

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.

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

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

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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.

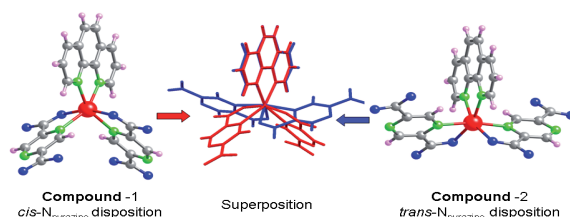


Figure 1. Superposition of the coordination environments of the Mn(II) atoms in compounds **1** and **2**.

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

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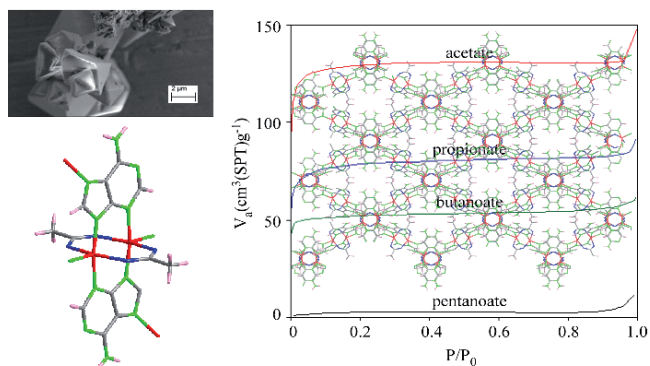
3D-copper-adeninate complexes with microchannels tailored by aliphatic acids

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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

rich structural chemistry and excellent gas sorption properties. In this type of compounds, we can functionalize the pores to direct their specific recognition capability towards small molecules, and therefore, the emerging porous MOFs serve as novel functional materials for gas storage, separation, heterogeneous catalysis and sensing [2]. The judicious choice of the organic ligands is a key step in designing multidimensional frameworks containing transition metal complexes as building blocks [3]. In this sense, the unsubstituted adenine nucleobase is a good candidate because it contains at least five donor sites and its versatility as a ligand is well-known [4]. Additionally, it is also known that paddle-wheel cores, with carboxylate and purine derivatives as bridging ligands, are able to build rigid and porous MOFs [5-7].

We present here the synthesis and characterization of a new family of three-dimensional porous metal-organic compounds, $[\text{Cu}_2(\mu_3\text{-ade})_2(\mu_2\text{-OOC}(\text{CH}_2)_n\text{CH}_3)_2] \cdot x\text{H}_2\text{O}$ [n from 0 (acetate) to 5 (heptanoate)]. Single-crystal X-ray analysis of acetate ($n = 0$) and butanoate ($n = 2$) compounds shows a covalent 3D network in which the copper(II) centers are bridged by tridentate $\mu\text{-}N3,N7,N9$ adeninato ligands and by $\mu\text{-}O,O'$ carboxylate ligands, with crystallization water molecules trapped in the pores which are decorated by the Watson-Crick faces of the adenine. The tunable permanent porosity of guest-free compounds was confirmed by gas adsorption measurements.



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Keywords: MOF, adsorption, bioinorganic

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Synthesis and characterization of the $\text{K}_{(1-x)}\text{Rb}_x\text{CuFe}(\text{PO}_4)_2$ ($0 \leq x \leq 1$) phosphates

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Transition metal phosphates are extensively studied for their attractive applications in catalysis, ion-exchange, conductivity and magnetism. Among them, iron phosphates are special interest due to their rich crystal chemistry owing to the possible +II/+III oxidation state of iron and the diverse linkage fashions of its coordination polyhedra. Our interest in these compounds concerns the synthesis of new materials and their structural and physical investigation.

As part of this study, we recently isolated a new solid solution $\text{K}_{(1-x)}\text{Rb}_x\text{CuFe}(\text{PO}_4)_2$ ($0 \leq x \leq 1$) using high temperature solid-state reaction technique. Its phase analysis by powder X-ray diffraction indicated the formation of a continuous solid solution. The cation distribution was evidenced by a single crystal X-ray study of the two limiting phases $\text{KCuFe}(\text{PO}_4)_2$ and $\text{RbCuFe}(\text{PO}_4)_2$. It was then found that this solid solution is formed by cationic substitution mechanism: $\text{K}^+ \rightarrow \text{Rb}^+$. The observed increase of the cell parameters with increasing Rb content is attributed to the difference between the ionic radii of K^+ and Rb^+ . The whole structure is built up from two structural units: isolated FeO_6 octahedra and Cu_2O_8 units of corners CuO_5 polyhedra. These units are corner-sharing to form crossing chains which propagate along the [011] and [01-1] directions. Such chains are interconnected by means of the PO_4 tetrahedra and the resulting 3D framework shows hexagonal tunnels running along the [101] directions, occupied by K^+ and Rb^+ cations.

The Infra-Red spectra are consistent with the presence of two distinct phosphorus sites in tetrahedral geometry. The Differential Thermal Analysis (DTA) showed a congruent melting of the products, the melting temperature being increased with increasing Rb content. The Mössbauer spectroscopy study of the $\text{KCuFe}(\text{PO}_4)_2$ phase gave clear evidence of the exclusive occurrence of octahedral Fe^{3+} ions and its magnetic susceptibility study indicated an antiferromagnetic ordering with $T_N = 36$ K.

Key words: phosphate, X-ray diffraction, spectroscopy study.

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Structure and crystallochemistry of four sepiolites from Madrid
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Sepiolite is a mineral frequently found in the Miocene sediments of the Madrid basin. This basin contains the world's largest sepiolite reserves, which is remarkable as far as the industrial value of this mineral, owing to its adsorbent properties, is well known [1,2].

Four materials, containing mainly sepiolite (>85% weight), have been selected from more than 20 high grade sepiolite specimens sampled in the Vicálvaro-Barajas (Madrid) zone.

Sepiolite structure consists of blocks and channels elongated in Z-axis direction, whereas each structural unit is built up of two tetrahedral silicate layers and a central trioctahedral layer. In the octahedral layer Mg^{2+} ions occupy two different structural positions: on the borders of the structural blocks, coordinated to water molecules and in the interior of the blocks, linked to hydroxyl groups, which can be substituted by fluorine due to the similarity of electronegativity and ionic radius values [3].

Chemical analyses were corrected for known mineral impurities, mainly dolomite and quartz, using the Rietveld method. Crystallochemical formulae were then calculated showing virtually