Polyoxophosphomolybdates

Role of Hydrogen-Bonded Interactions in the Crystal Packing of Phenylenediammonium Phosphomolybdates

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Abstract
Self-assembled synthesis of three new organic/inorganic hybrid solids (1?3) in the presence of isomeric phenylenediammonium ions (p-, m-, and o-) demonstrates the role of nonbonding interactions in the construction of phosphomolybdate-based solid-state assemblies. In 1, crystal packing is dominated by two kinds of supramolecular assemblies:? an unusual pentadecameric water cluster linked through p-phenylenediammonium (ppda) cations and a hydrogen-bonded assembly of a ppda cation with four phosphomolybdate anions. In 2, a pair of m-phenylenediammonium (mpda) cations linked through ?⋯? interactions envelops a phosphomolybdate anion from either side through hydrogen bonding mediated by water molecules forming butterfly-like supramolecular motifs. In 3, a new kind of O?W?O?W (organic?water) linker formed by alternate hydrogen bonding between o-phenylenediammonium (opda) and water molecules; such motifs are well decorated around a pentamolybdate cluster anion leading to the formation of the three-dimensional architecture. Crystal structures of 1?3 reveal that supramolecular synthons earlier observed between water and organic ammonium cations in the presence of octamolybdate anions are broken in the presence of diphosphopentamolybdates due to the latter anion’s strong affinity for hydrogen bonding with the cations.

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