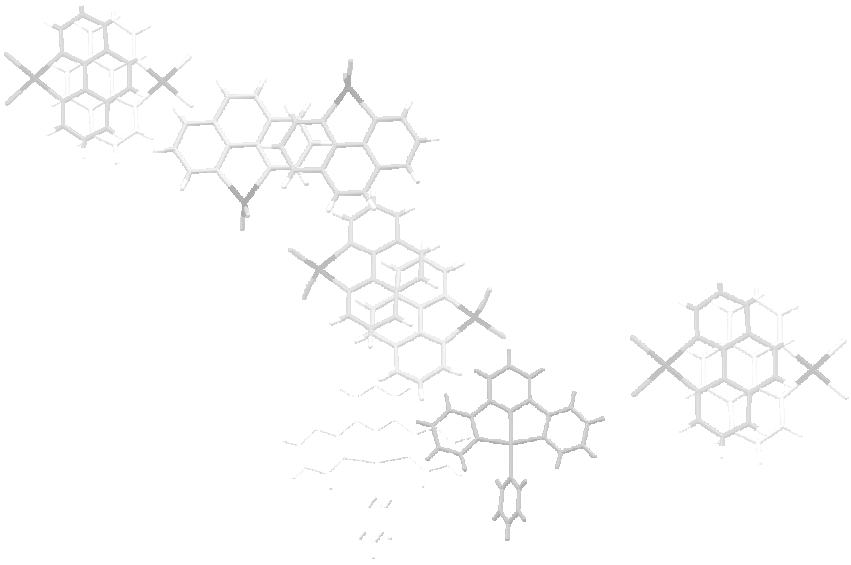
SECOND HUMBOLDT CONFERENCE ON NONCOVALENT INTERACTIONS

Vršac, Serbia
October 22-25, 2009



BOOK OF ABSTRACTS

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PROGRAM

Thursday, October 22, 2009

14:00-17:00 registration

17:00 Welcome remarks

Chair: Snežana Zarić

17:30 **Slobodan Macura, Mayo Clinic, Rochester, Minnesota, USA**
NMR Study of Water/Urea Interactions in Organic Solvents

18:00 **Cristoph Janiak, Universitaet Freiburg, Germany**
Applying non-covalent interactions for the stabilization of "naked" metal nanoparticles in ionic liquids

Friday, October 23, 2009

Chair: Matthias Ullmann

Noncovalent interactions in transition metal systems

9:00 **Natalia Belkova, Russian Academy of Sciences, Moscow, Russia**
Hydrogen bond structure as determinant for the protonation mechanism of transition metal hydrides.

9:30 **Michael Hall, Texas A & M University, U.S.A.**
Intermediate H---H contacts in transition metal complexes: Elongated bonding or compressed non-bonding?

10:00 **Rinaldo Poli, CNRS, Toulouse, France**
Transmission of non-covalent interaction: effect of the solvent on the cation through solvent···anion···cation interactions.

10:30 – 11:00 Coffee break

Noncovalent interactions in fluids

11:00 **Tzonka Mineva, Institut Charles Gerhardt, France**
Structures and dynamics of surfactant templates: phosphatidil choline lipids and n-alkylmethylamonium bromide salts.

11:30 **Radivoje Prodanović, Jacobs University Bremen, Germany**
High throughput screening system based on FACS and in vitrocompartmentalization for directed evolution of glucose oxidase toward improved affinity and activity for glucose.

12:00 **Goran Vladisavljević, Loughborough University, United Kingdom**
Noncovalent interactions in microfluidic devices

12:30 – 14:30 Lunch

Chair: Gabor Naray-Szabo

Noncovalent interactions in metal systems

14:30 **Jairton Dupont, Institute of Chemistry - UFRGS, Porto Alegre, Brazil**
The role of suparamolecular aggregates on the formation and stabilization of metal nanoparticles in imidazolium ionic liquids.

15:00 **Ryszard Kubiak, Polish Academy of Sciences, Poland**
Coordination compounds of metallophthalocyanines – the way to usable materials

15:30 **Miroslav Boca, Slovak Academy of Sciences, Slovak Republic**
Columbic interactions in high temperature molten salts.

16:00 - 16:30 Coffee break

Noncovalent interactions of π-systems

16:30 **Fanica Cimpoesu, Institute of Physical Chemistry, Bucharest, Romania**
Aromaticity and stacking effects in organic and coordination systems

17:00 **Miloš Milčić, University of Belgrade, Serbia**
Noncovalent interactions of π-systems in transition metal complexes

17:30 - 19:30 **Posters**

Saturday, October 24, 2009

Chair: Michael Hall

Noncovalent interactions in biological systems

9:00 **Ilza Pajeva, Bulgarian Academy of Sciences, Sofia, Bulgaria**
Ligand- and Structure-Based Modeling Studies of the ABC Transporter P-Glycoprotein

9:30 **Matthias Ullmann, University of Bayreuth, Germany**
pH-dependent pK_a Values in Proteins – A Theoretical Analysis of Protonation Energies with Practical Consequences for Enzymatic

10:00 **Gabor Naray-Szabo, Eotvous University Budapest, Hungary**
Mechanism of Enzymatic Phosphoryl Transfer Reactions: Associative vs. Dissociative Pathways

10:30 – 11:00 Coffee break

11:00 **Ernst-Walter Knapp, Free University Berlin, Germany**
Marriage of electrostatic and quantum chemistry to compute protonation and redox equilibria

11:30 **Georgi N. Vayssilov, University of Sofia, Bulgaria**
Computational modeling of the influence of hydrogen bonding and proton transfer on protein biosynthesis in ribosome.

12:00 **Jaroslav Burda, Charles University, Check Republic**
Comparison of thermodynamic and kinetic parameters for chosen interaction mechanisms of different metallodrugs

12:30 – 14:30 Lunch

Chair: Jean-Pierre Djukic

Noncovalent interactions in metal systems

14:30 **Marilena Ferbinteanu, University of Bucharest, Romania**
Long range effects in supramolecular architectures of lanthanide complexes.

15:00 **Pierre Braunstein, Institut de Chimie, CNRS, Strasbourg, France**
Non-covalent Interactions in Metal-Ligand and Metal-Metal Bonded Systems.

15:30- 16:00 Coffee break

16:00 **Per Brodersen, Alexander von Humboldt Foundation, Bonn, Germany**
Presentation of Alexander von Humboldt Foundation programmes

17:00- 19:00 **Posters**

Sunday, October 25, 2009

Chair: Horst Borrmann

Hydrogen bonds

9:00 **Rade Marković, University of Belgrade, Serbia**
Selected chemoselective reactions of stereodefined 2-alkylidene-4-oxothiazolidines in terms of structure-activity relationship

9:30 **Ingmar Persson, Swedish University of Agricultural Sciences, Uppsala, Sweden**
Hydration of Anions in Aqueous Solution.

10:00 **Miljko Sataric, Faculty of Technical Sciences,University of Novi Sad, Serbia**
Hydrogen Bonds within an Alpha-helix could be modeled by Toda potential

10:30 – 11:00 Coffee break

11:00 **Radu Silaghi-Dumitrescu, "Babes-Bolyai" University, Cluj-Napoca, Romania**
Walking the plank in small molecule activation by metalloenzymes and related centers

11:30 **Ivan Gutman, University of Kragujevac, Serbia**
Mathematical Chemistry - History and Recent Developments.

INVITED LECTURES

NMR Study of Water/Urea Interactions in Organic Solvents

Slobodan Macura[a], Nenad Juranić[a] and Franklyn G. Prendergast[a]
[a]*Department of Biochemistry, Mayo Clinic, Rochester, Minnesota 55905, USA*

Urea is well known protein denaturant but it is still debated whether it attacks protein directly or by the way of disrupting the solvent water structure. Either view has been supported by numerous experiments and simulations. Such diversity of evidence is caused by complex nature of the system, i.e., presence of numerous noncovalent interactions among protein, solvent and other solutes. To probe the interaction between urea and water we studied them dissolved in organic solvents where the number of interactions is significantly reduced. Namely, interactions with organic solvents are much weaker than hydrogen bonding between polar solutes and organic solvent breaks the H-bond network leaving solutes as isolated molecules or their clusters. Using magnetization exchange spectroscopy, assisted with variation of isotope composition of solutes, we were able to discern homomolecular and heteromolecular noncovalent interaction in a urea/water system.

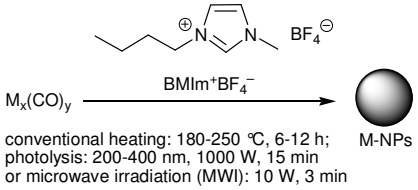
Applying non-covalent interactions for the stabilization of "naked" metal nanoparticles in ionic liquids

Engelbert Redel,[a] Michael Walter[b] and Christoph Janiak[a]

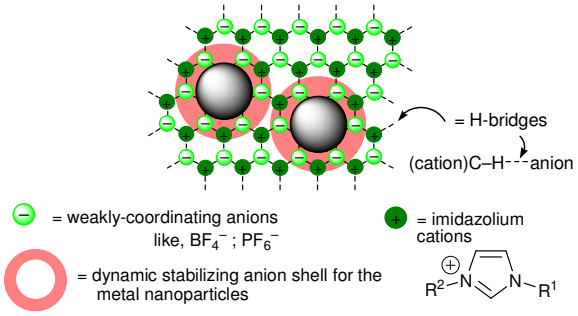
[a]*Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstr. 21, 79104 Freiburg, Germany, Email: janiak@uni-freiburg.de, Tel. 0761-203-6127*

[b]*Universität Freiburg, FMF (Freiburger Material Forschungszentrum), Stefan-Meier-Str. 21, D-79104 Freiburg, Email: michael.walter@fmf.uni-freiburg.de*

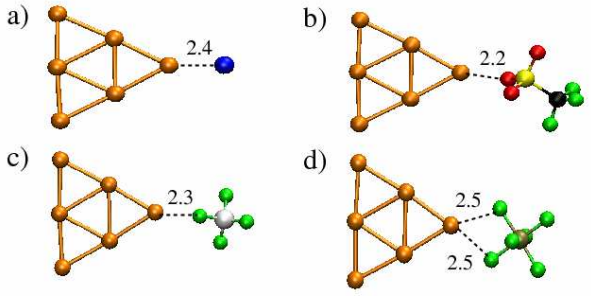
The synthesis of defined and stable metal nanoparticles (M-NPs) is of high importance for various applications. Stable Cr-, Mo-, W-, Mn-, Re, Fe-, Ru-, Os-, Co-, Rh- and Ir-NPs have been reproducibly obtained by microwave, thermal or photolytic decomposition from their metal carbonyl precursors $M_x(CO)_y$ in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIm^+BF_4^-$).[1,2,3] Ag- and Au-NPs were obtained from $AgBF_4$ and Au(CO)Cl or $KAuCl_4$, respectively, in $BMIm^+BF_4^-$.[4,5]



Ionic liquids (ILs) were demonstrated as a favorable template for the preparation of nanostructures. ILs stabilize M-NPs due to their high ionic charge, high polarity, high dielectric constant and ability to form supramolecular hydrogen bonding networks. ILs should provide an electrostatic and steric ("*electrosteric*") protection in the form of a "*protective shell*" for M-NPs, so that no extra stabilizing molecules are needed. The IL network contains weakly coordinating cations and anions that bind less strongly and are less deactivating to the metal surface than traditional stabilizers or capping ligands.



Density functional theory (DFT) calculations on Au_n clusters favor interactions to IL anions instead of IL-cations. This suggests a Au···F interaction and anion–Au_n stabilization in fluorous ILs. Shown here are relaxed configurations of Au_6 bound to a) Cl^-, b) OTf^-, c) BF_4^- and d) PF_6^- (bond lengths in Å).[5]



[1] E. Redel, R. Thomann, C. Janiak, *Chem. Comm.* **2008**, 1789–1791.
[2] J. Krämer, E. Redel, R. Thomann, C. Janiak, *Organometallics* **2008**, *27*, 1976–1978.
[3] E. Redel, J. Krämer, R. Thomann, C. Janiak, *J. Organomet Chem.* **2009**, *694*, 1069-1075.
[4] E. Redel, R. Thomann, C. Janiak, *Inorg. Chem.* **2008**, *47*, 14–16.
[5] E. Redel,M. Walter, R. Thomann, C. Vollmer, L. Hussein, H. Scherer, M. Krüger, C. Janiak, *Chem. Eur. J.* **2009**, in press, http://dx.doi.org/10.1002/chem.200900301

Hydrogen bond structure as determinant for the protonation mechanism of transition metal hydrides

Natalia V. Belkova, Oleg A. Filippov, Lina M. Epstein, Elena S. Shubina
A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str, 28, 119991, Moscow, Russia
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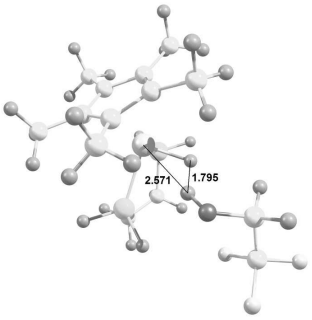
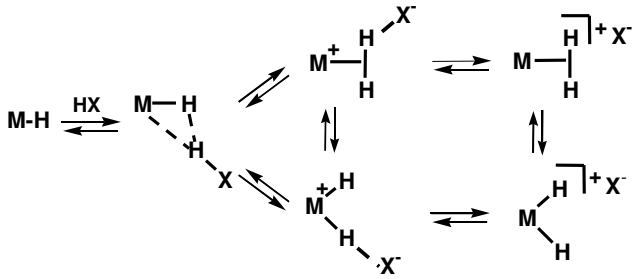
Recently found hydrogen bonds of new types: to a metal atom (XH…M) and to a hydride ligand (XH…HM)[1] are still under active investigation. These hydrogen bonded complexes are intermediates of proton transfer reactions playing key role in many chemical and biochemical (stoichiometric or catalytic) processes. In this communication the most recent results will be presented obtained by combination of spectroscopic (IR, UV, NMR) studies at 190-290 K with DFT calculations. The effect of the metal atom depending on its position in the Periodic Table on the structural and electronic characteristics of XH…HM complexes will be considered on the example of Cp*MH(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$, M = Fe, Ru, Os)[2] and Cp*MH_3(dppe) (M = Mo, W)[3] hydrides series. The analysis of hydrogen bonded complexes structure, energy and electron density distribution indicates an asymmetric bifurcated interaction (Figure) with significant impact of hydrogen bonding to the metal atom increasing down the group. Accordingly, the proton transfer pathway changes on going from 3d and 4d to 5d metal complexes (Scheme). Factors such as solvent nature (polarity and hydrogen bonding ability) and cooperative effect are found to determine stability of the species involved in the process and could affect the proton transfer equilibrium position, as is illustrated for [κ^4-$P(CH_2CH_2PPh_2)_3$]RuH_2.[4] The knowledge acquired shows steering role of hydrogen bonding between transition metal hydride and proton donor or specific solute-solvent interactions.





This work was financially supported by the Russian Foundation for Basic Research (Project No. 08-03-00464) and by the Division of Chemistry and Material Sciences of RAS.

1. (a) E.S. Shubina, N.V. Belkova, L.M. Epstein. *J. Organomet. Chem*., **1997**, *536-537*, 17-35; (b) Belkova, N. V.; Shubina, E. S.; Epstein, L. M. *Acc. Chem. Res.*, **2005,** *38*, 624-631.
2. (a) N. V. Belkova, E. Collange, P. Dub, L. M. Epstein, D. A. Lemenovskii, A. Lledós, O. Maresca, F. Maseras, R. Poli, P. O. Revin, E. S. Shubina, E. V. Vorontsov. *Chem. Eur. J.,* **2005**, *11*, 873-888; (b) N. V. Belkova, P. A. Dub, M. Baya and J. Houghton, *Inorg. Chim. Acta* **2007**, *360*, 149–162.
3. N. V. Belkova, M. Besora, M. Baya, P. A. Dub, L. M. Epstein, A. Lledós, R. Poli, P. O. Revin, E. S. Shubina, *Chem. Eur. J.* **2008,** *14,* 9921-9934.
4. N. V. Belkova, T. N. Gribanova, E. I. Gutsul, R. M. Minyaev, C. Bianchini, M. Peruzzini, F. Zanobini, E. S. Shubina and L. M. Epstein, *J. Mol. Struct.* **2007**, *844*, 115-131.

Intermediate H---H contacts in transition metal complexes: Elongated bonding or compressed non-bonding?

Michael B. Hall and Xinzheng Yang
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mbhall@tamu.edu

Density functional theory is capable of yielding reasonably accurate fully optimized geometries on small and moderate sized molecules. When H_2 interacts with a transition metal the two most common results are (1) a σ-complex with H—H distance < 1.0 Å if the metal is electron poor or (2) oxidative addition to a dihydride with H----H contact > 1.6 Å if the metal is electron rich. Less common is the observation of intermediate H---H distances in the range 1.1 to 1.5 Å. Several examples will be presented including (1) (eta^5-C_5Me_5)$OsH_4(PR_3)$, where for R=Ph the system is a dihydrogen dihydride complex with the centrally located H-H bond perpendicular to the Cp ring and for R=Cy the system is a tetrahydride with the central hydrides now parallel to the Cp ring; and (2) $ReH_7(PR_3)_2$, where for R=tolyl an intermediate length H---H bond is observed, while most calculations predict two isomers of nearly equal stability, one with a short H—H and one with a long H----H.

Transmission of non-covalent interaction: effect of the solvent on the cation through solvent···anion···cation interactions

Rinaldo Poli,[a] Pavel A. Dub,[a,b] Jean-Claude Daran,[a] Natalia V. Belkova,[b] Oleg A. Filippov,[b] Elena S. Shubina,[b] Lina M. Epstein,[b] Agustí Lledós[c]

[a] *Laboratoire de Chimie de Coordination, UPR CNRS 8241, 205 route de Narbonne, 31077 Toulouse, France;* [b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, 119991 Moscow, Russia;* [c] *Departament de Química, Edifici Cn, Universitat Autónoma de Barcelona, 08193 Bellaterra, Spain*

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In contrast to the protonation of $CpMo(PMe_3)(CO)_2H$, giving directly H_2 evolution via a fleeting dihydrogen complex,[1] and that of $Cp^*Mo(PMe_3)_3H$, giving a stable dihydride product,[2] the low temperature (200K) protonation of compound $[Cp^*Mo(PMe_3)_2(CO)H]$, **1**, by $Et_2O{\cdot}HBF_4$ yields a different result depending on a subtle solvent change: the dihydrogen complex $[Cp^*Mo(PMe_3)_2(CO)(\eta^2\text{-}H_2)]^+$, **2**, is obtained in THF, whereas the tautomeric classical dihydride $[Cp^*Mo(PMe_3)_2(CO)(H)_2]^+$, **3**, is the only observable product in dichloromethane (Figure 1). Both products were fully characterized (ν_{CO} IR, ^1H, ^{31}P, ^{13}C NMR) at low temperature; they loose H_2 upon warming to 230 K at approximately the same rate of ca 10^{-3} s^{-1} (with no detection of the non-classical form in CD_2Cl_2), generating $[Cp^*Mo(PMe_3)_2(CO)(FBF_3)]$, **4**. The latter also slowly decomposes at ambient temperature. One of the decomposition products was crystallized and identified by X-ray crystallography as $[Cp^*Mo(PMe_3)_2(CO)(FH\cdots FBF_3)]$, **5**, featuring a neutral HF ligand coordinated to a transition metal through the F atom and to the BF_4^- anion through a hydrogen bond. The reason for the switch of relative stability between **2** and **3** was probed by DFT calculations based on the B3LYP and M05-2X functionals, with inclusion of anion (e.g. see Figure 2) and solvent effects through the conductor-like polarizable continuum model (CPCM) and by the explicit consideration of solvent molecules. Calculations at the MP4(SDQ) and CCSD(T) levels on the simplified $[CpMo(PH_3)_2(CO)H_2]^+$ model were also carried out for calibration. The calculations reveal the key role of non covalent anion-solvent interactions, which modulate the anion-cation interaction ultimately altering the energetic balance between the two isomeric forms.

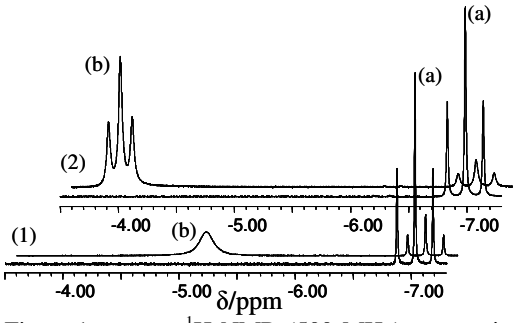
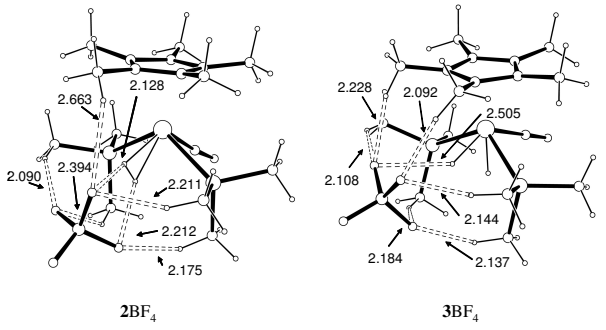


Figure 1. ^1H NMR (500 MHz) spectra in THF-d_8 (1) or CD_2Cl_2 (2) of: (a) compound **1** alone; (b) compound **1** in the presence of slightly less than **1** equiv of $Et_2O{\cdot}HBF_4$. [**1**] = 0.04 M; T = 200 K.



2BF_4 **3**BF_4

Figure 2. View of the M05-2X optimized geometries for the ion pairs $2BF_4$ and $3BF_4$.

1) E. A. Quadrelli, H.-B. Kraatz and R. Poli, *Inorg. Chem.* **1996**, *35*, 5154-5162.

2) M. Baya, P. A. Dub, J. Houghton, J.-C. Daran, R. Poli, N. V. Belkova, E. S. Shubina, L. M. Epstein and A. Lledós, *Inorg. Chem.* **2009**, *48*, 209-220.

Structures and dynamics of surfactant templates: phosphatidyl choline lipids and n-alkylmethylamonium bromide salts

Tzonka Mineva,[a] A. Goursot,[a], D. Talbi[b], B. Alonso[a], Tzonka Mineva[a]
[a] *UMR 5253 CNRS/ENSCM/UM2/UM1, Institut Charles Gerhardt Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier cedex 5, France*
[b] *Université Montpellier II - GRAAL, CNRS - UMR 5024, place Eugène Bataillon, 34095 Montpellier, France*
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Two types of surfactant templates, used in the synthesis of hybrid silica organic-inorganic materials are studied by means of DFT based methods. These are phsophatidyl choline lipids (PC) molecules and n-alkyltrimethylammonium bromide salts. The structures of these organic templates are mainly determined by noncovalent interactions. Detailed knowledge about template structures at atomistic level are highly desired as they are expected to contribute to the understanding of the reasons leading to the structuration of hybrid materials.

To describe accurately the noncovalent parts in the PC lipids and its interaction with water we have established a numerical protocol based on the use of Density Functional Method augmented with a damped empirical London dispersion correction (DFT-D) without any scaling factor [1]. The performance of this DFT-D protocol, associated with the choice of basis sets and exchange-correlation functionals will be first shortly analyzed for non-polar – non-polar and for non-polar – polar interactions. Further on, we will discuss results on conformational structures and dynamics of phosphatidyl choline (PC) lipid molecules with different chain lengths (C12, C14 and C16) [2] obtained with same DFT-D protocol. A quantitative analysis of the electronic factors elucidating the relationships between the conformational structures and the intramolecular interactions will be presented.

The second part of this talk is related to the use of ^{14}N and ^{81}Br nuclei as sensitive NMR probes of n-alkyltrimethylammonium bromide crystal structures, where the electrostatic interactions between the polar head and the halide counter-anions are predominant. DFT optimized structural parameters (within a periodic approach) and computed and measured nuclear quadruple coupling parameters were used for this study. The main results that will be presented demonstrate that the nature of the counter-anion has an indirect effect on ^{14}N NMR quadrupole interaction parameters by affecting the crystal structure and the symmetry of charges. Observed small variations of ^{14}N and ^{81}Br NMR parameters as a function the chain lengths are mainly related to small differences in C-N-C angles and in spatial distributions of cations and anions [3].

1) Goursot, A.; Mineva, T.; Kevorkyants, R.; Talbi, D. *J. Chem. Theory and Com* **2007**, 3, 755-763.
2) Krishnamurty, S.; Stefanov, M.; Mineva, T.; Begu, S.; Devoisselle, J. M.; Goursot, A.; Zhu, R.; Salahub, D. R. *J. Chem Phys B* **2008**, 112, 13433-13442.
3) Alonso, B.; Massiot, D.; Florian, P.; Paradies, H. H.; Gaveau P.; Mineva, T. *J. Phys. Chem. B* **2009,** 113, 11906–11920.

High throughput screening system based on FACS and in vitro compartmentalization for directed evolution of glucose oxidase toward improved affinity and activity for glucose

Dr. Radivoje Prodanovic,[a]
[a] *Institute of Biotechnology, faculty of Biology, RWTH Aachen*

The main objective of this study was to improve properties of glucose oxidase (GOx) from *Aspergillus niger* for its use in miniaturized biofuel cells implanted in a major blood vessel in order to power pacemakers, insulin pumps and miniaturized biosensor devices. GOx activity under physiological conditions in blood (4 mM glucose and pH 7.4) was improved by decreasing the K_m value of GOx for glucose and increasing enzyme activity at pH 7.4. This was achieved using novel fluorescent assay for GOx and high-throughput screening system based on FACS (fluorescence activated cell sorter) assisted sorting of yeast cells compartmentalized in double emulsions.

Noncovalent interactions in microfluidic devices

Goran T. Vladisavljević[a]
[a]*Department of Chemical Engineering, Loughborough University, Leicestershire, LE11 3TU, U.K.*

Noncovalent interactions play an important role in creation of microparticles in microfluidic devices. The examples of such microparticles fabricated in microfluidic devices using monodisperse single and multiple emulsion drops as templates are shown in Fig. 1. Colloidosomes are hollow shells composed of colloidal particles formed by self assembly at the interface of emulsion drops. Giant lipid vesicles (liposomes) are molecular structures greater than 1 μm in diameter formed by self assembly of phospholipids, such as phosphatidyl choline (PC) into concentric bilayers. Asymmetric liposomes have different lipid molecules in the inner and outer layer, e.g. 1-palmitoyl-2-oleoyl-phosphatidylcholine (POPC) and 1-palmitoyl-2-oleoyl-phosphatidyl-L-serine (POPS). Polymerosomes are vesicles formed by self assembly of diblock copolymers.

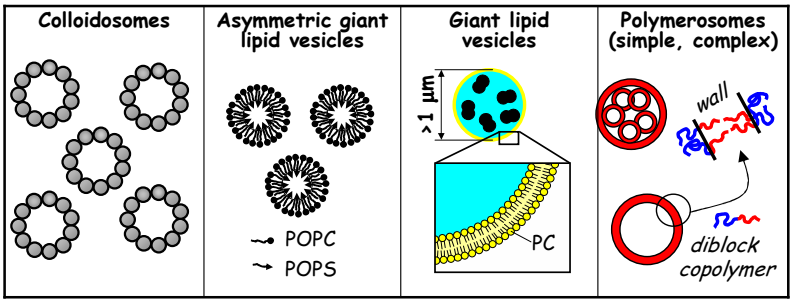

Fig. 1. Examples of microparticles created in microfluidic devices by particle or molecular self assembly.

These self-assembled vesicles can be fabricated in flow focusing microfluidic devices shown in Fig. 2. For example, polymerosomes can be produced using core/shell drops in which the shell fluid is a volatile mixture of organic solvent that contains dissolved diblock copolymers and both the inner and outer fluid is an aqueous solution (Fig. 3). After the solvent is evaporated, diblock copolymers self assemble into bilayer membranes. The hydrophobic parts tend to minimise the contact with water and attract each other, while the hydrophilic parts prefer contact with water and repel each other, forming the outer shells of membranes.

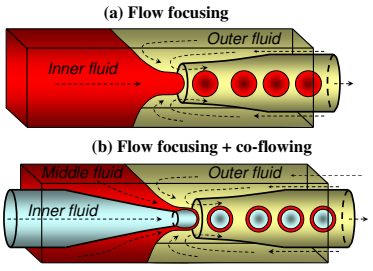

Fig. 2. Glass microcapillary devices for production of uniform simple and core-shell emulsion drops [1].

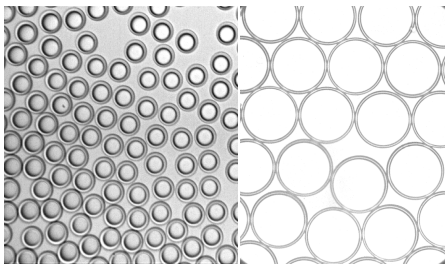

Fig. 3. Core-shell drops with a core diameter of 62 μm and a shell thickness of 8 μm produced by G.T. Vladisavljević using the device shown in Fig. 2b.

[1] Utada, A.S, Chu, L.-Y., Fernandez-Nieves, A., Link, D.R., Holtze, C. and Weitz, D.A. (2007): Dripping, jetting, drops, and wetting: the magic of microfluidics. *MRS Bull.* 32, 702-708.

The role of supramolecular aggregates on the formation and stabilization of metal nanoparticles in imidazolium ionic liquids

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It is now well accepted that imidazolium ionic liquids (IL) may provide a favorable environment for the formation of metal nanoparticles with, in most cases, a small diameter and size distribution under very mild conditions. In this respect, transition-metal NPs in imidazolium ILs are stabilized by protective layers of discrete supramolecular $\{[(DAI)_x(X)_{\tilde{x}n})]^{n+}[(DAI)_{x-n}(X)_x)]^{n-}\}_m$ (DAI is the dialkylimidazolium cation and X the anion) species through the loosely bound anionic moieties and/or NHC carbenes together with an oxide layer when present on the metal surface.[1] These loosely surface-bound protective species are easily displaced by other substances present in the media. This on the one hand is responsible to some extend for their catalytic activity, but on the other hand explains their relatively low stability that leads to aggregation/agglomeration and eventually to the bulk metal. Therefore the stability and the catalytic activity of transition-metal NPs in imidazolium IL are also highly influenced by coordinative strength of the aggregates with the metal surface and the type and nature of the substrates/products. The nature of these supramolecular aggregates was investigated in the condensate phase (X-Ray and ESI-MS) and in the gas phase by MS experiments. The shape and size of the nanoparticles can be modulated by playing with the structural organization of the polar and non-polar regions of the 1-alkyl-3-methylimidazolium IL and the ionicity of the metal precursor (Figure 1).[2, 3]

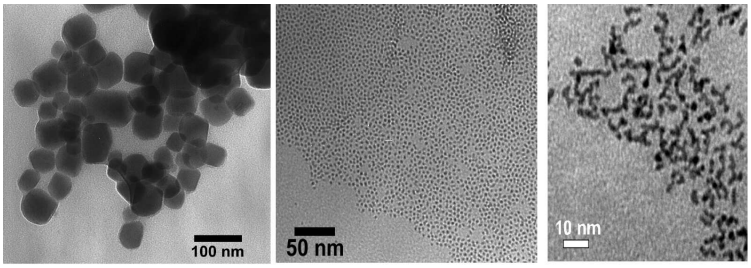

Figure 1. Examples of Co nanocubes, spherical Ru and warm-like Ir nanoparticles in imidazolium IL.

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Coordination compounds of metallophthalocyanines – the way to usable materials

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Phthalocyanines are important class of compounds for industry and are still very attractive materials for modern technology [1]. One of the ways of their functionalization is their thermal processing at various inorganic and organic species. In our laboratory we have been prepared and characterised many metallophthalocyanines in which the additive species is iodine or pyridine or pyridine derivatives [2,3]. The additives give rise to various weak intra- and intermolecular interactions changing the features of the parent phthalocyanines.

Recently much interest has been attracted by lanthanide double-decker phthalocyanines, which are very promising as single molecular magnets [4]. Therefore here the our results concerning the preparation and structural characterisation of the holmium(III) double-decker phthalocyanine, and its conversion at water free and at containing water acetylacetone (Acac) will be presented in more details. The reactive pathway leading to the respective conversions will be proposed. In particular the results have shown the still unexpected potential of metallophthalocyanines as chemical reactants and catalytic agents. On of such newly obtained by us compounds is holmium(III) semiphthalocyanine, Ho(semiPc)(Ac)(Acac), which is illustrated in Fig. 1. The new tetrapyrrole skeleton of the new moiety is named by as "semiPc".

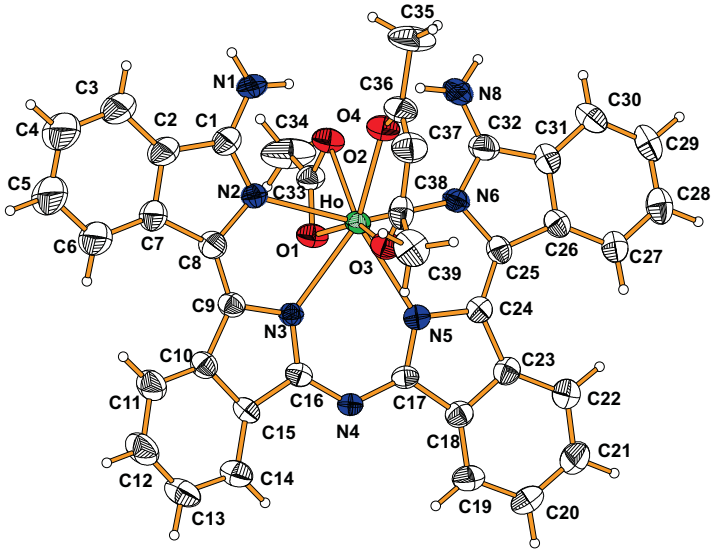

Figure 1. View of the holmium(III) semiphthalocyanine

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Coulombic Interactions in Molten Salts

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The contribution deals with basic introduction of the molten salts directed to the problem of ionic composition of the liquids at high temperature. Inorganic molten salts, being composed of cations and anions (simple ones, polyatomic ones or complex ones), can be described by several different approaches based on classical thermodynamics or computational chemistry.

The methods that helps to reveal ionic composition includes entire electromagnetic spectrum from NMR and EPR through vibrational and electronic spectroscopies ending with diffraction techniques.

The importance of knowledge of ionic composition in inorganic melts is demonstrated on the industrial application of the aluminium production. Modern applications of molten salts are presented.

Acknowledgment: This contribution/publication is the result of the project implementation: Centre for materials, layers and systems for applications and chemical processes under extreme conditions supported by the Research & Development Operational Programme funded by the ERDF .

Aromaticity and Stacking Effects in Organic and Coordination Systems

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In the early ages of theoretical chemistry, R. S. Mulliken noticed the ongoing tendency that ''*the more accurate the calculations become, the more the concepts tend to vanish into thin air*''. Indeed, with the advent of modern methods, the thesaurus of qualitative ideas like hybridization, electronegativity, aromaticity, became of rather secondary use for the theoretical chemistry itself. Such concepts changed their status from the initial *a priori* explanatory virtues, expressing the active causal agents, to the rather passive role, as subject of the eventual *a posteriori* recovery from the bare output of the electronic structure methods. Since the actual retrieving from the black box of calculations is, in fact, not that easy, such concepts are nowadays most often overlooked, or invoked in bare qualitative standard ways .

Here we pay our tribute to the aromaticity concept, treating the old keyword in new keys.[1,2] Graphenes and polyacenes are our organic study cases for interesting and magnetic and charge transport effects, as well as for models of van der Waals interactions.[3] The celebrated stacking and assembling effects in supramolecular chemistry are also treated with the help of aromaticity-based models, revealing interesting anti-aromaticity and aromaticity cases in coordination and cluster systems.[4] A particular route of theoretical treatment used the model known as Heisenberg spin Hamiltonian. The frequent routine use of this model to the routine fit the magnetic susceptibility faded and deprecated its powerful virtues in interpreting the chemical bond itself, or even the subtle effect of long range effects. In fact the Heisenberg Hamiltonian is conceptually parallel to the Valence Bond language, another "*vintage*" method that fell into a sort of undeserved oblivion. We revalorise here these tools of "*good old times*" putting them at work aside with state of the art computational methods, for sake of extracting heuristic meaning from the approached case studies.

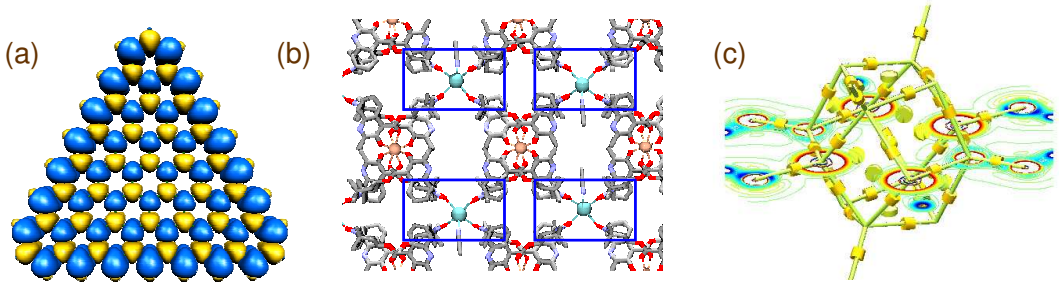

Figure 1. Synopsis on aromaticity-antiaromaticity case studies: (a) spin polarization and magnetism in triangular graphenes (b) a inedited case of supramolecular anti-aromaticity in the 2D coordination assembling of a system based on a TEMPO-type ligands. (c) a carbalane cluster with $\{Al_8C_6\}$ core and 3D-surface aromaticity.

Acknowledgement: This work is supported by the CNCSIS Grant PCE-174/2007.

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Noncovalent interactions of π-systems in transition metal complexes

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The noncovalent interactions of π-systems have been extensively studied in recent years. These interactions are important for many molecular systems from molecular biology to crystal engineering. Noncovalent interactions involving metal atoms have gained particular attention with recognition that metal cations can bind to the phenyl ring by cation-π-type interactions. Cationic metal complexes are involved in similar metal-ligand aromatic cation-π (MLACπ) interactions, where ligands coordinated to the metal interact with π-systems. These can be considered also as a type of XH/π hydrogen bonds.

Recently, it has been observed that planar chelate rings with delocalized π-bonds can be involved in noncovalent interactions in a manner similar to that in organic aromatic rings, indicating that these chelate rings could have aromatic character. Both CH/π[1] and stacking[2] interactions with chelate rings were observed. Analysis of the crystal structures of the metal complexes and quantum chemical calculations show that a chelate ring can be a hydrogen atom acceptor in CH/π interactions. Energy of the CH/π interactions with the chelate ring was evaluated by quantum chemical calculations to be about 2 kcal/mol. Geometries and energies of these interactions are similar to the CH/π interactions with organic aromatic rings. Chelate rings of the coordinated porphyrin can be also hydrogen acceptors in CH/π interactions[1b].

The idea of aromaticity of chelate rings was introduced by Calvin and Wilson in year 1945. Metalloaromaticity stabilizes coordinated chelate ligands, allows electrophilic substitution reaction to take place on the ligand, affects π-electron distribution, and allows charge-transfer complexes to form with chelates. Furthermore, both spectroscopic and magnetic properties of these complexes are affected by the degree of the aromaticity. The nucleus-independent chemical shift (NICS) index defined by Schleyer became well accepted as one of the most efficient tools for understanding aromaticity. Calculations of NICS values on number of complexes with acetylacetonato (acac) and *o*-benzoquinonediimine (bqdi) ligands coordinated to different metals show that most of these chelate rings do not have large negative NICS values, indicating that these chelate rings do not satisfy this magnetic criterion for aromaticity. Among calculated chelate rings, there is only the Ru^{2+}-bqdi chelate ring with large negative NICS values, indicating aromaticity by magnetic criterion.[3]

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Ligand- and Structure-Based Modeling Studies of the ABC Transporter P-Glycoprotein

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Since its discovery in 1976 P-glycoprotein (P-gp) constantly remains in the focus of the research interest because of its involvement in a number of physiologically and pharmacologically important phenomena. Besides its decisive role in cancer multidrug resistance (MDR), the protein acts also as a protector of normal issues against xenobiotics and is a significant factor for the absorption, distribution, metabolism, and excretion (ADME) of the drugs.

Up to 2009, when the X-ray structure of mouse P-gp was resolved, the modeling studies were mostly restricted to ligand-based approaches. Recently structure-based approaches are actively applied.

The lecture will first give a short overview of the previous ligand-based applications to study protein-ligand interactions. Next, the most recent findings will be presented related to combined pharmacophore modeling of selective P-gp inhibitors, homology modeling of human P-gp in different conformational states, ligand docking and analysis of the ligand-protein interactions.

The studies are performed in cooperation with Institute of Pharmacy, University of Bonn, Germany (Prof. Dr. M. Wiese).

pH-dependent pK_a Values in Proteins – A Theoretical Analysis of Protonation Energies with Practical Consequences for Enzymatic

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Because of their central importance for understanding enzymatic mechanisms, pK_a values are of great interest in biochemical research. It is common practice to determine pK_a values of aminoacid residues in proteins from NMR or FTIR titration curves by determining the pH at which the protonation probability is 50%. The pH dependence of the free energy required to protonate this residue is then determined from the linear relationship Gprot = RT ln 10 (pH − pK_a) where R is the gas constant and T the absolute temperature. However, this approach neglects that there can be important electrostatic interactions in the proteins that can shift the protonation energy. Even if the titration curves seem to have a standard sigmoidal shape, the protonation energy of an individual site in a protein depends non-linearly on pH. To account for this non-linear dependence, we define pK_a values for individual sites in proteins that depend on pH. Two different definitions are discussed. One definition is based on a rearranged Henderson-Hasselbalch equation, the other definition is based on an equation that was used by Tanford and Roxby to approximate titration curves of proteins. In the limiting case of weak interactions, the two definitions are equivalent. We discuss how these two differently defined pK_a values are related to the free energy change required to protonate a site. Using simple examples, we demonstrate that the interactions between protonatable residues in proteins can help to maintain the energy required to protonate a site in the protein nearly constant over a wide pH range. We show with the example of RNase T1 that such a mechanism to keep the protonation energy constant is used in enzymes. The pH dependence of pK_a values may be an important concept in enzyme catalysis. Neglecting this concept, important features of enzymes may be missed and the enzymatic mechanism may not be fully understood.

Mechanism of Enzymatic Phosphoryl Transfer Reactions: Associative vs. Dissociative Pathways

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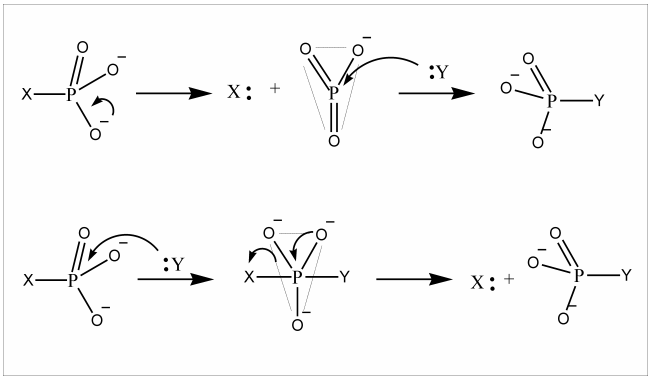
It is generally supposed that enzymatic phosphoryl transfer may follow two pathways (see Figure) [1]. In the dissociative mechanism (top) a trigonal metaphosphate intermediate is



formed, while the associative mechanism (bottom) involves a relatively stable, trigonal bipyramidal intermediate, which refers to a local energy minimum on the reaction path [2,3]. However, a third option has to be mentioned, too, this is the classical S_N2 mechanism with a trigonal bipyramidal transition state, referring to a maximum on the energy path [4]. The preferred pathway is determined by the nature of the phosphorus electrophile, the nucleophile, and the reaction medium (solvent or enzyme active site). Earlier computer simulations indicate that associative and dissociative mechanisms are similarly favored in the aqueous phase, and also calculations for different enzymes support either dissociative or associative pathways depending on a variety of factors. I will present some examples for all three types of reaction and stress the importance of the quantum mechanical approach in the appropriate interpretation of experimental data.

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Marriage of electrostatic and quantum chemistry to compute protonation and redox equilibria

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Electron and proton transfer (ET, PT) processes are the most elementary chemical reactions in proteins. PT processes occur between titratable groups (Glu, Asp, His, Arg, Lys). ET processes involve redox-active compounds, which can be organic molecules or often transition metal complexes (TMC) appearing as cofactors in proteins. To characterize these processes energetically we need to know pK_A values and redox potentials of these compounds with an accuracy of one pH unit or 50 mV, respectively. If experimental values are available for model compounds in solution we can compute the shift between solvent and protein environment just by evaluating electrostatic energies. But, in some particular important cases such model compounds are not available or their redox potentials or pK_A are not known. Hence, accurate and generally applicable methods for *ab initio* computations of redox potentials and pK_A values are needed. So far *ab initio* methods were not accurate and general enough to match these requirements. We have developed a combination of quantum chemical and electrostatic energy computations, which tries to solve this problem. For pK_A values high level DFT methods combined with tuned electrostatic methods are appropriate. For the computation of redox potentials DFT alone is not appropriate. Therefore, we use for redox-active organic compounds an MP2 approach with post SCF correction term (G3MP2), while for transition metal complexes we use DFT with an adjusted functional and post SCF correction combined with electrostatic energy computation.

Computational modeling of the influence of hydrogen bonding and proton transfer on protein biosynthesis in ribosome

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The aim of the study is elucidation of the influence of different types of hydrogen bonds and proton transfer processes on the mechanisms of protein biosynthesis in ribosome by studying congruent model systems. Initially, we used formylethanediol model as the obtained results showed its applicability to the studied processes.[1] Due to its small size and the ease of handling, the model allows numerous computational experiments for specifying small effects on the reaction rate. However, the most substantial disadvantage of this model is the exclusion of the ribosomal ring at 3' end adenosine from it. Thus, in order to define the influence of the vicinal hydroxyl in the reaction of ammonolysis in a system closer to the real one, the monoformylated tetrahydrofurane-3,4-diol is a felicitous choice for a substrate in a more precise model system (Fig. 1).

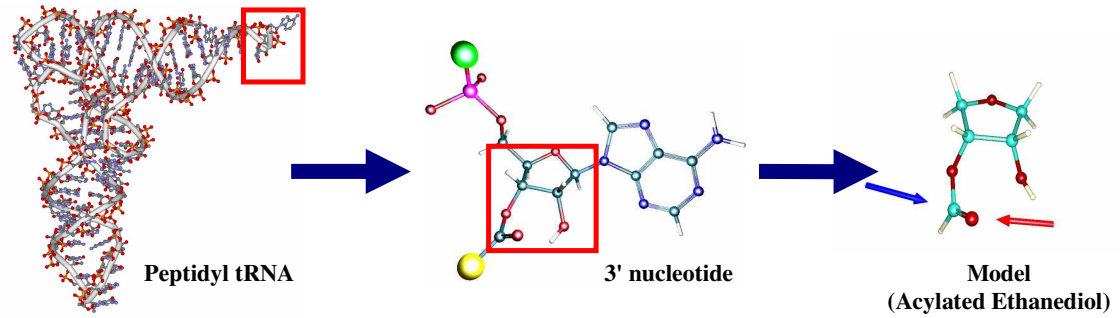

Figure 1. Defining the model system that will be applied in the simulation of the ammonolysis process.

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Comparison of thermodynamic and kinetic parameters for chosen interaction mechanisms of different metallodrugs

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Cisplatin (diammine-dichloro-platinum(II) complex) and its derivatives are known for their high activity in the anticancer treatment. The physico-chemical background of the activation of these drugs in the hydration process of replacing chloro-ligards by water molecules was examined. Thermodynamic and kinetic parameters were determined for this hydration reaction. Comparing with experimental data it can be seen very good agreement of both characteristics. The process of cisplatin activation can be understand purely on the thermodynamic footings as formation of less stable Pt-complexes under the LeChatelier-Braun-van Hoff's principle of chemical equilibrium. On this basis hydration rate and cytotoxicity index were compared for several platinum complexes.

Also some other transition metals were explored. Detachment of the chloro-ligand in [ruthenium(II)(arene)(en)Cl]$^{+}$ was studied and compared with cisplatin activation. Thermodynamic potentials and rate constants for activation and interactions with purine nucleobases bases were estimated. Comparison with measured data demonstrates a power of such computational tools for further investigations.

Long Range Effects in Supramolecular Architectures of Lanthanide Complexes

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The lanthanide ion complexes received in the recent years a growing attention,[1] with special focus on their intrinsic magnetic anisotropy, a key factor for designing molecular and nano-scale magnets. The lanthanide complexes draw challenges also from the perspective of supramolecular and crystal engineering concepts, since the preponderantly ionic regime of their bonding determines a rather extreme versatility in the constitution and conformation of the coordination spheres and a low predictability of the interacting manner.

We present, in the continuation of our previous results,[2] original perspectives and strategies approaching the open questions and challenges of the field. The true complexity of the structure and properties of lanthanide systems can be accounted only including in the focus the theoretical subtleties related with the intricate electronic configuration factors[3] interplayed with the long range fine effects. We outline here new conceptual and methodological developments, in both experimental and theoretical respects, aiming to fill the gaps between the chemistry and physics related with the structure and properties of lanthanide units and extended systems.

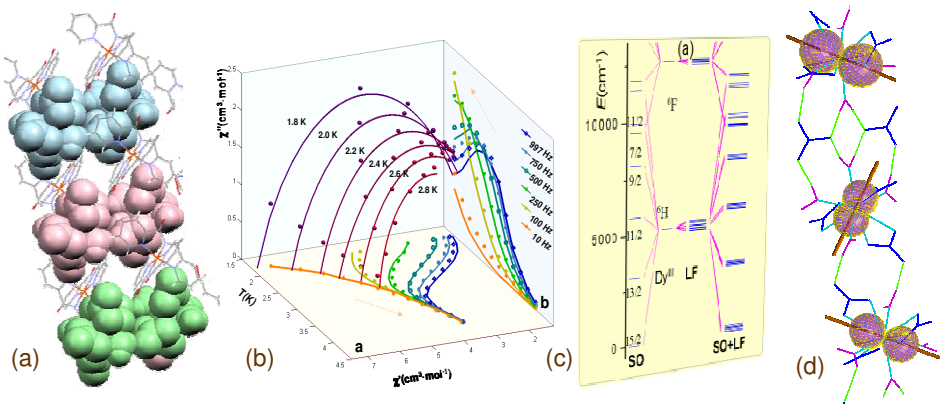

Figure 1. Synopsis suggesting the variety of magneto-structural issues in lanthanide coordination chemistry: (a) molecular structure and crystal packing (b) dynamic magnetic properties, (c) complicate electronic structure tuned by Ligand Field and Spin-Orbit effects, (d) magnetic anisotropy.

Acknowledgement: This work is supported by the CNCSIS Grant PCE-467/2009

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Non-Covalent Interactions in Metal-Ligand and Metal-Metal Bonded Systems

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Relatively weak interactions are capable to significantly modify the structure and reactivity of a single molecule (intramolecular effects) or of a collection of mutually interacting molecules (intermolecular effects).

Exemples will be discussed where metalloligands are used for the selective construction of multinuclear coordination complexes. The isolobal analogy can often be of great help to rationalize and predict the outcome of a given reaction and this will be illustrated in the case of phosphinoenolate complexes.[1]

Following the synthesis of the first heterometallic complexes containing a metal-metal bond between a group 11 d^{10} ion and another transition metal,[2] a considerable interest for such compounds has developed.[3] In some cases, such complexes feature additional, noncovalent d^{10}—d^{10} interactions between the metal centres, which are of current interest from an experimental and a theoretical point of view.[4] We shall discuss a series of heterometallic, metal-metal bonded complexes and clusters in which combined experimental and theoretical data suggest that d^{10}—d^{10} interactions are responsible for their unique features.

We are grateful to Drs. M.-M. Rohmer and M. Bénard (Strasbourg) for theoretical analyses and thank the CNRS, the Ministère de l'Enseignement Supérieur et de la Recherche, the Agence Nationale de la Recherche (ANR-06-BLAN-410) and the franco-german collaborative research programme GRK (Graduiertenkolleg) 532 for funding.

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Selected chemoselective reactions of stereodefined 2-alkylidene-4-oxothiazolidines in terms of structure-activity relationship

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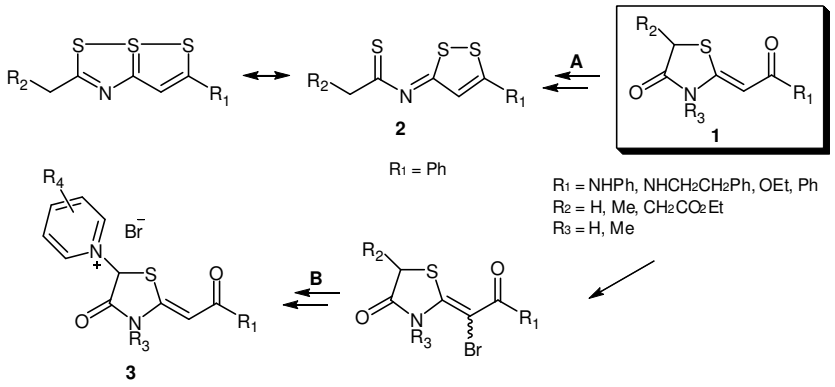
Over the last decade we investigated the chemistry of an extensive series of 5-substituted and unsubstituted 4-oxothiazolidines **1** (Scheme), bearing the trisubstituted exocyclic C-C double bond at position C-2.[1] They belong to a class of *push-pull* compounds,[2] usually represented by a general formula D-π-A, whereas D and A denote electron donor(s) and electron acceptor(s), respectively, connected via C-C double bond or π-conjugating spacer.

Several structural features of compounds **1**, *e.i.*, their polifunctional nature, the stereogenic center at the C-5 position of the thiazolidine ring, the *Z* or *E* geometry of the exocyclic C=C bond with incorporated electron-donors and electron-acceptors, and also importantly, the *cis*-configured –S-C=C-C=O moiety of the Z-isomers, make them interesting substrates for investigating their properties and reactivity. Thus, configurational isomerization of stereodefined (*Z*)-5-substituted and unsubstituted 2-alkylidene-4-thiazolidinones **1** in a solution and solid state as well, to give Z/E mixtures in various ratios, can be explained in terms of intermolecular and intramolecular hydrogen bonding interactions. In addition, they undergo a number of synthetically useful transformations into diverse heterocyclic systems, including 1,2-dithioles **2**, 1,3-thiazines, pyridinium salts **3** containing a 4-oxothiazolidinyl moiety, tetrahydrofuro[2,3-*d*]thiazolo derivatives and other thiazolidine-condensed 5-, 6- and 7-membered heterocycles.



Scheme

Based on molecular modelling calculations, employing extensive experimental spectro-scopic data of **1**, **2** and **3** in conjunction with already solved and new crystal structures of reactants and products, such as 4-oxothiazolidines **1** and 1,2-dithioles **2**, we shall discuss the chemoselective reactions **A**[3a] and **B**[3b] in terms of a structure-activity relationship, based on abovementioned innate structural properties of particular substrates **1**.

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Hydration of Anions in Aqueous Solution

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Inorganic anions are hydrated through hydrogen bonds in aqueous solution. The strength of these hydrogen bonds is preferably determined by the double difference infrared spectroscopy method.[1,2] Anions forming stronger hydrogen bonds to the surrounding water molecules than the hydrogen bonds in bulk water are regarded as structures makers, while those forming weaker hydrogen bonds are regarded as structure breakers. The hydrogen bond strength is also reflected in the exchange rate as shown by theoretical simulations.[3] The structure of hydrated anions in aqueous solution is determined by large angle X-ray scattering (LAXS) to get information about distances, bond angles and approximate number of water molecules bound in the first coordination sphere. A survey of the methods used will be presented. An overview of studied hydrated metal ions will be given as well as some recent results.

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Hydrogen Bonds within an Alpha-helix could be modeled by Toda potential

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Directional biological motion of motor proteins requires that the cell be able to convert stored chemical energy into mechanical work. Understanding how the mechano-chemical energy transduction occurs and how small biological forces, on the order of piconewtons, generated at the molecular level, are organized to produce (large) cellular –scale movement is fundamental to understanding cell motility.
Here we have examined the relay helices(RH) of these complex machines. On the basis of experimental evidencies, we theoretically examined the motion of RH, by paying special attention to internal degrees of freedom associated with hydrogen bonds within the alpha-helix backbone. The presence of hydrogen bonds in RH is the key departure point in our model of chain oscillations using a nonlinear Toda potential(1).Alpha-helices by being composed of amino acids with not much different masses, are especially favorable for sustaining Toda soliton(TS). TS are robust and stable along length of RH. We estimated energies and forces involved in energy conversion through RH, and critically compared this TS model with some other theoretical approaches (2).

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Walking the plank in small molecule activation by metalloenzymes and related centers

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Recent computational data from our group will be presented on reaction pathways involving small molecule activation by metalloenzymes. In cytochromes P450, heme high-valent iron-oxo complexes known as Compound I, derived from dioxygen or peroxide, are believed to be the reactive intermediates performing hydrocarbon activation under very mild conditions, either by hydrogen atom abstraction or by oxygen atom insertion. Intricate electronic structure details of these Compound I species (e.g., two-state spin-dependent reactivity, biradical nature, "push effect") are often implied as essential in dictating reactivity. Other reactions of Compound I-type compounds are halogen activation, as seen in chloroperoxidase or myeloperoxidase, or hydrogen peroxide oxidation, as seen in catalase.

Here, reaction pathways for hydrocarbon and halide activation will be examined and compared for Compound I and related species. Besides the canonical ferryl+porphyrin cation radical structures typical of Compound I, their protonated versions are also discussed in light of experimental data suggesting that at least some ferryl groups can be protonated; the performance of ferric-peroxo species, which in enzymes are often precursors of Compound I and have been proposed as alternative oxidants in special cases, is also discussed. Also discussed is the case of non-heme cognates of Compound I, where Fe(V) states for iron *in vivo* have to be implied. Last but not least, the hydrocarbon-activating abilities of these dioxygen-derived species (Compound I, peroxo) are compared to those of a much less studied class of oxygen atom-donating metallocomplexes – iron-nitrite adducts. Examination of potential energy curves will reveal structures found at the edge between bonding and weak bonding, offering new insight into the factors controlling the remarkable reactivity of these complexes, and, indirectly, into the fascinating electronic structure of ferryl centers. Pitfalls of computational procedures in discussing such topics will also be noted.

Acknowledgement: the work shown here has been supported by the Romanian Ministry for Education and Research (ID565/2007, CEEX98/2006).

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Mathematical Chemistry – History and Recent Developments

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In the main part of the lecture the more than two thousand years long history of the interplay between mathematics and chemistry will be presented, including the first (erroneous) result of mathematical chemistry (Plato), Jabir ibn Hayyan's magic number 17 (VIII century), alchemical geometry, the first theorem of "mathematical chemistry" (1741), the mathematical background of the XIX century structural chemistry, the knot theory of atoms (Lord Kelvin), the chemical origin of graphs, and the over-optimism of the 1930s. Then the present status of mathematical chemistry will be briefly commented, revealing its successes and failures.

We conclude the lecture by offering an answer to the question:

What is, and what is not Mathematical Chemistry?

POSTERS

INTERACTIONS OF FUMONISIN B_1 WITH NATURAL ZEOLITIC TUFF AND ORGANOZEOLITES

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The natural zeolitic tuff was modified with different amounts (2, 5 and 10 mmol M^+/100g) of octadecyldimethylbenzyl ammoinum (ODMBA) ions and the samples were denoted as OZ-2, OZ-5 and OZ-10. The starting material and organozeolites were characterized by determination of the point of zero charge (pH_{pzc}). *In vitro* sorption of fumonisin B_1 (FB_1) was studied at different surface coverage of the zeolitic tuff with ODMBA, different amounts of sorbent in suspension and at different pHs (3, 7 and 9).

The determined pH_{pzc} for natural zeolitic tuff was 6.8 ± 0.1, while for OZ-2, OZ-5 and OZ-10 pH_{pzc} was 7.0 ± 0.1. This suggests that surface of natural zeolitic tuff and organozeolites is positively charged at pH 3, and not charged at pH 7 and 9. Fumonisin B_1 is a large organic molecule containing one NH_2-group, three hydroxyl and four carboxylic groups (Fig. 1), suggesting that it may exist in anionic form even at pH 3.

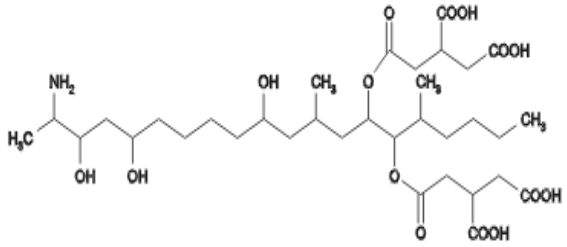

Fig. 1 Chemical structure of fumonisin B_1

High sorption of FB_1 by the natural zeolitic tuff in acidic solution suggested electrostatic interactions between anionic FB_1 and positively charged zeolitic surface. At pH 7 and 9, adsorption of FB_1 is prevented by anionic FB_1 that can not be adsorbed at uncharged surface. For organozeolites, it was found that presence of ODMBA at the zeolitic surface greatly improved sorption of FB_1, especially at pH 7 and 9. The sorption of ionizable FB_1 varied with pH of solution at lower amounts of ODMBA at surface (OZ-2 and OZ-5) with the highest sorption achieved at pH 3, while its sorption was practically independent on the pH when the zeolitic surface was totally covered with ODMBA. From determined pH_{pzc} for organozeolites, it is possible that for OZ-2 and OZ-5, at pH 3, the electrostatic interactions between the positive uncovered surface and anionic form of FB_1 in combination with specific interactions between FB_1 and ODMBA ions contribute to the FB_1 adsorption, while at pH 7 and 9 there is only possibility for specific interactions. For OZ-10, FB_1 sorption was not dependent on the form of FB_1 in solution suggesting only specific interactions between ODMBA and FB_1.

Experimental charge density study of intermolecular interactions in the crystal structure of *N*-o-Vanillylidene-L-histidine

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Electron density distribution in the crystal structure of *N*-o-vanillylidene-L-histidine (OVHIS) was modelled using Hansen-Coppens multipole model [1] and a high-resolution, low-temperature, single-crystal X-ray diffraction data set. A topological analysis of the total electron density, based on Bader's Quantum Theory of Atoms in Molecules (QTAIM) [2], confirmed the existence of 12 intermolecular interactions and corresponding (3,–1) bond critical points (BCPs). Two strong charge-assisted N–H···O hydrogen bonds (N3–H···O2 and N2–H···O4) are much stronger than the rest of the intermolecular interactions and have quite short H···O distances of 1.61 Å and a high $\rho(r_{bcp})$ value at BCP (0.26 and 0.37 e Å^{-3}).

Molecular electrostatic properties have been also analysed using experimental charge density data. It was found that the OVHIS molecule is highly polarized (Fig. 1) and has a very high molecular dipole moment of 42.4 D in the solid state. It seems that intermolecular hydrogen bonds significantly contribute to a large molecular dipole enhancement which occurs upon crystallization.

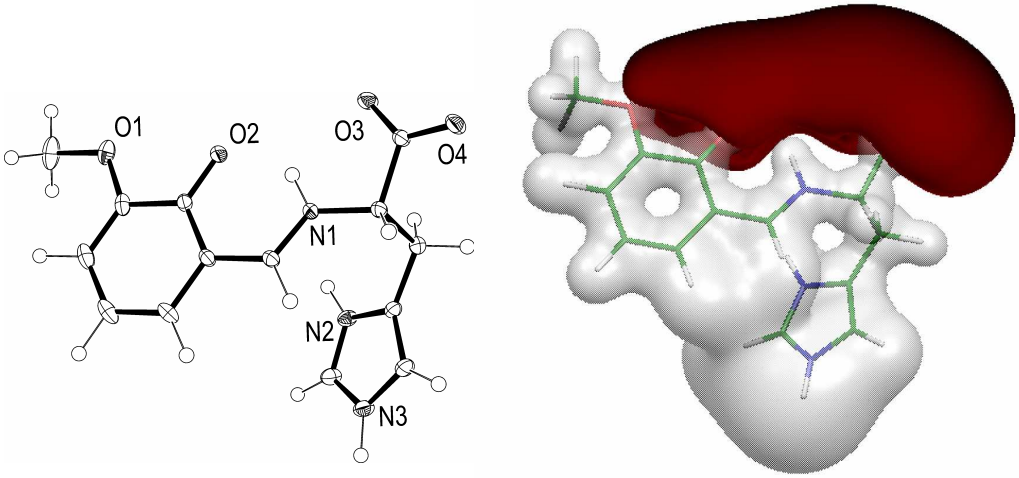

Figure 1. Isosurfaces of experimental electrostatic potential of OVHIS (right side): transparent light gray surface corresponds to the positive electrostatic potential of +0.15 au while solid black surface corresponds to the negative electrostatic potential of –0.15 au.

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Theoretical determination of Hydrogen-bond lengths of DNA base-pairs

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Hydrogen-bond lengths of Adenin-Thymin (A-T) and Guanine-Cytosine (G-C) base-pairs, including the sugar-phosphate group, of DNA are calculated at several levels of the density functional (DFT) as well as Hartree-Fock theory. Comparison of the obtained DFT results for hydrogen-bond lengths of N-HN, NH-O of A-T pair and O-HN, NH-N, NH-O of G-C pair with experimental data show a systematic improvement over previous theoretical studies.

Acknowledgement: This work is supported from the FP7 nanoDNAsequencing project.

The B4(XQ3)LYP-approach solving lactam-lactim tautomerism

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The energetics of lactam-lactim equilibria of 2-pyridinone, 2-quinolinone, 1-isoquinolinone, 3-isoquinolinone, 4-pyrimidinone, 4-quinazolinone, 2-pyrazinone, 2-quinoxalinone, cytosine, isocytosine, thymine and uracil were studied in vacuum using the B4(XQ3)LYP approach [1] applied to geometries optimized on the B3LYP/6-31G** level of theory as implemented in Jaguar V7.5 [2]. Predicted energies of tautomerization show root-mean-square deviation of 1.3 kcal/mol as compared with the experimental data [3] where available, or more accurate coupled cluster calculations [4]. The B4(XQ3)LYP approach performs only slightly better compared with B3LYP. To obtain tautomerization energies in aqueous solutions of mentioned compounds, the electrostatic contribution to the solvation energies of tautomers were obtained solving the Poisson equation for atomic charges generated by fitting the electrostatic potential derived from the molecular wave functions in vacuum. The comparison of tautomerization energies in solution with available experimental data [5] shows, that the electrostatic solvation model still needs to be optimized.

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DFT study of phosphine-borane adducts as frustrated Lewis acid-base pairs and their interaction with hydrogen

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Due to their specific properties, frustrated Lewis acid-base pairs (FLPs) have recently been thoroughly investigated by means of both experimental and theoretical methods. Since such systems are known to activated dihydrogen, they have found application in the catalytic metal-free hydrogenation processes in organic synthesis [1,2]. On the other hand, the reversible hydrogen uptake / release observed in the case of phosphine-boranes adducts [3] could be helpful for developing novel hydrogen storage materials on the base of FPLs. However, despite the available experimental and theoretical information the detailed mechanism of hydrogen activation remains unclear.

Hereby we present a theoretical study of the interaction of dihydrogen with a series of model FLP (Fig. 1). The quantum-mechanical calculations are performed at DFT level of theory with different functionals – B3LYP, MPW1K and M06-2X. The obtained results show that in the case of the modeled ethene B, P derivatives the hydrogenation of the double C-C bond is energetically more favorable than the formation of the corresponding B, P hydrogenated products. Taking into account the solvent effect results in stabilization of structures by due to formation of zwitterionic structures with higher dipole moment.

The investigation is supported by the National Center of Advanced Materials UNION under the project DOO2-82/08 with Bulgarian National Science Fund.

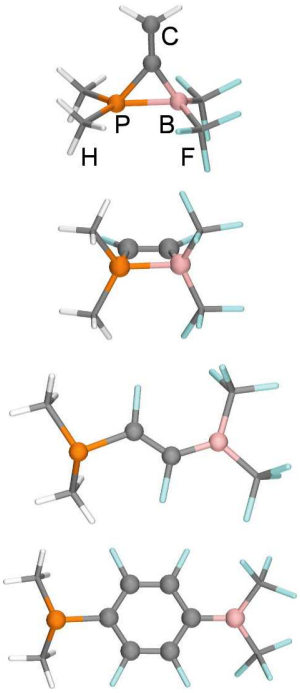

Figure 1. Model FLPs.

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Inclusion complexes of amlodipine bezylate and cyclodextrine

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Amlodipine, 3-O-ethyl 5-O-methyl (4R)-2-(2-aminoethoxymethyl)-4-(2-chlorophenyl)-6 -methyl-1,4-dihydropyridine-3,5-dicarboxylate is the blocker of calcium channels of the dihyropyridine group. Amlodipin decreases the number of attacks of angina pectoris and nitrate consumption, substantially decreases ischemic changes of physical load and prolongs the time between appearances of angina pectoris. Its basic disadvantage, in spite of its good characteristics is its photosensitivity. Under the influence of light 1,4 dihydropyridine ring turns into pyridine ring. New pyridine derivative of amlodipine causes the loss of pharmacological activity, also manifesting certain toxicity and it is also a potential cancer source. In order to protect amlodipine and similar drugs from photodegradation, various protective coatings were used. Recently, a new approach to the drug protection from photodegradation was developed based on the possiblity of using chemical complexes with corresponding photoprotective carriers: cyclodextrines, liposomes and microspheres. Supramolecular structures also substantially correct the physical characteristics of the drugs, such as small solubility, which is most often the limiting factor of the drug application as a successful humane therapeutics.

The aim of this work is the preparation of inclusion complexes of amlodipine besylate with β-cyclodextrine and hydroxipropyl-β-cyclodexstrine and their structural characterisation. Molecular inclusion complexes of amlodipine besylate are prepared by the method of coprecipitation and characterised by the application of spectroscopic methods FTIR, ^{1}H NMR and XRD. Also the photosensitivity of amlodipine besylate in inclusion complexes was determined with respect to noncomplexed agent. Suitable method for following the photosensitivity of amlodipine besylate in solid state in various forms was FTIR method. DSC method used for observing thermal effects arising from physical transformations of amlodipine besylate in pure and complexed state. DSC curves show the loss of the expressed peak from melting of amlodipine besylate at about 200 °C in inclusion complexes, indicating to its inclusion into host cavities. The inclusion of amlodipine besylate with cyclodextrine increased the stability, i.e. decreased the photosensitivity of amlodipine.

Acknowledgements: This paper was supported by Ministry of Science and Technological Development – Republic of Serbia, project TR-19048 and OI-142037.

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A MODEL INVESTIGATION OF NUCLEOBASE PARTICIPATION INTO NUCLEOSIDES INTERMOLECULAR HYDROGEN BONDS

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During the protein biosynthesis peptide bond formation in the ribosome interior is a key reaction for all living organisms. So far the mechanism of the process catalysed by ribosome remains non-revealed. It is mainly due to obscurity in the chemical processes mechanism and the ways for catalysis of that reaction in the ribosome interior. Because of proton donor and proton acceptor positioned close to reaction centre. Because of the possibility for general acid base catalysis it is important to know their ability for hydrogen bonding. In this study we calculate lengths and energies of hydrogen bonds between nucleobases and methanol or water.

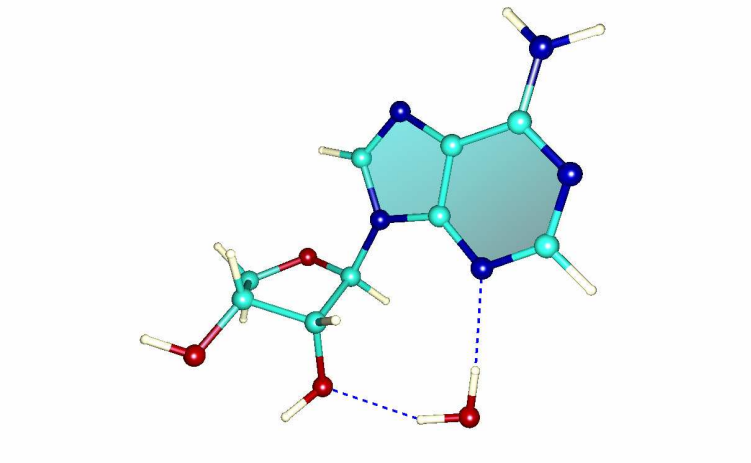

Fig. 1. Optimised structure for formation of hydrogen bonds of water molecule with nucleoside.

The investigation is supported by project DVU-191 with Bulgarian National Science Fund.

Electronic and topological properties of the non-covalent interactions in derivative of benzoylacrylic acid

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(*E*)-4-(2,4-diisopropylphenyl)-4-oxo-2-butenoic acid belongs to the aroylacrylic acids, class of compounds that exert significant antibacterial and antineoplastic activity (1). It has been observed that the introduction of branched alkyl chains on phenyl ring significantly increases antiproliferative potency, compared to unsubstituted derivative. By analysing larger set of congeners it is clear that such increase of potency cannot be attributed to mere increase of overall lipophilicity. This finding emphasizes the importance of the weak non-covalent interactions between the active compound and its biological target(s).
High-resolution X-ray diffraction experiment and the multipole refinement (2) were used for detailed description of the electron density distribution in (*E*)-4-(2,4-diisopropylphenyl)-4-oxo-2-butenoic acid. This approach has also provided the details about the electronic features of the intermolecular interactions in the crystal packing. Along the analysis of the charge density distribution between the interacting atoms, all intermolecular interactions have been quantitatively studied by topological analysis based on the Bader's quantum theory of Atoms in Molecules (AIM) (3). The polar, 4-oxo-2-butenoic fragments of the molecule are involved in cyclic O-H…O hydrogen bond, typical for carboxylic acids (H…O = 1.6500 (9) Å, O-H…O = 175.95(6)°). According to the topological analysis, the amount of density in the bond critical points and the value of the Laplacian for this, the strongest non-covalent interaction are: ρ_{bcp} = 0.27 e.Å^{-3}, $\nabla^2\rho_{bcp}$ = 4.73 e.Å^{-5}. Interactions which involve only aryl fragments of the molecules are of the C-H...π type. The values for ρ_{bcp} and $\nabla^2\rho_{bcp}$ in three bond critical points are in ranges 0.02-0.03 e.Å^{-3} and 0.26-0.52 e.Å^{-5}, respectively. Among the interactions related to both 4-oxo-2-butenoic and the aroyl moieties, the strongest interaction is of the C-H…O type with ρ_{bcp} = 0.04 e.Å^{-3} and $\nabla^2\rho_{bcp}$ = 0.57 e.Å^{-5}. The experimental charge density analysis also allowed the determination of the electrostatic potential (4). This important property has been used for the analysis of the electrostatic complementarities which led to the mutual recognition of the interacting fragments.

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Novel apolar β-peptide foldamers; the role of axis chirality on β-peptide sheet stability

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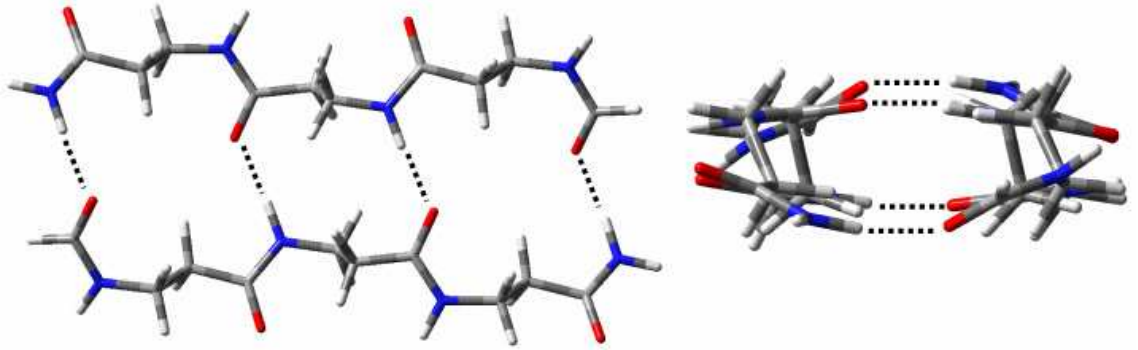
This study is on structure and stability of sheet-like conformers of β-peptides; never seen new foldamers are reported. Single- and double-stranded structures are analyzed: the seeds of large β-layers and biocompatible nanomaterials. Both the monomeric, HCO-(β-Ala)$_3$-NH$_2$, and the dimeric forms, [HCO-(β-Ala)$_3$-NH$_2$]$_2$, of oligo-β-alanines[1] are evaluated by geometry optimizations and frequency calculations at an adequate level of theory B3LYP/6-31G(d) for peptides of this size. Local backbone folds, with the central μ torsion angle set to an *anti* orientation were all probed. These novel secondary structural elements of β-peptides are structural analogs of β-pleated sheets of proteins. Sheet structures built up of strands with carbonyl groups monotonically facing the same spatial direction, **polar strands**, were previously assigned and synthesized [1]. Novel β-peptide sheets of alternating carbonyl group orientations, **apolar strands** (see figure), are described here. These extended like foldamers are stable supramolecular complexes, more firm by ~8-10 kcal.mol^{-1} than the aforementioned polar strands. Furthermore, apolar strands lack the overall twisting of β-layers present in polar strands. Once the effect of substitution of Hβ1 and/or Hβ2 atoms are revealed on foldamer stability, short peptide sequence could be designed and synthesized. These new, conformationally optimized β-sheet-like nanostructures of increased stability, with little or no twisting could be used as enzymatically resistant biomaterials. They will enlarge the arsenal of already used durable polyesters of similar chemical constitution (*e.g.* -[O-CH(CH$_3$)-CH$_2$CO]$_n$- and -[O-CH(COOH)-CH$_2$CO]$_n$-) as artificial heart valves for example[2].



Schematic representation of the most stable apolar sheet structure of HCO-(β-Ala)$_3$-NH$_2$]$_2$

[1]β-alanine, β-Ala: 3-aminopropanoicacid, H$_2$N-C$^{\beta}$H$_2$-C$^{\alpha}$H$_2$-COOH

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Hydrogen bonding of methanol as a probe molecule to hydrocarbons containing CN group

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Using Density Functional Theory we studied hydrogen bonding between methanol as a probe molecule and various hydrocarbons containing CN group. Studied hydrocarbons were chosen to have different carbon chain length containing up to eight carbon atoms (R-CN, Ar-CN). Calculation were done by Gaussian03 with hybrid (B3LYP) exchange correlation functional combined with basis set at triple dzeta quality 6-311++G (d,p). The corresponding energies of the complexes with methanol were corrected for BSSE and ZPE. We studied not only binding energy of methanol to nitrite compounds but also energy of core level of N atom from CN group, proton affinity (PA) [i], and electrostatic potential on the N atom from CN group as descriptors of proton acceptors in hydrogen bonded complexes. Energy of the H – bond in studied complexes vary from 14.40 to 16.13 kJ/mol, depending on the type of the hydrocarbon chain. We found energy of core level of N atom from CN group vs. proton affinity and electrostatic potential of N atom from CN group as sensitive with respect to discrimination of primary and secondary nitrile compounds.

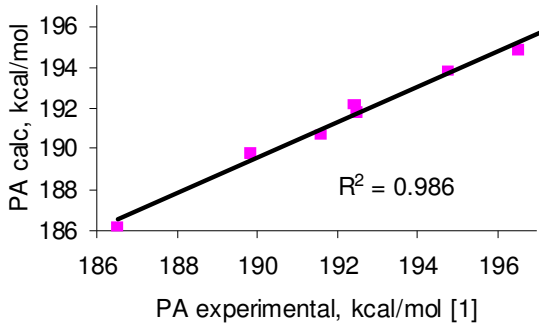

Figure 1. Calculated vs. experimental proton affinity of series of nitriles

The investigation is supported by project DVU-191 with Bulgarian National Science Fund.

[1] National Institute of Standards and Technology (NIST)
http://webbook.nist.gov/chemistry/form-ser.html

Significant consequences of subtle changes within two Mn(III) complexes with *naften* ligands

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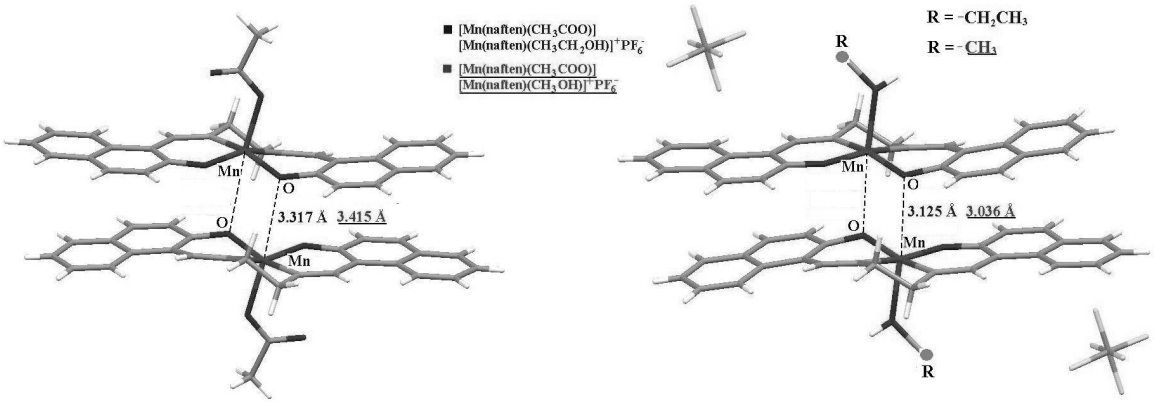
Complex compound was synthesized by reaction of manganese(III) acetate with N,N'-ethylene-bis((2-hydroxy-1-naphthyl)-methaniminato) (H_2naften) in methanol in presence of NH_4PF_6. Recrystallisation from ethanol produced an isostructural complex in which only solvent ligand is substituted. As revealed from single crystal X-ray analysis the triclinic structures are mainly characterized by two different Mn(III) naften out-of-plane-of-dimers in the unit cell. Next to neutral entities $[Mn(naften)CH_3COO]_2$ complex cations $([Mn(naften)ROH]^+)_2$ with PF_6^- as counterions are observed (see Fig. 1). Deprotonated quadridentate naften ligands coordinate the Mn ions *via* NNOO donor atom set.

Centrosymmetric dimers are connected *via* Mn-O interactions where respective distances reflect expected trend due to local and overall net charges of the molecules. However, very significant trends are induced by different solvent ligands. In the supposedly unaffected dimeric entities containing acetate, Mn-O distances within the dimers are shortened by 0.1 Å upon replacement of methanol by ethanol. This is even more surprising since respective elongations in the solvent-containing dimers amount to 0.09 Å only. Detailed analysis has to evaluate, to which extent hydrogen bonding between acetate and solvent ligands induces these changes. Clearly, significant influence on magnetic properties has to be expected. Stacking interactions between naphthyl fragments in the dimers are slightly different. Variation in normal distances between naphtyl groups are not only caused by different overall net charges of complexes but also due to noncovalent interactions with PF_6 anions.



(a) (b)

Fig. 1: Mn(III) naften out-of-plane-dimers in analysed crystal structures.
(a) $[Mn(naften)CH_3COO]_2$; (b) $([Mn(naften)ROH]^+)_2\ 2PF_6^-$.

Building of a π Complex and Hydrogen Bonds - Crutial Moments of Oxidative Addition of Iodobenzene to the Low-Ligated Diethanolamine Palladium(0) Complex in Heck Reactions

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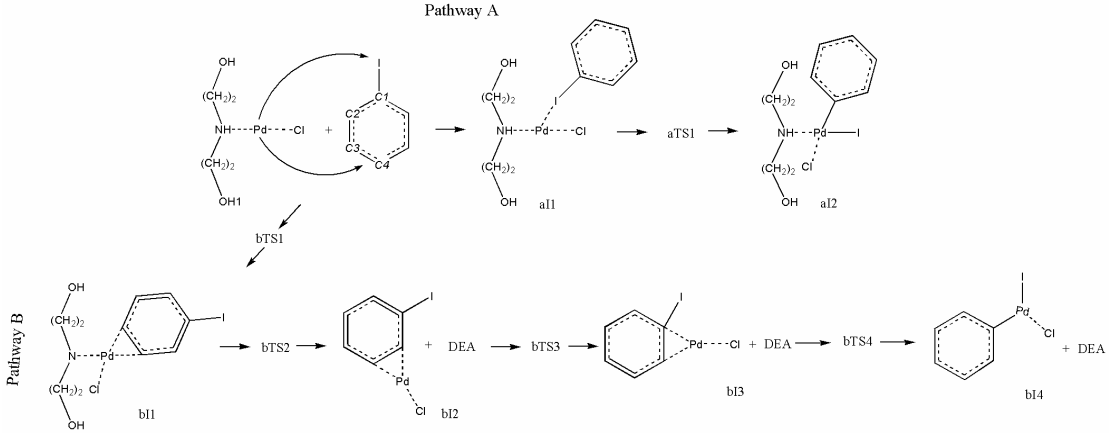
In our previous studies we have elaborated the preactivation steps of a phosphine-free Heck reaction, where as a precatalyst we used *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex (*trans*-[$PdCl_2(DEA)_2$]). It was established that DEA-Pd(0)-Cl was obtained as catalytically active species in the preactivation process of the investigated reaction [1,2].

The next step in the Heck catalytic cycle is oxidative addition of iodobenzene to Pd(0) species. The aim of this DFT study is to investigate possible mechanistic pathways of oxidative addition of iodobenzene to the activated Pd(0) complex. The general outline of two revealed mechanisms is presented in Scheme 1. The first mechanism begins with a nucleophilic attack of palladium on iodine, thus forming the intermediate tetracoordinated complex aI2 (pathway A). The second mechanism (pathway B) begins with an attack of palladium on benzene ring. This proces occurs via π complexes, which result from the interaction between electron rich Pd of the activated complex and π electron system of iodobenzene. The tricoordinated intermediate complex (bI4) is here yielded. The energetics of the two pathways and structures of final intermediates indicate that pathway B provides significantly more favorable mechanism for the oxidative addition of iodobenzene to the DEA-Pd(0)-Cl complex.

The presence and formation of hydrogen bonds of DEA (as solvent) with intermediates bI2-bI4 lower the activation energies for the formation of all transition states in pathway B.



Scheme 1. Proposed mechanism for the catalytic cycle of the Heck reactions

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Diethanolammonium Acetate as Ionic Liquid and Ligand Precursor in Green Heck Reaction Protocol

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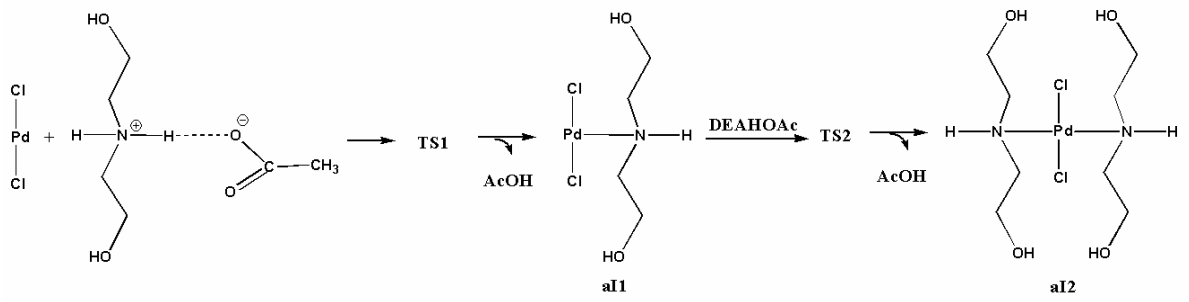
The palladium-catalyzed arylations of olefins, known as the *Heck* reactions, deserve considerable attention due to its synthetic versatility. This important reaction for C-C bond formation, may be used for the synthesis of many multifunctional compounds, such as natural products and bioactive compounds, pharmaceutical, agricultural and other useful materials [1].

Ionic liquids have received considerable attention as green solvents for organic synthesis and catalysis. This is mainly because of their superior properties compared with conventional organic solvents, such as nonvolatility, nonflammability, low toxicity, high thermal stability, wide liquid range, and reusability. Also, ionic liquids have been employed as good solvents in Heck reactions [2,3]. The aim of this study is to evaluate application of diethanolammonium acetate as ionic liquid in green Heck protocol, as well as mechanism of synthesis of trans-dichlorobis(diethanolamine-N)palladium(II) complex (aI2) by using DFT methods.

The mechanism of formation of Heck pre-catalyst aI2 is depicted in Scheme 1. The reaction begins with nucleophilic attack of diethanolammonium acetate on electron sufficient palladium atom *via* TS1, with parallel braking of hydrogen bond of ionic liquid affording aI1. The reaction continues in the same way *via* hydrogen bond braking in TS2, giving complex aI2.

The obtained experimental results are showing that usage of this ionic liquid increases the yield of the desired Heck coupling products (85%-92%) in comparison to reaction in which diethanolamine is used as a weak base and trans-dichlorobis(diethanolamine-N)palladium(II) complex as pre-catalyst (71%-81%) [4].



Scheme 1: Mechanism of Heck pre-catalyst synthesis

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Quantum-chemical descriptors for QSAR modelling of flavonoids' antioxidant activity measured in stoichiometric assays

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Flavonoids, a group of widespread plant polyphenols, are claimed to be responsible for many of the beneficial effects of fruits, vegetables, tea, vines, etc. The biochemical and pharmacological effects of flavonoids are related to interactions with certain protein receptors, free radical scavenging in hydrophilic environments, mild prooxidant action leading to up-regulation of the enzymatic antioxidant defense, etc. It is shown that some of them exert also cytostatic and multidrug resistance-reversal effects important for efficient anticancer therapy.

The antioxidant/antiradical effects of many natural and synthetic mono- and polyphenolic compounds are extensively studied by a number of assays, most of them characterized by stoichiometric endpoints. While the selection of molecular descriptors for modelling kinetic assays is quite straightforward, the proper selection of descriptors useful in predicting antioxidant/antiradical properties in stoichiometric assays is not clear yet. The main obstacle for obtaining reliable models in this case is related to the presence of multiple centres with similar reactivity in the molecules.

In this study, antiradical activities of a number of flavonoids in the stoichiometric assays FRAP (1), ABTS and DPPH (2) were studied by QSAR analyses. The descriptors used were the total number of OH-groups and the number of OH-groups weighted by semiempirical quantum-chemical parameters characterizing the O–H bond dissociation in the flavonoid molecules and unpaired electron delocalization in the flavonyl radicals: activation energy of bond cleavage, difference between heats of formation of the molecule and its radical(s), maximal spin density on a single atom in the radical(s), etc. The number of OH-groups weighted by the O–H bond dissociation parameters correlated much better with the antioxidant activity than the total number of OH-groups. The impact of these results on estimating the antioxidant/antiradical activities of the compounds is discussed.

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The imino bond cleavage in Schiff base ligand, N,N'-bis(4-dodecyloxy-benzylidene-N-propyl)piperazine. The study of the new obtained Cu(II) and Ni(II) complexes containing piperazine as ligand.

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Polidentate ligands of the Schiff bases type, which contain the piperazine bridge, have attracted the interest of researchers in many different areas because of the various coordination modes they can display. These ligands are readily available, versatile and, depending on the nature of the starting materials (primary amine, carbonyl precursors), they exhibit various functionalities. Moreover, the number, the nature, and the relative position of the donor atoms of a Schiff base ligand allow a good control over the stereochemistry of the metallic center [1].
In this respect, we designed and further obtained the Schiff base ligand N,N'-bis(4-dodecyloxy-benzylidene-N-propyl)-piperazine (L) which contains two N_2 donor sets simmetrically separated by a piperazine fragment, a relative rigid unit. The formation of a rigid core by complexation of the aminic groups failed due to the destruction of the imino bonds and formation of N,N'-bis(3-aminopropyl)piperazineperchloratocopper(II) and Ni(II).
Here we report the synthesis and spectral properties of the new Cu(II) and Ni(II) complexes containing N,N'-bis(3-aminopropyl)piperazine as ligand.
The nature of the complexes was established by elemental analyses (AAS), molar electric conductibility , UV-Vis and IR spectroscopy.

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Obtaining and characterization of a new Zn(II) complex containing piperazine core

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The Schiff bases are widely employed as ligands in coordination chemistry [1, 2]. Schiff base metal complexes have been studied extensively for years due to the synthetic flexibilities of these Schiff base ligands and their selectivity as well as sensitivity towards the transition metal ions.
A binuclear Zn(II) complex was obtained starting from N,N'-bis(4-decyloxysalicyliden-N-n-propyl)-piperazine (L) as ligand [3] and $Znac_2$ dihydrate using 1/2 molar ratio. The obtained compound was analysed by AAS, UV-Vis and IR spectroscopy, and also electrical molar conductibility.

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Studies of Co(II) complex containing N,N'-tetra-(4-antipyrylmethyl)-1,2 diaminoethane(TAMEN) as ligand

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A large number of reports are available on the chemistry of transition metal complexes containing Mannich bases as ligands. Because of their different coordination possibilities with metal ions and to their flexible complexing behavior, the synthesis and structural studies of this ligands and their metal complexes has drawn the attention of many researchers . Mannich bases complexes have been widely studied in the last years, since they are becoming increasingly important as biochemical and antimicrobial agents. In this paper we report the synthesis and characterization of new Co(II) complex, $Co_2(TAMEN)Br_4 \cdot 2H_2O$ were TAMEN=N,N'-tetra-(4-antipyrylmethyl)-1,2 diaminoethane. The synthesized complex has been characterized by elemental analysis, IR and UV-VIS spectroscopy, and molar conductibility data. The citotoxic activity of the complex was studied by MTT assay method on human glioblastoma multiforme cells, 8 MGBA cells, (brain tumor).

The Impact of Accuracy of Experimental Data on the Selection of Descriptors for Prediction of Aqueous Solubility

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Aqueous solubility of a drug is an important parameter which can influence its absorption, distribution and elimination in the body. Development attrition resulting from poor solubility could potentially be reduced with the help of a reliable tool for the prediction of solubility from molecular structure. Numerous predictive models have been proposed. One of the factors which can significantly affect their performance is the consistency of data used in the training set.[1, 2]

To examine the impact of experimental data consistency on model training, three data sets were used: Data Set 1 consisted of solubility data carefully compiled from various literature sources (n=319); Data Set 2, created by substituting 28 values from the first set with solubility data determined experimentally under uniform conditions; and Data Set 3 (n=375), created by including an additional 56 components to Data Set 2, for which solubility values were determined using the same uniform experimental protocol. Structures were optimized using the AM1 semi-empirical method and a large number of molecular descriptors were then calculated using CODESSA software. The heuristic method was applied for the selection of the most significant descriptors.

Significance of individual descriptors for the prediction of solubility using Data Set 1, Data Set 2 and Data Set 3 were then compared. It was observed that within a descriptor group (constitutional, geometrical, topological, electrostatic, quantum-chemical (QM)), individual descriptors largely retain their order of significance, with some reordering of closely related descriptors. Electrostatic and QM descriptors, selected as the most significant ones, were derived from H-bond donor/acceptor surface areas, relative charges and polar surface areas. Most of the constitutional descriptors account for aromaticity and overall hydrophobicity of a molecule. Descriptors selected using the heuristic method can, thus, account for both the hydrophobicity of a molecule and its ability to engage in polar interactions. In Data Set 3, there is also a consistent increase in individual descriptor correlation coefficients.

Multiparameter correlations obtained by the heuristic method show a much greater degree of diversity in descriptors selected using three different data sets. The interpretability of these QSPR equations in terms of the solubility phenomenon they reflect is largely affected by the choice of experimental data in the training set. In overall, greater data uniformity within the training set favors the selection of more readily interpretable descriptors and increases the statistical performance of the resulting equation.

Aqueous solubility remains a difficult property to predict and while significant progress has been made in developing new modeling techniques, there is an emerging consensus that improving the reliability of existing models will require large, diverse sets of uniformly determined experimental data. The findings presented in this work prove such a statement.

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Hydrogen bonding and structure - activity analysis of some potential steroidal aromatase inhibitors

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Estrogens are involved in numerous physiological processes including the development and maintenance of the female sexual organs, the reproductive cycle, reproduction, and various neuroendocrine functions. On the other hand, estrogens enhance growth and proliferation of certain target cells, such as breast epithelial cells and estrogen-dependent mammary carcinoma cells, and induce formation and secretion of various growth factors in established cell lines such as MCF-7. Estradiol, the most potent endogenous estrogen, is biosynthesized from androgens by the cytochrome P450 enzyme complex called aromatase [1]. Aromatase is present in breast tissue, and intratumoral aromatase is the source of local estrogen production in breast cancer tissues [2]. Inhibition of aromatase is an important approach to reducing growth stimulatory effects of estrogens in estrogen-dependent breast cancer [3].

Steroidal inhibitors that have been developed to date build upon the basic androstenedione nucleus and incorporate chemical substituents at varying positions on the steroid [3].

Examination of the structures of compounds having high affinity for aromatase enzyme led to the suggestion that steroid-enzyme binding is primarily the result of interactions between the enzyme and the steroidal D ring [4]. Especially, of the great importance for the binding are the position and the possible hydrogen bonds of H-atom from 17β-hydroxyl group. Activity of steroidal aromatase inhibitors might be also controlled by the A ring and 3-oxo or 3-hydroxyl group [4].

In our study of some androstene and adrostane derivatives with potential antiaromatase properties a number of compounds were synthesized, structurally analyzed and tested for biologic effects [5]. In this paper our attention was directed toward the examination of their hydrogen bonding characteristics.

As a part of our study, the influences of molecule flexibility and substituents on the structure-activity relationship were also examined. The crystal structures of the compounds were determined by the single crystal X-ray diffraction methods.

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The noncovalent interactions in phenol-O_2^+ cation dimer. A gradient-corrected density functional and MP2 study

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Noncovalent interactions in the phenol-O_2^+ cationic dimer were explored at several DFT and MP2 levels of theory. In the DFT approach, several combinations of exchange and correlation functionals were employed, such as: B3LYP, PBE1PBE, HCTH/407, MPW1B95 etc. The global minimum on all of the explored potential energy hypersurfaces was shown to correspond to the nearly-linear hydrogen bonding arrangement of the monomeric units. A second minimum was also detected at some theoretical levels, corresponding to the stacked □-bonded arrangement, in agreement with the available experimental data. Anharmonic vibrational frequency shifts of the OH stretching mode were also calculated at all theoretical levels. The HCTH combination of functionals was shown to perform best with respect to prediction of experimental anharmonic frequency shifts, being even superior to MP2, regardless of the basis set used. This was attributed to the spin contamination problems in the reference HF wavefunction.

QSAR and pharmacophore modelling of pyrrole hydrazones as new anti-tuberculosis agents

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Research for novel ant-tuberculosis drugs is a priority set forth by the World Health Organization due to the huge number of people affected by tuberculosis. Additional motivation is the resistance of the tuberculosis bacilli developed to some anti-tuberculosis drugs. Preliminary investigations of our research team has proven the perspectives of some pyrrole hydrazones to inhibit 90-100% of tuberculosis bacilli, however the lack of activity of other structural analogues was left unclear.

In the current work the anti-tuberculosis activity of a series of pyrrole hydrazones was investigated by different computer-aided drug design approaches in order to find compound structural features which are important for the activity. An in-house series of 57 pyrrole hydrazones was used; the compound activity varied from 0 to 100 % inhibition of tuberculosis bacilli. 2D QSAR analysis and pharmacophore modelling were applied.

For 2D QSAR analysis different constitutional, topological, physicochemical, and quantum-mechanical descriptors of the chemical structure were calculated. Before the analysis logit transformation was applied to the percentage bacillus inhibition. This transformation approximates $\log IC_{50}$ and performs correctly in the range of 10-90% inhibition, therefore compounds outside this range were excluded, leaving 30 compounds for the analysis. Multiple linear regression was used to relate the biological activity to the structural descriptors. Molecular flexibility and shape (Kier molecular flexibility index, number of rotatable bonds, globularity index), and magnitudes of charged molecular surfaces areas and hydrophobic volumes appeared to influence the activity.

Next, the compounds were grouped as active and non-active, with percentage inhibition equal to or less than 10% or equal to or greater than 90%, respectively (28 compounds in the both group, 8 active, 20 non-active). Classification threes approach was tried in order to identify descriptors which distinguish between the two groups. The presence of chlorine substitutient in the compounds and the molecule shape (globularity) influenced significantly the activity.

In order to find structural features responsible for the compound interactions with their biological target in the 3D space, pharmacophore analysis using explicit 3D conformations was initially applied. Possible pharmacophore consists of three hydrophobic centres and a projected location at the binding site of a potential H-bond acceptor. It was present in all active compounds, and distingwished them from the non-active compounds by an accuracy of 0.6 (with accuracy 0.0 meaning non-distingwish and accuracy 1.0 meaning complete distingwish). Currently other options of pharmacophore serach are also expolored.

SYNTHESIS OF MULTIDOPED CERIA BASED NANOPOWDERS

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Mulitidoped ceria nanopowders with different particle sizes were produced by two different methods. The following compositions were prepared: $Ce_{0.8}Nd_{0.01}Sm_{0.04}Gd_{0.04}Dy_{0.04}Y_{0.07}O_{2-\delta}$ and $Ce_{0.8}Sm_{0.005}Gd_{0.005}Dy_{0.095}Y_{0.095}O_{2-\delta}$, as well as pure ceria for comparison. Parameters of the MGNP synthesis process were investigated by variation of glycine to nitrate ratio from 0.6 to 1.0, which affected powders properties like specific surface area, crystallinity, as well as crystallite size.

In addition, the room temperature self propagating synthesis was applied to synthesize the same compositions.

Characterization of the obtained powders revealed that all the samples were single phase ceria solid solutions, while the particle size of the powders prepared by the two mentioned mehtods, differed by an order of magnitude. It is interesting to note that with powders obtained at room temperature inspite of very small particle size (2-4 nm) crystallinity was very high, which was proved by XRD, TEM as well as by Raman spectroscopy.

POTENTIOMETRIC DETERMINATION OF THE STABILITY CONSTANTS OF THE BINARY COMPLEXES OF SOME DIVALENT METAL IONS (CO(II), CU(II)) WITH 1H-3-MERCAPTO-5-UNDECYL-1,2,4-TRIAZOLE

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The interest in the synthesis of the complexes of some transition metals with 1,2,4-triazoles has considerable increased because 1,2,4-triazoles are used to inhibit the growth of tumours and cancer in mammals and to threat the viral as well as bacterial infections.

In this paper we present the potentiometric study of the binary complexes of some divalent metal ions (Co(II), Cu(II)) with 1H-3-mercapto-5-undecyl-1,2,4-triazole.

Potentiometric measurements were performed with a TitroLine alpha plus-TA 10 plus-Schott Instruments. The following factors have been considered: acido-basic behavior of the free ligand, metal:ligand molar ratio and pH of solutions. All the studies have been performed at constant concentration of the ligand. The value of protonation constants of the ligand were calculated with Superquad program and the stability constants of metal complexes with Psequad program. The speciation diagrams in the aqueous binary systems was plotted by the program HYSS 2006.

QSAR and Docking study of binding affinities to steroid-binding globulins

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In the presented QSAR study was developed method for theoretical evaluation of steroids binding affinity to corticosteroid-binding globulin (CBG) and sex hormone-binding globulin (SHBG). The binding affinities of steroids to the CBG and SHBG have influence on the half-life, distribution, and efficacy of these agents.

Thirty one steroids of different structures were used in theoretical QSAR and docking study of binding affinities to CBG) and SHBG. Plasma CBG and SHBG also bind synthetic glucocorticoids and sex hormones, and therefore influences the half-life, distribution, and efficacy of these group of drugs. Performed theoretical study has developed QSAR models for prediction of the steroids binding affinities for SHBG and CBG.

The compounds examined in the study demonstrated a wide range of experimentally measured binding affinities (K: 10^{-5}–10^{-9} M^{-1}). Constitutional, geometrical, physico-chemical and electronic descriptors were computed for the examined structures by use of the Chem3D Ultra 7.0.0 [1], the Dragon 5.4 [2], the MOPAC2009 [3], and the Chemical Descriptors Library (CDL) [4] program. Partial least squares regression (PLSR), has been applied for selection of the most relevant molecular descriptors and development of the QSAR models.

Optimal QSAR models with six and eight variables, R^2>0.789 and cross-validation parameter Q^2>0.682, were selected and compared.

Finally, the ligands docking were performed with help of FRED docking program at the CBG and SHBG active sites. Results of the QSAR and docking study were compared in order to define physicochemical, electronical and structural requirements for selective and effective binding to the CBG and SHBG.

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Postdocking Optimization of Protein-ligand Complexes using AMMOS Software Tool

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A software tool AMMOS (Automated Molecular Mechanics Optimization tool for in silico Screening) for structural refinement of compound collections and energy minimization of protein-ligand complexes has been developed for virtual ligand screening purposes. The tool carries out an automatic procedure for minimization, based on molecular mechanics, at different levels of atom flexibility. Five proteins of completely different geometries and physicochemical properties of the binding sites (estrogen receptor, thymidine kinase, coagulation factor X, ribonuclease and neuraminidase) have been selected for AMMOS testing. The presented tool significantly improves the enrichment after pre-docking with 40 to 60% of the initially added active compounds in the top 3% to 5% of the entire compound collection. AMMOS is open source program and can be used by scientists working in the field of in silico drug design.

Modelling the infrared spectrum of the acetic acid dimer

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The acetic acid dimer possesses a double hydrogen bond, and thus represents a prototype for DNA base pairs. Upon a formation of the dimer, the two local O-H stretches combine into symmetric (Raman active) and antisymmetric (infrared active) mode.

The infrared spectrum of the acetic acid dimer is quite complex in the region of the O-H stretching vibration, which makes its modelling a real challenge. The reason for the rich substructure of the spectrum is twofold: First, apart from the most stable structure, the two conformers that are located at the top of the barrier for single and double methyl rotation are also present in the spectrum, each of them giving its own contribution to the overall spectrum. Secondly, the double hydrogen bond is responsible for the pronounced anharmonicity of the potential energy surface, which results in appearance of overtone and combination transitions that involve vibrational degrees of freedom that the O-H stretching mode is coupled to. Those degrees of freedom are identified by analyzing cubic and semi-diagonal quartic anharmonic force fields that involve the antisymmetric O-H stretching, $\nu_{OH,a}$. This analysis reveals that the mode of interest exhibits the strongest coupling to its symmetric counterpart, $\nu_{OH,s}$, and to the two out-of-plane bending modes, $\gamma_{OH,a}$ and $\gamma_{OH,s}$. The resulting 4D models capture the most significant features of the O-H stretching band.

Additionally, the low frequency region contains a few sharp peaks, and the fact that their intensity is high can be explained by considering oscillator strength borrowing through coupling to the $\nu_{OH,a}$ mode. According to the values of the harmonic frequencies, they represent combinations and overtones of the O-H in-plane-bending modes ($\beta_{OH,a}$ and $\beta_{OH,s}$) and the C-O stretching vibrations ($\nu_{CO,a}$ and $\nu_{CO,s}$). This brings us to 8D model, built by computing the 4D potential on the grid (it involves the strongly coupled modes $\nu_{OH,a}$, $\nu_{OH,s}$, $\beta_{OH,a}$ and $\beta_{OH,s}$), whereas the additional four degrees of freedom are included through force fields up to the fourth order. We employed the Multi Configuration Time Dependent Hartree[1] ansatz for the wavefunction and computed the spectrum by performing a Fourier transform of the dipole autocorrelation function from a 1 ps run. The resulting spectrum[2] reproduces the experimental one in the O-H stretching region quite satisfactory and shows the origin of the high intensity peaks in the low frequency region.

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Raman Spectrum of Aqueous OH^- Ion: A Sequential Monte Carlo - Quantum Mechanical Study

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A sequential Monte Carlo – quantum mechanical (S-MC-QM) methodology is used to simulate the Raman spectrum of aqueous hydroxide anion. Series of statistically uncorrelated configurations taken from an equilibrated MC simulation were sequentially used to compute the in-liquid anharmonic OH stretching potential in a variety of possible environments by quantum mechanical approach (employing HF, B3LYP and MP2/6-31++G(*d*,*p*) levels of theory) and subsequently calculate the anharmonic OH stretching frequencies by solving the vibrational Schrödinger equation. In the QM calculations, first hydration shell water molecules were included explicitly, while the remaining "bulk" molecules were included either as sets of point charges or as a polarizable continuum. The average *frequency shift* from the gas phase value computed at MP2 level is in excellent agreement with the experimental data (+78.1 *vs.* + 77 cm^{-1}). HF and B3LYP levels of theory were found to overestimate significantly the experimental blue shift (the corresponding values being +195.0 and +129.4 cm^{-1} respectively). "In-liquid" instantaneous correlation curves between ν(OH) and r_e(OH) values are also presented. According to the statistical analysis of the hydrogen bonding between the hydroxide ion and the first-shell water molecules, it was found that when the OH^- ion is treated by a charged-ring (CR) representation, the average number of h-bonds accepted by the solute ion is 4.6, while within the simple charge (SC) representation this number is 6.4. Both representations of the OH^- species in the MC simulations, however, predict insignificant number of h-bonds in which the solute species acts as a proton-donor (0.0 in the CR and 0.1 in the SC model).

Interactions in active site of *E. coli* β-glucuronidase: mechanism of action and pH optimum control

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E. coli β-glucuronidase (GUS, EC.3.2.1.31) has been widely used as a reporter enzyme and as an analytical/synthetic reagent. However, its structure and mechanism of action remain unsolved. Despite its exceptionally high activity compared to human β-glucuronidase, its immunogenicity hampers application in humans for targeted tumor therapy, enzyme replacement therapy or anti-aging related therapies. Understanding the mechanism of action of the E. coli enzyme may help overcome the immunogenicity problem by allowing the creation of humanized enzymes with improved properties.

We solved the crystal structure of recombinant E. coli β-glucuronidase with and without an inhibitor in the active site and applied a semi-rational approach aiming to identify catalytic groups and determine the mechanism of catalysis and factors controlling the pH optimum.

Despite overall low similarity at the DNA and amino acid level, E. coli β-glucuronidase excellently resembles the 3D structure of human β-glucuronidase. Both are homo-tetramers in which each monomer consists of three domains. The active site is situated in a third, C-terminal TIM barrel domain. Active sites are highly conserved with E413 and E504, corresponding to E451and E540 in human β-glucuronidase respectively, acting as catalytic groups. The distance and orientation of the groups indicate retention type acid-basic hydrolysis (Fig.1).

Site-directed mutagenesis of glutamic acids in the active site to alanine greatly decreased the activity. Chemical rescue of residual activity of the alanine mutants by azide and formate demonstrated that E413 acts as an acid-base and E504 acts as a nucleophile, while R327 and Y468 act as nucleophile stabilizing groups. Modeling substrate orientation based on the inhibitor orientation revealed H-network with amino-acids responsible for the specificity. Surprisingly, the glucuronic acid's carboxy group was stabilized by interactions with Y472 and W549, opposite of what was presumed in human β-glucuronidase.

Despite extreme similarity of the active sites, E. coli β-glucuronidase was about 200 times more active than human β-glucuronidase at neutral pH. Expected pH control by an H-network around E413 was not confirmed. Instead, mutations that changed the polarity and flexibility of the active site bearing backbones resulted in dramatic change of the pH profile. We anticipate that this study could be applied to improve human β-glucuronidase for clinical applications.

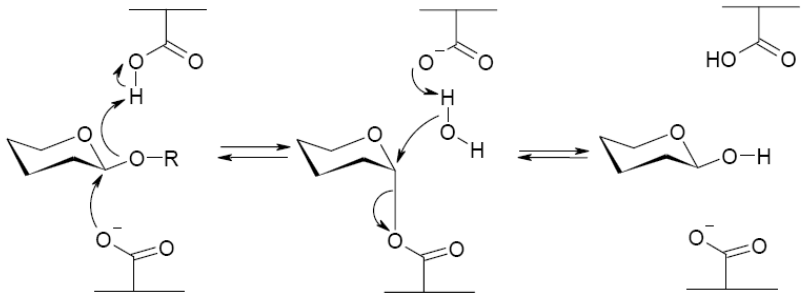

Fig.1: Retention-type acid-base hydrolysis: E413 as the acid-base and E504 as the stabilizing group

PREPARATION AND PROPERTIES OF NANO-GRAINED MULTI DOPED CERIA

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Multiply doped ceria nanopowders were synthesized by applying MGNP (modified glycine/nitrate procedure). The overall concentration of dopants was kept constant (x=0.2) whereby Gd ion as the main dopant was gradually substituted by Sm and by Sm+Y. The compositions of solid solutions were calculated by applying defect model introducing anion vacancy radius. Characterization of powders involved BET, TEM, XRD and chemical analyses. Densification was performed at 1500°C, in an oxygen atmosphere for 1 h. The results showed that with increasing number of dopants, specific surface area of powders increased, followed by decrease of crystallite and grain sizes. Densification degree was also found to rise with increasing number of dopants. According to impedance measurements it was found that ionic conductivity was the highest1.14×10^{-3} Scm^{-1} at 450°C in sample doped with Gd, Sm and Y simultaneously.

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The thermal and oxidation stability monitoring of copper(II) complexes with polysaccharide by conductometric method

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Bioactive copper complexes with polysaccharide pullulan or dextran are the subject of intensive research mainly because of their possible application in veterinary and human medicine. The thermal and oxidation stability of the Cu(II) complexes with reduced low-molar pullulan(RLMP) or dextran (RLMD) were carried out by conductometric method in this paper. Forced degradation studies were performed on bulk sample of complexes using heat (25, 50, 60 and 70 ºC) and oxidation agent (0.1, 0.5, 1.0 and 10.0% v/v hydrogen peroxide). According to the results obtained by the conductivity investigation during forced degradation studies it can be concluded that the Cu(II) complexes shows the greatest stability to both assays.

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The Study ML_2 Building Blocks Based on an Ambidentate Ligand with N-N-N Tridentate and O-O Chelate Functions.

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We devote here a detailed attention to the structural features of the ligand bis(2-pyridyl-carbonyl) amine, (denoted bpca in its anionic form) that have the interesting feature of N-N-N tridentate coordination resembling the terpyridine topology and a bidentate side of diketonate type. The ligand itself is known since long time,[1] being exploited first only in the chemistry of *d*-transition elements.[2] Relatively recently[3] we realized the capacity of the $[M(bcpa)_2]^{q-2}$ units to act as metallo-ligands engaging, by the external diketonate moiety, coordination and assembling towards oxophyle lanthanide ions. We designed in this way a rational strategy for obtaining *d-f* systems with special magnetic properties (Single Molecule Magnets and magnetic anisotropy features).[3] This synthetic strategy was exploited afterwards by other groups also.[4] Focusing on the structural particularities of the complex, we used special features of the ADF (Amsterdam Density Functional) DFT code, revealing by proper analysis a seducing rationalization in terms of the Ligand Field heuristic reasons. The approach was applied also at analysis of the crystal packing and *d-f* assembling based on the discussed units.

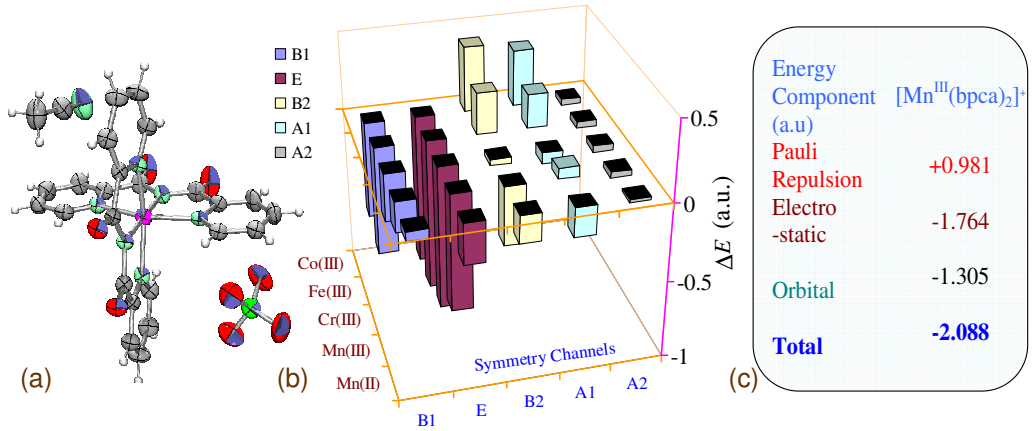

Figure 1. Synopsis illustrating: (a) the structure of discussed structural prototype, (b) the dichotomy of orbital energy on symmetry channels (with respect of D_{2d} group) for a series of $[M(bcpa)_2]^{q-2}$ complexes and (c) a sample of energy decomposition for the Mn(III) complex.

Acknowledgement: This work is supported by the CNCSIS Grant PCE-467/2009

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Manganese (III) Chain Complexes with Single *Syn-Anti* Carboxylate Bridges.

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The interest in developing functional materials has steadily increased during the past decade, molecular magnetism being a hot and appealing area. The paradigms of supramolecular chemistry serve the goal in helping to design extended systems on the basis of appropriate building blocks carrying the necessary properties, such as large spin and magnetic anisotropy. In this context, a novel perspective for designing new magnetic materials is offered by dimeric units of Mn(III) salen and naften analogues as ferromagnetic building blocks, but simple molecules like carboxylate group used as connectors. The orientation towards the discussed systems was justified by previous successes in the assembling of the Mn(III) salen analogues into multi-dimensional magnetic materials[1] combined with the interest in exploiting the versatility of carboxylate groups. We obtained 1D Mn(III) complexes with carboxylate groups as bridges, coordinated in a *syn-anti* fashion.[2] The individual Mn(III) complexes present elongated octahedral pattern. There are two alternating types of dimeric $\{Mn_2O_2\}$ units, each of them intrinsically ferromagnetic and anisotropic, but mutually coupled antiferromagnetically along the chain. Magneto-structural correlations were derived with the help of ab initio calculations in order to understand the subtle factors of local magnetic anisotropy, the factors of 1D assembling and magnetic ordering.

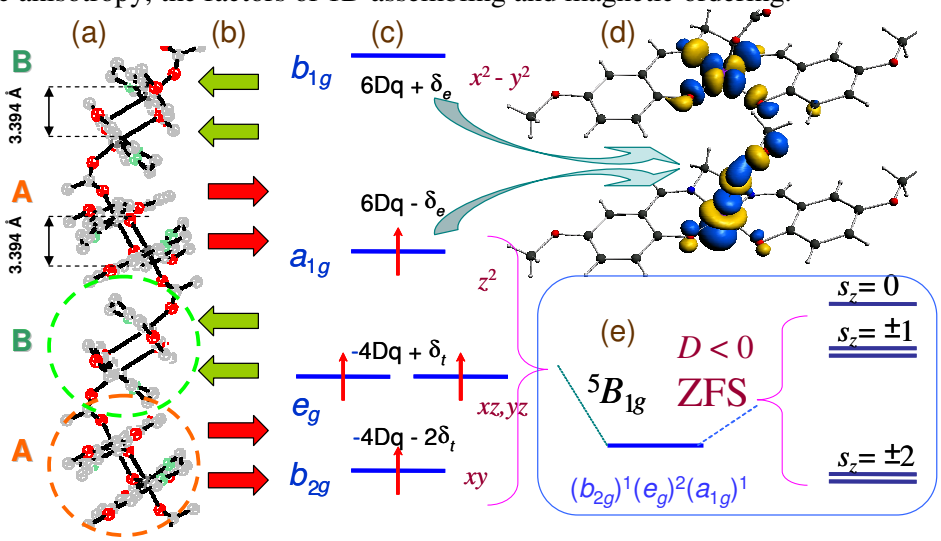

Figure 1. Synopsis of magneto-structural aspects: (a) the chain of $\{Mn_2\}$ dimeric units; (b) magnetic ordering, ferro inside $\{Mn_2\}$ and antiferro in long range; (c) idealized Ligand Field scheme (d) frontier MOs from DFT calculations, and (e) the ZFS split of the ground state, with $D<0$ anisotropy.

Acknowledgement: Financial support from A.v.Humboldt Foundation is acknowledged.

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Structural Features of the Chelate NO_2^- and Diketonate Units in Mixed Ligand Nickel (II) Complexes.

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We present here structural aspects concerning mixed-ligand nickel (II) complexes with the general formula [Ni(*diam*)(*β-dike*)(NO_2)], where *diam* is a series of diamines and *β-dike* are the anions of selected *β diketones*. This type of systems is interesting for rather challenging synthetic issues, solved with respect of particularities of each *diam-dike* ligand couple.[1] We succeeded in obtaining[2] new mononuclear compounds with three different chelate ligands, using this opportunity to explore particular structural features of the presented coordination spheres and their supramolecular packing. Effects such as the ring strain due to the small bite angle NO_2^- chelate ligand and the aromaticity of diketonate moieties are discussed. The analysis of the packing pattern in attempted in quantitative manner, using energy decomposition procedures subsequent to DFT calculations. A particularly interesting part is the theoretical analysis devoted to the simulation the electronic spectra via TD-DFT routine methods and their characterization in a rather inedited way, with the help of density difference maps.

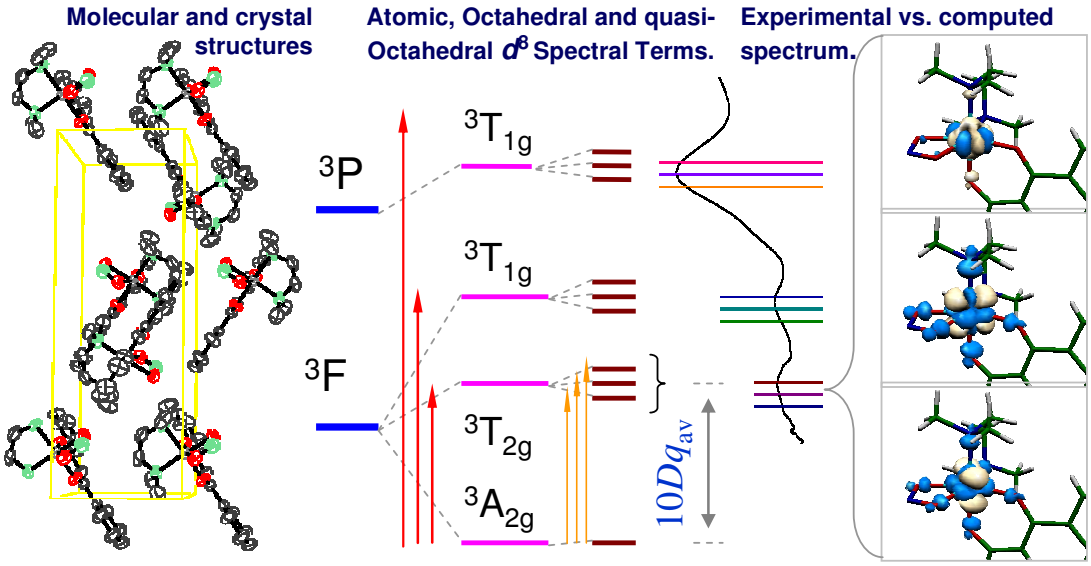

Figure 1. Synopsis of discussed issues: molecular structure and crystal packing of mixed ligand Ni(II) complexes, experimental and electronic spectra and their analysis by density difference maps.

Acknowledgement: Financial support from A.v.Humboldt Foundation is acknowledged.

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Noncovalent interactions revealed from crystal structures of two Ni (II) mixed ligand complexes with *demen* and *dibm*.

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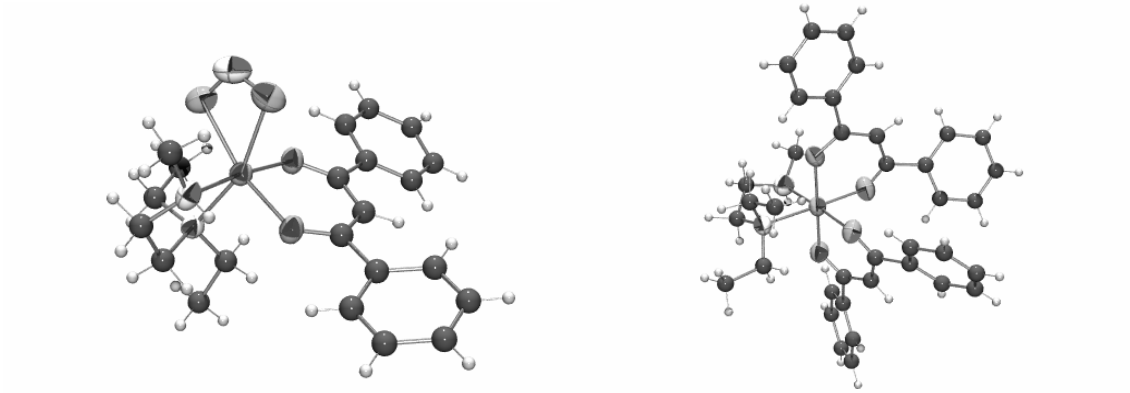
Via reaction of $K_4[Ni(NO_2)_6]$ with N,N-diethyl-N'-methyl-ethylenediamine (demen) and Dibenzoylmethane (Hdibm) in methanol, two Ni(II) complexes, $[Ni(demen)(dibm)(NO_2)]$ (**1**) (green crystals) and $[Ni(demen)(dibm)_2]$ (**2**) (brown crystals), were obtained. The structures of both complexes were determined by single crystal X-ray diffraction methods. In both structures Ni(II) ions are located in pseudo-octahedral environment, where each nickel is coordinated by chelate arms of three bidentate ligands. Much larger distortion from octahedral geometry is induced in (**1**) as consequence of the small nitrito group while coordinated in a chelate fashion and therefore inducing a small bite angle along with a less favorable four-membered chelate ring. This is very well reflected in the difference between the two O_{ax}-Ni–O_{ax} angles (160.81(8)° for (**1**), but 175.53(4)° for (**2**)).

The two compounds pack differently, as mainly reflected in different conformations of phenyl groups within dibm ligands. In addition one ligand exhibits larger deviation from planarity. The dihedral angles in the bent dibm ligand, orientation of phenyl groups as well as short contacts reflect different number of CH-C_{sp2} interactions. In analysing the noncovalent interactions in these structures, we found smaller number of interactions with phenyl groups that are almost in same plane to the chelate ring. However, conformations of demen ligands are in both structures very similar.



Molecular structures of $[Ni(demen)(dibm)NO_2]$ (**1**) (left), and $[Ni(demen)(dibm)_2]$ (**2**) (right)

Crystallographic data: (**1**) $C_{22}H_{29}N_3O_4Ni$, Mr = 458.19, monoclinic, space group C2/c, a = 40.431(3), b = 6.9875(4), c = 16.2274(13) Å, β = 102.454(4)º, V = 4476.6(5) Å^3, Z = 8, R_1 = 0.059, wR2 = 0.112. (**2**) $C_{37}H_{40}N_2O_4Ni$, Mr = 635.42, monoclinic, space group $P2_1/a$, a = 17.3766(9), b = 10.5179(5), c = 18.6548(11) Å, β = 99.293(3)º, V = 3364.7(3) Å^3, Z = 4, R_1 = 0.061, wR2 = 0.139.

Interactions of coordinated water molecule with C_6-aromatic group

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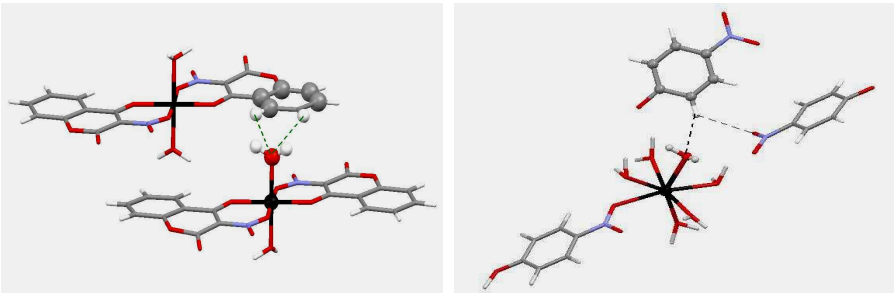
The interactions of coordinated water molecules and π–system of C_6-aromatic group, called metal ligand aromatic cation-π (MLACπ) interactions were recognized and studied in crystal structures of metalloproteins and metal complexes [1,2]. However, coordinated water molecules can also form CH···O interactions with C_6-aromatic groups where water molecule is hydrogen atom acceptor.

Here we present results of intermolecular C-H···O interactions between coordinated water molecules and C6-aromatic groups. Study of interactions was based on analysis of crystallographic data. Crystal structures archived in the Cambridge Structural Database (CSD) involving coordinated water molecules and C_6-aryl groups were screened for intermolecular contacts. We search for structures in which the distance between the O atom of the water molecule and the H atom of the C_6-aromatic ring is less than 3.2 Å, and the angle α larger than 110°. In the CSD crystal structures we found 2355 short intermolecular contacts which satisfy these criteria. The geometric analysis show that non linear arrangement is favored in cristal structures. Visual analysis of structures showed that one of the reason for non linear arrangement is steric effect, because interacting groups are usually voluminous. Since the substituent, on the neighboring carbon atom, can interact with the water molecule, the analysis of the type of atom at this position (X position) is done. In most of the structures on the X position is hydrogen atom. In these structures there is a similar number of simultaneous and bifurcated C-H···O interactions. In structures, in which carbon, oxygen or nitrogen atoms are on the X position, there is a tendency for simultaneous C-H···O interactions (Figure)



(a) (b)

Figure Examples of structures with bifurcated (a) and simultaneous (b) C-H...O interaction.

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Chelate-chelate stacking interactions in crystal structures of square-planar transition metal complexes

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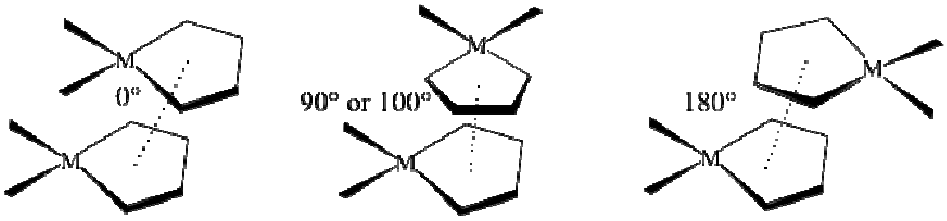
Noncovalent interactions of aromatic and other π-systems are very important in various molecular systems, from biomolecules to crystal engenieering. Recently, number of new methods have been developed and stacking interactions have been studied very intensively. Our previous results show that there are stacking interactions between chelate and C_6-aromatic rings exist in crystal structures of square-planar transition-metal complexes. [1,2]

In this work we found evidences of chelate-chelate stacking interactions analyzing crystal structures from the Cambridge Structural Database. Our study showed that chelate-chelate stacking interactions occur in large number in crystal structures of neutral square-planar complexes that posses planar five and/or six-membered chelate rings. We separately analyzed structures with isolated and fused chelate rings because size of the planar system has influence on the stacking interactions. We used the criteria of search that interaction existed if the dihedral angle between mean planes of two chelate rings less than 10°, distance between the center of two chelate rings less than 4.6 Å, and angle between the normal to the chelate ring and line that connect the centers of two chelate rings $\beta < 35°$. According to this criteria we found 89 interactions in structures which posess isolated chelate rings and 892 interactions in structures in which chelate ring is part of extended π-systems. In crystal structures with fused chelate rings there are three main conformations of interacting chelate rings: parallel, cross and antiparallel, while in structures with isolated chelate rings there are very small number of examples with cross conformations. The torsion angles ($metal_1$-$centroid_1$-$metal_2$-$centroid_2$) in cross conformation for five and six-membered chelate rings are 100 and 90º respectively, that is the consequence of the geometry of these rings.



Parallel Cross Antiparallel

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Noncovalent Interactions Between Chains in Hfq protein from *E.coli*

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One of the most complex levels of structural organization in biological molecules are protein-protein interactions. These interactions are involved in many biological processes. The specificity of protein-protein interactions is of crucial importance for a specific biological function as to form a defined multimeric structure.

The Hfq protein was first discovered in *Escherichia coli* as a host factor for the Qβ phage RNA replication[1]. In last 15 years it was shown that Hfq protein is involved in many RNA processing events. A link between Hfq protein from *E.coli* and spliceosomal Sm proteins was indicated by remote sequence homology. The crystal structure of *E.coli* Hfq protein[2] showed that its monomer displays a charachteristic Sm-fold and forms a homo-hexamer in a ring-like morphology.

We have attempted to study noncovalent interactions between the chains in crystal structure of Hfq protein (PDB code 1HK9) using molecular dynamics calculations. All the calculations were done with CHARMM force field and program. By solving poisson-boltzman equations with CHARMM, Karlsberg and H++ programs we determined protonation state of each aminoacid from Hfq protein. These calculations have shown that each chain is positively charged (+3).

Analyzing the interaction energies between chains it was shown that there are repulsive electrostatic interactions between each two chains in the hexamer unit. This interactions are least repulsive between chains that are in vdW contact (neighboring chains). Van der Waals interactions between neigbouring chains are attractive. These calculations enabled to analyse the types of noncovalent interactions responsible for polymerisation in Hfq protein.

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Identification of Hot spots in Sm protein interfaces

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The Sm family of proteins are closely associated with RNA metabolism throughout all of life. These proteins form homomorphic and heteromorphic rings consisting of six or seven subunits with a characteristic central pore, the presence of which is critical for binding U-rich regions of single-stranded RNA. This study aims to characterize the interface hot spot residues of subunits in Sm proteins. We performed an analysis of the X ray structure of 15 Sm motif containing proteins from the Protein Data Bank (PDB) and summarize physicochemical properties in an effort to understand the origin of their stabilizing contributions to protein–protein associations.

Homo-oligomer interfaces have greater number of interface residues and hydrophobic residues (Ala, Val, Leu, Met, Ile, Phe) are predominant at the homo-oligomer interfaces. However, the study shows that charged residues (Asp, Glu, Lys, Arg) and hydrophilic residues (Asn, Thr, Ser, Gln, His, Trp, Tyr) are dominant at the hetero-oligomer interfaces. Analysis of amino acid enrichment in hot spots shows that some residues are more favorable. The most frequent ones, Met, Arg, Pro, Thr and Tyr, are critical due to their capability of making multiple types of favorable interactions and lowered effective dielectric environment of hot spots.

Our results show that low relCompASA is critical for a residue to be a hot spot. Though many of the hot spot residues have similar relCompASA values with nonhot spot residues, they have different mean values (hot spots: 5.1%, non-hot spots: 29.1%). The *P*-value for relCompASA is less than 0.05, which indicate that hot spots located near the center of the interface are a general property of the interfaces, and largely protected from bulk solvent (corresponding to low relCompASA). RelΔASA indicates the change in the solvent accessibility of a residue, and correlate significantly with relCompASA. Additionally, knowledge-based pair potentials of residues is statistically significant to discriminate hot spots and non-hot spots (P-value = 5.7×10^{-6}). These results indicate that hot spots are mostly buried, tightly packed and form a network of favorable interactions with other residues.

Structurally conserved residues and hot spots correlate significantly, and demonstrate that hot spots play an important role in the stability of oligomers.

Theoretical study of C-H···O interactions between water molecules and C_6-aromatic groups

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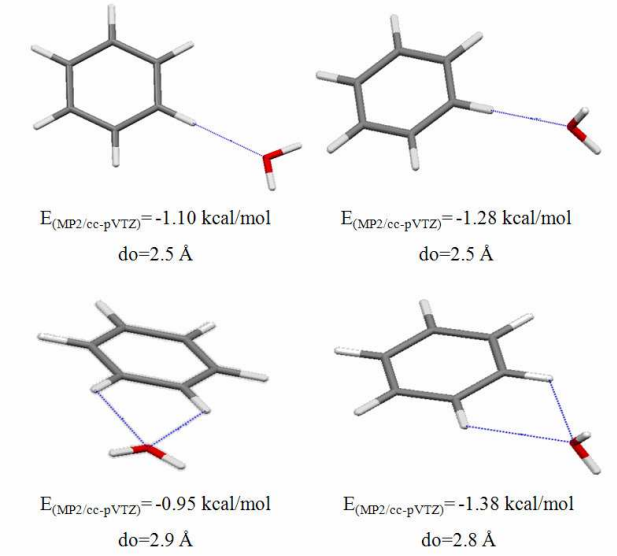
C-H…O interactions are of great importance in chemistry, biology and biochemistry. They have been observed in different molecular systems and it is known that they play significant role in crystal packing, conformational control, enzyme-substrate recognition, stabilizing protein structures and DNA base pairs.

The results of geometrical analysis of intermolecular C-H...O interactions between C_6-aromatic group and non-coordinated water molecule in crystal structures archived in Cambridge Structural Database are presented. High level *ab initio* calculations were also performed. The statistical study was based on the crystal structures archived in the Cambridge Structural Database. In the CSD crystal structures we found 3576 short intermolecular contacts between water and a C_6- aromatic ring, satisfying criteria for C-H…O interactions (1,2). High level a*b initio* calculations were carried out on model system water-benzene. It was observed that in C-H...O interactions between C_6-aromatic group and water molecule linear alignment of donor carbon atom, hydrogen and acceptor oxygen atom is not favored, although this is typical for C-H...O interactions in other systems. Visual analysis of structures and *ab initio* calculations showed that deviation from linear arrangement is consequence of tendency of water molecule to make energetically more stable bifurcated interaction with two adjoining hydrogen atoms from aromatic group.



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Intercalation of cryptolepine as antimalarial mechanism of action

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Malaria is caused by protozoa of genus Plasmodium. Because of its multidrug resistance there is urgent need for new antimalarial drugs . Among several plants used in tradition to cure malaria cryptolepis sanhuinolenta or (sida acuta) is one of the most studied, especially for the best promise expected for their alkaloids particularly cryptolepine (CLP) ,neocryptolepine (NCLP), benzo-delta-carboline (DCB). The indoloquinoline alkaloid cryptolepine has potent in vitro antiplasmodial activity, but it is also a DNA intercalator with cytotoxic properties that are hypothetically due to its abilities to intercalate into DNA and inhibit topoisomerase II as well as DNA synthesis.

According to experimental data cryptolepine intercalates for CG-rich sequences containing nonalternantig CC sites. The mechanism of action is partially inhibition of beta haematin formation (BHIA) and intercalation into parasite CGCG base pairs. Experimental data show good correlation between DNA intercalation (cytotoxicity) and biological activity of cryptolepines (CLPs) (for 15 compound) and there were no correlation between antimalarial activity and BHIA (on 8 compounds $r^2 = 0.0781$). In this work it is shown that cryptolepine and new synthesized derivatives interacts with CG – base pairs in a base – stacking intercalation mode and that their activity depends on interaction with DNA chain.

Density functional theory of steric and electronic influence on the structure of molybdenum trihydride complexes

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Experimental data show that complexes $[(1,2,4\text{-}C_5{}^tBu_3H_2)Mo(PMe_3)H_3]^+$ **($\mathbf{a}^+$)** and $[(C_5{}^iPr_4H)Mo(PMe_3)_2H_3]^+$ **($\mathbf{b}^+$)** undergo H_2 release by oxidatively induced reductive elimination (OIRE mechanism) yielding $[(1,2,4\text{-}C_5{}^tBu_3H_2)Mo(PMe_3)H]^+$ and $[(C_5{}^iPr_4H)Mo(PMe_3)_2H]^+$.

The results of a density functional theory study of these molybdenum trihydride complexes are presented in this work. Different substituents on the Cp ring in **a** and **b** influence the orientation of Cp ring with respect to the phosphines and hydrogen positions and this influence may be of steric or electronic origin. To investigate this influence, geometries and energies of number of different isomers were calculated. The nature of the somewhat shortened H···H contacts in neutral complexes **a** and **b** and the even shorter contacts in corresponding cations $\mathbf{a}^+$ and $\mathbf{b}^+$ were also examined. Monohydride products of OIRE were also examined in order to explain the different stabilities of $\mathbf{a}^+$ and $\mathbf{b}^+$ species towards H_2 elimination. The computational results are in good agreement with the experimental ones.

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Parallel alignment of water molecule and C_6-aromatic rings – evidence for the interactions

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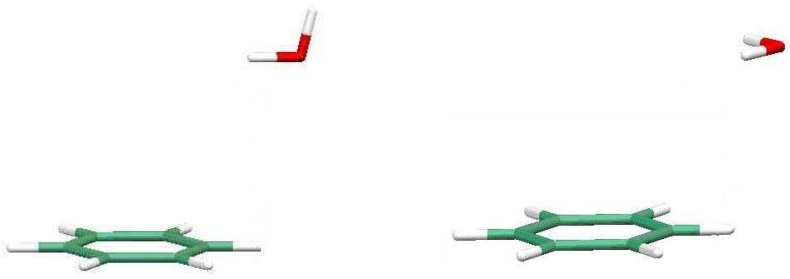
Water plays an essential role in nature and its high polarity and size define its capabilities and the complexity of its behavior. Most important is its hydrogen-bonding ability. Water molecules also form weaker interactions with less polar molecules. These interactions have been observed in various molecular systems. In particular, the interactions of water molecule with aromatic groups have been the subject of extensive theoretical investigation. The study of the interactions between water molecule and the π-electrons of aromatic groups of amino acids in crystal structures of proteins confirmed relatively frequent occurrence of these interactions.

Here, we present a situation in which the whole water molecule or one of its O-H bonds is parallel to the C_6-aromatic ring. These important new geometric features were discovered by analyzing the interactions in crystal structures from the Cambridge Structural Database (CSD) and by *ab initio* quantum mechanical calculations of the water-benzene dimer model systems including coupled cluster electron correlation treatment (CCSD(T)) and complete basis set extrapolation.

In our previous work horizontal distance of 2.0 Å was used as one of geometric criterions[1]. Here the statistical study was based on broadening this parameter to 2.5 Å, in order to determine if there are interactions in the area beyond 2.0 Å. By searching CSD we found 893 short intermolecular contacts with mutually parallel alignment. Among these interactions we found 134 contacts with parallel alignments of the whole water molecule and 481 contacts with parallel alignment of O-H_1 bond. The analysis of the geometries shows that most water molecules are positioned above the region of the C-H bonds. In the new search a significant number of structures was found in the region of the horizontal distance of 2.0-2.5 Å.

A number of model systems with the parallel alignment of the whole water molecule and with one of the O-H bonds parallel to the ring plane were studied by *ab initio* calculations. The calculated normal distances are shorter for the water molecule above the C-H region (3.0 – 3.3 Å) than above the ring (3.4 -3.6 Å) in all model systems. The computed normal distances are in coherence with the distances found in the crystal structures.



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Classification of stacking interactions geometry between terpyridyl square-planar complexes in crystal structures

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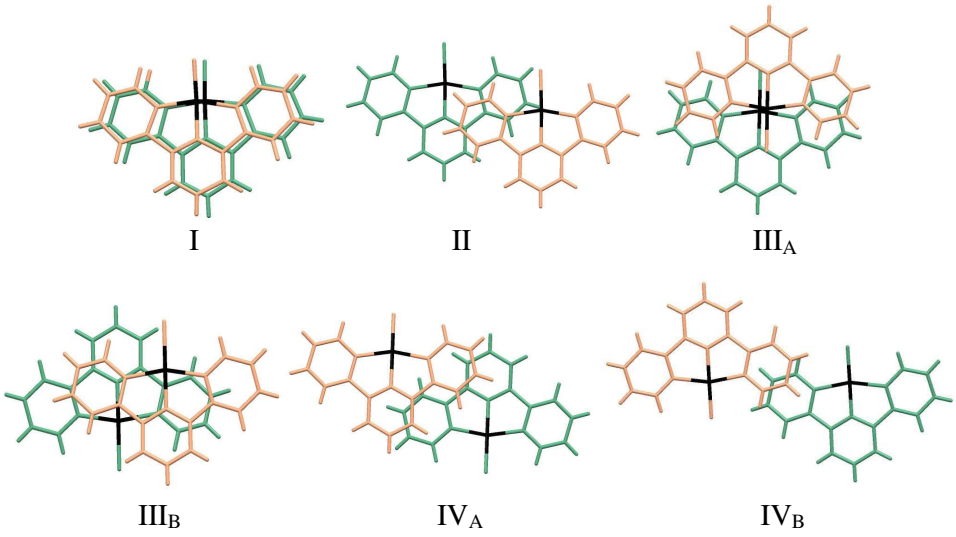
Stacking interactions are generaly studied between aromatic organic molecules or fragments. However, other planar molecules and fragments can be also involved in stacking interactions. Planar chelate rings with delocalized π-bonds can also build stacking interactions similar to aromatic organic molecules.[1] Recently, we showed that water molecule forms parallel alignment interactions with C_6-aromatic rings.[2]

Terpiridine molecule coordinating to a metal ion forms large planar system of five rings, three pyridine fragments and two chelate rings. This planar system has propensity to form stacking interactions. In order to gain better view in stacking interaction of terpy complexes we analyze the geometries of π-π stacking interactions between the terpyridyl ligands of square planar transition metal complexes in crystal structures from the Cambridge Structural Database (CSD). We classified mutual terpyridyl ligands overlaps in six types: I, II, III_A, III_B, IV_A and IV_B. Types of the overlap are defined by geometric parameters. The most numerous are structures with overlap types III_A, III_B with „head to tail" orientation of the two terpy complexes, and quite large area of overlap. The normal distances in these structures are between 3.1 and 3.7 Å. This range is typical range for stacking interactions of two aromatic rings. The shortest normal distances are noticed in the structures of type I and III_A with short metal-metal distance indicating that metal-metal interaction contribute significantly to the interaction.



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The Protection of Nifedipin from Photodegradation Due to Complex Formation with β-Cyclodextrin

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Nifedipin [1,4-dihydro-2,6-dimethyl-4-(2-nitrophenyl)-3,5-pyridine carboxylate] is a derivative of 1,4-dihydropyridine. It belongs to the group of active substances with therapeutic use as a calcium channels blocker and a coro β-cyclodextrin nary vasodilator. It is a highly unstable compound and, under the influence of light, it readily oxidizes to nitroso derivatives [4-(2-nitrosophenyl)-2,6-dimethyl-3,5-dimethoxycarbonyl pyridine] and nitro derivatives [4-(2-nitrophenyl)-2,6-dimethyl-3,5-dimethoxycarbonyl pyridine]. These products lead to the loss of the pharmacological activity of nifedipin. They show certain toxicity in the organism, while the nitroso derivative is potentially cancerous. The high photosensitivity and low solubility of nifedipin are a limiting factor for use of this medicine for clinical purposes [1-5].

The scope of this work is the preparation of the nifedipin inclusion complex with β-cyclodextrin, with inhibited degradation under the influence of light to nitro and nitroso derivatives undesirable during the medicine application. The complex is prepared by use of the coprecipitation method, with 1:1 guest to host mol ratio. The nifedipin degradation products in the free and complexed state, produced by irradiation with 350 nm light, were monitored by using liquid chromatography. It was proven that the photostability of nifedipin in the complex was multiply increased. In solid state, nifedipin degradation also shows increased photostability in the complex. These changes were monitored by infrared spectroscopy. The increased photostability of nifedipin makes possible a safer application for clinical purposes, i.e. minimum stress that may be caused by the photodegradation products.

Acknowledgements: This research is part of the project "Working out of formulations and technology of pharmaceutical and cosmetic products based on lipozomes, microspheres and inclusion complexes" (project No. 19048) which is financially supported by the Ministry of Science of the Republic of Serbia.

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Long-range interaction and LO-TO splitting in powdered and single crystal samples of Alum crystals

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An investigation on the long-range forces in crystals of Alums was performed, and the LO-TO splitting of the modes have been discussed. For that, reflectance spectra from single crystals and the corresponding polycrystalline samples have been obtained. A dispersion analysis employing downhill simplex iteration method gave optical and dielectric parameters of the corresponding crystals [1]. The comparison between the fitted and the recorded spectra appeared to be very well even for the polycrystalline sample. The values for the transversal and longitudinal phonons have been evaluated using two different approaches [2]. Apart from the dispersion analysis, a Kramers-Krönig transformation was applied in obtaining the optical and dielectric parameters of the investigated crystals [3]. The calculated parameters using both methods were compared.

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Molecular and crystal structures of N-heteroaromatic hydrazones and corresponding Cd(II) complexes

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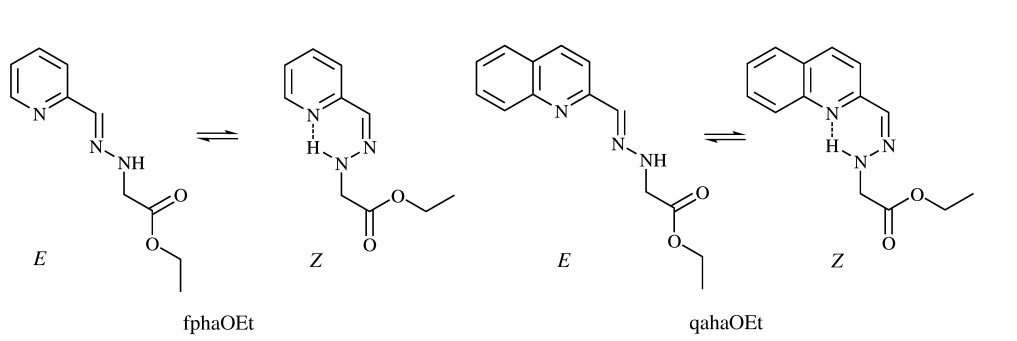
Two novel ligands ethyl-2-{[pyridine-2-ylmethylene]hydrazino}acetate (fphaOEt) and ethyl-2-{[quinoline-2-ylmethylene]hydrazino}acetate (qahaOEt) were synthesized via condensation reaction of ethyl hydrazinoacetate hydrochloride (haOEt·HCl) with 2-formylpyridine (fp) or 2-quinolinecarboxaldehyde (qa), respectively. Both ligands were characterized by single crystal diffraction, as well as NMR spectroscopy in DMSO-d_6. A common feature of crystal packing for both structures are N–H···N_{py} intermolecular hydrogen bonds connecting adjacent molecules, and thus give rise to the formation of infinite 1D supramolecular chains. In freshly prepared DMSO-d_6 solutions of the ligands the presence of both *E* and *Z* interconvertible isomeric forms are observed (Scheme 1). The *E* form exists in both cases in higher concentrations.

Cd(II) complexes with both ligands were obtained by template reactions starting from $CdCl_2·H_2O$, haOEt·HCl and appropriate carbonyl compound. The complexes were characterized in the solid state by X-ray crystallography, while structural characterization in DMSO-d_6 solution was done by means of NMR spectroscopy.



Scheme 1.

Acknowledgment: S.M.gratefully acknowledges DAAD for a scholarship.

Investigation of the reaction of Quercetin with oxygen.

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Bearing in mind the reactivity of OH groups of quercetin (Q) obtained on the basis of the BDE values, we take a step further in this work, and investigate the reactions of 3' and 4' OH groups of Q with oxigen. Our calculations reveal that detachment of H atom by oxygen can be performed with both catehol hydroxyl groups of Q. Both reactions proceed via one transition state and one intermediate (corresponding radical). The values of total energies, enthalpies, and free energies of all relevant species are given in Table 1.

Table 1. Total electronic energy Ee, zero point vibrational energy ZPVE, termal correction to enthalpy TCE, thermal correction to Gibbs free energy TCG. Values of Ee+ZPEV, Ee+TCE, and Ee+TCG are scaled using appropriate scaling factors. All values of energy are in Hartree.

	Ee	ZPVE	TCE	TCG	Ee+ZPEV	Ee+TCE	Ee+TCG
Q	-1104.1486	0.2346	0.2532	0.1889	-1103.9226	-1103.9080	-1103.9702
HOO	-150.8826	0.0147	0.0185	-0.0075	-150.8684	-150.8650	-150.8896
OO	-150.2963	0.0040	0.0074	-0.0159	-150.2963	-150.2932	-150.3152
QO4'	-1103.5148	0.2214	0.2378	0.1772	-1103.3016	-1103.2888	-1254.8385
QO3'	-1103.5119	0.2218	0.2391	0.1778	-1103.2982	-1103.2846	-1254.8392
QO4'TS	-1255.0235	0.2465	0.2679	0.1959	-1254.7861	-1254.8385	-1103.3474
QO3'TS	-1255.0234	0.2463	0.2677	0.1950	-1254.7862	-1254.7690	-1103.3440

During the reaction of 3'OH and 4'OH groups with oxigen, partial detachment of H atom from oxygen of catehol moiety is observed in transition states. The distance between O-H in TS's are increased with respect to corresponding bonds in Q by 32.7 and 30.7 %, whereas the distances between H and O from molecule of oxygen are longer than O-H bond in hydrogen peroxide (0.964 Å) by 17.3 and 19.3 % for reactions in positions 3'OH and 4'OH. The activation energy ΔG associated with both reactions is calculated as the difference in the total free energy between the transition state and corresponding reactant. The activation energies was showed that reaction in position 4'-OH is slightly faster then in 3'-OH.

A detailed analysis of the charges of the transition states shows that the QO and OO fragments carry negative charge, while transferred H has a positive charge in bouth cases. In addition, spin density is also located on OO and QO fragments. Actually, spin density associated with QO moiety is increased, while that associated with OO fragment is decreased, in comparison to the reactants. However, there is no spin density associated with a transferred hydrogen atom. The NBO indicates that there is a hydrogen atom transfer in both cases, as it was concluded in the research of Dhaouadi et al. on the reactions of 4OH group of Q with OH radical [1, 2].

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Non-Covalent Interactions in Framework Compounds Containing Isophthalate Ion

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The design of inorganic-organic coordination frameworks is very intriguing for their various structural topologies and potential applications (1). Anions of benzenepolycarboxylic acids together with some aromatic N-donor ligands are important in maintaining the dimensionality of the coordination compounds and provide potential supramolecular recognition sites for π-π aromatic stacking interactions and hydrogen bonding to form interesting framework structures (2).

To explore the structural diversities in ternary transition metal complexes containing dianion of isophthalic (1,3-benzenedicarboxylic) acid, ipht, on the supramolecular architectures and their dimensionality, crystal structures of three novel framework compounds: $[Co(bipy)(ipht)]_n$ (**1**), $[Ni(bipy)(H_2O)_4](ipht)$ (**2**) and $\{[Cu(ipht)(dipya)]\cdot H_2O\}_n$ (**3**), where *bipy* = 2,2'-bipyridine and *dipya* = 2,2'-dipyridylamine, are described here.

In **1**-**3** N-donor ligands are coordinated as usual chelates, while ipht anions are coordinated in very different manners. Two different ipht exist in **1**: one ipht bridges two Co atoms acting as bis-chelate ligand and another ipht bridges three Co atoms with one bridging and one chelating COO group. The structure **2** consists of individual $[Ni(bipy)(H_2O)_4]^{2+}$ entities and counter ipht ions. In **3**, ipht anion acts as bridging tridentate ligand with monodentately and chelately coordinated COO groups. The coordination polyhedra around both Co(II) atoms in **1** and Ni(II) atom in **2** are highly distorted octahedra, while Cu(II) atoms in **3** are in a very deformed trigonal bipyramidal environment.

The centrosymmetric double chains extending along *b*-axis are formed in **1**. *Bipy* ligands are oriented outwards of the chains and thus play an important role in the crystal packing. Adjacent chains are stacked in the zipper-like fashion into 3D framework through significant intramolecular π-π interactions. The face to face (centroid to centroid) distances are 3.666 and 3.747 Å. Besides π-π, there are numerous C–H···O interactions in **1**.

Cations and anions in **2** are connected by the network of hydrogen bonds building centrosymmetric double layers parallel to *ab*-plane. These layers further construct 3D framework structure *via* a system of π-π stacking interactions between hydrophobic parts of the layers where *bipy* exist. The shortest distance between C atoms from neighboring *bipy* ligands of 3.819 Å approves weak π-π interactions.

In **3** one hydrogen bond involves uncoordinated H_2O molecule and the other hydrogen bond connects adjacent zigzag chains running along *c*-axis. The zigzag chains are stacked into 3D architecture in the lattice through hydrogen bonds and π-π interactions. The shortest distances between C atoms from neighboring *dipya* ligands are 3.304 and 3.434 Å confirming strong face to face π-π interactions.

3D networks in all compounds are essentially determined by non-covalent interactions.

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Could hydrogen bond network dynamics determine the behaviour of the chemical oscillator?

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The object of investigation is Bray Liebhafsky (BL) oscillatory reaction which is known to proceed in two complex, periodically dominating steps:

$$2IO_3^- + 2H^+ + 5H_2O_2 \rightarrow I_2 + 5O_2 + 6H_2O_2 \quad (1)$$

$$I_2 + 5H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \quad (2)$$

After the initial accumulation of iodine through the reaction (1), the reaction (2) is initiated removing iodine from the system faster than it is produced in (1). After some time reaction (1) becomes dominant again and the dynamics repeats. This is the example of spontaneous ordering in the system, through the periodic appearance of iodine (as well as other less stable intermediates through which (1) and (2) proceed). Despite the thermodynamic base of spontaneous ordering is established, detailed mechanism of the whole process is still unknown. The main problem is process (2) which, although thermodynamically favorable, is extremely slow. It indicates great activation energy and it is still unknown by which mechanism process (2) may become a dominant one. Possible explanation can be related with the appearance of a nonequilibrium energy distribution, favoring oxidative properties of hydrogen peroxide. Appearance of such mechanism is of high interest because it anticipates the active involvement of water hydrogen-bonded network. Water is present in great excess over all components and due to the large heat capacity should contain the most part of energy released in chemical reactions. Therefore, it should be involved in controlling all energy rearrangements in the system. Although energy contained in hydrogen bonds is not high, changed hydrogen-bond network dynamics can influence reaction paths especially in systems close to the bifurcation points separating regions with different reaction kinetic. Testing this assumption is performed by the microwave (MW) heating of the reaction mixture at the same temperature as in conventional experiments. Microwave heating of the solution is known to proceed through constant breaking and reforming of weak hydrogen bonds, (either by effects of conduction or dipolar polarization) influencing their dynamics. The constant temperature of the BL mixture is achieved by the external circulating water bath. Experiments with different levels of emitted microwave power showed considerable influence of MW`s on the reaction mechanism. Due to the same temperature as in conventional experiments as well as the close values of electrode potentials by which the process is monitored, effect of microwaves could be ascribed to nonthermal effects. Because of the specific mechanisms of MW heating, it can be correlated with the changed dynamics of hydrogen-bond network. This assumption is supported by previous results of NMR recordings during the chemical oscillations and effects of heavy water. Because of the great importance of water (and hydrogen bonds) in biochemical processes, further investigations in this field are justifiable.

Considering an ordered model of hydrogen atoms in the framework of methane hydrate and related clathrates

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High-flying hopes but also dramatic risks are associated with large reserves of methane clathrate in the oceans as well as in permafrost regions, e.g. in Siberia. Hopes are connected with the enormous reservoir of energy stored in clathrates. However, any methane released will influence the global carbon cycle but also will largely contribute to global warming due to high activity of methane as greenhouse gas. Despite abundance and importance of methane clathrate, its detailed structure in the solid state is not yet well understood. Current models are based on a cubic structure containing a tetrahedral network of water molecules (Fig. 1). However, this model presents an averaged situation as due to symmetry requirements each oxygen atom is connected to four hydrogen atoms at equal distances. Accordingly each position of hydrogen atoms is only half occupied. Since the formation of clathrates is certainly the most common templated reaction, but also with respective to Si- or Ge-based compounds being considered for thermoelectric applications, a better understanding of the basic structure seems highly desirable. We have considered an old-fashioned method in order to cope with particular problems induced by a frustrated situation in the five-membered rings enclosing the cavities. Two distinct starting models are compared with focus on transferability from are local model towards an extended structure.

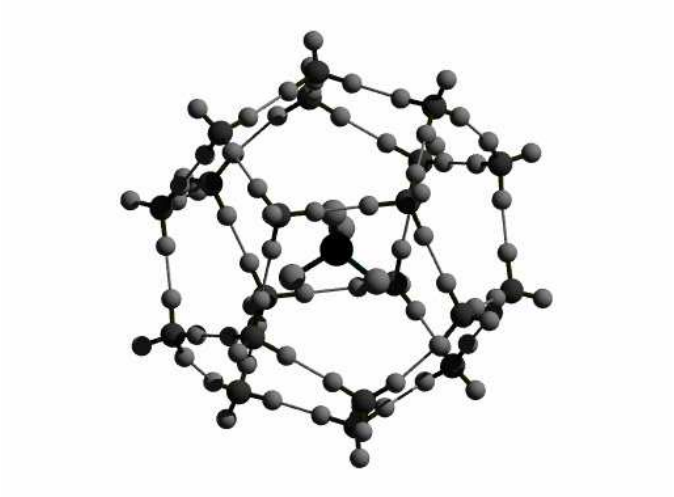

Fig. 1: Dodecahedron type cage in clathrate-I structure with enclosed methane molecule at the centre. Hydrogen atom positions in the framework are only half occupied, the disordered methane molecule is depicted in one idealized orientation.

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Evaluation of the influence of tagged protein analogue on enzymatic activity of recombinant glutathion *S*-transferase (rGST)

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Glutathion *S*-transferase (GST) is an enzyme that takes part in major red-ox reactions in living cells. Depending on the tissue, enzyme has different catalytic activities and K_m values. In molecular biotechnology, it is one of the most common protein tags used for the prokaryotic expression of proteins with high number of disulphide bridges, which are usually targeted in inclusion bodies of *E. coli*. GST helps tagged proteins to get their correct three-dimensional structures, and enables their easier purification. For the enzymatic studies we used recombinant GST (rGST) from *Schistosoma japonicum* (pGEX-4T-1 vector, Amersham Biosciences). Because enzyme assays are more convenient method for detection of expressed protein than immunoassays, the aim of the study was to analyze the influence of tagged protein analogue on enzymatic activity of rGST in different concentrations of urea. Different concentrations of urea were used for the evaluation of rGST enzymatic activity in the presence of equimolar concentration of tagged protein analogue. Although there are studies that describe the activity of rGST in different buffers and different concentration of urea, none of them considered the effect of interactions of tagged protein on the enzyme kinetic.

Research and development of blood derived Hemoglobin for animal usage

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Iron deficiency (ID) affects over one billion people, particularly children and women. If untreated, iron deficiency leads to anemia, reduced work capacity, diminished learning ability, increased susceptibility to infection, and greater risk of maternal and childhood mortality. Anemia is a lack of hemoglobin, the constituent of blood that transports oxygen trough the body. The main objective of this process is to develop a new heme-iron product attained from pig blood wasted in slaughterhouses, that should be used in prevention of anemia as a food additive. The aim of the R&D is to apply a new procedure for isolation and purification of hemoglobin performed in an original pilot device. The main activities include the standardization of new procedures for erythrocyte separation from whole blood and hemoglobin purification, development and optimization of a novel bio reactor system for hem-iron production, as well as establishment of the optimal product form, that would provide iron in a stable, highly bio available form.

The Crucial Role of London-Dispersion in Non-Covalent Metal-Metal "Bonds" with 3d metals

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The literature contains numerous examples of compounds whereby weak interactions have been suspected to play a major role in the stabilization and the cohesion of the molecular structure. In some cases this types of inter-metallic interactions have been coined "heterodox" because from the point of view of covalence there is no obvious electron sharing and density overlap that would support a strong chemical bond. Recently, several classes of compounds of this kind have been revisited using the latest quantum chemical methods that are able to account at different levels for the contribution of dispersion forces in the bonding energy. In this communication, selected classes of compounds presenting this sort of dispersion-supported interactions will be addressed [1] and the nature "heterodox" metal-metal bonds in bimetallic indenyl systems will detailed thanks to the use a new high-level electronic structure analysis procedure based on perturbation theory within a localized molecular orbital basis.[2]

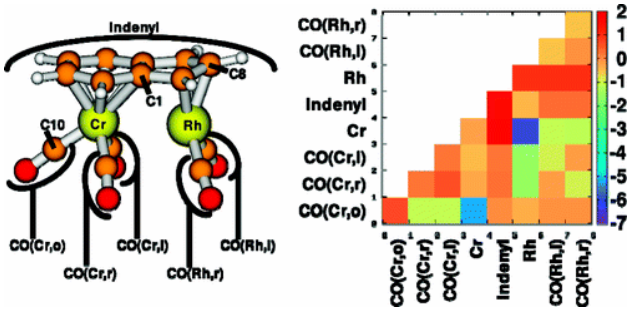

Figure 1 Change in intra- (diagonal elements) and inter-fragment (off-diagonal elements) correlation energies (kcal mol^{-1}) between *syn* and *ant-facial* isomers at the SCS-MP2 level.

In most cases it is noticed that rather strong metal-metal interactions can be found and their origin in London-dispersion effects can be uncovered and established, thus underlining the importance of intermolecular van-der-Waals interactions even for quite small organometallic systems.

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Structural and spectroscopic characterisation of the holmium double-decker partially oxidised and bi-radical phthalocyanine complexes with iodine

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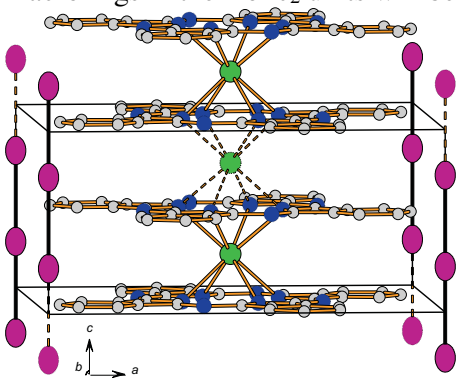
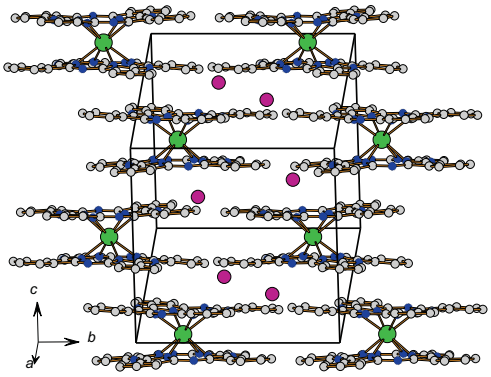
Lanthanide(III) double-decker phthalocyanines ($LnPc_2$) are well known and are still of significant interest due to their intriguing electronic features, making them especially promising as molecular magnetic materials for modern technology [1].

There are relatively few reports concerning the X-ray single crystal investigation of iodne-doped lanthanide diphtalocyaninato complexes comparing to the structural reports of iodine-doped metallophthalocyanines of the transition metals [2]. Within the lanthanide, the structural investigation of the iodine-doped diphthalocyanines have been performed only for the praseodymium $[PrPc_2]_2I_3I$ [3] and ytterbium $[YbPc_2]I_2$ [4] containing different quantity of the iodine doped atoms. Therefore we decided to synthesise the holmium, as selected lanthanide, diphthalocyaninato complexes in presence of various quantity of iodine. The structural sngle crystal investigations, magnetic and spectroscopic characterisation of two double-decker holmium diphtahlocyaninato complexes with different quantity of iodine: tetragonal $HoPc_2I_{5/3}$ and monoclinic $HoPc_2I$ containing different oxidised phthalocyaninato macrorings in the $HoPc_2$ units will be presented.



tetragonal $HoPc_2I_{5/3}$



monoclinic $HoPc_2I$

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