Title:	Two pillared-layer metal–organic frameworks based on the pinwheel trinuclear carboxylate-clusters of Zn(ii) and Co(ii): synthesis, crystal structures, magnetic study, and Lewis acid catalysis
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Abstract:	Using a dicarboxylic acid, [1,1′-biphenyl]-4,4′-dicarboxylic acid (H2L1) and an exobidentate ligand, (1E,1′E)-N,N′-(1,4-phenylene)bis(1-(pyridin-4-yl)methanimine) (L2), two 3D interpenetrated networks, {[Zn3(L1)3(L2)]·9H2O}n (Zn-MOF) and {[Co3(L1)3(L2)(DMF)]·0.5DMF}n (Co-MOF), have been prepared in good yields. The crystal structure analysis of Zn-MOF and Co-MOF revealed that both have a 3D pillared-layer structure based on pinwheel trinuclear metal–carboxylate clusters as secondary building units (SBUs). Furthermore, the structures also exhibited three-fold interpenetration. Although the overall networks in Zn-MOF and Co-MOF showed significant resemblances, there are marked differences in their crystal structures, which are associated with the coordination environment of the metal centre and the binding modes of the carboxylates. Gas adsorption studies (N2 at 77 K and 1 bar) indicated that Co-MOF is more porous than Zn-MOF. Magnetic measurements on Co-MOF indicate a significant antiferromagnetic interaction (45 K to 303 K) between trimeric Co(II) S = 3/2 spins through syn–syn carboxylato bridges. Both MOFs were studied for the Lewis acid catalyzed Knoevenagel condensation reactions between benzaldehydes and malononitrile with an active methylene group, where Zn-MOF was found to be a better catalyst than Co-MOF. This was supported by the Monte Carlo simulations indicating the better substrate binding ability of Zn-MOF than Co-MOF.
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