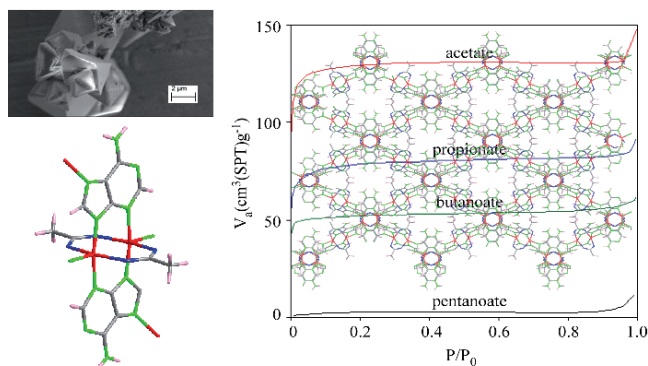


rich structural chemistry and excellent gas sorption properties. In this type of compounds, we can functionalize the pores to direct their specific recognition capability towards small molecules, and therefore, the emerging porous MOFs serve as novel functional materials for gas storage, separation, 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

## MS25.P14

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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  $\text{K}^+$  and  $\text{Rb}^+$ . The whole structure is built up from two structural units: isolated  $\text{FeO}_6$  octahedra and  $\text{Cu}_2\text{O}_8$  units of corners  $\text{CuO}_5$  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  $\text{PO}_4$  tetrahedra and the resulting 3D framework shows hexagonal tunnels running along the [101] directions, occupied by  $\text{K}^+$  and  $\text{Rb}^+$  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  $\text{Fe}^{3+}$  ions and its magnetic susceptibility study indicated an antiferromagnetic ordering with  $T_N = 36$  K.

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

## MS25.P15

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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  $\text{Mg}^{2+}$  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

sepiolite ideal composition for two of them, which origin was from two thick (>1m) high grade sepiolite layer in Vicálvaro and Barajas (Table). Specimens sampled from less developed sepiolite layers showed a slight excess in F, Si and lower Mg occupation than ideal sepiolite [4]. It is observed a correlation between the high fluorine content and low magnesium occupation of the studied samples with the loss of ideal structure.

Sample	Corrected Formulae
TS4	Si <sub>12.02</sub> (Mg <sub>7.97</sub> )(OH) <sub>3.14</sub> F <sub>0.86</sub> )
S41733	Si <sub>12.04</sub> (Al <sub>0.05</sub> Mg <sub>7.84</sub> )(OH) <sub>3.35</sub> F <sub>0.65</sub> )
S4284	Si <sub>12.17</sub> (Al <sub>0.03</sub> Mg <sub>7.63</sub> )(OH) <sub>2.80</sub> F <sub>1.20</sub> )
S13392	Si <sub>12.16</sub> (Mg <sub>7.68</sub> )(OH) <sub>3.04</sub> F <sub>0.96</sub> )

Ordering and degree of occupancy of Mg and F ions are being studied in order to explain the structural anomalies found in sepiolite.

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**Keywords: sepiolite, structural anomalies, fluorine**

## MS25.P16

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### Investigations of barium and strontium dicarboxylates – ‘new metalorganic compounds’

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Synthesis and study of new salts of dicarboxylic acids with metals reveal new types of structures, which are interesting from the viewpoint of crystal engineering and practical applications. These compounds can be layered, three dimensional micro- and macroporous materials. Properly selected dicarboxylic acids synthesized with appropriate compounds used as templates may be ‘building blocks’ of complex three-dimensional hierarchical materials, [1]. Some salts of uranium and simple dicarboxylic acids are known and well characterized [2], additionally the poor solubility of this kind of compounds of metals such as calcium is known. Therefore, these systems can be used in the design of materials which may be useful for removing of heavy metals from solutions. Increasing interest in the compounds such as MOF (Metal-Organic Frameworks) is related to their possible use, similar to zeolites, including sorption and gas separation, ion exchange and catalytic properties.

In our study we obtained a group of barium and strontium dicarboxylates with chain length from 5 to 12 carbon atoms. For all obtained compounds XRPD studies were performed (phase analysis and lattice parameters). In four cases single crystal analysis was also performed (Table 1). Compound (I) forms isolated layers of the Ba ions and molecules of glutaric acid, while the structures (II-IV) are built of the Ba-O layers connected with each other by dicarboxylic acids. Further structure studies for the obtained substances, using

both single crystal and powder methods are in progress. Additionally, obtained samples were characterized by thermal decomposition and spectroscopic studies.

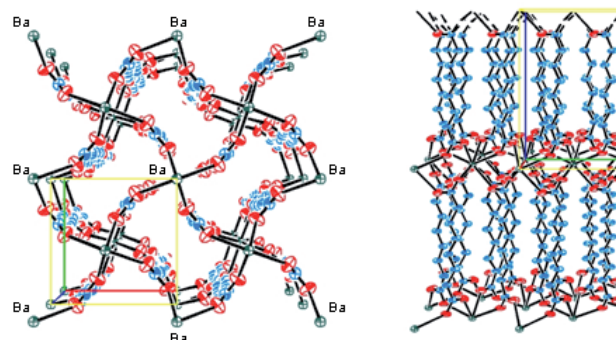


Fig. 1. Structure of BaC<sub>16</sub>H<sub>26</sub>O<sub>8</sub> (II): view along c (left), packing of the molecules in the direction perpendicular to the layers (right)

Table 1. Cell parameters obtained by single crystal analysis

Chemical formula	BaC <sub>5</sub> H <sub>6</sub> O <sub>4</sub> ·6H <sub>2</sub> O (I)	BaC <sub>16</sub> H <sub>26</sub> O <sub>8</sub> (II)	SrC <sub>9</sub> H <sub>14</sub> O <sub>4</sub> (III)	SrC <sub>24</sub> H <sub>40</sub> O <sub>8</sub> (IV)
SG	Pnma(62)	P-4b2(117)	I222(23)	Ccca(68)
a [Å]	12.149(1)	12.0906(4)	8.4750(2)	36.0410(1)
b [Å]	7.532(1)	12.0906(4)	8.8411(3)	9.3710(3)
c [Å]	13.294(1)	13.0713(5)	28.0506(7)	7.9310(3)
V [Å <sup>3</sup> ]	1187.5(2)	1910.8(1)	2101.7	2678.6
wR2, R1	0.0497, 0.0200	0.0337, 0.0137	0.1445, 0.0691	0.1461, 0.0612

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**Keywords: barium, strontium, carboxylate**

## MS25.P17

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### Crystal structure of new alkaline diphosphates in the A<sub>2</sub>MnP<sub>2</sub>O<sub>7</sub> family

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Two new members of the A<sub>2</sub>MnP<sub>2</sub>O<sub>7</sub> diphosphate family have been evidenced: Rb<sub>2</sub>MnP<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O and Cs<sub>2</sub>MnP<sub>2</sub>O<sub>7</sub>. The crystal structures of both compounds were resolved and refined using single crystal X-ray diffraction. The crystals of the rubidium based phase presented systematically a non-merohedral twinning so a Rietveld refinement of powder XRD data was also performed.