

SYNTHESIS, STRUCTURAL AND CHEMICAL CHARACTERIZATION OF $\text{Ca}(\text{HO}_3\text{PCH}_2)_2\text{-N}(\text{H})\text{-(CH}_2)_6\text{-N}(\text{H})\text{-(CH}_2\text{PO}_3\text{H})_2\cdot 2\text{H}_2\text{O}$

L. León-Reina^a, A. Cabeza^b, R.M.P. Colodrero^b, M.A.G. Aranda^b,
E. Barouda^c, K.D. Demadis^c

^aServicio Central de Apoyo a la Investigación, Universidad de Málaga, 29071-Málaga, Spain

^bDepartment of Inorganic Chemistry, University of Málaga, 29071-Málaga, Spain

^cDepartment of Chemistry, University of Crete, Voutes, Heraklion GR-71003, Crete, Greece

The structural and functional chemistry of inorganic-organic hybrid materials have recently attracted considerable attention due to a plethora of potential applications such as gas storage, catalysis, and ion exchange [1]. In the area of metal phosphonates, special attention has recently been placed on the use of tetraphosphonates for the preparation of new crystalline compounds with open structures. Phosphonic acids are versatile ligands that allow synthetic access to a great number of structural motifs varying from closely packed 3-D to pillared-layered or open framework structures depending on the nature of the organic groups and the metal ion used [2].

We have focused our study on the synthesis, structural and chemical characterization of a new calcium hexamethylenediamine-*tetrakis*(methylenephosphonate) material, $\text{Ca}(\text{HO}_3\text{PCH}_2)_2\text{-N}(\text{H})\text{-(CH}_2)_6\text{-N}(\text{H})\text{-(CH}_2\text{PO}_3\text{H})_2\cdot 2\text{H}_2\text{O}$ (**I**). This compound has been prepared as polycrystalline powder at room temperature and also by hydrothermal procedure. The x-ray thermodiffraction study in combination with thermal analysis shows the existence of an anhydrous phase at 250°C, (**II**). The rehydration of **II** occurs spontaneously and reversibly at room temperature. Both phases crystallize in triclinic unit cells and their structures have been solved by *ab initio* methodology from strictly monochromatic laboratory X-ray powder diffraction data. The frameworks have been refined by the Rietveld method. **I** and **II** show layered frameworks with the tetraphosphonate groups bridging Ca^{2+} centers (Figure 1). The layers are held together only by H-bonding.

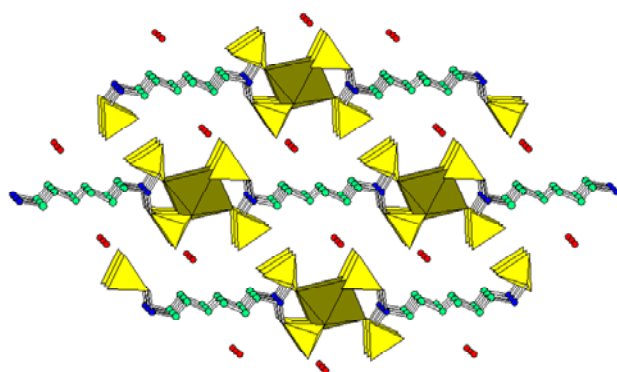


Figure 1. Structure of **I** with the water molecules as red spheres between the organo-inorganic layers.

References

- [1] F. Constantino, T. Bataille, N. Audebrand, E.L. Fur, C. Sangregorio, *Cryst. Growth Des.* 7, **2007**, 1881.
- [2] K.D. Demadis in: “*Progress in Solid State Chemistry Research*”, Ed. Ronald W. Buckley, 2007, 109.

The water molecules are situated in the interlamellar space, interacting by H-bonds and their loss at 250°C causes a reversible “sliding” of the layers to give the anhydrous phase.

The intercalation of NH_3 in **I** led to a new crystalline phase.

The relationship between the crystal structures of the different phases will be reported.