

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^[2]. In this work, seven sandwich-type POMs were obtained with organic cations of distinct symmetry: $(\text{CH}_3)\text{NH}_3^+_{10}\text{Na}[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{ORE})_3\text{CO}_3]$ (**RE-MA**; RE = Tb, Dy, Er and Y; MA = methylammonium), $(\text{CH}_3)_2\text{NH}_2^+_{11}[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OTb})_3\text{CO}_3]$ (**Tb-DMA**, DMA = dimethylammonium), $(\text{CH}_3)_3\text{NH}^+_{8}\text{Na}_3[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OTb})_3\text{CO}_3]$ (**Tb-TriMA**, TriMA = trimethylammonium), and $(\text{CH}_3)_4\text{N}^+_6\text{Na}_5[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OTb})_3\text{CO}_3]$ (**Tb-TMA**, TMA = tetramethylammonium). Two highly centrosymmetric space groups of $P6_3/m$ and $R\bar{3}m$ in crystal **RE-MA** and **Tb-TMA**, and two polar space groups of $Pna2_1$ and $Cmc2_1$ in crystal **Tb-DMA** and **Tb-TriMA**, were achieved, respectively, by adjusting the symmetry organic cations. $\text{MA}^+(C_{3v})$, $\text{DMA}^+(C_{2v})$, $\text{TriMA}^+(C_{3v})$ and $\text{TMA}^+(T_d)$ cations possessing 3, 2, 1 and 0 hydrogen-bond sites are exploited, in which only MA^+ cations constructed hydrogen-bond network of C_3 symmetry with sandwich-POM anions and water molecules utilizing three hydrogen-bonding sites at $-\text{NH}_3^+$ moiety. Especially, hydrogen-bonding supramolecular units $\{(\text{MeNH}_3^+)_m(\text{H}_2\text{O})_n\}$ having C_{3h} 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 D_{3h} symmetry, in which the RE_3 -triangle is equilateral having C_3 axis perpendicular to the plane. Successfully, equilateral RE_3 -triangle is achieved in crystal **RE-MA** and **Tb-TMA** under the influence of high symmetric hydrogen-bonding supramolecular cation (C_{3h}) and TMA^+ cation (T_d). Magnetic measurements indicate that **RE-MA**, **Tb-DMA**, **Tb-TriMA** and **Tb-TMA** exhibit field-induced single molecular magnetic behaviors.

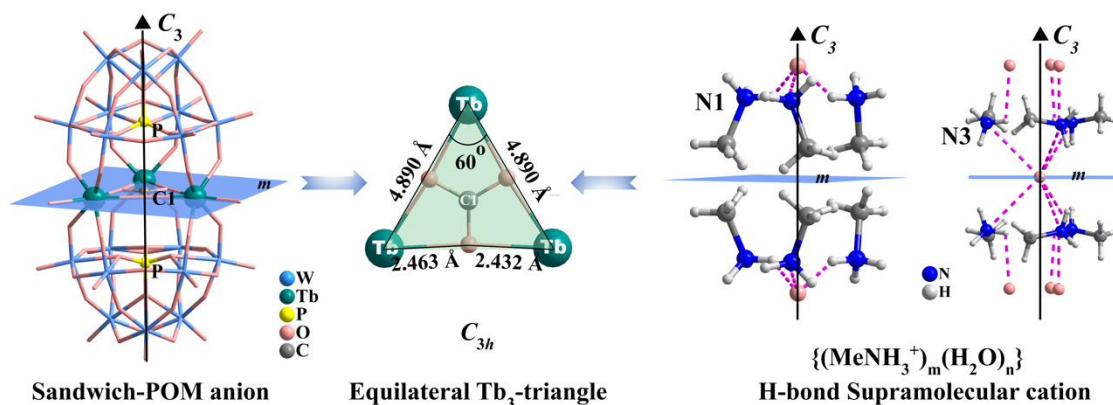


Fig. 1. The crystal structure of $(\text{CH}_3)\text{NH}_3^+_{10}\text{Na}[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OTb})_3\text{CO}_3]$ (**Tb-MA**).

References

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