Assemblies of Two New Metal-Organic Frameworks Constructed from Cd(II) with 2,2'-Bipyrimidine and Cyclic Oxocarbon Dianions $C_nO_n^{2-}$ (n =4, 5)

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Two extended networks of Cd(II) with 2,2'-bipyrimidine (bpym) and cyclic oxocarbon dianions $C_nO_n^{2-}$ (n = 4, 5) with formulas $[Cd(C_4O_4)(bpym)_{0.5}(H_2O)]$ (1) and $[Cd(C_5O_5)(bpym)_{0.5}(H_2O)]$ (2) have been synthesized and characterized by singlecrystal X-ray diffraction studies. Structural determination reveals that, in compounds 1, each Cd center lies in a seven-coordinate environment bonded to two bpym nitrogen atoms and five oxygen donors from four squarate and one water molecules. The squarateacts as a bridging ligand with two different binding modes, a tetramonodentate (í4) and a bis-bridging (í4) coordination mode, linking the Cd(II) ions to form a two-dimensional (2D) metal-squarate layer. Adjacent layers are then mutually linked via bridges of bis-bidentate bpym ligands constructing a three-dimensional (3D) triangular metal-organic framework (MOF). In compound 2, each Cd center lies in an eight-coordinate environment bonded to two bpym nitrogen atoms and six oxygen donors from three croconate ligands and one water molecule. Each croconate ($C_5O_5^{2-}$) adopts a new bis-bidentate/monodentate (í5) bridging mode and links crystallographically identical Cd ions, forming a one-dimensional (1D) bichain. Adjacent bichains are then mutually linked via the bridges of bis-bidentate bpym ligands constructing a 2D layered MOF, which is then extended to a 3D supramolecular architecture by two intermolecular ð-ð interactions between the pyrimidyl rings of bpyms and between cyclic five-membered rings of croconates. Both MOFs are thermally stable, as evidenced by thermogravimetric analysis and in-situ powder X-ray diffraction measurements.