

$C_2B_9H_{9.91}]^-$ anion in salt **1** presented in Figure 1. The dicarbollide ligands are mutually rotated by 180° producing *transoid* conformation.

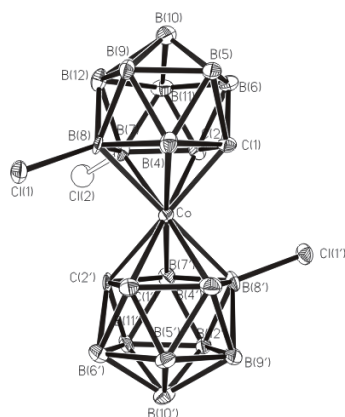


Fig. 1. The anion in (**1**). Hydrogen atoms omitted for clarity.

All radical cation salts prepared were found to be semiconductors, the room temperature conductivities are 2, 10^{-5} , $0.5 \Omega^{-1}cm^{-1}$, respectively.

Acknowledgements: The authors want to acknowledge Russian Foundation for Basic Research

Keywords: molecular conductors, X-ray study, materials

MS66.P06

Acta Cryst. (2011) A67, C639

Solvent-tuned Magnetic Behaviors of Manganese(III) Corroles

Mei Ding,^a Bingwu Wang,^a Zheming Wang,^a Junlong Zhang,^a Olaf Fuhr,^b Dieter Fenske,^b Song Gao,^a ^aBeijing National Laboratory of Molecular Science, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871 (China). ^bKarlsruher Institut für Technologie (KIT), Institut für Nanotechnologie and Institut für Anorganische Chemie, Karlsruhe (Germany). Email: dingmei.pku@gmail.com

Mn(tpfc) (tpfc = the trianion of 5,10,15-tri(pentafluorophenyl)corrole) is a good magnetic anisotropy motif. Compared to intense efforts on its catalytic performance [1, 2], rare research concentrates on its magnetic behaviors. We get three Mn(tpfc) solvates from methanol (**1**), ethyl acetate (**2**) and ethanol (**3**), respectively. Though they share the same magnetic repeating unit, they show quite different magnetic behaviors due to solvent-tuned different packing in crystal lattices. **1** and **2** are supramolecular 1D chains while **3** forms dimers. **1** with slow relaxation of magnetization below 2 K and magnetization hysteresis loop at 0.5 K is the first spin canted supramolecular single-chain magnet stemming from intermolecular $\pi-\pi$ interaction. **2** is an antiferromagnetic chain without ordering or slow magnetization relaxation down to 0.5 K while **3** shows field-induced single-molecule magnet-like behaviors below 2.5 K.

Such control of solvent on magnetic behaviors comes from different relative orientations of magnetic anisotropy axes induced by solvents and shows clear magneto-structural correlation.

We acknowledge the support of NSFC, the National Basic Research Program of China.

[1] Z. Gross, G. Golubkov, L. Simkhovich *Angew. Chem. Int. Ed.* **2000**, *39*, 4045-4047. [2] M.J. Zdilla, M.M. Abu-Omar *J. Am. Chem. Soc.* **2006**, *128*, 16971-16979.

Keywords: solvent, manganese, magnetism

MS66.P07

Acta Cryst. (2011) A67, C639

Multifunctional Gd^{III}-core nanoparticles directed by alkylnitrosopyrazolones

Jorge Pasán,^a Julio Belmar,^b José Quezada,^b Claudio A. Jiménez,^b Fernando Lahoz,^c Alberto Hernández-Creus,^d Miguel Julve,^e Catalina Ruiz-Pérez,^a ^aLaboratorio de Rayos X y Materiales Moleculares (MATMOL), dpto. Física Fundamental II, Universidad de La Laguna, La Laguna (Spain). ^bLaboratorio de Síntesis Covalente y no Covalente, Dpto. Química Orgánica, Universidad de Concepción, Concepción (Chile). ^cDpto. Física Fundamental y Experimental, Electrónica y Sistemas, Universidad de La Laguna, La Laguna (Spain). ^dDpto. Química Física, Universidad de La Laguna, La Laguna (Spain). ^eDpto. Química Inorgánica, Instituto de Ciencia Molecular, Universitat de València, Valencia (Spain). E-mail: jpasang@ull.es

The area of gadolinium(III) labelled nanoparticles for use as MRI contrast agents is rapidly increasing. They are usually envisaged as an inorganic nanoparticulate core of a Gd-containing species (i.e. Gd₂O₃) coated with a polymeric shell.[1] Our strategy consists in developing Gd(III) coordination clusters where specific organic molecules act as chelating and coating agent simultaneously. For this function we have selected a pyrazolone-derivative.

Pyrazolones constitute a wide family of organic heterocyclic compounds that are very relevant because of chemical, biological and medicinal points of view. The tautomerism that they exhibit, their use in dyes, as derivatizing agents in carbohydrate analysis and also as chelating ligands are among the most appealing chemical points of these heterocycles. Concerning their biological/medicinal aspects, two illustrative examples are the analgesic antipyrine still in use in several countries and Edaravone[®], a radical quencher that is used to treat brain ischemia.

Here we report the synthesis, crystal structure and magnetic properties of the complex [Gd₅L₁₁(μ₃-O)₂(H₂O)₂]-H₂O where L = 1-hexyl-3-phenyl-4-nitroso-5-pyrazolone. This compound is formed by nanoparticles of ca. 3.5 nm diameter that are stable in solution, a situation that has been confirmed by AFM studies. The luminescence of the nanoparticles has also been characterized.

[1] M. Bottrill, L. Kwok, N.J. Long, *Chem. Soc. Rev.* **2006**, *35*, 557-571. [2] (a) J.S. Casas, M.S. García-Tasende, A. Sánchez, J. Sordo, A. Touceda, *Coord. Chem. Rev.* **2007**, *251*, 1561. (b) Y. Higashi, D. Jitsuiki, K. Chayama, M. Yoshizumi, *Recent Pat. Cardiovasc. Drug Discovery*, **2006**, *1*, 85. (c) H. Hammouda, *Arch. Pharm. Res.*, **1992**, *15*, 1.

Keywords: nano, luminescent, gadolinium

MS66.P08

Acta Cryst. (2011) A67, C639-C640

Synthesis and structural characterization of [H₃N(CH₂)₄NH₃][Y(hedpH)][hedpH₂]

Eva Fernández-Zapico,^{a,b} Jose Montejó-Bernardo,^a J. Rubén García,^b Santiago García-Granda,^a ^aDepartamento de Química Física y Analítica, ^bDepartamento de Química Orgánica e Inorgánica, Universidad de Oviedo-CINN, Oviedo, Asturias (Spain). E-mail: fernandezeva.uo@uniovi.es

We have recently reported the synthesis and crystal structure of a family of [H₃N(CH₂)₄NH₃]_n[Ln(hedpH)_n][hedpH₂], with Ln = La, Pr, Sm, Eu, Gd, Tb and Er [1, 2].

These phosphonates are based on 1-hydroxyethane-1,1-diphosphonic acid [hedpH₄, H₂O₃PC(OH)(CH₃)PO₃H₂], which has been widely used as a strong chelating agent in the preparation of functional

metal diphosphonates and found to bind strongly to numerous metal ions.

Following with our line of work, we have synthesized one new member of this family, $[H_3N(CH_2)_4NH_3]Y[hedpH][hedpH_2]$, with Y as central atom, being found, as expected, that this new compound is isostructural to all the other members.

Here we present the synthesis, structural studies by single crystal and synchrotron powder x-ray diffraction, and characterization studies by SEM-EDX and TG-MS and DSC techniques.

Now, we are trying to obtain similar compounds with the other elements of Y group, to compare their structures.

Acknowledgements. Financial support from Spanish MICINN (MAT2006-01997, MAT2010-15095 and 'Factoría de Cristalización' Consolider Ingenio 2010), Universidad de Oviedo and Banco Santander is acknowledged. FEDER support is also acknowledged.

[1] F.-Y. Liu, L. Rocas, R.A. Sa Ferreira, S. García-Granda, J.R. García, L.D. Carlos, J. Rocha, *Journal of Materials Chemistry* **2007**, *17*, 3696-3701. [2] E. Fernández-Zapico, J. Montejo-Bernardo, S. García-Granda, J.R. García, G.R. Castro, F.-Y. Liu, J. Rocha, *Zeitschrift für Kristallographie (Supplement Proceedings of EPDIC12)* **2010**, accepted.

Keywords: yttrium phosphonates, crystal structure, thermal characterization.

MS66.P09

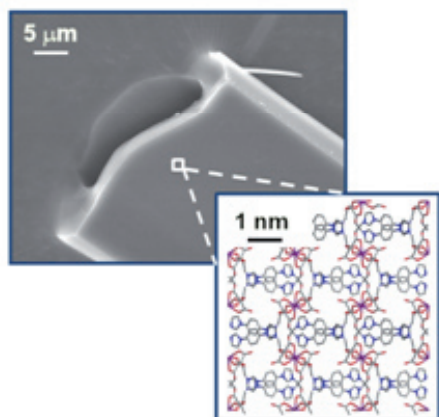
Acta Cryst. (2011) **A67**, C640

Elaboration of nanoporous hydrogen-bonded Metal-Organic frameworks (MOF)

Carine Duhayon, Georges Mouchaham, Nans Roques, and Jean-Pascal-Sutter, *CNRS, Laboratoire de Chimie de Coordination, UPR 8241, 205 Route de Narbonne, F-31077 Toulouse, (France)*. E-mail: duhayon@lcc-toulouse.fr,

During the last decade, the synthesis and the characterization of porous metal-organic frameworks (MOFs) have attracted much attention owing to their potential applications in gas storage, sensing, catalysis or as functional materials. MOFs reported in the literature are classically obtained through solvothermal synthesis, and result from the direct assembly of metal ions and bridging ligands yielding, during the association process, secondary building units that govern the final network topology.

Alternatively, an emerging trend towards the development of MOFs consists in using preformed complexes as building-blocks to assemble *via* coordination chemistry and/or charge assisted H-Bonding. These building units, which possess given geometries and linking abilities, form the nodes of the network, and contribute to govern the net topology in association with linkers such as metal ions or organic molecules. We have shown charge assisted H-Bonding to be valuable to design open-framework architectures [1,2]. These compounds were characterized by single crystal X-ray crystallography. In this communication, recent striking results obtained using this



approach will be presented: supramolecular architectures with interesting sorption properties [3] and crystal morphology control to afford supramolecular materials showing hierarchical porosity [4].

[1] I. Imaz, A. Thillet, J.-P. Sutter, *Crystal Growth & Design* **2007**, *7*, 1754. [2] G. Mouchaham, N. Roques, I. Imaz, C. Duhayon, J.P. Sutter, *Crystal Growth & Design*, **2010**, *10*, 4906-4919. [3] F. Thetiot, C. Duhayon, T.S. Venkatakrisnan, J.-P. Sutter, *Crystal Growth & Design*, **2008**, *8*, 1870. [4] G. Mouchaham, N. Roques, A. Kaiba, P. Guionneau, J.-P. Sutter, *CrystEngComm*, **2010**, *12*, 3496.

Keywords: MOF, X-Ray, structure

MS66.P10

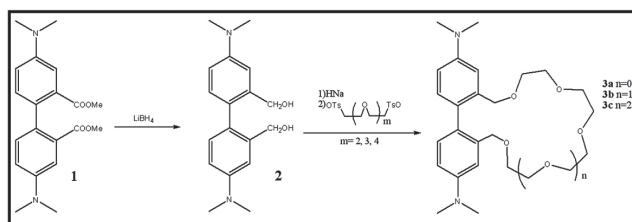
Acta Cryst. (2011) **A67**, C640

Electrochemical and Photophysical Sensors derived from biphenyl. Structural Studies

Katherine Chulvi,^a Ana M. Costero,^a Rosario Andreu^a, Luis E. Ochando^{a,b}, Rosendo Pou-Américo,^c ^a*Centro de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Unidad Mixta UPV-UV, Dep. Química Orgánica, Facultad de Químicas.* ^b*Dep. Geología,* ^c*Dep. Química Física, Universidad de Valencia, Burjassot, Valencia (Spain)*. E-mail: katchuli@alumni.uv.es

Chemosensors containing in their structures biphenyl moieties have demonstrated to be useful systems for both anion and cation sensing. First of all, modifications in the dihedral angle between the aromatic rings in the biphenyl structure have strong influence on the photophysical properties of the compound [1]. Secondly, appropriately substituted biphenyls present interesting electrochemical properties that can be modulated by the presence of different analytes [2]. In order to connect the recognition event with the transduction mechanism (modification of the dihedral angle), coronands directly bond to the 2,2' position of the 4,4'-Bis(dimethylamino)phenyl have been prepared. Varying the number of oxygens in the crown ether, changes the size of the cavity enabling a selective answer by the sensor between different cations [3]. As there is a clear relationship between ligand and complex conformations and their photophysical or electrochemical properties [4], a comparative crystallography study between different related compounds has been carried out. Dihedral angle between planar aromatics was 81.7°, 72.7° and 83.6° for **3a**, **3b** and **3c** respectively. For compound **1**, dihedral angles between aryl groups was 56.5° 56.2°, and 88.7° for compound **2**.

Moreover, a structural study with quantum chemical calculations of these sensors using density functional methods will be done.



[1] A.C.Benniston, A.Harriman, P.V.Patel, C.A.Sams. *J.Org.Chem.* **2005**, *21*, 4680-4686. [2] A.M. Costero, C. Andreu, R. Martínez-Máñez, J. Soto, L.E. Ochando, J.M. Amigó. *Tetrahedron* **1998**, *54*, 8159-8170. [3] A.M. Costero, E. Monrabal, C. Andreu, R. Martínez-Máñez, J. Soto, M. Padilla-Tosta, T. Pardo, L.E. Ochando, J.M. Amigó. *J. Chem. Soc., Dalton Trans.* **2000**, 361-367. [4] G. Delogu, D. Fabbri, M.A. Detori, M. Sallé, F. Le Derf, M.J. Blesa, M. Allain. *J.Org.Chem.* **2006**, *71*, 9096-9103.

Keywords: sensor, crystallography, angle.