Equilateral and symmetry breaking rare-earth triangles in sandwich-type polyoxometalates regulated by simple organic cations

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The sandwich-type polyoxometalates (POMs) formed by sandwiching a carbonate-bridged lanthanide equilateral triangle between two lacunary Keggin POMs have a possibility to give interesting magnetic properties, such as spin frustration[1], toroidal magnetic moment[2] and single molecule magnets[3]. In this work, seven sandwich-type POMs were obtained with organic cations of distinct symmetry: (CH₃)₃NH⁺Na⁺[(PW₆O₃₄)₂(H₂O)₁₀]RECO₃] (RE-MA; RE = Tb, Dy, Er and Y; MA = methylammonium), (CH₃)₃NH⁺[(PW₆O₃₄)₂(H₂O)₁₀]TbCO₃] (Tb-DMA, DMA = dimethylammonium), (CH₃)₃NH⁺[(PW₆O₃₄)₂(H₂O)₁₀]C₂O₃] (TriMA, TriMA = trimethylammonium), and (CH₃)₃N⁺[(PW₆O₃₄)₂(H₂O)₁₀]TMA] (Tb-TMA, TMA = tetramethylammonium). Two highly centrosymmetric space groups of P63/m and R3m in crystal RE-MA and Tb-TMA, and two polar space groups of Pna2₁ and Cmc2₁ in crystal Tb-DMA and Tb-TriMA, were achieved, respectively, by adjusting the symmetry of organic cations. MA⁺(Cₓₗₗ), DMA⁺(C₂ₙ), TriMA⁺(C₃ᵥ) and TMA⁺(Tₗₗ) cations possessing 3, 2, 1 and 0 hydrogen-bond sites are exploited, in which only MA⁺ cations constructed hydrogen-bond network of C₃ symmetry with sandwich-POM anions and water molecules utilizing three hydrogen-bonding sites at -NH₃⁺ moiety. Especially, hydrogen-bonding supramolecular units {[(MeNH₃⁺)ₖ(H₂O)ₖ]} having C₃h symmetry and compatible size with sandwich POM anions are constructed in crystal RE-MA as shown in Fig. 1. An ideal sandwich POM anion should display D₃h symmetry, in which the RE₃-triangle is equilateral having C₃ axis perpendicular to the plane. Successfully, equilateral RE₃-triangle is achieved in crystal RE-MA and Tb-TMA under the influence of high symmetric hydrogen-bonding supramolecular cation (C₃h) and TMA⁺ cation (Tₗₗ). Magnetic measurements indicate that RE-MA, Tb-DMA, Tb-TriMA and Tb-TMA exhibit field-induced single molecular magnetic behaviors.

References