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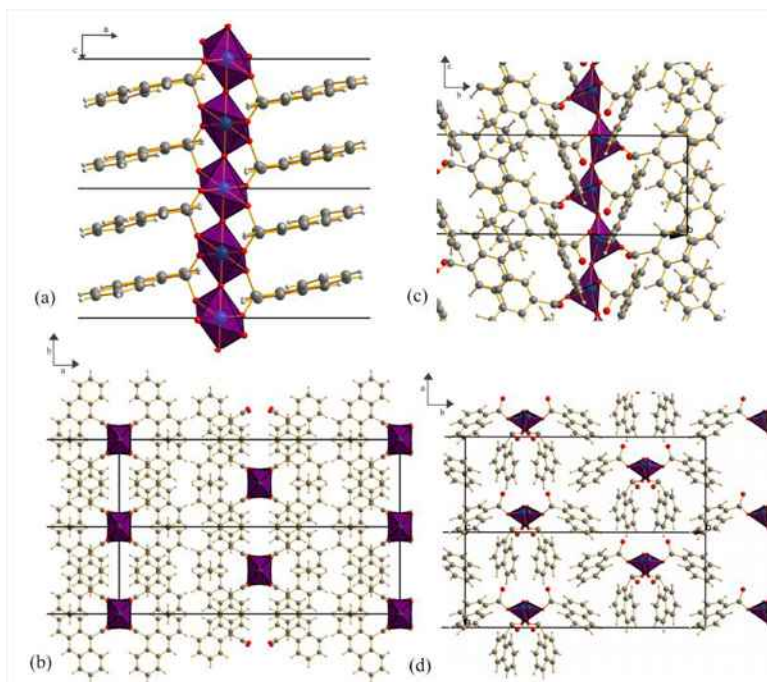
Crystal Structures Of Several Inorganic-Organic Hybrids Solved From Powder XRD

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When dealing with the crystal structure solving of low-crystalline materials, it is of paramount importance to combine DFT geometry optimization with direct-space methods in order to find the correct structural model. Particularly, in the case of inorganic-organic hybrids prepared by solvothermal route, finite dimensional single crystal is very difficult to obtain. Hence, we present several successfully elucidated crystal structures from the powder XRD of the low-crystalline inorganic-organic hybrids: Cr(HL)Cl₃, HL=Hbdmpza (1), [1] VO(C10H7COO)₂ (2), VO(C14H9COO)₂ (3). All of these structures have been solved from powder XRD data, either from laboratory or synchrotron source, by combining direct-space methods (simulated annealing), DFT geometry optimization, and constraint Rietveld refinement. The solid compound 1 was isolated in acetonitrile by starting CrCl₃·9H₂O and HL only in a concentrated solution, from which microcrystalline aggregates precipitated. Additionally, the presence of a carboxylate proton in HL stabilizes the structure by H-bonds, but also enables adsorption of moisture. Other two hybrids were synthesized in o-xylene by reacting vanadium (V) triisopropoxide with 1-naphthalenecarboxylic [2] or 9-anthracenecarboxylic acid. [2] They contain one-dimensional chain of corner-sharing tetrahedra in the case of VO(C10H7COO)₂ (Figure 1(a), (c)), and corner-sharing octahedra for VO(C14H9COO)₂ (Figure 1(b), (d)) oriented along orthorhombic/monoclinic c-axis, respectively. While VO(C14H9COO)₂ exhibits bidentate bridging binding of organic moiety to the metal center, VO(C10H7COO)₂ shows monodentate mode as evidenced from DFT and infrared spectroscopy. The obtained crystal structures were further verified by direct methods (ab initio approach). I. D. acknowledges financial support from the Unity through Knowledge Fund (www.ukf.hr) of the Croatian Ministry of Science, Education and Sports (Grant Agreement No. 7/13).

[1] N. Kitanovski, N. Borsan, M. Kasunič, V. Francetič, J. Popović, I. Djerdj, X. Rocquefelte, J. Reedijk, B. Kozlevčar, *Polyhedron*, 2014, 70, 119-124, [2] I. Djerdj, J. Popovic, J. Stare, G. Ambrozic, S.D. Skapin, B. Kozlevcar, D. Pajic, Z. Jaglicic, Z. C. Orel, *J. Mater. Chem.* 2012, 22, 10255-10265



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