

Formation of a Kagome Lattice with Huge Channels by Very Large Spherical Anions

A very large spherical polyoxometalate anion known as the Keplerate, $[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$, has been crystallized into an unprecedented hexagonal phase with the unit cell dimensions of $a = 61.530(1)$ and $c = 63.896(1)$ Å when precipitated with Sr^{2+} cations. Single-crystal X-ray diffraction at the AR-NW2A beamline revealed that the compound shows a unique structure where the large spherical anions with the I_h symmetry are packed into a superposed kagome lattice possessing huge channels with the approximate diameter of 3.0 nm.

Nature abhors a vacuum and, as a consequence, crystals prefer close packed structures. Ionic crystals are no exception; a frequently adopted mechanism to achieve a dense packing for an ionic crystal is to arrange larger ions into a close-packed structure and smaller ones into the interstices between the larger ones. For example, the sodium chloride structure is regarded as a cubic close-packed array of the chloride anions with the sodium cations in its octahedral interstices. In principle, the larger the discrepancy between the radii of the cation and the anion is, the more effectively this mechanism should work. Therefore, it seems reasonable that the extremely large Keplerate-type spherical polyoxometalates, the $[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ anion (abbreviated as $\{\text{Mo}_{132}\}$ hereafter) [1] and its derivatives that measure approximately 3.0 nm in diameter, crystallize into cubic or trigonal space group types where the huge spherical anions adopt strict or slightly distorted cubic close packing arrays.

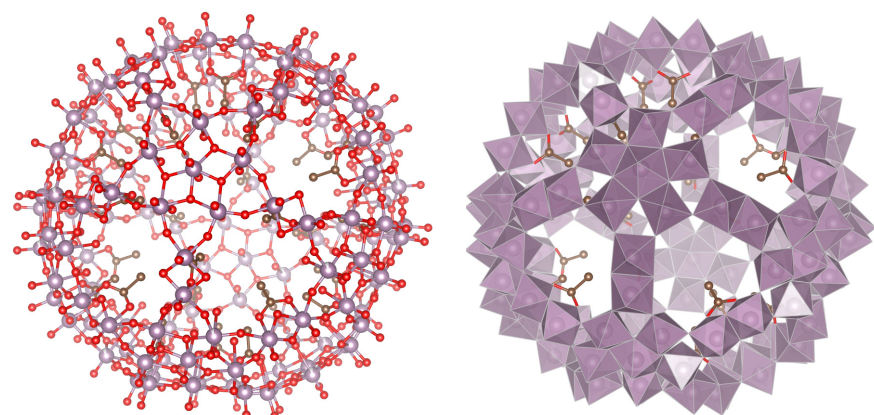


Figure 1: Structure of the $[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ anion in ball-and-stick (left) and polyhedral (right) representations (prepared by using VESTA 3.1.6 [3]).

However, the $\{\text{Mo}_{132}\}$ anion that consists of 12 pentagonal $[\text{Mo}^{\text{VI}}_6\text{O}_{21}(\text{H}_2\text{O})_6]^{6-}$ and 30 $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})]^+$ units (Fig. 1) does not adopt the completely spherical symmetry but better approximates the I_h symmetry. The I_h symmetry is not compatible with the site symmetry of the spheres in any type of close packings (O_h for the cubic close packing and D_{3h} for the hexagonal one, for example). Therefore, introduction of intermolecular interactions specific to the structures of $\{\text{Mo}_{132}\}$ could lead to a different and less dense arrangement of the anions. A looser arrangement of the anions thus constructed would yield interstices with larger volume than those in the close packed structures. It is worth noting that the use of the large spherical anions as building blocks will intrinsically preclude the formation of interpenetrating structures, which often form when thin stick-like building blocks are employed. By using Sr^{2+} , a multivalent cation that can potentially interact with $\{\text{Mo}_{132}\}$ in a site-specific manner, we obtained a new hexagonal crystal of $\text{Sr}_{18.5}(\text{NH}_4)_5[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}] \cdot 149.25\text{H}_2\text{O}$ (compound 1).

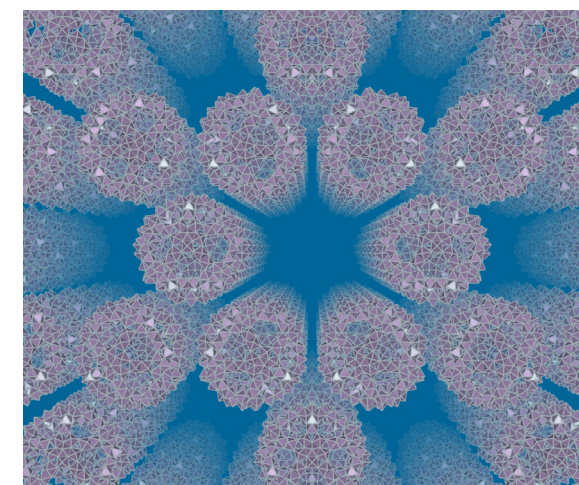


Figure 2: Crystal packing of the Sr^{2+} salt of $[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ anion viewed along the c axis (prepared by using VESTA 3.1.6 [3]).

Compound 1 crystallizes in the space group $P6_3/mmc$ with the unit cell dimensions of $a = 61.530(1)$ and $c = 63.896(1)$ Å. Single-crystal X-ray diffraction at the AR-NW2A revealed that $\{\text{Mo}_{132}\}$ anions are located at the $2/m$ sites to make a superposed kagome lattice. The $\{\text{Mo}_{132}\}$ anions are connected so as to sandwich hydrated Sr^{2+} cations with their Mo_9O_9 pores, each of which is surrounded by three $[\text{Mo}^{\text{VI}}_6\text{O}_{21}(\text{H}_2\text{O})_6]^{6-}$ and three $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})]^+$ units. Each connection is supported by two additional Sr^{2+} cations that are directly bound to the terminal O atoms of the two $\{\text{Mo}_{132}\}$ anions. Due to the I_h symmetry, $\{\text{Mo}_{132}\}$ 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 $\{\text{Mo}_{132}\}$ spanning parallel to the crystallographic ab plane. Six $\{\text{Mo}_{132}\}$ surrounding the large void point their $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})]^+$ moieties to the space and they cannot establish similar interactions with another $\{\text{Mo}_{132}\}$ in this cavity. As a result, the cavity is left unoccupied and presumably filled with disordered water molecules. The kagome-lattice sheets are superposed to form a three-dimensional framework as shown in Fig. 2. The sheets are connected by a similar interaction between two $\{\text{Mo}_{132}\}$ through their Mo_9O_9 pores. 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, whose diameter measures approximately 3.0 nm.

In summary, we have successfully prepared an unprecedentedly arranged array of the Keplerate type $[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ anion, whose structure was successfully determined by exploiting synchrotron radiation. The current strategy for the design of crystals with huge channels could be applied to the development of catalyses, ionic conductors and small molecule storing materials.

REFERENCES

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BEAMLINE

AR-NW2A

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