Synthesis and structure of porous ionic crystals based on delta-Keggin-type aluminum polyoxocation

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Aluminum is the third most abundant element in the earth's crust and has complex solution chemistry. The hydrolysis of aluminum salts in water produces an array of polyoxoaluminum clusters with various sizes, widely used in catalysis, water treatment, and as pillaring agents.[1] Among the polyoxoaluminum clusters, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (**Al₁₃**) has five possible isomers of the Baker–Figgis–Keggin (Keggin) structure: α, β, γ, δ, and ε. We have previously obtained all-inorganic porous ionic crystals (PICs) by combining oppositely charged molecular ions (macroions) with T_d symmetry, ε-Keggin-type cation $[\varepsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (ε-$\mathbf{Al_{13}}$) and α-Keggin-type anions (e.g., $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$).[2] However, isomers/derivatives of δ-$\mathbf{Al_{13}}$ have been rarely reported in recent years. The present study describes the synthesis and structural characterization of a PIC of $[\delta\text{-}Al_{13}O_4(OH)_{25}(H_2O)_{11}][\alpha\text{-}CoW_{12}O_{40}]\cdot 29H_2O$ [**I**].

The all-inorganic PIC of **I** crystallized through a dissolution−recrystallization reaction in water for 3 days. Single crystal X-ray diffraction analysis reveals that oppositely charged macroions are combined, δ-$\mathbf{Al_{13}}$ with C_{3v} symmetry (Figure 1a) and $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$ with T_d symmetry (Figure 1b). Compound **I** contains 1D-channels with large apertures (ca. 13 Å × 6.5 Å) along the *b*-axis (Figure 1c) and is applicable as a solid catalyst in environmentally friendly acid reactions. To the best of our knowledge, this is the first example of isolating δ-$\mathbf{Al_{13}}$ polycation without capping sodium ions in the solid-state.[3,4]

(a) (b) (c)

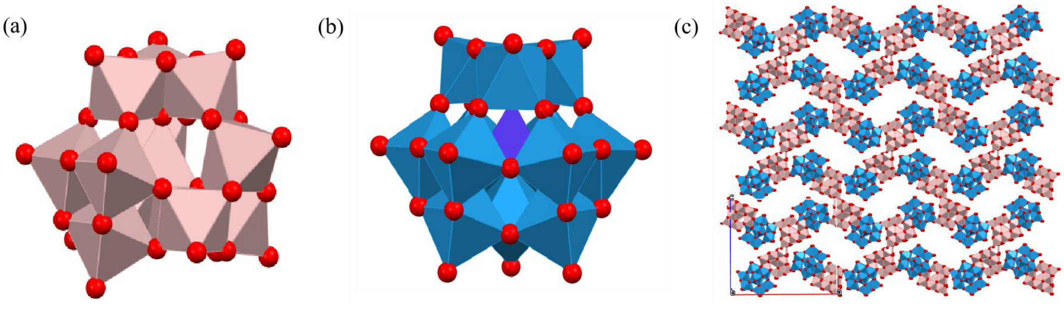

Figure 1.The crystal structure of (a) δ-Al_{13} (b) α-$CoW_{12}O_{40}^{6-}$ and (c) **I** along *b*-axis

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