

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 _{12.02} (Mg _{7.97})((OH) _{3.14} F _{0.86})
S41733	Si _{12.04} (Al _{0.05} Mg _{7.84})((OH) _{3.35} F _{0.65})
S4284	Si _{12.17} (Al _{0.03} Mg _{7.63})((OH) _{2.80} F _{1.20})
S13392	Si _{12.16} (Mg _{7.68})((OH) _{3.04} F _{0.96})

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

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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.

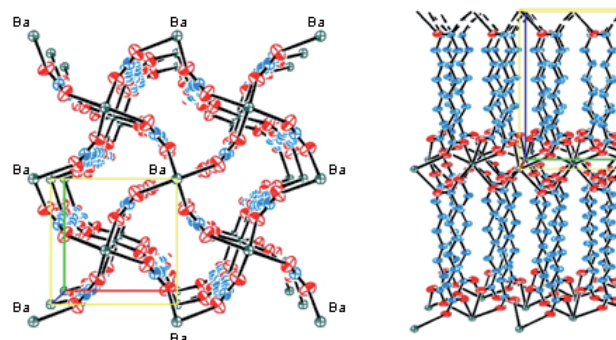


Fig. 1. Structure of BaC₁₆H₂₆O₈ (II): view along c (left), packing of the molecules in the direction perpendicular to the layers (right)

Table 1. Cell parameters obtained by single crystal analysis

Chemical formula	BaC ₅ H ₆ O ₄ ·6H ₂ O (I)	BaC ₁₆ H ₂₆ O ₈ (II)	SrC ₉ H ₁₄ O ₄ (III)	SrC ₂₄ H ₄₀ O ₈ (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 ³]	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

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Crystal structure of new alkaline diphosphates in the A₂MnP₂O₇ family

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Two new members of the A₂MnP₂O₇ diphosphate family have been evidenced: Rb₂MnP₂O₇·H₂O and Cs₂MnP₂O₇. 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.

Although from the same family, the two phosphates adopt two different crystal structures. $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic $P2_1/c$ space group with lattice parameters $a = 5.3845(5) \text{ \AA}$, $b = 10.241(1) \text{ \AA}$, $c = 15.566(2) \text{ \AA}$, $\beta = 93.15(1)^\circ$, $Z = 4$, $V = 857,00(4) \text{ \AA}^3$. $\text{Cs}_2\text{MnP}_2\text{O}_7$ crystallizes in the orthorhombic $Pnma$ ($n^\circ 62$) space group and the unit cell parameters are $a = 16.3398(3) \text{ \AA}$, $b = 5.3872(1) \text{ \AA}$, $c = 9.8872(2) \text{ \AA}$, $Z = 4$, $V = 870,33(3) \text{ \AA}^3$. Both structures are however closely related. They can be described by a single axis stacking of undulating $[\text{MnP}_2\text{O}_{10}]_\infty$ layers; alkaline cations occupy the interlayer spaces. The water molecule in $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ is positioned also between the $[\text{MnP}_2\text{O}_{10}]_\infty$ layers. Its presence is confirmed by the 1607cm^{-1} , 3173cm^{-1} and 3545cm^{-1} absorption bands observed in the infrared spectrum.

Some parallel can be made between the structures of $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ / $\text{Cs}_2\text{MnP}_2\text{O}_7$ [1] and some phosphates of the enlarged $\text{A}_2\text{MP}_2\text{O}_7$ family like $\text{K}_2\text{CuP}_2\text{O}_7$ [2]. On the other hand, within the entire $\text{A}_2\text{MnP}_2\text{O}_7$ ($A = \text{Li, Na, K, Rb, Cs}$) family itself, every phosphate adopts a different crystal structure with either layered or 3D $[\text{MnP}_2\text{O}_7]$ framework and various Mn coordination [1, 3 - 5].

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Keywords: phosphate, structure, layered

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Three-dimensional lanthanide MOF based on a linear ditopic dicarboxylate

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Since its first appearance, the MOF-type materials (Metal-Organic Frameworks) has shown a promising future into the materials science, due to their big applications in all fields, from structural materials (giving light and resilient structures), to their magnetic properties (opening a new field of research in the information store devices.)

For the last ten years, our research group has centered its attention upon the field of MOF-type materials, with special interest into the magnetic properties. In the preparation of these materials our strategy has been based on carboxylic ligands, using transition metal and lanthanide ions as paramagnetic centres and organic molecules containing this substituent as ligands.

We have selected the *trans,trans*-muconic acid (**Figure 1**, H_2ttmuc) because it is a linear, ditopic ligand with a rigid rod-like configuration. This ligand has two connection sites at both extremes, giving as a result a ligand which can act as edges in three-dimensional MOFs where the formation of cavities is favoured. The muconic acid is a dicarboxylic acid. The double unsaturated muconic acid has three isomeric forms, designated *trans,trans*-muconic acid, *cis,trans*-muconic acid, and *cis,cis*-muconic acid, which differ by the geometry around the double bonds.

Previous results of this ligand include the preparation of transition metal complexes, such as Fe[1], Cu[1], Ni[2] and Co[3], to form networks of different dimensionalities. However, the use of lanthanides remains unexplored, and thus here in we present the preliminary results

on the crystal structure of the praseodymium(III) compound (**Figures 2a & 2b**), that show that the MOF formed is three-dimensional with cavities where water molecules are hosted.

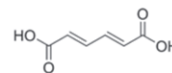


Figure 1. *trans,trans*-Muconic Acid (H_2ttmuc)

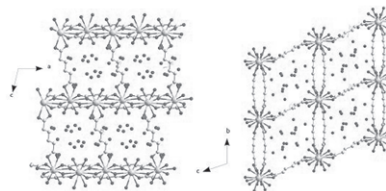


Figure 2a & 2b. Crystalline structure of *Pr [tt-muc]*. a, c

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Keywords: muconic acid, mof-type materials.

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Formation of LC-phase in concentrated solutions of mono-carboxylic acids by SANS

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Mono-carboxylic acids (bent non-saturated oleic acid (OA) and strictly linear saturated stearic (SA) and myristic (MA) acids) show different efficiency in stabilization of ferrofluids, in particular, regarding nano-magnetite in organic non-polar carriers [1]. The difference can be related to the interaction between acid molecules in organic non-polar solutions added to stabilized ferrofluids at the preparation stage. To clarify this point we study the concentration effects in pure solutions of OA, MA, SA based on deuterated benzene and decalin by means of small-angle neutron scattering (SANS). The behavior of the studied acids in the two solvents is quite similar. The increase in the concentration of MA and SA results in vigorous growth of solution viscosity followed by the formation of a new jelly-like phase. We associate this effect with the transition into the liquid crystalline (LC) state, which is well-known in the thermodynamics of stiff rod-like polymers. At the same time, such transition is not observed in the OA solutions.

The characteristic size of the acid molecules (2 nm) is close to the resolution limit of the SANS method. This means that only the Guinier region of the scattering curves can be reliably treated in the case of diluted isotropic solutions [2]. The important feature of the used analysis is that the dependence of the forward scattering intensity on the solute concentration is determined only by the isotropic part of the particle interaction potential [3]. The excluded volume repulsion is found to dominate over the attraction (presumably van der Waals forces) for OA and MA. In its turn, for SA the attractive component is higher than the repulsive one. This results in a shift of the transition into the liquid