

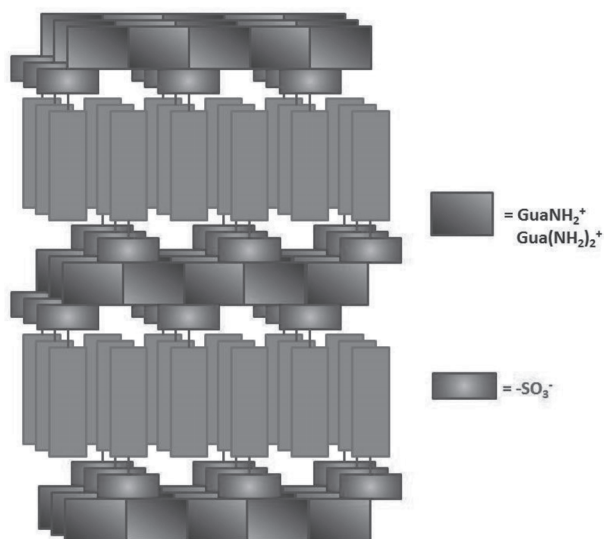
MS25-P9 Aminoguanidine and diaminoguanidine as adaptive cationic building blocks in organosulfonate structures. Arie van der Lee,^a Yves-Marie Legrand,^a Dan Dumitrescu,^b Mihail Barboiu^a ^a*Institut Européen des Membranes, Place Eugène Bataillon CC047, 34095 Montpellier Cedex 5, France,* ^b*Politehnica University of Bucharest, Spl. Independentei 303a, Bucharest, Romania*
E-mail: avderlee@univ-montp2.fr

Crystal engineering is a very delicate process which depends on many factors, and, as a consequence the final structure can rarely be predicted. Crystal engineering usually overcomes these obstacles by relying on strong, directional interactions like hydrogen bonding and dipolar forces.

The structural backbone of one of the most versatile and widely used systems, guanidinium-sulfonate assemblies, is a honeycomb lattice of $R_2^2(8)$ H-bond rings which assemble into ribbons and larger $R_6^3(12)$ patterns. The numerous papers published on this subject provide ample amounts of data on the effect of organic R substituent on crystal packing and overall structure type (bilayer, brick etc.).

To our knowledge no attempt was made to change the cationic component in these systems, the guanidinium moiety. The aim of the current work is to investigate the structural versatility of aminoguanidine and diaminoguanidine as cationic components together with representative organic sulfonates.

The 7 new crystal structures demonstrate the versatility of these new cationic components to form supramolecular hydrogen-bonding assemblies. Furthermore, aminoguanidine proved to be adaptable, by forming a $R_2^2(10)$ dimer in the structures where the total number of hydrogens available of H-bonding exceeds the total number of H-bond acceptors. Diaminoguanidine presented this motif in all the structures studied, with the orientation of the elongated dimer mimicking the width of the organic group from the sulfonates.



Schematic representation of a new $\text{Gua}(\text{NH}_2)_2^+\text{R-SO}_3^-$ structure

Keywords: crystal engineering; hydrogen-bond patterns; supramolecular assemblies

MS26-P1 Luminescent proton conducting lanthanide carboxyphosphonate open-framework hybrids. M.A.G. Aranda,^a R.M.P. Colodrero,^a P. Olivera-Pastor,^a E.R. Losilla,^a A. Cabeza,^a K.E. Papathevasiou,^b N. Stavgiannoudaki,^b K.D. Demadis,^b D. Choquesillo-Lazarte,^c J.M. Garcia-Ruiz,^c ^a*University of Malaga, Spain,* ^b*University of Crete, Greece,* ^c*CSIC-Granada, Spain*
E-mail: g_aranda@uma.es

A new family of multifunctional open-framework lanthanide-carboxyphosphonates [$\text{Ln}=\text{La, Ce, Pr, Sm, Eu, Gd, Tb}$ or Dy ; and ligand=2-hydroxophosphonoacetic acid: H_3HPA] has been prepared. All compounds, $\text{Ln}_3(\text{H}_{0.75}\text{O}_3\text{PCHOHCOO})_4 \times x\text{H}_2\text{O}$ ($x=15-16$, LnHPA) are orthorhombic, $V \sim 4000 \text{ \AA}^3$, and two types of structures were isolated: series-I and series-II crystallize in $\text{Iba}2$ and $\text{Pca}n$ space groups, respectively. Crystal structures were derived from microcrystal diffraction and Rietveld refinement of powder diffraction data. The synthetic outcome depends on the pH of synthesis and the ionic radius of Ln. For both series, the 3D frameworks result from the linkage of similar organo-inorganic layers, in the ac -plane, by central lanthanide cations, which yield trimeric units. Large oval-shaped 1D channels (see attached figure) are formed by the spatial separation of the layers along the b -axis and filled with lattice water molecules. LnHPA products were studied by powder X-ray (thermo)diffraction, infrared spectroscopy, solid state ^{31}P and ^1H NMR spectroscopy, thermal analysis, scanning electron microscopy and photoluminescence. LnHPA materials undergo a remarkable crystalline-to-amorphous-to-crystalline transformation upon dehydration and rehydration cycles. Two representative members, LaHPA-I and GdHPA-II, were studied for characterizing their proton-conducting behavior. For LaHPA-I σ_T was $5.6 \cdot 10^{-6} \text{ S} \times \text{cm}^{-1}$ and for GdHPA-II σ_T was $3.2 \cdot 10^{-4} \text{ S} \times \text{cm}^{-1}$, both at 98% of relative humidity and 21°C . The dehydration-rehydration chemistry was also followed by photoluminescence spectroscopy. It is shown that loss and re-uptake of water molecules are accompanied by clear changes in the corresponding spectra and lifetimes of the EuHPA-II.

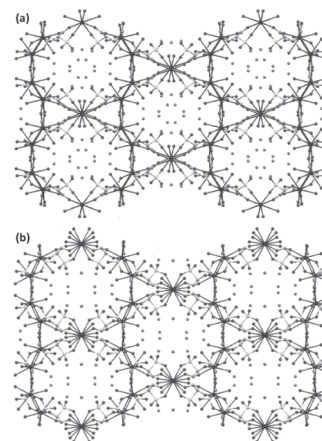


Figure. c-axis view of the crystal structures of (a) LaHPA-II and (b) LaHPA-I.

Keywords: MOFs, powder diffraction, transformations