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A superposed kagome-lattice Crystallization of a Keplerate-type polyoxometalate

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1 Introduction

A frequently occurring packing mechanism for an ionic crystal is to arrange larger ions into a close-packed array and smaller ones into the interstices between the larger ones. In this context, it seems reasonable that the exceedingly large Keplerate-type spherical polyoxometalates, the $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ anion (hereafter, abbreviated as $\{Mo_{132}\}$), prefer to crystallize into cubic or trigonal space group types where the huge spherical anions (approximate diameter of 30 Å) adopt strict or slightly distorted cubic close packing arrays. However, the $\{Mo_{132}\}$ anion, which consists of 12 pentagonal $[Mo^{VI}_6O_{21}(H_2O)_6]^{6-}$ and 30 $[Mo^{V}_2O_4(CH_3COO)]^{+}$ moieties (Figure 1), is not completely isotropic but approximates to the I_h symmetry. It is incompatible with the site symmetry of the spheres in any type of close packings. Therefore, introduction of intermolecular interactions specific to the local structures of $\{Mo_{132}\}$ could lead to a different and less dense arrangement of the anions. By using Sr^{2+} as counter cations, we succeeded in crystallizing $\{Mo_{132}\}$into an unprecedented superposed kagome-lattice structure with huge channels.[1]

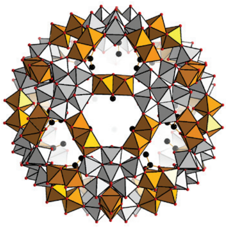

Fig. 1: Structure of $\{Mo_{132}\}$.

2 Experiment

A 15.0 mL aqueous solution dissolving 0.50 g of $(NH_4)_{42}\{Mo_{132}\}\cdot ca.300H_2O\cdot ca.10CH_3COONH_4$ was mixed with a 15.0 mL aqueous solution containing 1.26 g of $SrCl_2\cdot 6H_2O$. The mixed solution was heated to 65 °C for 1.5 h and kept at 40 °C for two weeks. After the solution cooled down to the room temperature, dark red hexagonal prismatic crystals of $Sr_{18.5}(NH_4)_5[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot mH_2O$ (**1**) were precipitated. Single crystal X-ray diffraction experiment was carried out at the NW2A beamline of PF-AR.

3 Results and Discussion

Compound **1** crystallizes in the space group $P6_3/mmc$. The $\{Mo_{132}\}$ anions are located at the $2/m$ sites to make a superposed kagome-lattice. The $\{Mo_{132}\}$ anions are connected so as to sandwich hydrated Sr^{2+} cations with their Mo_9O_9 pores. Each connection is supported by two additional Sr^{2+} cations that are directly bound to the terminal O atoms of the two $\{Mo_{132}\}$ anions. At the connections parallel to the crystallographic *a*, *b* or *a*+*b* axes (perpendicular to the *c* axis, Figure 4a), two O–Sr–O linkages stem from the Mo atoms that belong to the Mo_9O_9 pores but belong to different $[Mo^{VI}_6O_{21}(H_2O)_6]^{6-}$ moieties. The two Mo_9O_9 pores are almost parallel to each other with the dihedral angle of 11.16(1)° and the distance between two $\{Mo_{132}\}$ is 30.765 Å. Due to the I_h symmetry, $\{Mo_{132}\}$ can accommodate up to only four Mo_9O_9 pores on a great circle. Therefore, this type of interaction leads to a kagome-lattice sheet of $\{Mo_{132}\}$ spanning parallel to the crystallographic *ab* plane. Six $\{Mo_{132}\}$ surrounding the large space at the origin of the unit cell point their $[Mo^{V}_2O_4(CH_3COO)]^{+}$ moieties to the space and they cannot establish similar interactions with another $\{Mo_{132}\}$ in this cavity. As a result, the cavity is left unoccupied by $\{Mo_{132}\}$ and presumably filled with disordered water molecules.

The kagome-lattice sheets are superposed to form a three-dimensional framework as shown in Figure 2. The sheets are connected by a similar interaction between two $\{Mo_{132}\}$ through their Mo_9O_9 pores. The dihedral angle of the two Mo_9O_9 pores is as large as 39.55(1)°. Thus the two O–Sr–O linkages supporting this connection stem from two Mo atoms that belong to the same $[Mo^{VI}_6O_{21}(H_2O)_6]^{6-}$ moiety but are not in the Mo_9O_9 at the rim of the pore. As a result, the kagome-lattice sheets are arranged so that the cavities of one sheet fall exactly above those of the sheet below, leading to a channel running through the crystal along the *c* axis.

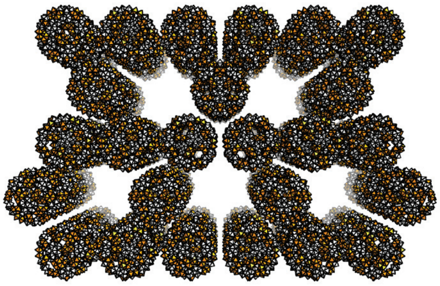

Fig. 2: Superposed kagome lattice of $\{Mo_{132}\}$.

References

[1] M. Saito, T. Ozeki, Dalton Trans. (2012) in press, DOI: 10.1039/C2DT30582H.

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