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The aim of this work is the study of weak intermolecular interactions in molecular crystals, by both diffraction methods and *ab initio* calculations using the new version of the *CRYSTAL* [1] program, which is designed to treat infinite periodic systems. Two molecular systems were chosen: *i) formamide* [2]: each molecule is linked to three other molecules by two types of hydrogen bonds; *ii) boric acid* [3]: each molecule forms six almost equivalent hydrogen bonds with three neighbouring molecules. The *CRYSTAL03* calculations were carried out employing the HF and DFT (B3LYP) methods with the 6-31G(d,p) basis set, also using the new geometry optimisation options. The electron density, the electrostatic potential, the binding energies and the structure factors were derived. In formamide the cooperative effects of packing on the hydrogen bond interactions leading to the formation of linear chains and on those connecting the chains were analyzed. Hydrogen bonded molecules of boric acid form layers held together by weak B--O interactions, which may play a role in dictating the inter-layer packing. The comparison of the experimental and theoretical results and the most recent results obtained using the geometry optimisation facilities in *CRYSTAL03* will be presented.

[1] Saunders V.R., et al., *CRYSTAL03*, www.crystal.unito.it [2] Stevens E.D., *Acta Cryst.*, 1978, B34, 544. [3] Gajhede M., Larsen S., Rettrup S., *Acta Cryst.*, B42, 545, 1986.

Keywords: hydrogen bond, weak interactions, *ab-initio* calculations

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Orientations of Axially Coordinated Ligands in Model Systems of Cytochromes

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Many properties of cytochromes and model systems depend on orientations of axial ligands. In this work we elucidated role of substituents of porphyrin on orientation of axial ligands in model systems of cytochromes. The orientations of axially coordinated imidazoles and pyridines in crystal structures of model systems of cytochromes were analyzed and data were compared with previous quantum-chemical calculations.

The results show that eight ethyl groups on porphyrin ring strongly favor parallel orientation, hence, in all these complexes axial ligands, pyridines or imidazoles, are mutually parallel. Four phenyl or mesityl groups at *meso*-carbons also favor parallel orientation but less strong. Hence, in most of the bis-imidazole complexes orientation is parallel, while in bis-pyridine complexes orientation of pyridines depends on oxidation state of Fe.

In Fe(II) complexes orientation is parallel, in Fe(III) it is orthogonal. In Fe(III) complexes influence of the interaction of pyridine with porphyrin ring, dominates over influence of phenyl or mesityl groups on porphyrin ring, and the orientation is parallel. Namely, by previous quantum chemical calculations it was shown that in bis-pyridine Fe(III) porphyrinato complexes without substituents orthogonal orientation is favored by 16 kcal/mol.

Keywords: ligands, porphyrins, cytochromes

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CH/ π Interactions between Chelate and Phenyl Rings in Acetylacetonato Complexes

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By coordinating to metal atom with acetylacetonato ligand makes planar chelate ring, with delocalized bonds. Hence, coordinated acetylacetonato ligand could be involved in CH/ π interactions with

phenyl ring in two ways, as hydrogen atom donor, or as hydrogen atom acceptor. In first case hydrogen atoms of acetylacetonato ligand could make MLAC π interactions with phenyl ring. Acetylacetonato ligand has negative charge, but by coordinating to metal cation partial positive charge is transferred from the metal cation to the ligand. If enough positive charge is transferred hydrogen atoms of acetylacetonato ligand will get enough positive charge to be involved in MLAC π interactions. In second type of interactions phenyl ring and chelate ring change roles; phenyl ring is hydrogen atom donor whereas chelate ring with delocalised π -system is hydrogen atom acceptor.

Here we report on CH/ π interactions between acetylacetonato chelate rings and phenyl rings in acetylacetonato complexes. The results were obtained by searching and analyzing crystal structures in Cambridge Structural Database (CSD) and by quantum chemical calculations. Dependence of CH/ π interactions on delocalization in chelate rings that is connected with type of metal in the ring was studied. To the best of our knowledge this is the first time that influence of metal in a chelate ring on CH/ π interactions in metal complexes was studied.

Keywords: CH/ π interactions, DFT, chelates

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Structural Characterisation of *p*-semiquinone Radical in a Crystal: X-ray Structure and EPR Evidence

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In membrane-located proteins, quinone system plays a significant role in electron-transfer reactions. The described work illustrates that semiquinone radical is stabilized in the solid state.

Thin dark-red plate-like crystals of *p*-semiquinone radical were grown by evaporation of mildly alkaline, saturated water solution of hydroquinone. Although stable in air, larger single crystals decay after ca. 20 h exposure to X-rays or UV radiation producing amorphous yellow substance identified as a mixture of quinone and quinhydrone.

Solid-state electronic paramagnetic resonance spectra of crystalline *p*-semiquinone detected its paramagnetic properties revealing four symmetrically equivalent protons.

Crystal structure was determined at 100 and 150 K (monoclinic, space group P 21/c, a = 3.78 Å, b = 5.98 Å, c = 10.79 Å, β = 90.66°). In both of them, *p*-semiquinone molecule is centrosymmetric (four protons are, therefore, equivalent), with C-O bond length of 1.295 Å, corresponding to bond order of 1.5. Molecules are hydrogen bonded into infinite chains (O-H...O distance of 2.70 Å with the proton disordered between two oxygen atoms. This packing is very similar to that of quinhydrone; the unit cell can be transformed into a half of the unit cell of quinhydrone.

Keywords: radical, *p*-semiquinone, EPR

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Crystal Structure and Synthesis of New Trinuclear 3d-metal Trifluoroacetates

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Anhydrous acid trinuclear trifluoroacetates of divalent metals [M₃(CF₃COO)₆(CF₃COOH)₆][CF₃COOH] where M = Ni (I) and Co (II), and partially hydrated nickel trifluoroacetate [Ni₃(CF₃COO)₄(CF₃COOH)₄(H₂O)₄](CF₃COOH)₂ (III) were synthesized and studied by X-ray diffraction. Compounds I and II were obtained by crystallization from solutions of Ni(CF₃COO)₂·4H₂O (I), Co(CF₃COO)₂·4H₂O (II) in trifluoroacetic anhydride in the presence of phosphoric anhydride as the drying agent. Compound I crystallizes in trigonal system, space group R $\bar{3}$, Z=27, a = 13.307(2), c = 53.13(1) Å, V = 8148(2) Å³, R₁ = 0.1112. The structure is molecular; trinuclear linear unit is formed by three metal

atoms linked by trifluoroacetic bridges. Side atoms are connected with three trifluoroacetic acid molecules. Compound II crystallizes in triclinic system, space group $P\bar{1}$, $Z=2$, $a = 13.199(6)$, $b = 14.649(6)$, $c = 15.818(6)$ Å, $\alpha = 90.04(4)$, $\beta = 114.32(4)$, $\gamma = 108.55(4)^\circ$, $V = 2611.3(19)$ Å³, $R_1 = 0.0480$. Its structure resembles I, but it's more distorted. Compound III was obtained by crystallization from solution of $Ni(CF_3COO)_2 \cdot 4H_2O$ in trifluoroacetic acid (99%) in the presence of phosphoric anhydride as the drying agent. According to X-ray diffraction the data it crystallizes in triclinic system space group $P\bar{1}$, $Z=1$, $a=9.121(18)$, $b=10.379(2)$, $c=12.109(2)$ Å, $\alpha=84.59(3)$, $\beta=72.20(3)$, $\gamma=82.80(3)^\circ$, $V=1080.9(4)$ Å³, $R=0.0334$. Unlike the previous compounds, here the metal atoms are linked by two trifluoroacetic groups and one water molecule.

Keywords: nickel trifluoroacetate, cobalt trifluoroacetate, crystal structure

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Structural and Electronic Properties of Carbenes as Ligands

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In developing the basis for a ligand knowledge base (LKB), we have studied a test group of ligands, carbenes, in order to gauge their electronic, structural and steric properties when complexed to a metal centre. Data is collected from mining structural databases, from structural studies of new complexes determined and from computational studies, and then organised using informatics methods.

Forty different carbenes, chosen to span a range of electronic and steric properties, were optimised using density functional theory (DFT) at the BP86/6-31G* level of theory, both as the free carbene and as a ligand attached to a number of metal fragments. Various geometric, electronic and steric parameters were calculated for each of the carbenes and their complexes.

These data were analysed using principal component analysis (PCA) and the data scrutinised in order to remove highly correlated parameters and parameters for which there was insignificant variation. About 75% of the variance in the data could be represented by 5 principal components. Rated by their factor scores against a particular principal component, carbenes of a similar nature cluster together in ligand space (LS). Apparently unrelated carbenes which mimic one another may be identified by their similar positions in LS.

Carbenes may be characterised by objective LS parameters. This approach may offer opportunities to design new catalysts with specific and desirable properties.

Keywords: DFT, carbene, informatics

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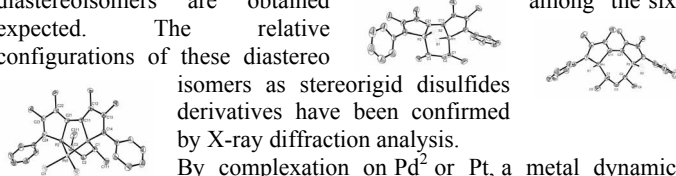
Chirality Control in 2,2'-biphosphole Ligands Leading to Enantio-pure Complexes

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The use of stereochemically dynamic 2,2'-biphosphole (BIPHOS), after spontaneous resolution by crystallization and complexation on Pd center, proved to be as effective as well known chirally rigid diphosphines in asymmetric allylic substitution¹. In order to generalize the use of 2,2'-biphosphole type ligands in asymmetric catalysis, the control of chirality could be achieved in two steps: selective formation of diastereoisomers by using a chiral controller and enantiomer-selective coordination to a metal center. The partial chirality control of the 2,2'-biphosphole framework as only 3 diastereoisomers are obtained among the six expected.

The relative configurations of these diastereoisomers as stereorigid disulfides derivatives have been confirmed by X-ray diffraction analysis.

By complexation on Pd²⁺ or Pt, a metal dynamic



resolution occurs leading to enantio and diastereomerically pure 2,2'-biphosphole complexes as confirmed by X-ray diffractions studies. Applications of these complexes in asymmetric catalysis are currently underway.

[1] Tissot O., Gouygou M., Dallemer F., Daran J.-C., Balavoine G.G.A., *Angew. Chem. Int. Ed.*, 2001, **40**, 1076-1078. [2] Ortega C., Gouygou M., Daran J.-C., *Chem Comm.*, 2003, 1154-1155.

Keywords: chirally flexible ligand, metal dynamic resolution, diphosphines

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Molecular Mechanism of ADP-ribose Pyrophosphatase from *Thermus thermophilus* HB8

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The nudix pyrophosphatases share a highly conserved amino acid sequence, called the "nudix motif". Recent genome analyses have revealed a wide distribution of nudix proteins from phage to human, although as yet their function has not been fully established. To elucidate a detailed molecular function we have analyzed nudix proteins from *Thermus thermophilus* HB8. Here, we report the structural and mutational study of ADP-ribose pyrophosphatase (*Tt*ADPRase), a major group within the nudix protein family.

We have determined the crystal structure of *Tt*ADPRase with its ligands [1]. To further investigate the substrate recognition and catalytic mechanism in detail, we performed a mutational analysis based on the structural data. From kinetic studies, we identified several residues involved in recognition of ADP-ribose. In addition, the results strongly suggested that *Tt*ADPRase employs a *two-metal ion mechanism*, in which a water molecular is coordinated by two cations and activated to be a nucleophile. This catalytic mechanism differs from that of other nudix proteins, including 8-oxo-dGTPase (*MutT*). These results also reveal the diversity in molecular function of nudix proteins both in terms of substrate recognition and catalysis.

[1] Yoshiba S., *et al.*, *J. Biol. Chem.*, 2004, **279**, 37163-37174.

Keywords: hydrolase, mutational analysis, nucleotide metabolism

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Synthesis and Thermal Behaviour of New Lanthanide Oxalato-squarates

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During the course of our synthetic efforts on metal carboxylates with open architectures employing mixed dicarboxylates to obtain potential properties as porosity, cation-exchange as well as non-linear optical characteristics [1], a series of hydrated lanthanide compounds was produced by hydrothermal reactions. Results of the first X-ray single crystal structure analysis indicate the formation of a new low water content lanthanum oxalato-squarate, $La_2(C_2O_4)_2(C_4O_4) \cdot 2H_2O$, whose structure features a novel dense 3D network. It crystallizes with orthorhombic symmetry, $a = 7.7326(1)$, $b = 18.2553(2)$ and $c = 18.3299(2)$ Å, S.G. *Cmca* and $Z = 8$. The structure is built from edge-sharing LaO_9 tricapped trigonal prisms resulting in chains running along [100]. The rôles of the $C_2O_4^{2-}$ anions is to enforce the connection within a chain acting as bridging monodentate groups and to link the chains together according to a bidentate mode. A tunnel framework along [100] results, showing strongly bonded water molecules inside the smallest pores while planar tetra-monodentate squarate groups fill the widest voids bridging four LaO_9 polyhedra.

Additionally, in order to determine if the new materials exhibit any particular thermal behaviour, the decomposition mechanisms into nanocrystalline Ln_2O_3 oxides, through the loss of water molecules and the departure of gases such as CO, CO₂, were investigated by using