

Structures of Carbonate-Bridged Lanthanoid Triangles Sandwiched by Lacunary Keggin Polyoxometalates

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1. Introduction

Polyoxometalates (POMs) which are metal–oxygen clusters with versatile structural topologies have been attracting much attention in diverse fields such as catalysis, magnetism, and biological systems.^[1] The lacunary Keggin POMs are constructed by removing a triad of MO₆ octahedra units from Keggin type POMs, and can act as ligands toward carbonate-bridged Lanthanoid triangles. In this way sandwich-type POMs can be formed with different spin topologies, and in general are reasonably well separated from one another by the bulky nonmagnetic POMs.^[2] Such Lanthanoid-containing sandwich-type POMs have the possibility to give interesting properties such as single-molecule magnet (SMM) behavior with spin frustrated topology. In this work, five kinds of sandwich-type POMs with different cations, X_{11-n}Na_n[(PW₉O₃₄)₂(H₂OTb)₃CO₃] (0 < n < 11; X = Na⁺ (**1**), methylammonium (**2**), dimethylammonium (**3**), trimethylammonium (**4**), tetramethylammonium (**5**)), were synthesized to investigate the effect of organic cations to the structure of POMs in the crystals.

2. Experimental

TbCl₃·6H₂O was dissolved in water, and the pH was adjusted to 6.1 using a solution of Na₂CO₃. Na₈H[(PW₉O₃₄)] was added into the aqueous solution with stirring for 1 h at 80 °C. Insoluble material was removed by centrifugation, and counter cation was added into the solution. The colorless crystals were obtained by slow evaporation.

3. Results and discussion

The absorption bands of ν_{C-N} (1415 cm⁻¹) and ν_{C-O} (1470 cm⁻¹), as well as ν_{P-O} (1060 cm⁻¹, 1010 cm⁻¹) and ν_{W-O-W} (700 cm⁻¹ - 950 cm⁻¹) in IR spectra for crystals **2-5** indicated the presence of organic cations and the formation of sandwich-type POMs, respectively. Single crystal structural analyses revealed that the three terbium ions were bridged by carbonate ion between two lacunary Keggin POMs, forming Tb triangle in sandwich-type POMs (Fig. 1). The triangle shapes and POM arrangement were different in the crystals: the triangles in crystals **2** and **5** were equilateral with C₃ axis though the triangle plane and the sandwich-type POM anions were arranged along the c-axis (Fig. 2 (a)), whereas the triangles in crystal **1** and **4** were distorted and POM anions were not arranged in the same direction as the symmetric axis (Fig. 2 (b)).

4. References

- [1] D. Long, *et al.*, *Angew. Chem.*, **2010**, 49, 1736.
- [2] A. Muller, *et al.*, *Am. Chem. Soc.*, **1998**, 239-231.

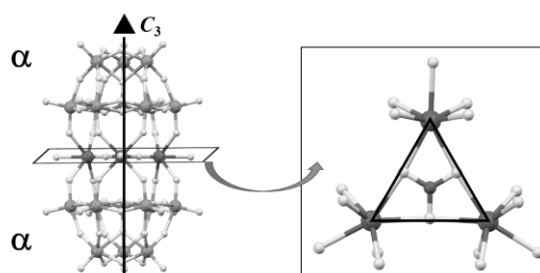


Fig. 1. The structure of the sandwich-type POM and carbonate-bridged Tb triangle in crystals **2** and crystal **5**

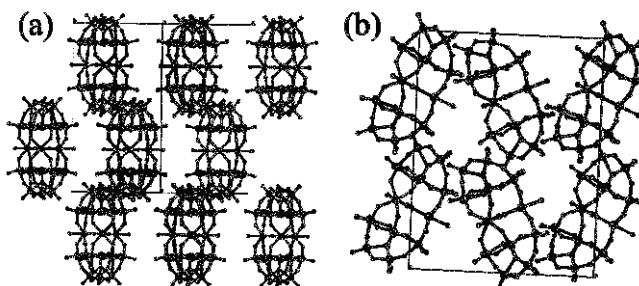


Fig. 2. The packing structures of (a) crystal **2** and (b) crystal **4**.