

A microporous cationic MOF has been prepared by our research group while investigating the lanthanide/2,5-pyridinedicarboxylic acid system [3]. Large crystals of framework $[\text{Ce}_2(\text{pydc})_2(\text{Hpydc})(\text{H}_2\text{O})_2]\text{Cl}\cdot(9+y)\text{H}_2\text{O}$ (**1**) (where pydc^{2-} is the diprotonated residue of 2,5-pyridinedicarboxylic acid) were directly isolated from the hydrothermal reaction vial via filtration. A second phase was also systematically present and was identified as identical to the structure reported by Huang et al.: $[\text{Ce}_2(\text{pydc})_3(\text{H}_2\text{O})_2]$ [4].

A systematic change of the reaction conditions to promote the sole preparation of **1** proved to be unsuccessful: we found that we could only improve the ratio between the desired microporous phase **1** and $[\text{Ce}_2(\text{pydc})_3(\text{H}_2\text{O})_2]$ to 4:1. Nevertheless, the considerable difference in particle size allowed an easy segregation of **1** for further detailed X-ray diffraction studies.

1 has a single crystallographically independent Ce^{3+} . The nine-coordination sphere is composed of one water molecule, six oxygen atoms from *syn*, *skew*- or *syn,syn*-bridging carboxylate groups, plus a *N,O*-chelate. The coordination polyhedron resembles a highly distorted dodecahedron. This MOF (*ca.* 43% of accessible volume) contains prominent channels (cross section *ca.* $12 \times 7 \text{ \AA}^2$) running parallel to the [001] direction housing disordered charge-balancing chloride anions and water molecules of crystallization. The BET surface area of the degassed material was calculated as approximately $106 \text{ m}^2/\text{g}$. The solvent (water) could be partially exchanged by chloroform or benzyl alcohol by crystal immersion at ambient temperature over a period of several days.

This material (**1**) was treated as an anion exchanger by immersion of the individual crystallites in methanolic solutions of several anions, such as Br^- , I^- , NO_3^- , PF_6^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, PO_4^{3-} . We note that the presence of the secondary phase, $[\text{Ce}_2(\text{pydc})_3(\text{H}_2\text{O})_2]$, is an advantage as it can be used as an internal standard. Structural details of the exchanged materials (solvent and anion), were investigated by using in tandem X-ray diffraction (single-crystal and powder), electron microscopy (SEM and EDS), and FT-IR spectroscopy.

Acknowledgments We are grateful to CICECO and to FCT for their financial support (R&D project PTDC/QUI-QUI/098098/2008) and for the Ph.D. scholarship SFRH/BD/46601/2008 (to PS).

[1] S. Bureekaew, S. Shimomura, S. Kitagawa, *Sci. Technol. Adv. Mater.* **2008**, *9*, 014108. [2] J. Klinowski, F.A.A. Paz, P. Silva, J. Rocha, *Dalton Trans.* **2011**, *40*, 321-330. [3] P. Silva, A.A. Valente, J. Rocha, F.A.A. Paz, *Cryst. Growth Des.*, **2010**, *10*, 2025-2028. [4] Y. Huang, Y. S. Song, B. Yan, M. Shao, *J. Solid State Chem.* **2008**, *181*, 1731-1737.

Keywords: metal-organic framework, microporosity, anion-exchange

MS25.P12

Acta Cryst. (2011) A67, C396

1D systems based on pyrazine-2,5-dicarboxylate linkers and $[\text{Mn}(\text{phen})]^{2+}$ nodes

Mónica Lanchas, Garikoitz Beobide, Oscar Castillo, Javier Cepeda, Antonio Luque, Sonia Pérez-Yáñez, Pascual Román, Jintha Thomas-Gipson, Daniel Vallejo-Sánchez, *Inorganic Chemistry Department, University of the Basque Country, P. O. 644, E-48080 Bilbao (Spain)*. E-mail: monica.lanchas@ehu.es

In recent years, the area of inorganic crystal engineering [1] has become one of intense research activity because of the growing need for novel solid-state architectures with potential applications as functional materials in fields such as catalysis, conductivity, zeolitic behaviour, and magnetism [2]. The judicious choice of the metal ion, a good understanding of the coordination preferences of the bridging entities, and a careful selection of the terminal ligands are key steps for

the rational design of metal-organic coordination polymers with novel topologies and specific chemical and physical properties [3]. In this context, π -conjugated N-donor bridging ligands, such as pyrazine and its polycarboxylic derivatives, have appeared to be well-suited tools for the construction of extended arrays of metal ions with interesting physical properties in molecular magnetism or selective guest adsorption fields [4].

Two new metal-organic compounds based on the bridging ligand pyrazine-2,5-dicarboxylate (Pzdc) have been synthesized and chemically and crystallographically characterized in the present work: $\{[\text{Mn}(\mu\text{-Pzdc})(\text{Phen})]\cdot 2\text{DMSO}\}_n$ (**1**) and $\{[\text{Mn}(\mu\text{-Pzdc})(\text{Phen})]\cdot \text{CH}_3\text{O}\cdot \text{H}\cdot \text{H}_2\text{Pzdc}\}_n$ (**2**), with Phen = 1,10-phenanthroline, DMSO = dimethyl sulphoxide. Compound **1**, obtained using DMSO as solvent, crystallizes in the C2/c space group and it is built up by zig-zag chains in which the metal centers are joined by bisbidentate Pzdc bridging ligands and the phenanthroline molecule acts as blocking ligand avoiding further polymerization. The compound loses crystallinity out of the mother liquors, so the employed solvent was changed to methanol in order to get a more stable structure, obtaining the compound **2**. The complex crystallizes in the P2/c space group and although it is also made up of $[\text{Mn}(\mu\text{-Pzdc})(\text{Phen})]_n$ chains, the increase of the supramolecular interactions gives rise to a more robust structure. The metal coordination environment in both compounds is similar but not equal as can be observed in figure 1.

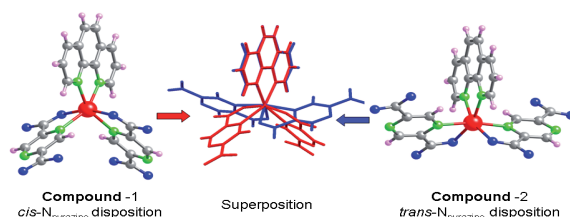


Figure 1. Superposition of the coordination environments of the Mn(II) atoms in compounds **1** and **2**.

[1] D. Braga, L. Brammer, N. R. Champness, *CrystEngComm.* **2005**, *7*, 1-19, [2] S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276-288, [3] D. Braga, G. R. Desiraju, J. S. Miller, A. G. Orpen, S. L. Price, *CrystEngComm.* **2002**, *4*, 500-509, [4] S. Konar, S. C. Manna, E. Zangrando, N. R. Chaudhuri, *Inorg. Chim. Acta* **2004**, *357*, 1593-1597.

Acknowledgements. This work has been supported by the Ministerio de Ciencia e Innovación (MAT2008-05690/MAT), the Gobierno Vasco (IT477-10) and UPV/EHU (predoctoral fellowships).

Keywords: coordination-polymer, pyrazine-2,5-dicarboxylate, manganese.

MS25.P13

Acta Cryst. (2011) A67, C396-C397

3D-copper-adeninate complexes with microchannels tailored by aliphatic acids

Sonia Pérez-Yáñez, Garikoitz Beobide, Oscar Castillo, Javier Cepeda, Mónica Lanchas, Antonio Luque, Pascual Román, Jintha Thomas-Gipson, Daniel Vallejo-Sánchez, *Inorganic Chemistry Department, University of the Basque Country, P. O. 644, E-48080 Bilbao (Spain)*. E-mail: sonia.perez@ehu.es

The emerging field of coordination polymers offers a means to a novel class of potentially designable materials because their metrics and chemical functionality can be carefully adjusted for specific applications [1]. In recent times, porous metal organic frameworks (MOFs) have attracted increasing attention because they possess a