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STRUCTURAL VARIABILITY IN MULTIFUNCTIONAL METAL Xylenediaminetetraphosphate HYBRIDS

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The two cornerstones in the field of MOFs are the Secondary Building Units (SBU's or "bricks") and the organic linkers. The structural tunability of crystalline MOFs coupled, when possible, with high chemical and thermal robustness, makes them suitable materials to correlate structure with function [1]. Hence, the research focus has been set recently to the potential applications of some of these compounds, including phosphonate-based MOFs [2].

We report two families of isostructural divalent (Ca, Mg, Co, Zn) hybrid phosphonate MOFs based on the tetraphosphonate ligands 1,4- and 1,3-bis(aminomethyl)benzene-*N,N'*-bis(methylenephosphonic acid), (H₂O₃PCH₂)₂-N-CH₂C₆H₄CH₂-N(CH₂PO₃H₂)₂, (designated as **p-C₁₂H₂₀O₁₂N₂P₄** or **m-C₁₂H₂₀O₁₂N₂P₄**, respectively). The use of these two functionalized ligands, otherwise chemically and structurally quite similar, represents a good example of how small stereochemical changes in the organic linker may dramatically affect structural features and dimensionality of the resulting solids and, hence, their final properties. The crystal structures of representative compounds of each family were solved ab initio from synchrotron powder diffraction data ($\lambda=0.2998$ Å, beamline ID31-ESRF) and were used as starting models for the Rietveld refinements of the remaining components. **M-p-C₁₂H₂₀O₁₂N₂P₄** (M = Mg, Co and Zn) present low dimensionality (1D) within a wide range of experimental conditions (figure 1). In contrast, solids containing the linker **m-H₈L**, **M-m-C₁₂H₂₀O₁₂N₂P₄** (M = Mg, Ca and Zn) tend to acquire a 3D pillared open-framework for a wide range of metal ion sizes (figure 2). Two representative members, **Mg-p-C₁₂H₂₀O₁₂N₂P₄** and **Zn-m-C₁₂H₂₀O₁₂N₂P₄**, were studied for characterizing their proton-conducting behavior. At 98 % RH and T = 297 K, σ are close to $9.4 \cdot 10^{-5}$ S·cm⁻¹ for both compounds [3]. Their crystal structures, thermal stability and proton conductivity properties will be reported and discussed.

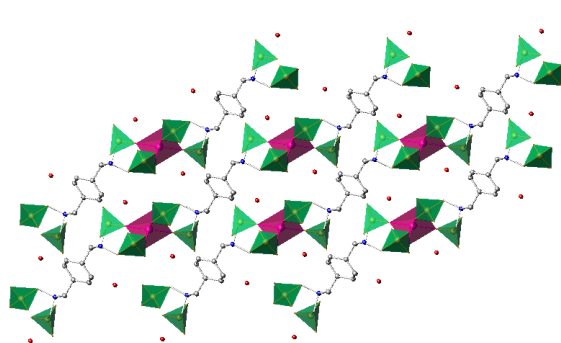


Figure 1. Packing of the hybrid chains in the crystal structure of $M-p-C_{12}H_{20}O_{12}N_2P_4 \cdot 4H_2O$ ($M = Mg, Co, Zn$)

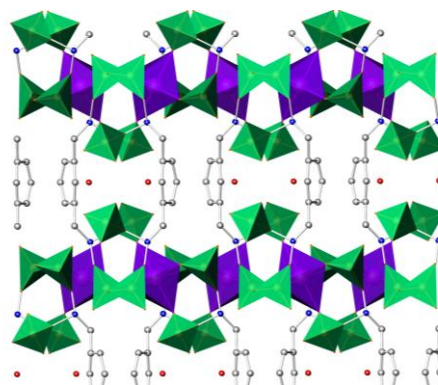


Figure 2. 3D open-framework of $M-m-C_{12}H_{20}O_{12}N_2P_4$ ($M=Ca, Mg, Zn$), viewed along the [010].

REFERENCES

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