

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,  $\alpha = 90.04(4)$ ,  $\beta = 114.32(4)$ ,  $\gamma = 108.55(4)^\circ$ ,  $V = 2611.3(19)$  Å<sup>3</sup>,  $R_1 = 0.0480$ . 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,  $\alpha=84.59(3)$ ,  $\beta=72.20(3)$ ,  $\gamma=82.80(3)^\circ$ ,  $V=1080.9(4)$  Å<sup>3</sup>,  $R=0.0334$ . 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

#### P.08.09.3

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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

#### P.08.09.4

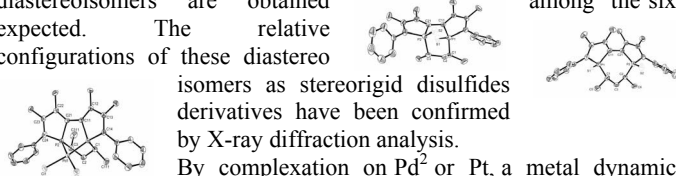
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#### Chirality Control in 2,2'-biphosphole Ligands Leading to Enantio-pure Complexes

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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 substitution<sup>1</sup>. 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 Pd<sup>2+</sup> 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

#### P.08.09.5

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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 molecule 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

#### P.08.09.6

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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, CO<sub>2</sub>, were investigated by using