

**P.07.01.41***Acta Cryst.* (2005). A61, C304**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  $[M_2(\mu\text{-PyPz})_2(\text{CO})_2]$ ,  $[M_2(\mu\text{-PyPz})\text{Cl}(\text{COD})_2]$  or  $[M(\text{COD})(\mu\text{-PyPz})M'(\text{PPh}_3)]$ . 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  $[M(\text{CO})_2(\mu\text{-PyPz})\text{MCl}(\text{CO})_2]$  ( $M = \text{Rh}, \text{Ir}$ ).

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

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

**P.07.01.42***Acta Cryst.* (2005). A61, C304**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] methodology. 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  $[M(\text{CH}_3)_4]$  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] Zabrdošky 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

**P.07.01.43***Acta Cryst.* (2005). A61, C304**Structure Determination of Twinned and Disordered Cyclopentadienyl Complexes**

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$\text{Cp}_3$  lanthanides ( $\text{Cp} = \text{cyclopentadienyl}$ ) represent one of the best investigated agents in modern organolanthanide chemistry [1]. However, only eight of the 14 possible solvent free lanthanide  $\text{Cp}_3$  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  $\text{Cp}$  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.

$\text{HoCp}_3$  and  $\text{CeCp}_3$  crystallize in different crystal shapes, depending on the temperature at which they were crystallized. Pseudomerohedral and reticular pseudomerohedral 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

**P.07.02.1***Acta Cryst.* (2005). A61, C304**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-Salen 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

**P.07.03.1***Acta Cryst.* (2005). A61, C304-C305**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