Title:	Crystal Engineering and Magnetostructural Properties of Newly Designed Azide/Acetate-Bridged Mn12 Coordination Polymers
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Abstract:	Crystal engineering of the coordination polymers where polynuclear clusters are building blocks constitutes an emerging class of chemistry. The fine-tuning of the structural motifs leads to interesting and varying magnetic properties. Owing to such properties, two rare μ6-oxo centered mixed-valent, azide or acetate-bridged coordination polymers viz, [{MnII2MnIII10Na2(μ6-O)2(N3)10(NO3)(H2O)4(thme)8}·3(Et3NH)]n (1) and [{MnII3MnIII9Na7(μ2-O)2(μ6-O)2(O)5(CH3O)(CH3CO2)11(thmp)8}·4(O)]n (2), with retention of a Mn12 metallic core in both polymers are obtained using tripodal polyalcohol 1,1,1-tris (hydroxymethyl)ethane (H3thme) and 1,1,1-tris (hydroxymethyl)propane (H3thmp) ligands, respectively. X-ray analysis shows that 1 is a one-dimensional coordination polymer where Mn12 units are propagating by bridging azide function. 1 shows the underlying net of 2,2,3C6 topological type. 2 forms a cyclic ring as a result of repeating Mn12 zigzag chains bridging by sodium and H2O. The topology of 2 results in a 31-nodal underlying 3,3,3,3,4,4,4,4,4,4,4,4,4,4,5,5,5,5,5,5,6,6,6,6,6,6,6,6,7,7-c net with a point symbol of the net of {3.4.5}2{3.47.52}2{32.410.52.6}{32.410.53}4{32.43.5.203.21}{32.43.5}6{32.44}2{32.46.52.63.7.8}{32.46.52}{34.44.52}{34.46.54.64.72.8}2{412.52.6}2{42.6}2{43}{45.5}3{45.6}{46.63.8}. In 1, a magnetic study ascertains the presence of antiferromagnetic interaction and shows single molecule magnet-like behavior with an energy barrier of 75.5 K. However, 2 exhibited strong antiferromagnetic interaction in dc studies. The super-paramagnetic-like slow relaxation of its magnetization was not observed for 2 in out-of-phase ac magnetic susceptibility due to the absence of a large enough energy barrier. Magnetization versus an applied dc field exhibited a hysteresis loop at 2 K with a coercivity of 1069.10 Oe and remanent magnetization of 0.374 μB in 1, while 2 has no coercivity in the hysteresis loop even at the lowest temperature (2.0 K), and no saturation was observed up to 7.0 T field supporting antiferromagnetic interactions present in the polymer.
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