

P.07.01.37*Acta Cryst.* (2005). A61, C303**Unit Cellmates: the *Cis* and *Trans* Isomers of an Iron(II) Complex Co-crystallize**

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The crystal structure of dichloro-bis(2-picolyamine)-iron(II) contains a 1:1 ratio of the *cis* and *trans* isomers. The former lies on a two-fold axis whereas the latter lies on an inversion centre. The equatorial chlorine and NH₂ ligands of the two isomers lie in the same crystal planes exhibiting an intricate 2D hydrogen bond network with four eight-membered rings around each iron constructing a tiling pattern throughout the layer. These hydrogen bonded layers are interconnected through extended π - π interaction between the axial pyridine ligands.

The number of crystal structures with co-crystallized isomers found in the CSD is very limited. In fact only one analogous, ordered example with *similar* ligand atoms (MN₄Cl₂) seems to exist [1].

The rare occurrence of this phenomenon may be understood intuitively from the facts that firstly, both isomers, which are expected to have different energies and most probably also different synthesis conditions, must happen to be present during crystallization, and that secondly, the formation of the co-crystal must be more favourable in thermodynamic and/or kinetic terms than the formation of crystals containing the individual isomers only.

[1] Zhu D., Xu Y., Yu Z., Guo Z., Sang H., Liu T., You X, *Chem. Mater.*, 2002, **14**, 838.

Keywords: iron(II) complex, isomers, co-crystallization

P.07.01.38*Acta Cryst.* (2005). A61, C303**Influence of the R Group in [Mo₂(μ -R)(μ -PCy₂)(CO)₂Cp₂], R=H, CH₃, Ph, Bz**

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The experimental geometry obtained from single-crystal X-ray diffraction for the dimolybdenum complexes [Mo₂(μ -R)(μ -PCy₂)(CO)₂Cp₂] (R=H, CH₃, Ph, Bz) are compared with the results of DFT calculations with the B3LYP, B3PW91 density functionals and the Lan12dz basis set [1]. The crystal structure of the methyl derivative presents a symmetric bridging group whereas the calculations are in accordance with an asymmetric Mo-CH₃-Mo moiety that exhibits an agostic interaction on one of the two molybdenum centers. The agostic interaction is clearly evident in the crystal structure of the benzyl derivative, in agreement with the geometry obtained from the calculations. The geometry of the phenyl derivative was obtained by optimisation of a partial solution from a poor data set of X-ray data where the connectivity of all the non-hydrogen atoms was unambiguously determined. The phenyl ring is symmetrically bound, and it presents a π interaction with the two molybdenum atoms. The nature and the strength of the agostic and π interactions were analyzed by means of the AIM (atoms in molecules) [2] and the NBO (natural bond orbitals) [3] theories.

[1] Gaussian Inc., Pittsburgh PA, 2001, *Gaussian 01*. [2] Bader R.F.W., *Atoms in Molecules*, Oxford University Press, Oxford, 1990. [3] Reed A. E., Curtiss L.A., Weinhold F., *Chem. Rev.*, 1988, **88**, 899.

Keywords: molybdenum, crystal structure, ab-initio calculations

P.07.01.39*Acta Cryst.* (2005). A61, C303**Synthesis and X-ray Study of the P₅-polyphosphorus Rhodium Complex [(dppm){Ph₂PCH₂P(Ph₂)PPP}Rh]OTf**

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The development of selective procedures for the preparation of organophosphorus compounds directly from P₄ is an important goal in modern phosphorus chemistry. In this respect, particular attention has been devoted to the rationalization of the reactivity patterns ruling the formation of organometallic complexes bearing in their coordination sphere oligophosphorus moieties. The cobalt derivative [Co{Ph₂PCH₂P(Ph₂)PPP(Ph₂)PCH₂PPh₂}]BF₄ (**1**) was reported a few years ago from the thermal reaction of P₄, dppm and [Co(H₂O)₆](BF₄)₂ in boiling *n*-BuOH.^[1,2] The mechanism of this intriguing reaction has not yet been fully understood even if a double nucleophilic attack of the activated P₄ molecule to two PPh₂ ends from two distinct dppm ligands, has been proposed to account for the formation of **1**.

Herein we present an X-ray study of the related rhodium complex [(dppm){Ph₂PCH₂P(Ph₂)PPP}Rh]OTf possessing a new pentaphosphorus ligand and discuss about its possible role as model intermediate in the formation of **1**.

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[1] Cecconi F., Ghilardi C.A., Midollini S., Orlandini A., *J. Am. Chem. Soc.*, 1984, **106**, 3667. [2] Cecconi F., Ghilardi C.A., Midollini S., Orlandini A., *Inorg. Chem.*, 1986, **25**, 1766.

Keywords: white phosphorus, Rh-complex, P₅-ligand

P.07.01.40*Acta Cryst.* (2005). A61, C303**Structural Analysis of New Early-late Heterobimetallic Tetranuclear Metallomacrocycles**

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Coordination-driven self-assembly has shown remarkable potential in the construction of solid-state architectures with interesting physico-chemical properties. Mononuclear complexes with strong covalently bound ligands and accessible donor sites have been used as building blocks for the synthesis of mixed heterometallic moieties using a modular approach.

Interestingly, very few heterometallic macrocycles containing metalocenes and late transition metals are known. A reduced number of Ti/Pt metallomacrocycles have been assembled using the flexible bis(pyridine-4-carboxylate)titanocene as building block; also Cp₂MCl₂ (M = Ti, Zr) complexes reacted with phosphino-alkylcyclopentadienyl ligands to produce tetranuclear M/Rh metallo-macrocycles.

We are studying the preparation and structural characteristics of new angular flexible metalloligands based on (alkoxymethyl)-diphenylphosphine (μ -OCH₂PPh₂) ligand, designed for the modular assembly of d⁰-d⁸ early-late metallomacrocycles. In our poster, we will describe the structural details of two analogous but different tetranuclear Zr₂M₂ complexes, [Cp₂Zr(μ -OCH₂PPh₂)M(diolef)]₂ (BF₄)₂ (M = Rh, Ir). We will analyze metal environments and the geometric characteristics of the bifunctional ligand.

Keywords: structure of coordination complexes, early-late metallomacrocycles, heterometallic compounds