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Structural Aspects of Pyridyl-pyrazole Dinuclear Rh and Ir Complexes

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The design of new synthetic strategies and the study of structure/activity relationships in dinuclear and polynuclear complexes is the key stone towards the understanding of most of their interesting properties in the field of homogeneous catalysis. A particular well-studied bridging ligand is the pyrazole unity, which has been shown to confer high stability to dinuclear frameworks, while simultaneously allowing a wide range of intermetallic separations.

We are currently investigating the new possibilities, in terms of different structures and properties of complexes, the additional presence of a classical pyridine substituent could bring to this peculiar type of dinucleating ligands [1].

In our poster we will describe the preparation and discuss the structural analysis of a family of dinuclear homo and heterodinuclear complexes containing Rh and Ir as central metals and pyridyl-pyrazole as bridging moiety. Complexes included will be of the types $[M_2(\mu\text{-}PyPz)_2(CO)_2]$, $[M_2(\mu\text{-}PyPz)Cl(COD)_2]$ or $[M(COD)(\mu\text{-}PyPz)M'(PPh_3)]$. The role of metal-metal weak interactions will be considered for the understanding of a particular situation where two different packing structures were observed for two identical molecular structures $[M(CO)_2(\mu\text{-}PyPz)MCl(CO)_2]$ (M = Rh, Ir).

[1] Martínez A.P., et al., *Inorg. Chim. Acta*, 2005, **358**, 1635.

Keywords: structure of organometallic complexes, metal-metal interactions, intermolecular packing

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Spin State and Stereochemistry in Tetracoordinate Complexes of d^n Transition Metals

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We will present a theoretical study of the structural preferences of tetracoordinate transition metal compounds with d^n electronic configuration. The structural choice of tetracoordinate transition metal compounds has been established recently from the available experimental structural data with the help of the Continuous Shape Measures (CShM)[1] metodology. In that work, different structural preferences were found for the tetracoordinate transition metal compounds as a function of the electron configuration of the metal[3].

Using the Density Functional Theory with the B3LYP hybrid functional we have calculated the potential energy surfaces for simple $[M(CH_3)_4]$ models in different spin states of all the d^n electron configurations. By using the CShM methodology we analyze the distribution of more than 12000 structures along the minimal distortion pathway[2] for the tetrahedron to square interconversion, and find that it mirrors the calculated potential energy curves for each d^n family of complexes.

[1] Zabrdosky H., Peleg S., Avnir D., *J. Am. Chem. Soc.*, 1992, **114**, 7843. [2] Cirera J., Alemany P., Alvarez S., *Chem.-Eur. J.*, 2004, **10**, 190. [3] Casanova D., Cirera J., Llunell M., Alemany P., Avnir D., Alvarez S., *J. Am. Chem. Soc.*, 2004, **126**,1755.

Keywords: continuous shape measures, spin state, transition metal complexes

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Structure Determination of Twinned and Disordered Cyclopentadienyl Complexes

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Cp_3 lanthanides (Cp = cyclopentadienyl) represent one of the best investigated agents in modern organolanthanide chemistry [1]. However, only eight of the 14 possible solvent free lanthanide Cp_3 complexes have been yet characterized successfully by X-ray diffraction methods [2]. Many problems in the synthesis of suitable crystals and refinement of the crystal data have been reported [3].

We observed the intrinsic twinning and/or disorder in the crystal structure of the Cp complexes of cerium and holmium. Single-crystal X-ray and powder diffraction measurements at different temperatures have been elaborated in order to explain this phenomenon from a crystallographic and chemical point of view.

$HoCp_3$ and $CeCp_3$ crystallize in different crystal shapes, depending on the temperature at which they were crystallized. Pseudomerohedral and reticular pseudomerohedrical twinning as well as disorder were detected in monoclinic primitive crystal systems. The sharing of one C atom between the molecular units of the complex produces polymeric zigzag chains along the cell axis.

[1] Schumann H., Meese-Marktscheffel J.A., Esser L., *Chem. Rev.*, 1995, **95**, 865. [2] Rebizant J., Apostolidis C., *Acta Cryst.*, 1988, **C44**, 614. [3] Eggers S.H., Hinrichs W., Kopf J., Jahn W., Fischer R.D., *J. Organomet. Chem.*, 1986, **311**, 313.

Keywords: organometallic crystal structures, lanthanides, crystal disorder

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X-ray Studies of some Tetradentate Schiff Base Oxovanadium(IV) Complexes

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Vanadium chemistry has attracted attention due to its interesting structural features and biological relevance. In recent years, various vanadium complexes of dianionic tetradentate Schiff bases have been proposed for potential use as insulin mimetic agents. These ligands are of particular interest because they provide coordination environments which efficiently stabilize different oxidation states of vanadium, while still providing active sites capable of binding other molecules [1]. These compounds also show a great catalytic reactivity towards organic substrates, in particular the oxidation of organic substrates such as alkenes and sulfides. When chiral Schiff bases are used as ligands, vanadyl complexes can effectively catalyze asymmetric oxidation of sulfides, disulfides and dithioacetals [2].The free ligand and the corresponding vanadyl complexes with Schiff bases derived from trans-Salcn were characterized by elemental analysis (C,H,N) and X-ray diffraction. A monocrystal of each compound was sent to the Enraf Nonius CAD4 diffractometer and submitted to its routine analysis using the WINGX [3] program. The structure resolutions were obtained with Patterson and the several refinements were obtained by SHELXL program.

[1] Thompson K.H., Orving C., *Coordination Chemistry Reviews*, 2001, **219-221**, 1033. [2] Lyang S., Derveer D.V., Qian S.Y., Sturgeon B., Bu X. R., *Polyhedron*, 2002, **21**, 2021. [3] Farrugia L.J., *J. Apply Crystallogr.*, 1999, **30**, 565.

Keywords: Schiff bases, coordination compounds, vanadyl

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Metal Complexes of Fullerene Fragments

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Nowadays metal complexes of fullerenes constitute the largest class of fullerene derivatives. In contrast, study of open geodesic polyarenes that map onto the fullerene surfaces and therefore referred to as ‘fullerene fragments’ is a new area of research. To form metallated products of fullerene fragments, we use gas phase deposition reactions with volatile transition metal complexes. In contrast to traditional solution studies, this technique readily affords metal complexes in crystalline form to allow their X-ray structural characterization. Using co-deposition, we have successfully prepared the first metal complexes of corannulene [1], dibenzo[*a*,*g*]corannulene [2], and hemifullerene [3]. X-ray structural analysis revealed an η^2-rim coordination of the above fullerene fragments in their Rh(II) and Ru(I) complexes. Importantly, multiple metal coordination to a ligand was readily achieved under gas phase conditions to force rare polydentate bridging modes of fullerene fragments. This has resulted in unique complexes ranging from discreet to extended 1D, 2D, and 3D networks. The type of supramolecular architecture is dictated by the geometry and curvature of the fullerene fragment.

[1] Petrukhina M. A., Andreini K.W., Mack J., Scott L.T., *Angew. Chem. Int Ed.*, 2003, **42**, 3375. [2] Petrukhina M.A., Andreini K.W., Tsefrilas V.M., Scott L.T., *Organometallics*, 2005, *in press*. [3] Petrukhina M.A., Andreini K.W., Peng L., Scott L.T., *Angew. Chem. Int. Ed.*, 2004, **43**, 5477.

Keywords: fullerene fragment, structure, metal coordination

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Structures of Three 36-azametallacrown-12 Complexes

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Metallacrowns are a new class of metallamacrocycles, which have gained increasing attention over the past decades[1-2]. A novel pentadentate *N*-substituted-salicylhydrazide ligand, pentadentate *N*-substituted-picoloylhydrazide ligand and three 36-azametallacrown-12 complexes have been synthesized. A dodenuclear ring of twelve metal atoms linked by twelve N-N groups is an important structural characterization for the one Mn metallacrown and two Ni metallacrowns. Twelve metal ions and twelve ligands construct a 36-membered ring based on the M-N-N-M linkage. The flexibility around the N-N single bond and the conformational adaptability of the pentadentate ligand allow for the formation of the title dodecanuclear complexes and for the propeller configuration of the metal ions. There are some solvent molecules in the 'host' cavity of three azametallacrowns. There are many kinds of intramolecular and intermolecular hydrogen bonds in the title compound.

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Keywords: supramolecular chemistry, transition metals, complexes

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A Lower Rim Tert-butyl Calix[4]arene Derivative that Binds Ag(I)

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The X-ray structures of a *tert*-butyl calix[4]arene derivative with –O–H and –O–$(CH_2)_2$–NH–(P=S)$(OCH_2CH_3)_2$ pendant arms (**EPS**) as molecular complexes with methanol, **EPS**(MeOH), **1**, with dichloromethane, **EPS**(Cl_2CH_2), **2**, and its complex with silver(I) and acetonitrile, Ag**EPS**(MeCN)K.$(ClO_4)_2$.H_2O, **3**, were determined. The structures were solved from 17027 (**1**), 8810 (**2**) and 7729 (**3**) reflections with I>2σ(I) collected at T=100 K, and refined to R1-factors of 0.054 (**1**), 0.049 (**2**) and 0.090 (**3**). In all compounds, a pair of strong O–H…O(pend) bonds in the lower rim produces relatively open chalices. This, in turn, promotes the hydrophobic interaction with the solvent molecules found included in these cavities. The upper half of the **EPS** pendant arms is anchored by N-H…O(ox) intra-molecular bonds where now the phenol oxydryl oxygen atoms act as H-bond acceptors. Despite the relative rigidity of the upper half of the hydrophilic cavity, the lower half is pre-organized towards soft metal ion complexation at the thiophosphorous sulphur binding site by unhindered torsion movements, mainly around the N-P σ-bond. The silver(I) complex with **EPS**, exhibits an approximate C_2 symmetry around the calix axis. The Ag(I) ion is sited on this axis, linearly coordinated to the sulphur atoms of the pendant arms [Ag-S distances of 2.414(2) and 2.422(2) Å, ∠(S-Ag-S)=171.99(8)°]. We thank FAPESP (Brazil) and EU (Contract ICA CT 2000-30006) for support.

Keywords: calixarene complexes, environmental chemistry, supramacromolecules

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Two Isomeric Calix(4)arene Complexes with Mercury(II)

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The X-ray structures of two isomeric complexes of partially derivatized 5,11,17,23-tetra-tert-butyl[25,27-bis(hydroxy)-26,28-bis(ethylthio ethoxy)]-calix[4]arene (L) with mercury(II) were determined at 120K. The one obtained by slow evaporation from ethanol solvent, $LHg(ClO_4)_2$, crystallizes in the space group Pbca with a=15.568(1), b=18.696(1), c=40.322(1) Å, and Z=8. The other one, obtained from an acetonitrile solution, $LHg(ClO_4)_2$.2MeCN, crystallizes in the space group Pccn with a=21.794(1), b=45.754(1), c=12.395(1) Å, and Z=8. The structures were solved from 6870 [$LHg(ClO_4)_2$] and 7660 [$LHg(ClO_4)_2$.2MeCN] reflections with I>2σ(I) and refined to R1-values of 0.053 and 0.073, respectively. The calix[4]arene ligand in both complexes shows hydrophobic cavities with a quite similar squashed cone conformation. In contrast, the hydrophilic cavities exhibit substantial differences in the conformation adopted by the opposite sulfur-containing pendant arms: in $LHg(ClO_4)_2$ they are roughly related by a pseudo two-fold axis, while in $LHg(ClO_4)_2$.2MeCN these pendant arms are approximately related through a local mirror plane. Despite these lower rim conformational differences, the Hg(II) ion in both complexes is in a similar environment, *trans* coordinated to the sulfur atoms of the opposite pendant arms, conforming a nearly linear S-Hg-S bond. We thank FAPESP (Brazil) and EU (Contract ICA CT 2000-30006) for support.

Keywords: calixarene complexes, environmental chemistry, supramolecules

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2D Supramolecular Sheet Generated by π Interactions for Cadmium(II) Compounds

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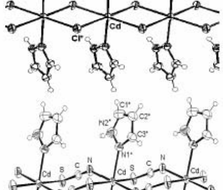
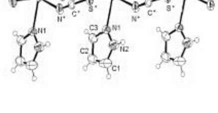
The X-ray structure determinations showed that the coordination polymers $[Cd(\mu\text{-}Cl)_2(HPz)_2]_n$ (**1**) and $[Cd(\mu\text{-}1,3\text{-}SCN)_2(HPz)_2]_n$ (**2**) (HPz = pyrazole) exhibited chain structures made by linear arrays of Cd(II) bridged by chlorine (**1**) (see Fig. 1) or 1,3-SCN (**2**) (see Fig. 2) ions with the pyrazole ligands at the apical sites.

The crystal packing structure of **1** consists of two-dimensional infinite chains along the **b** axis. Hydrogen bonding is the responsible for the self-assembly of linear chains of **1**, yielding a 2D network Intramolecular hydrogen bonds also occur between N- H and Cl.



(1)



(2)