

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 $\text{Ni}(\text{CF}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ 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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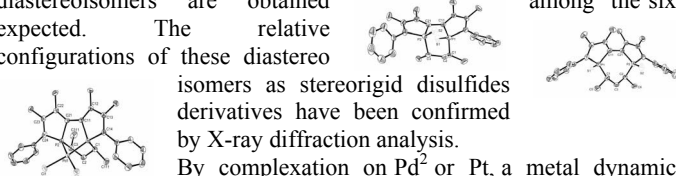
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Chirality Control in 2,2'-biphosphole Ligands Leading to Enantio-pure Complexes

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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 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

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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, $\text{La}_2(\text{C}_2\text{O}_4)_2(\text{C}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$, 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 $\text{C}_2\text{O}_4^{2-}$ 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_2 , were investigated by using

complementary methods, TDXD and simultaneous TG-MS coupling techniques.

[1] Vaidhyanathan R., Natarajan S., Rao C.N.R., *J. Solid State Chem.*, 2004, **177**, 1444.

Keywords: hydrothermal, mixed carboxylates, thermal analysis

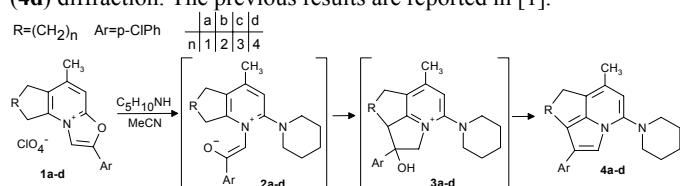
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Diffraction Study of Recyclization of Oxazolopyridinium Salts to Indolizines

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In the course of our systematic study of structure/reactivity relationships for heterocycles, the reaction of recyclization of oxazolo[3,2-*a*]pyridinium salts with annelated cycloalkane fragments of different size revealed some unexpected peculiarities. All obtained compounds were studied by single crystal (**1a-d**, **3c**, **4b,c**) or powder (**4d**) diffraction. The previous results are reported in [1].



As discovered earlier, compounds **1b,d** easily gave corresponding indolizines **4b,d**. In the case of compound **1c** the reaction suddenly stopped at the non-predicted intermediate **3c** (with ClO_4^- anion). It can be explained by the less distortion of 7-membered ring connected to a non-planar bicycle than in **4c**. Dehydration of **3c** led to **4c**. Compound **1a** was also attacked by piperidine, but only resin was formed. In this case, the unstable intermediate **2a** is unable to react further because compounds **3a** and **4a** have high angle distortions as the AM1 molecular model shows.

[1] *Acta Cryst.*, 2004, **E60**, o1096-o1097, o1301-o1302, o2313-o2314.

Keywords: structure/reactivity relationship, organic chemistry, powder diffraction

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Structure and Properties of Safe and Powerful Noble-Metals Oxidation Reagents

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Molecular CT-complexes obtained by reacting acceptors such as diiodine with S-donor molecules, have been extensively studied mainly due to their intrinsic structural, spectroscopic, chemical and physical properties and, recently, to their applicability as conducting materials or as oxidation reagents towards transition metals. With the view to synthesize complexing-oxidizing agents capable to dissolve noble-metals (NMs) in mild conditions, we have chosen exa- and epta-atomic cyclic dithioamides as bidentate S,S-donors. By reacting the N,N' -dialkyl-perhydrodiazepine-2,3-dithione ($R_2\text{dazdt}$, $R=\text{Me}$ (**a**), Et (**b**)) class of ligands with I_2 the expected 1:2 CT-complexes, $R_2\text{dazdt}\cdot 2\text{I}_2$ (**1**), have been obtained as proved by structural and spectroscopic characterization.^[1] Instead, by using the N,N' -dialkyl-piperazine-2,3-dithione ($R_2\text{pipdt}$, $R=\text{Me}$, Et , Pr^i (**c**)) class, which shows an exa-atomic ring in spite of the hepta-atomic one in $R_2\text{dazdt}$, the unexpected triiodide salt of the protonated donors, $[R_2\text{pipdtH}]\text{I}_3$ (**2**), have been isolated. The different nature and structure of the two class of reagents is reflected on a different reactivity towards NMs: while class **1** adducts are capable to oxidize Pd and Au metal but are inactive towards Pt, class **2** reagents are capable to dissolve Pt metal too. Further studies are in progress in order to clarify the different

behaviour of the two class of ligands and the source of H^+ in the reaction.

[1] Serpe A., et al., *Chem. Commun.*, 2005, 1040, and refs therein.

Keywords: charge-transfer complexes, halogens, noble-metals

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Nickel(II) Carbosilane Dendrimers: Structure and Polymerization Catalysis

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Nickel(II) compounds containing sterically demanding α -diimine ligands, and related chelates, have been found to be attractive catalysts for the production of polyolefins.^[1] Dendrimers can be used as well-defined supports for active centers in homogeneous phase, which catalytic applications are being widely studied,^[2] including those in polymerization processes.^[3] In this work, a series of carbosilane dendritic compounds $G_n\text{-ONNMe}_m\text{NiBr}_2$ ($n = 0, 1, 2, 3$; $m = 0, 2, 3$), from monometallic to metallo-dendritic structures containing up to sixteen ($n = 3$) terminal pyridylimine nickel complexes, have been synthesized, and the crystal structure of some model compounds have been determined. The nickel complexes, in combination with methylaluminoxane (MAO), convert ethylene into mixtures of toluene-insoluble polyethylene and oily oligomers. The variation of the pyridylimine ligand framework by m methyl substituents has a decisive influence on the activities of the nickel compounds. Also, the generation of the dendritic precursor (n) acutely affects the catalyst performance and the microstructure of the insertion products as well. Thus, higher generation catalysts show superior oligomerization activities and produce less branched polyethylene.

[1] Ittel S.D., Johnson L.K., Brookhart M., *Chem. Rev.*, 2000, **100**, 1169. [2] Astruc D., Chardac F., *Chem. Rev.*, 2001, 101, 2991. [3] Müller C., Ackerman L.J., Reek J.N.H., Kamer P.C.J., van Leeuwen P.W.N.M., *J. Am. Chem. Soc.*, 2004, **126**, 14960.

Keywords: nickel, dendrimers, polymerization

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Solid-state Formation of a Coordination Polymer Starting from a Monomeric Thiodiacetate Manganese Complex

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Compounds $[\text{Mn}(\text{tda})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Mn}(\text{tda})(\text{H}_2\text{O})]_n$ (**2**) (tda = thiodiacetate, $\text{S}(\text{CH}_2\text{COO})_2^{2-}$) were obtained by the reaction of aqueous solutions of manganese dichloride and a 1:1 mixture of Na_2CO_3 and thiodiacetic acid with the appropriate work-up. The X-ray study of **1** shows that the complex is a monomer containing the typical tridentate thiodiacetate ligand with a facial configuration. For compound **2**, as previously reported by us [1], we propose a structure similar to that published for the homologous cadmium derivative [2], namely a 2D-polymer with $\{\text{Mn}(\text{tda})(\text{H}_2\text{O})\}$ subunits bridged by the carboxylate groups of tda.

In this communication we will report the unprecedented solid-state polymerization of compound $[\text{Mn}(\text{tda})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (**1**) to afford $[\text{Mn}(\text{tda})(\text{H}_2\text{O})]_n$ (**2**). The formation of a coordination polymer from the corresponding monomer occurred in the solid state and the process can be monitored straightforwardly by IR spectroscopy.

Additionally, we will describe some preliminary results concerning the use of these derivatives and the related oxydiacetate compounds as catalyst precursors in the oxidation reaction of alcohols to aldehydes with dioxygen, a "clean reagent".

[1] Grirrane A., Pastor A., Galindo A., Ienco A., Mealli C., *Chem. Commun.*, 2003, 512. [2] Whitlow S.H., *Acta Cryst.*, 1975, **B31**, 2531.

Keywords: thiodiacetate, crystal structures, oxydiacetate