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Crystal Engineering through Face Interactions between Tetrahedral and Octahedral Building Blocks: Crystal Structure of $[\epsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]_2[V_2W_4O_{19}]_3(OH)_2 \cdot 27H_2O$

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A new intercluster salt crystal $[\epsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]_2[V_2W_4O_{19}]_3(OH)_2 \cdot 27H_2O$ (**1**) was synthesized from the reaction of octahedral Lindqvist-type polyoxometalate $[V_2W_4O_{19}]^{4-}$ and truncated tetrahedral Keggin-type $[\epsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ cluster ions. The crystal structure shows that the oppositely charged cluster ions are arranged alternately and have their contacting faces parallel to each other for maximal interactions, both electrostatic and hydrogen bonding. The face-to-face interaction mode of the clusters allows analysis of the crystal structure in an analogy to the bond directionality of conventional inorganic crystals. Therefore, the packing of clusters in **1** is that of As_2O_3 (Claudetite-II). With the bond directionality, the crystal has large one-dimensional channels with a cross-sectional area of 14.17 × 13.88 Å^2 that are filled by lattice water and charge-balancing OH^-.

Introduction

Crystal engineering using building blocks is an important emerging area of chemistry research with the desires to develop general strategies of forming crystals with various internal structures and functionalities for applications such as sorption media and catalysts.[1] Several different modes of interactions between building blocks, including coordination bonds,[2] hydrogen bonds,[3] and ionic interactions,[4] have been proposed and widely explored. Toward this end, we have recently introduced a method, namely, ionic interactions between oppositely charged cluster ions.[5] Through these works we have learned that there are several rules that govern the cluster packing: First, the electrostatic interactions between differently charged cluster ions arrange them alternately. Second, in addition to the electrostatic interactions, there are numerous hydrogen bonds between neighboring cluster ions. Third, to optimize these electrostatic and hydrogen-bonding interactions between the cluster ions, the cluster ions are arranged in such a way to ensure maximal

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contacts between them with their faces nearly parallel to one another. With these observations, it is a logical consequence to attempt reactions of cluster ions that are shaped as Platonic solids. The face-to-face contacts between cluster ions of regular shapes might be considered as a means to control the directionality of cluster arrays, an analogy to the directional bonds of conventional inorganic solids. Here we report a new crystal structure, wherein octahedral Lindqvist-type $[V_2W_4O_{19}]^{4-}$ (V_2W_4) clusters and truncated tetrahedral Keggin-type $[\epsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}) clusters are assembled through interactions between their triangular faces.

$$[\epsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]_2[V_2W_4O_{19}]_3(OH)_2 \cdot 27H_2O\ (\mathbf{1})$$

The regular packing of the cluster ions through face contacts and the subsequent large pores in **1** demonstrate a new strategy of crystal engineering.

Experimental Section

Synthesis and Characterization. Al_{13} Solution.[6] A 2 M NaOH solution was dropwisely added into a 0.2 M $AlCl_3 \cdot 6H_2O$ solution until the OH^-/Al^{3+} ratio became 2.3. The turbid solution was aged in an oven at 85 °C for 4 h to make a clear Al_{13} solution of pH 4.

V_2W_4 Solution.[7] A 0.1 M $NaVO_3$ solution and a 0.1 M $Na_2WO_4 \cdot 6H_2O$ solution were mixed to make a solution of V:W ratio 1:2. The pH of the solution was adjusted to 5 by adding a 6 M HCl solution.

The crystals of **1** were synthesized by a diffusion reaction between Al_{13} and V_2W_4 solutions using the crystal growth apparatus described previously.[5c] Briefly, we have assembled two glass ampules and a tube into a reactor that has three partitions separated by membrane filters for a slow diffusion reaction. Al_{13} and V_2W_4 solutions in the molar ratio 2:3 were placed in each end of the reactor, and the center partition was filled with distilled water. The assembled reactor was kept undisturbed for a few days. Bright-orange colored rhombic crystals formed among a yellow precipitate in the middle tube after a few days. The crystals were separated from the precipitate by decantation and filtration. The yield of the crystals was 6.5% based on Al. IR spectra were obtained with a Nicolet 1700 FT-IR spectrometer using KBr disks dispersed with sample powders in the 4000−400 cm^{-1} range. The bands in the IR spectra are in accordance with the reported spectra of the each cluster (cm^{-1}): 1069 (w), 966 (w), 796 (m), 707 (m), 591 (s), 458 (s).[8]

Thermogravimetric (TG) analyses were carried out by using the simultaneous TGA-DTA analysis module of a TA4000/SDT2960 thermogravimetric analyzer with a heating rate of 5 °C/min up to 1200 °C in an air flow. The TG curve showed weight loss of about 8.18% until 110 °C due to the loss of crystallization water, which agrees well with the water content found from the crystal structure refinement (27 H_2O/2 Al_{13}). Further weight loss of 14.44% occurs until 800 °C due to the loss of OH and H_2O ligands of Al_{13}.

^{51}V solid-state magic angle spinning (MAS) NMR spectra were obtained with a Bruker DSX 400 spectrometer. Solid-state ^{51}V MAS NMR of the crystals showed a peak at $\delta = -514$ ppm, evidence for the V_2W_4 clusters in **1**.[9]

X-ray Single-Crystal Structure Determination. A crystal was carefully coated with epoxy resin and quickly put into a glass capillary tube with mother liquor, and the tube was sealed with wax for single-crystal X-ray structure determination to prevent crystal decay. Crystal and intensity data were collected at 293(2) K using a Siemens 1K SMART CCD diffractometer with graphite-monochromated Mo Kα radiation (0.710 73 Å). A hemisphere of reflection data was collected as ω scan frames with a width of 0.3°/frame and exposure time of 20 s/frame. Cell parameters were determined and refined by the SMART program.[10] Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects.[11] An empirical absorption correction was applied with the SADABS program.[12] The positional parameters of the metal atoms and most of the cluster oxygen atoms were determined by direct methods (SHELXS-97).[13] Several cycles of refinement and difference Fourier synthesis (SHELXL-97) revealed the other atoms including the lattice water molecules.[14] The oxygen atoms of the lattice water molecules were located by inspection of the difference Fourier maps. The O···O distances around these oxygen atoms are all in the range of hydrogen bonds. These were refined with partial occupancies. Two lattice water oxygen atoms should be that of OH^- to meet the charge-balancing condition but could not be located because of the disordered nature of the water molecules. Hydrogen atoms could not be found in the crystal structure refinements because of their low electron densities. Vanadium and tungsten atoms in the V_2W_4 cluster have positional disorder, occupying the same sites. Restraints were applied for all of the vanadium/tungsten atoms to have the same atomic coordinates and atomic displacement parameters. The site occupancies of V and W were refined: those are close to the theoretical random distribution. All of the atoms were refined with anisotropic temperature factors. The crystal structure has, at least, three types of disorders: disorder of the lattice water molecules; random distribution of V and W atoms; positional uncertainties of the ligand oxygen atoms of V_2W_4 clusters. These effects, all combined, probably give rise to the rather high wR value. Detailed crystallographic parameters are given in Table 1.

Results and Discussion

In this study, we utilized highly symmetric polyoxometalate ions as building blocks. The V_2W_4 clusters have octahedral shape (O_h) with eight nearly flat triangular faces each consisting of six oxygen ligands (Figure 1a). The Al_{13} clusters have truncated tetrahedral shape (T_d) with four hexagonal faces, each consisting of six OH ligands (bridging oxygens) at the center forming a triangle similarly to the faces of V_2W_4 and six H_2O ligands (terminal oxygens) at the periphery (Figure 1b).

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Table 1. Crystallographic Data for **1**

chem formula	$Al_{13}O_{82.10}V_3W_6$
fw	2915.89
space group	$C2/c$ (No. 15)
a (Å)	44.567(10)
b (Å)	25.766(7)
c (Å)	20.626(5)
β (deg)	104.526(14)
V (Å^3)	22928(9)
Z	8
D_{calcd} (g·cm^{-3})	1.689
μ (mm^{-1})	6.391
$R_1{}^a/wR_2{}^b$ (F_o, $I > 2\sigma$)	0.0670/0.1739
$R_1{}^a/wR_2{}^b$ (F_o, all data)	0.2153/0.2345

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = [2F_c{}^2 + \max(F_o{}^2,0)]/3$.

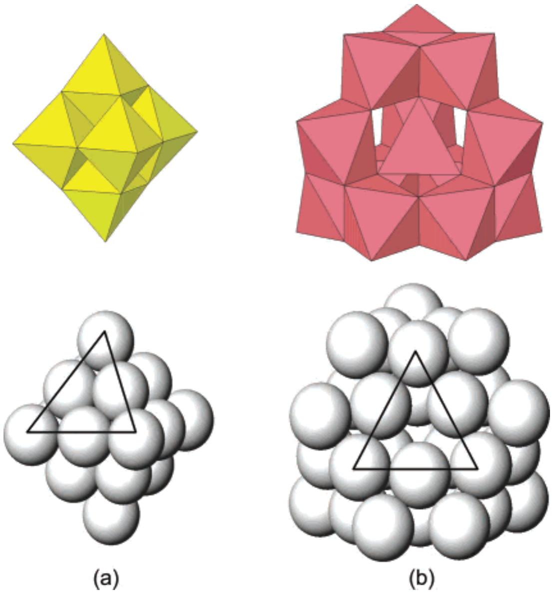

Figure 1. Structures of the cluster ions in **1** in polyhedral (top) and space-filling (bottom) representations. (a) The octahedral V_2W_4 cluster has eight nearly flat triangular faces each consisting of six oxygen ligands. Each metal atom site is occupied by approximated 1/3 V and 2/3 W atoms. (b) The truncated tetrahedral Al_{13} cluster has four hexagonal faces, each consisting of six OH ligands (bridging oxygens) at the center forming a triangle similarly to the faces of V_2W_4 and six H_2O ligands (terminal oxygens) at the periphery.

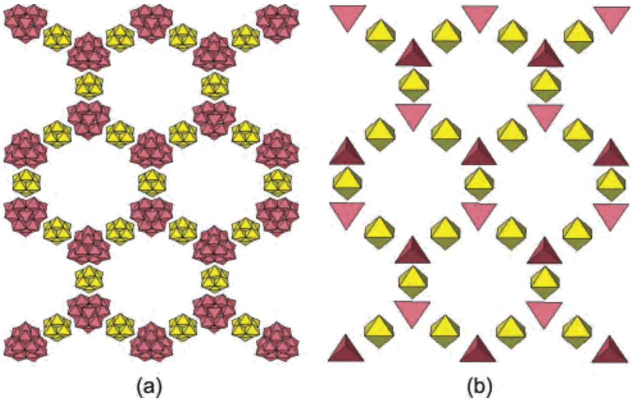

Figure 2. (a) Honeycomb net layer of the clusters in the crystal structure of **1** seen perpendicular to *ab*-plane: Al_{13}, purple; V_2W_4, yellow. (b) Approximated polygon arrangement of tetrahedra and octahedra.

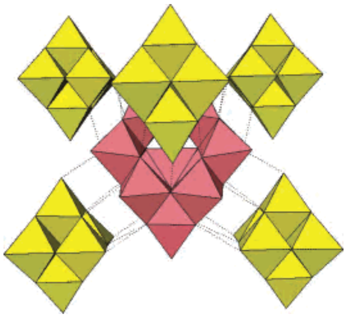

Figure 3. Hydrogen bonds around Al_{13}. Three V_2W_4 in the front side are within the same honeycomb net layer with face-to-face hydrogen bonds with Al_{13}, and the other two V_2W_4 in the adjacent honeycomb net are edge-to-edge hydrogen bonded with Al_{13}.

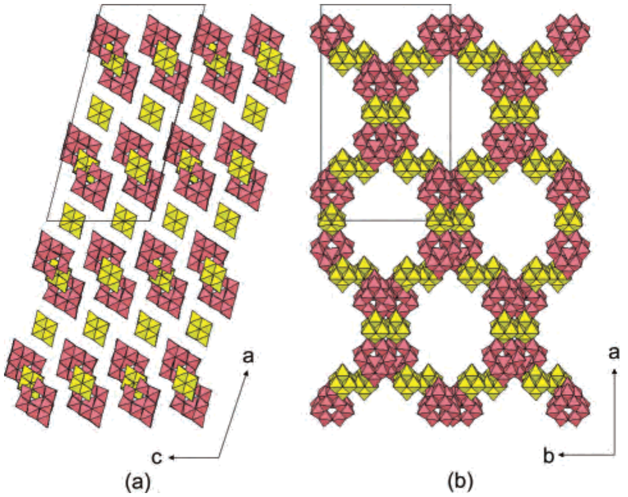

Figure 4. Structure of **1** seen along (a) [010] and (b) [001] directions. Four honeycomb net layers stacked along the *c*-direction are shown.

The basic structural motif in the crystal structure of **1** is a large 12-membered hexagonal ring composed of six Al_{13} and six V_2W_4, which extends along the *ab*-plane to form a honeycomb net layer (Figure 2a). The Al_{13} clusters are at the corners of the hexagons acting as tripodal linkers between the V_2W_4 clusters. Three of the four hexagonal faces of each Al_{13} are in close contacts with the triangular faces of three adjacent V_2W_4. The V_2W_4 clusters are at the centers of the hexagon edges and linearly link Al_{13} clusters by their two opposite triangular faces. Each pair of these contacting faces has six hydrogen-bonded O···O pairs with distances in the range of 2.75−2.96 Å between six O^{2-} ligands of V_2W_4 and six OH^- ligands of Al_{13} (Figure 3). The contacting faces of Al_{13} and V_2W_4 are almost parallel to each other with angles of 0.52−1.12° between them. Assuming that the shapes of the cluster ions are regular polygons, the structure of **1** can be approximated as an assembly of tetrahedra (Al_{13}) and octahedra (V_2W_4) (Figure 2b), with their triangular faces exactly matching each other. Due to the tetrahedral shape of Al_{13}, the hexagonal rings are distorted like cyclohexane in the chair form. The crystal structure of **1** shows that the ionic nature of this compound governs the disposition of the cluster ions and the local interactions such as hydrogen bonds influence the relative orientations of the cluster ions. On the other hand, while the cluster ions within the honeycomb nets show face-to-face interactions, the honeycomb nets are stacked along the *c*-direction through edge-to-edge interactions between the cluster ions with fewer hydrogen bonds per cluster (Figure 4a).

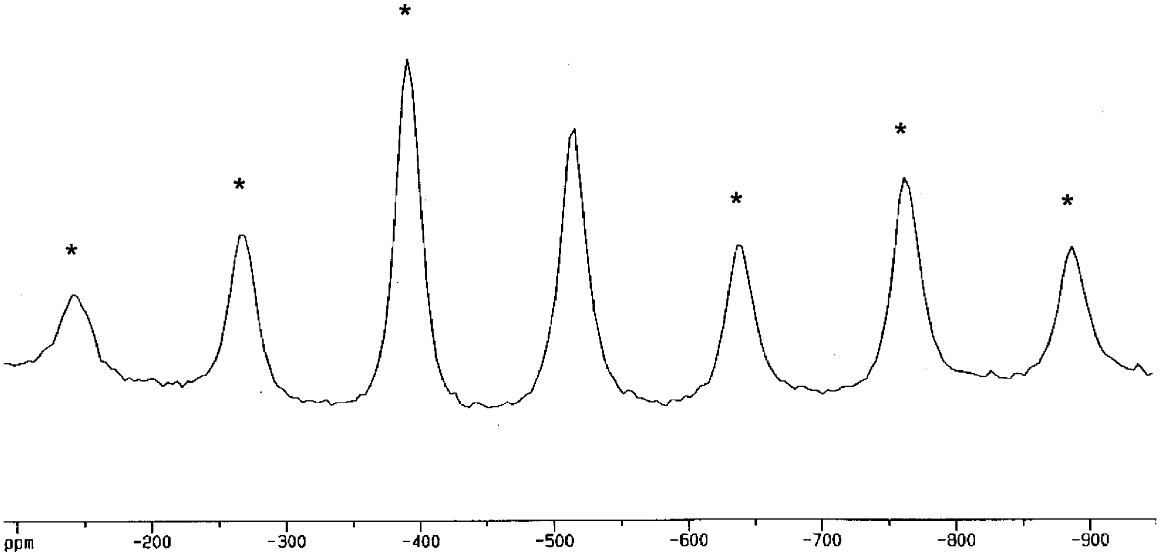

Figure 5. ^{51}V solid-state MAS NMR spectra of compound **1**. Spinning sidebands are marked by asterisks.

The structure of **1** possesses large one-dimensional channels of cross-sectional area 14.17 × 13.88 Å^2 along the *c*-direction through the hexagon arrays, which are occupied by water molecules and charge-balancing OH^- ions (Figure 4b). The pore diameter was calculated by excluding van der Waals radii of surface oxygen atoms of the clusters. Charge-balancing OH^- ions could not be located in the disordered lattice water region. Although we do not have direct evidence for the OH^- ions, there are several reasons to believe their presence: First, the charges of the cluster ions only do not balance and require anions. One may suspect that the V_2W_4 clusters are reduced to $V^{IV}{}_2W_4O_{19}{}^{6-}$ ($V^{IV}{}_2W_4$), which would exactly balance the charges of Al_{13}. However, the peak position and sharp peak shape of the ^{51}V solid-state NMR data clearly show that the V atoms are all in +5 oxidation state (Figure 5). The yellow color of the crystal, characteristic of V^V oxo compounds also supports this; the $V^{IV}{}_2W_4$ cluster is reportedly red-brown.[15] Second, some of our previously reported intercluster salts show OH^- ions whose oxygen environments could be well distinguished from those of lattice water molecules.[5a] The channel volume was calculated to be 56.3% of the total volume,[16] much higher than 35.8−48.2% of other intercluster salts.[5] As anticipated from the analogy to the bond directionality as the prerequisite for porous structures in inorganic solids, we understand that the large pores in **1** are the direct consequence of the directional bonds—contacts—between the faces of regularly shaped cluster ions, a manifestation of crystal engineering. Unfortunately, the crystals collapse losing the lattice water when dried in the air and their structure is not recovered by storing in water vapor, probably because the intercluster hydrogen bonds are not strong enough to sustain the highly porous structure without the water molecules. This instability without lattice water precludes any characterization of the pores. We are currently investigating the stability of the crystals in mixed solvents of water. Those results may provide better understanding of our crystals, which may lead to ways to modify them for future applications.

The crystal structure of **1** is similar to that of the As_2O_3 (Claudetite-II) structure that is composed of 12-membered hexagon net layers with arsenic atoms at the vertexes and oxygen atoms at the middle of edges.[17] Arsenic atoms are acting as tripodal linkers due to their lone pair electrons. The hexagon nets in As_2O_3 are more distorted than those in **1**, because the oxygen links are bent owing to their sp^3 hybrid orbital, in contrast to the octahedral V_2W_4 acting as linear linker in **1**.

Conclusions

We have synthesized a novel intercluster salt compound $[\epsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]_2[V_2W_4O_{19}]_3(OH)_2\cdot 27H_2O$ built by interactions between the faces of polygon-shaped cluster ions. Highly symmetric shapes of the clusters and exact face-to-face contacts between the clusters produced highly regular array of the clusters with large pores. The simple analogy to the bond directionality of conventional inorganic compounds utilizing the faces of clusters may be a useful way to direct the local bonding—contacting—modes. By choosing cluster ions of the right charges, sizes, and shapes, one may be able to synthesize crystals of a variety of architectures, a new approach for crystal engineering.

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Supporting Information Available: Detailed crystallographic data in CIF format for $[\epsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]_2[V_2W_4O_{19}]_3(OH)_2\cdot 27H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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