

industrial, biochemical, and medicinal application [1]. Although rare earth metal cations are widely used, little is known about the stability and the structure of their complexes in solution. In the absence of strongly stabilizing ligands, the complex formation is often precluded by the competition for the coordination sites from the solvent molecules and the counteranions. Metal complexes of phenanthroline and other structurally related ligands are of increasing importance in studies with DNA. Obviously, investigation on rare earth metal complexes of phenanthroline are of significant value for modern coordination chemistry [2,3].

Herein, we report crystal structure of  $\text{Ho}(\text{phen})_2(\text{NO}_3)_3$ . The branched tube method was employed for the preparation of suitable single crystals.  $\text{Ho}(\text{phen})_2(\text{NO}_3)_3$  was synthesized from the mixture of  $\text{Ho}(\text{NO}_3)_3$  and phenanthroline in stoichiometric amount. The title compound was placed in one arm of a branched tube, methanol was carefully added to fill both arms, the tube sealed and the compound containing arm immersed in a bath at  $80^\circ\text{C}$ , while the other was at ambient temperature. After 2 days, crystals were deposited in the cooler arm which was filtered off, washed with ether, and air dried. The tencoordinate Ho(III) ion is chelated by four N atoms from two phenanthroline (phen) ligands and six O atoms from three bidentate nitrate groups. The environment around the Ho atom can be described as a distorted bicapped square antiprism. It is believed that the Phen ligand may displace the coordinated water molecules. Almost all of the complexes were crystallized in the monoclinic space group  $C2/c$  [4]. In the title compound, four nitrogen atoms (from two phen ligands) and six oxygen atoms from three bidentate nitrate groups are coordinated to the central Ho(III) ion. Bond lengths and angles have normal values. In the crystal structure, short intermolecular distances between the centroids of six-membered rings prove an existence of  $\pi\text{-}\pi$  interactions, which link the molecules into stacks extended in direction. The crystal packing is further stabilized by the weak intermolecular  $\text{C}\cdots\text{H}\cdots\text{O}$  hydrogen bonds.

In conclusion, synthesis and crystal structure of  $\text{Ho}(\text{phen})_2(\text{NO}_3)_3$  has been investigated.

[1] M.Frechette, I.R.Butler, R.Hynes, C.Detellier, *Inorg.Chem.* **1992**, *31*, 1650-1656. [2] Q.-Y.Lin, Y.-L.Feng, *Z.Kristallogr.-New Cryst.Struct.* **2003**, *218*, 531-532. [3] D.L.Kepert, L.I.Semenova, A.N.Sobolev, A.H.White, *Aust. J.Chem.* **1996**, *49*, 1005-1008. [4] Y.-Q. Zheng, L.-X. Zhou, J.-L. Lin, S.-W. Zhang, *Z.Anorg.Allg.Chem.* **2001**, *627*, 1643--1646

**Keywords:** holmium, phenanthroline, rare earth elements

## MS24.P68

*Acta Cryst.* (2011) **A67**, C383

### X-Ray diffraction and photophysical studies on new platinum complexes

Sara Fuertes, Paul R. Raithby, *Department of Chemistry, University of Bath, Bath, (UK), BA2 7AY*. E-mail: S.F.Lorda@bath.ac.uk

Non covalent interactions highly contribute to the arrangement of smaller molecules into more elaborate structures generating a diverse number of different architectures. They have also been recognized to play an important role in molecular recognition, crystal engineering, self assembly and molecular electronics [1-3]. Besides, some of these weak interactions ( $\pi\cdots\pi$  or  $\text{Pt}\cdots\text{Pt}$ ) can display rich photoluminescent properties fairly different from the observed in the single molecules.

We report the preparation of a new 2, 6-diphenylisonicotinic derivative, its mono- and bis-cycloplatination, using a slightly modified version of the Rourke's method [4]. Reactions of this new compound  $[(\text{EtO}_2\text{C}-\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{Pt}(\text{DMSO})]$  with a range of monodentate

and bidentate ligands as well as with some metallic species gave rise to a brand new series of platinum (II) complexes which were analitically and spectroscopically characterized.

Solid state structures of these complexes have also been determined by X-ray diffraction studies, showing, the presence of weak inter- and intramolecular interactions (metal---metal,  $\pi\text{---}\pi$ ,  $\text{C-H}\text{---}\pi$  and  $\text{C-H}\text{---}\text{X}$ ). All these weak non-covalent interactions lead to the generation of different supramolecular bi- and tridimensional structures.

Photophysical studies have been performed on these complexes whether in solid state or in solution, showing a correlation between the crystalline structures and the emissive behaviour.

[1] J. Lehn *Angew. Chem., Int. Ed. Engl* **1990**, *29 (11)*, 1304. [2] C.A. Hunter *Chem. Soc. Rev* **1994**, 101. [3] C.A. Hunter, J. Singh, J. Thornton *J. Mol. Biol.* **1991**, *218*, 837. [4] G.W.V. Cave, F.P. Fanizzi, R.J. Deeth, W. Errington, J.P. Rourke *Organometallics* **2000**, *19*, 1355.

**Keywords:** platinum, photophysics, X-Ray diffraction

## MS24.P69

*Acta Cryst.* (2011) **A67**, C383-C384

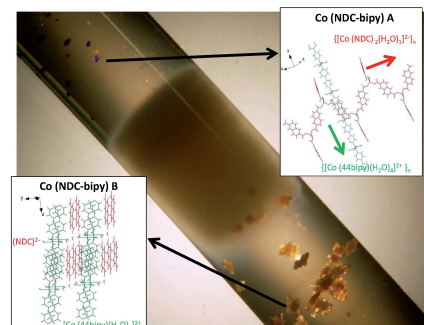
### Gel-based dimensionality control in multifunctional coordination polymers

Francisco Javier Martínez Casado, Duane Choquesillo-Lazarte, Juan Manuel García-Ruiz, *Laboratory for Crystallographic Studies, Instituto Andaluz de ciencias de la Tierra, CSIC-UGR, Armilla-Granada (Spain)*. E-mail: fmarcas@lec.csic.es.

The use of gels as a crystal growth media of a wide range of compounds has been reported in the literature including inorganic salts, organic molecules, coordination compounds and also proteins. Gel media enables a mass transport in a convection-free diffusive regime, reducing the nucleation rate and generally improving crystal quality. In addition, higher degrees of supersaturation without instantaneous nucleation can be reached with crystallization in gels, enabling the access to metastable phases and inducing polymorphism. On the other hand, the use of gels can tune the ratio metal to ligand ratio when used in advanced crystallization techniques such as the counter diffusion method and thus lead to the formation of compounds with different dimensionalities [1].

The properties of metal-organic compounds depend to a large extent in the different dimensionality they may present (isolated complexes, 1D, 2D, or 3D coordination polymers). Moreover, the same ligands and metal atoms can form different dimensioned polymorphs and hydrates [2]. The aim of this research work is to control systematically the obtaining of the different polymorphs and hydrates of the coordination polymers prepared by diffusion through different gel media (varying the conditions), and in studying the nature and properties of the crystals obtained.

A family of coordination polymers with transition metals (Mn, Co, Ni, Cu, Zn) and mixed ligands (2,6-Naphthalenedicarboxylic acid: *NDC*, and 4,4'-bipyridine: *44bipy*) has been analyzed. Isolated (0D) structures and 1D paddle-wheel complexes of this family of compounds are found in the literature with Co, Ni and Zn, all of them obtained by hydrothermal synthesis [3-4].



The experiments we have carried out with these compounds in gel media demonstrate the formation of different and new structures, even in the same U-tube (see Figure). This kind of experiment shows the possibility to tune the conditions to prepare new phases of these coordination polymers.

[1] L. Carlucci, G. Ciani, J.M. García-Ruiz, M. Moret, D.M. Proserpio, S. Rizzato, *Crystal Growth & Design* **2009**, *9* (12), 5024–5034. [2] C. Daiguebonne, A. Deluzet, M. Camara, K. Boubekeur, N. Audebrand, Y. Gérault, C. Baux, O. Guillou, *Crystal Growth & Design* **2003**, *3* (6), 1015–1020. [3] L.-P. Hsu, J.-Y. Wu, K.-L. Lu, *J.Inorg.Organomet.Polym.Mater.* **2007**, *17* (1), 259-265. [4] F. A. Almeida Paz, Y.Z. Khimyak, J. Klinowski, *Acta Cryst.* **2003**, *E59*, m8-m10.

**Keywords:** gel media, crystal growth, coordination polymers.

## MS24.P70

*Acta Cryst.* (2011) **A67**, C384

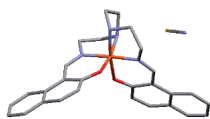
### New iron (III) two-step spin crossover compounds

Isabel C. Santos, Bruno J.C. Vieira, Laura C.J. Pereira, Vasco Gama, *Dep. Química, ITN/CFMC-UL, 2686-953 Sacavém, (Portugal)*. E-mail: icsantos@itn.pt

In recent years researcher's developed an effort to obtain molecular-based functional materials exhibiting properties of technological interest. Spin Crossover (SCO) emerges as a very powerful tool to be employed in such research.

In octahedral ligand fields, transition metal ions with d4-d7 configuration can assume a high-spin (HS) or a low-spin (LS) electronic arrangement, depending if the crystal field energy is lower or higher than the main spin pairing energy. In some of these cases bistability can take place, i.e. LS-HS transitions occur at different temperatures, they can be gradual or occur abruptly, eventually with an hysteresis loop. These materials possess increased interest in view of their possible application as display, memory and switching devices [1,2].

The two-step spin crossover of a new iron(III) compound [Fe<sup>III</sup>(Nst)]SCN is studied by magnetic and crystallographic methods revealing two spin transitions with an ordered intermediate phase built by the repetition of the [HS-LS] motif. Crystallographic data were collected on a single crystal temperatures between ; 50 and 294K. The structures collected at 50, 150 and 294 K are reported here.



[1] P. Gütllich, A. Hauser, H.C. Spiering, *Angew. Chem. Int. Ed.* **1994**, *33*, 2024. [2] J.A. Real, A.B. Gaspar, M.C. Munoz, *J Chem. Soc. Dalton Trans.* **2005**, 2062 .

**Keywords:** spin crossover, X-ray diffraction

## MS24.P71

*Acta Cryst.* (2011) **A67**, C384

### Solid-state synthesis and structure solution of chiral co-crystals and salts

Laura Chelazzi, Fabrizia Grepioni, Dario Braga, *Department of Chemistry "G. Ciamician", University of Bologna, (Italy)*. E-mail: laura.chelazzi@unibo.it

Co-crystallization provides a new strategy for altering the chemical and physical properties of molecular solid forms. The possibility of co-crystallization has to take into account the competition with kinetic factors associated with the nucleation stage of the crystallization processes. A way to overcome the thermodynamic-kinetic dualism is the “solvent-free” condition. It has also been shown that, in some systems, chiral recognition can affect solid state reactions just as it does in solution chemistry, and that products of grinding and solution experiments can be different [1],[2].

In the present work we make use of solution experiments and mechano-chemical techniques to obtain co-crystals or salts of chiral compounds [3]. For this purpose, serine(-), serine(+), serine-/+ and dicarboxylic acids were chosen as starting materials. Salts and co-crystals obtained were studied by single-crystal and powder X-ray diffraction methods, showing the formation of different polymorphs depending on the synthetic method (crystallization from solution, grinding or kneading). The new salts were also studied by thermal analysis (DSC, TG) and variable-temperature X-ray powder diffraction to check their thermal stability.

[1] R. Kuroda, Y. Imai and T. Sato, *Chirality* **2001**, *13*, 588; [2] S. Chen, H. Xi, R. F. Henry, I. Marsden and G. G. Z. Zhang, *CrystEngComm* **2009**, *11*,427; [3] D. Braga, F. Grepioni and G. I. Lampronti, *CrystEngComm* **2011**, Advance Article DOI: 10.1039/C0CE00576B

**Keywords:** polymorphism, X-ray, amino acids

## MS24.P72

*Acta Cryst.* (2011) **A67**, C384-C385

### Single-crystal to single-crystal transformations of a flexible porous Zn(II) framework

Ilne Grobler, Vincent J. Smith, Prashant Bhatt, Leonard J. Barbour, *Department of Chemistry, Stellenbosch University (South Africa)*. E-mail: ilne@sun.ac.za

Host-guest complexation by metal-organic frameworks (MOF's) is a highly topical area of research owing to applications in storage, separation and delivery of guest molecules. In particular, dynamic frameworks with guest responsive properties are essential for improved selectivity and controlled uptake and storage purposes [1]. Guest removal and exchange processes often result in collapse of a host framework and/or loss of the single-crystal quality of the material. In exceptional cases, these processes occur as single-crystal to single-crystal transformations that can be studied directly using single crystal X-ray diffraction.

Our investigation centers on the permanent porosity and exchange of guest molecules, by a three-dimensional Zn(II) MOF ([Zn(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]CH<sub>3</sub>OH, see Fig. 1) that has well-defined one-dimensional, square-shaped channels. Significant structural changes occur when the host framework accommodates different guest molecules whilst retaining its single crystal-nature.

The MOF consists of two-dimensional layers or nets stacked on top of one another and interconnected by polymeric metal-water-metal coordination. The as-synthesized framework includes methanol molecules hydrogen bonded to the framework. The crystals are remarkably robust and remain transparent following removal of the methanol molecules at 150°C under reduced pressure. A series of exchange experiments were carried out, all of which occurred *via* a single-crystal to single-crystal process.