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Novel Large Aluminophosphite Cage Unit as the Building Blocks To Form a Framework Structure Containing Multidimensional 12-Ring Channels

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In this report, an open-framework aluminophosphite (denoted as NKX-6) with large cavities and channel structure has been synthesized hydrothermally. Two crystals of NKX-6 with truncated tetrahedron- and octahedron-like morphology have been prepared by using pseudo-boehmite and aluminum isopropoxide as the aluminum source, respectively. X-ray diffraction patterns simulated from the data of these two single crystals show they are the same phase. Single-crystal analysis reveals that the framework of NKX-6 is $[Al_7(HPO_3)_9(OH)_6]^{3-}$ and charge-compensated by 1,6-hexanediammoniums. It crystallizes in a cubic system, space group $P\bar{4}3m$ (No. 215), with $a = 17.5632(4)$ Å, $V = 5417.6(2)$ Å^3, $Z = 4$, $\mu = 0.513$ mm^{-1}, and $\rho_{calcd} = 1.707$ mg/cm^3 (CCDC number: 617596). Two novel super-AlHPO-cages (named as super-type A cage and super-type B cage, respectively) have been found in the structure of NKX-6. The super-type A cage is constructed from four turtleback-shaped clusters and six crown-shaped clusters. It is reminiscent of an extended truncated octahedron with each of the six corners of the super-octahedron being occupied by a crown-like unit of eight Al octahedra alternatively linked with each other through corners or edges. In this super-octahedron cage, two opposite facets of the extended octahedron are occupied by a 12-ring window and a turtleback-like unit, respectively. The super-type B cage is constructed from the stacking of eight super-type A cages. It has 10 12-membered-ring windows, four being arranged tetrahedrally (connect to four adjacent type A cages) and six being arranged octahedrally (connect to the six adjacent type B cages). The stacking of the super-octahedron cages also builds up the open framework of NKX-6 with large 12-ring channels extending along the crystallographic *a*-, *b*- and *c*-axes as well as the [101], [110], and [011] directions.

Introduction

Large cavity-containing materials such as zeolites and metal phosphates play important roles in the domain of materials.[1] They have highly desirable structural features for application not only in traditional uses as catalysts, adsorbents, and separators but also in a number of modern science areas, such as microelectronics, gas storage, and medical diagnosis.[2] Significant advances in the methodology for synthesizing cage-containing materials have led to the preparation of new cavity-containing materials with previously unseen compositions and framework topologies.[3] For example, investigations on the guest−host relationship between structure directing agent (SDA) and framework, including the geometry, bulkiness, rigidity, and hydrophobicity of SDA[4] and the degree of heteroatom lattice substitution of elements in the silicate framework, have opened up new avenues for finding novel high silica cages containing zeolite

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structures.[5] The structure direction method through host−guest charge density matching in the highly charged system has resulted in series of zeolite-like metal phosphates containing large cages interconnected by multidimensional large-pore channels (denoted as UCSB-*n*).[6]

Recently, synthesis of phosphorus-based microporous materials by incorporating the pseudo-pyramidal hydrogen phosphite group HPO_3^{2-} instead of tetrahedral phosphate group PO_4^{3-} into the desired structures exhibits the diversity of phosphorus-based materials. A new class of architectures, including one-dimensional chain compounds, two-dimensional layer materials, and three-dimensional open-framework structures, have been prepared.[7] However, there are few papers about aluminum phosphites as well as the rare finding of the cavity-containing frameworks in the family of metal phosphites.[8] In our previous work, a small cage structure was been obtained in an aluminophosphite NKX-2.[11a] The present work reports the synthesis and structure of a novel large cage containing aluminophosphite. A novel super cage (named type A cage hereafter), which is reminiscent of an extended truncated octahedron, contains large 12-ring windows along the facet directions of the super-octahedron cage. As the building blocks for constructing framework with multidimensional channels, the unit cage has the largest 12-ring windows.

Experimental Section

Synthesis and Characterization. The aluminophosphite $Al_7(HPO_3)_9(OH)_6 \cdot (C_6H_{12}N_2H_6)_{1.5}(H_2O)_{12}$ is synthesized from a mixture of aluminum isopropoxide ($[(CH_3)_2CHO]_3Al$) or pseudo-boehmite, 1,6-hexanediamine (HDA; $C_6H_{16}N_2$), H_3PO_3 (phosphorous acid), and water. In a typical procedure, aluminum isopropoxide (4.09 g), distilled water (10.60 mL), and 99% H_3PO_3 (1.66 g) were stirred together at room temperature for 2 h. HDA (0.58 g) was then added. The mixture was stirred until the HDA was completely dissolved with the pH = 2, and this gel was heated hydrothermally under static conditions. The filling of the autoclaves was three-fourths of 20 mL. The colorless, truncated tetrahedron morphology (at 200 °C for 7 days) or octahedral-like (at 170 °C for 6 days) single crystals were recovered after cooling, filtered from the reacting mixture, and washed with distilled water and dried at room temperature.

Table 1. Crystal Data and Structure Refinement for Aluminum Phosphite NKX-6

CCDC number	617596
empirical formula	$Al_7(HPO_3)_9(OH)_6 \cdot (C_6H_{12}N_2H_6)_{1.5}(H_2O)_{12}$
formula weight	1404.23
temperature	113(2) K
wavelength	0.71070 Å
crystal system, space group	cubic, $P\bar{4}3m$ (No. 215)
unit cell dimensions	$a = 17.5632(4)$ Å
volume	5417.6(2) Å^3
Z, calculated density	4, 1.707 Mg/m^3
absorption coefficient	0.513 mm^{-1}
F(000)	2908
crystal size	0.14 × 0.12 × 0.10 mm^3
θ range for data collection	1.15−25.00°
limiting indices	$-15 \leq h \leq 21$; $-17 \leq k \leq 6$; $-23 \leq l \leq 12$
reflections collected/unique	7638/2231 [R(int) = 0.0487]
completeness to $\theta = 25.00°$	99.7%
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2231/76/156
goodness of fit on F^2	1.131
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0653, wR2 = 0.1795
R indices (all data)	R1 = 0.0687, wR2 = 0.1830
largest diff. peak and hole	1.088 and −1.688 e·Å^3

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 diffractormeter with Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal morphology and electron probe microanalysis analyzing chemical compositions of the products were performed with a Hitachi X-650 scanning microscope. IR spectra were recorded on a Bruker FTIR spectrometer. Thermal analysis was performed on Netzsch STA 409 PC thermal analyzer at a heating rate of 10 °C /min in nitrogen. Element analysis was performed on an Elementar Varioel element analyzer. Its result shown NKX-6 with C, 6.89; H, 4.23; N, 2.70 (wt %) and was in good agreement with that calculated (C. 7.46; H, 4.26; N, 2.90 wt %) from single-crystal data (Table 1).

Structure Determination. Structural analysis of a single crystal (0.14 × 0.12 × 0.10 mm^3) was performed with a Rigaku MicroMax 007 diffractometer equipped with a Saturn 70CCD using Mo Kα radiation ($\lambda = 0.710\,70$ Å). The data were collected at $T = 113(2)$ K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-97.[9] The positional parameters for Al, P, and O atoms were located by direct methods. The remaining non-hydrogen atoms were routinely located from Fourier difference maps during the course of the refinement. The C and N atoms in highly disordered 1,6-hexanediaminium cations were positioned geometrically [$d(\text{N1}-\text{C1}) = d(\text{N2}-\text{C6}) = d(\text{N3}-\text{C7}) = d(\text{N4}-\text{C12}) = 1.50$ Å; $d(\text{C}-\text{C}) = 1.54$ Å]. The H atoms of HPO_3^{2-} groups were placed geometrically [$d(\text{P}-\text{H}) = 1.30$ Å]. The P(3) atom was disordered over two positions with P3 having an occupancy of 0.885, whereas it was 0.115 for P3′. All non-hydrogen atoms of the inorganic framework were refined anisotropically. The result of single-crystal refinement is listed in Tables S1−S3 (Supporting Information). The C, N, and 18 H atom positions in 1,6-hexanediaminium cations are partially occupied (Figure S1 in Supporting Information). Their occupancy factors

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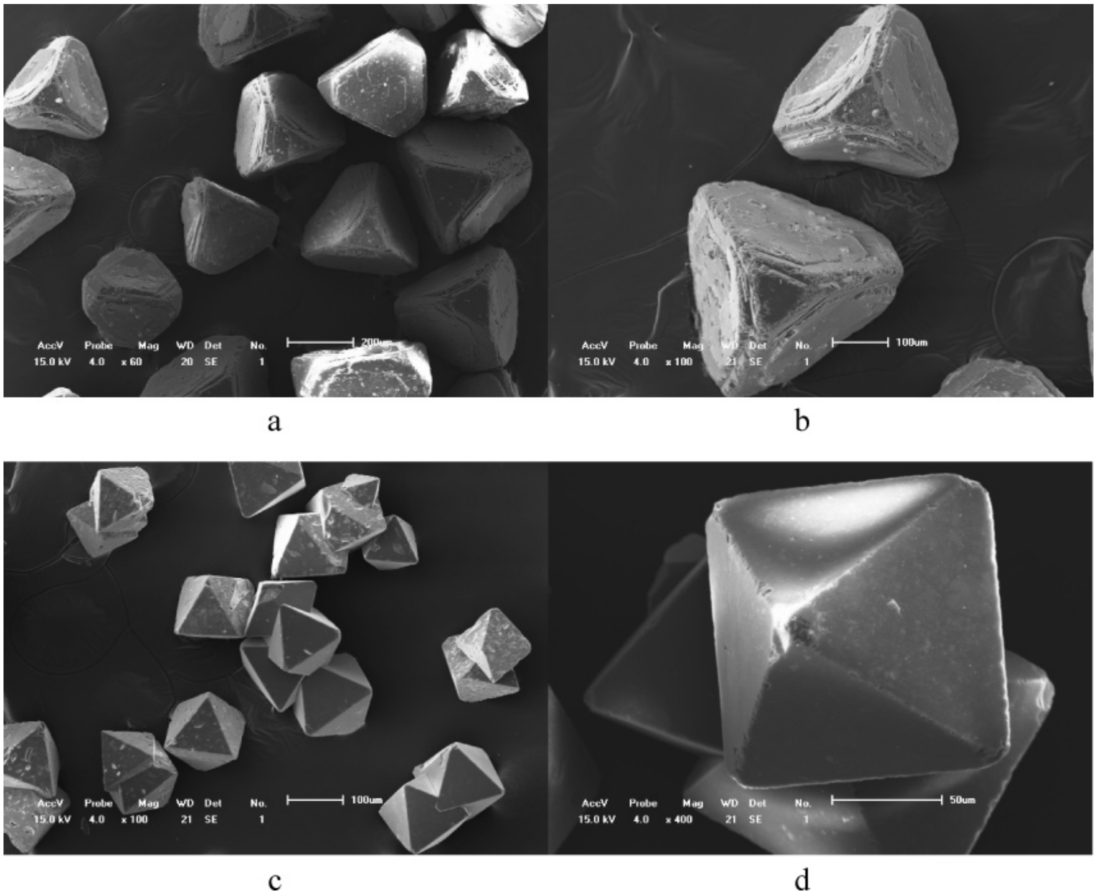

Figure 1. SEM images of the NKX-6 single crystals. (a, b) Truncated tetrahedron morphology synthesized using pseudo-boehmite as the aluminum source; (c, d) octahedron-like morphology synthesized using aluminum isopropoxide as the aluminum source.

were refined from the fragment of thermal ellipsoid and to match that of thermal analysis and element analysis.

Results and Discussion

The aluminophosphite NKX-6 has been first synthesized from the system using pseudo-boehmite as the aluminum source. The starting mixture is formed by reacting phosphorous acid with pseudo-boehmite in water with HDA as the SDA.

The concentration of HDA and content of water in the reacting mixture are important factors for the formation of NKX-6. It crystallizes in a narrow range with the molar ratio of $HDA/Al_2O_3 = 0.45-0.70$ and $H_2O/Al_2O_3 = 50-70$. The single crystal of NKX-6 has been obtained from the mixture with the molar ratio of $Al_2O_3/H_3PO_3/H_2O/HDA$ being 1.0:2.0:50:0.5 at 200 °C for 7 days. From the scanning electron microscopy (SEM) images showed in Figure 1a,b, it can be seen that the crystals are semi-transparent with truncated tetrahedron morphology. It is very interesting that when aluminum isopropoxide instead of pseudo-boehmite is used as the aluminum source, the octahedron-like crystals were obtained (Figure 1c,d). In this case, NKX-6 can be synthesized in a wide range with HDA/Al_2O_3 ranging from 0.25 to 1.25 and the H_2O/Al_2O_3 molar ratio ranging from 58 to 177. However, the quality of crystals is deeply affected by the concentration of HDA and the crystallization temperature. The perfect transparent single crystals of NKX-6 with octahedron-like morphology (Figure 1d) are obtained by crystallizing the mixture of $(PrO)_3$ $Al/H_3PO_3/H_2O/HDA = 2.0:2.0:117.8:0.5$ at 170 °C for 6 days. XRD patterns simulated from the single-crystal parameters show (Figure S2c,d, Supporting Information) that they are the same in their main diffractions but are not completely identical. This might result from little differences in the structures, for example, in the treatment of disordered guest species.

Single-crystal analysis reveals that the framework of aluminum phosphite NKX-6 is composed of $[Al_7(HPO_3)_9(OH)_6]^{3-}$ and charge-compensated with 1,6-hexanediammoniums cations. The asymmetric unit contains three crystallographically distinct P atoms and two crystallographically distinct Al sites with Al and P atoms in the form of AlO_6 octahedron and slightly distorted HPO_3^{2-} tetrahedron, respectively (Figure 2a). Each HPO_3^{2-} group shares three P−O bonds with Al atoms ($P-O_{av} = 1.528$ Å) and leaves a terminal P−H bond (the existence of P−H is also confirmed by the characteristic band of phosphite group [$\nu_{H-P} = 2360.7$ cm^{-1}] in the IR spectrum[10] in Figure 3). Two Al atoms are in octahedral environments with Al−O bond length (av 1.904 Å) being in agreement with those observed in other aluminophosphites.[11] The Al(2) atom in the structure is located on a threefold axis and connects six O atoms to nearby P atoms of three asymmetric units, forming an Al(2)-centric turtleback-shaped cluster composed of $[Al_7(HPO_3)_9(OH)_6]^{3-}$, which can be described as the secondary building unit (SBU) in the structure of NKX-6 (Figure 2b).

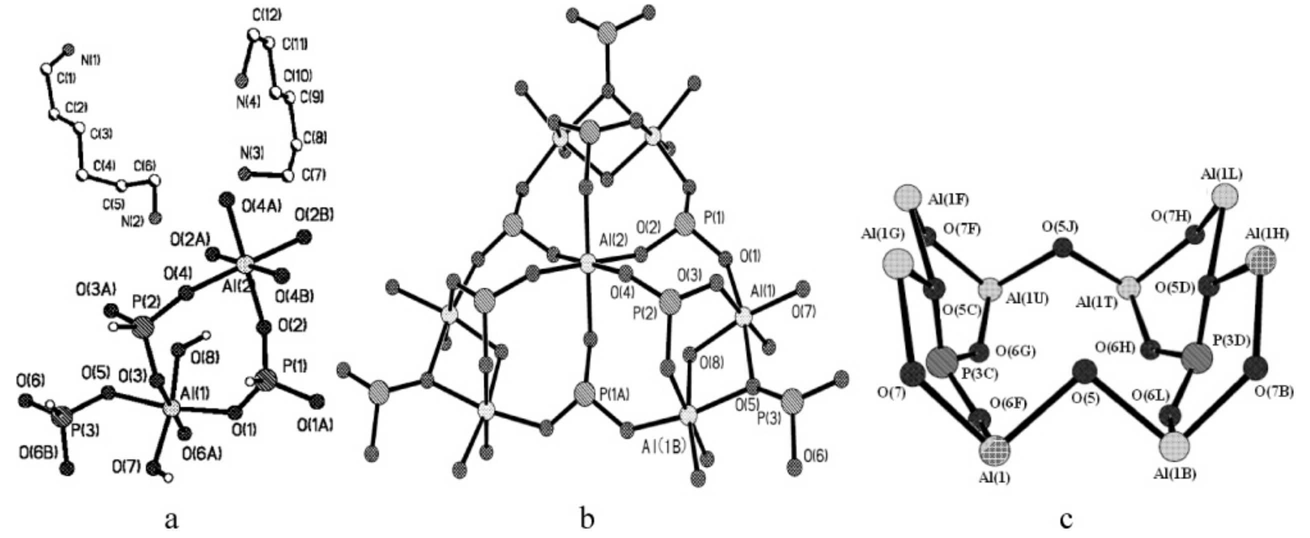

Figure 2. Cage unit structure of aluminum phosphite. (a) Asymmetric inorganic unit and 1,6-hexanediammoniums; (b) turtleback-like cluster with the inorganic composition of $Al_7(HPO_3)_9(OH)_6^{3-}$; (c) the crown-shaped clusters as the building unit in the structure of NKX-6.

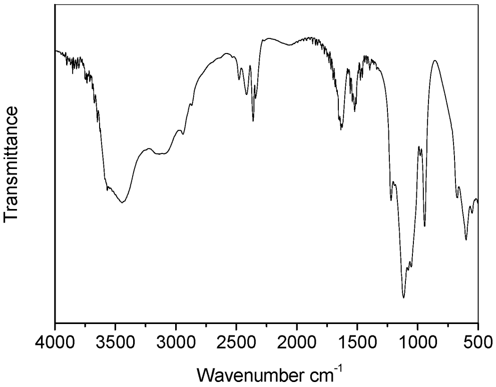

Figure 3. IR spectra of aluminum phosphite NKX-6.

Thereinto, adjacent four turtleback-shaped clusters join together through the linkages of Al(1)−O−P(3)−O−Al(1) in the six-ring of the crown-like units (a “cluster” of eight edge-sharing AlO_6 octahedra alternately linked with each other with free oxygen corners linking to two phosphite groups HPO_3^{2-}; Figure 2c) to form the type A cage sitting on the center of the unit cell (Wyckoff position 1b). The type A cage is a super-cage and reminiscent to an extended truncated octahedron with each of the six corners of the super-octahedron being occupied by a crown-like unit of eight Al octahedral, and each of the opposite facets of the extended octahedron are occupied by a 12-ring window and a turtleback-like unit, respectively (Figure 4a). In the super-octahedron cage, each of the four 12-ring windows is separated from the other by three 6-rings of the crown-like unit and colored differently to distinguish them from each other (Figure 4a,b). A closely related framework is encountered in an aluminum phosphate MIL-74,[8] showing an example of extension of the truncated octahedron with larger building units. Viewing along the direction of the crystallographic *a*-, *b*-, and *c*-axes, it has been found that via four Al−O−Al bonding, each type A cage links through Al(1) atoms on the 6-ring of the crown-shaped clusters with six adjacent type A cages (Figures 4c and 5a,b).

The open framework of NKX-6 is built up from the stacking of the super-type A cages. It results in the formation of a multidimensional large channels structure (Figure 5a). It is notable that the stacking of eight super-type A cages results in the formation of another super-AlHPO-cage (named type B cage hereafter, Figure 6), which has the same $\bar{4}3m$ symmetry and sits on the corners of the unit cell (Wyckoff position 1a). This cage, too, is constructed from four turtleback-shaped clusters arranged tetrahedrally and has 10 even 12-ring windows, four being arranged tetrahedrally (type A windows, connected to four adjacent type A cages) and six being arranged octahedrally (type B windows, connected to the six adjacent type B cages). The turtleback-shaped clusters of the type B cage are joined via the crown-shaped clusters mentioned above (as connecting the type A cages). Large multidimensional 12-ring channels in the framework extend along the crystallographic *a*-, *b*-, and *c*-axes (Figure 5a) and [101], [110], and [011] directions (Figure 5c), respectively. The channel system linking the centers of all the super-type A cages via the 12-rings is indeed rather complex but may be understood as follows: The windows of type B, being common to two type B cages, define channels running along the cube axes (⟨100⟩ directions). The windows of type A being common to one type B and one type A cage (along ⟨111⟩) define channels corresponding to two interpenetrating diamond nets. Channels mentioned above along [110], [101], and [011] actually correspond to diagonal views through 12-rings of type B cage (Figure 5c).

Some of the 1,6-hexanediammoniums cations are encapsulated in a type A cage. Others were located in a type B cage, with one end in cage B and the other end extended into the crown section. Their NH_3^+ groups were H-bonded with the framework oxygen atoms (Figure S1, Supporting Information).

Cage structures are the important building blocks to construct the frameworks with large cavities. However, almost all the large cavity-containing zeolites and metal phosphates such as Faujasite, EMC-2,[1] UCSB-6, UCSB-8, UCSB-10,[4] DAF-1,[12] MAPO-46,[13] and Cloverite[3e] are built up of cages with small windows. For example, zeolite Faujasite, and EMC-2 are built up of sodalite cage units with

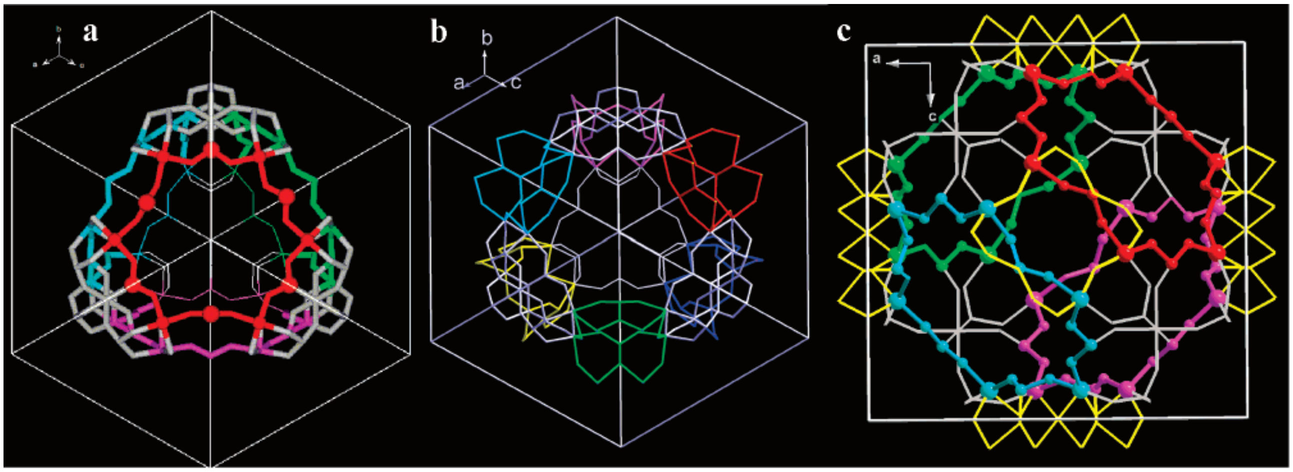

Figure 4. Type A cage containing four turtleback-like clusters in the structure (a) without the existence of crown-shaped clusters with the four 12-member rings are colored as red, green, magenta, and cyan, respectively; (b) containing crown-shaped clusters with each of them colored red, green, magenta, cyan, yellow, and blue; and (c) type A cage viewing along *b*-axis direction with the yellow colored crown-shaped clusters.

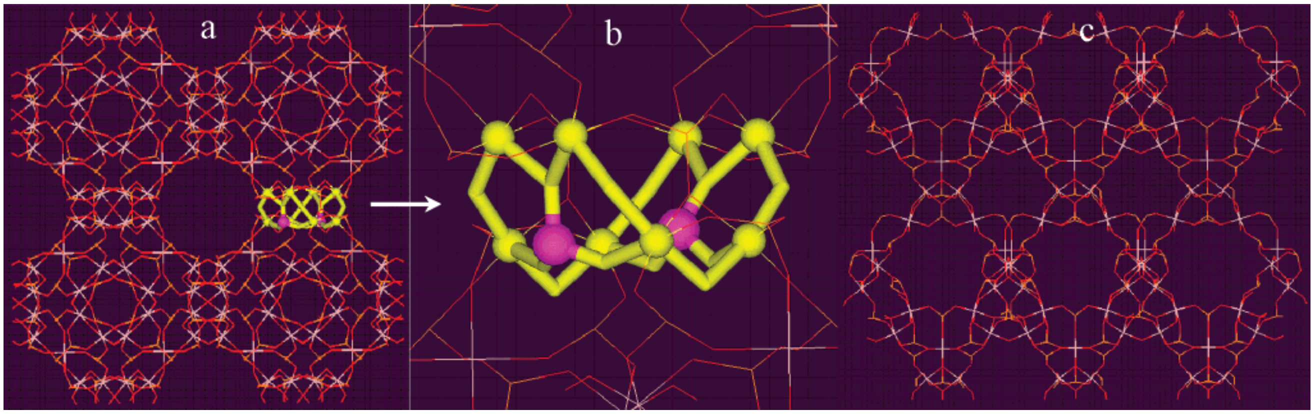

Figure 5. Inorganic framework of aluminum phosphite is formed by the stacking of novel AlHPO-cages type A. (a) Large 12-ring channels along axis direction; (b) the linkage between adjacent type A cages through a crown-like cluster; (c) another large 12-ring channel system formed from windows of type A cages in [110], [101], and [011] directions.

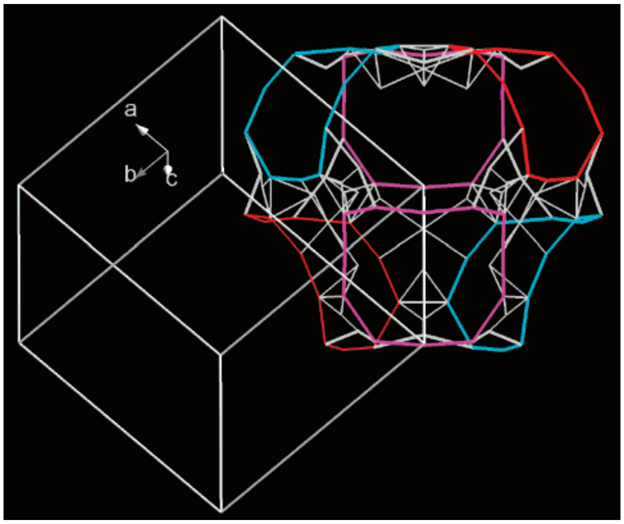

Figure 6. Type B cage structure of aluminum phosphite NKX-6.

6-ring windows; UCSB-6, UCSB-8, and UCSB-10 are formed from the stacking of CAN cage units (cancrinite) as well as Cloverite, which is formed by the connection of Alfa and Rpa cage units with 8-ring windows. It has been reported more recently that the building blocks used to stack the large-cavity zeolite ITQ-21 are also small cage units with 6-ring windows.[5c] The enviable progress on the preparation of large cage units in the porous materials has been achieved in the domain of metal-organic frameworks (MOFs).[14] So, although it is not an absolute tetrahedral framework structure, the super-type A cage is now a novel cage unit with 12-ring large windows used to construct open framework material. As the building blocks for constructing frameworks with multidimensional channels, the unit cage has the largest windows (12-ring).

Framework density (polyhedra number per 1000 Å^3) of materials indicates their void space. In the family of metal phosphites, NKX-6(11.8) has a lower framework density, higher than only a few members,[11,15] but close to the 11.6 of ZnHPO-CJ1, which is a zincophosphite and contains 24-ring channels in the structure.[7h−j] Compared to the large cavity-containing structures in Table 2, such as EMT(12.9),

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Table 2. Framework Density (polyhedra Number Per 1000 Å^3) of Materials with the Cubic-stacking of Cages

structure	material	framework density	reference
	ZnHPO-J1	11.6	7h
	NKX-6	11.8	present study
	MIL-74	8.9	11
−CLO	Claverite	11.1	3a
SBT	UCSB-10	12.1	6a
FAU	Faujasite	12.7	3a
SBE	UCSB-8	12.8	6a
SBS	UCSB-6	12.8	6a
EMT	ECM-2	12.9	3a
LTA	Linde A	12.9	3a
DFO	DAF-1	14.1	11
RHO	RHO	14.1	3a
KFI	ZK-5	14.6	3a
SAS	STA-6	15.3	3a

FAU(12.7), SBE(12.8), SBS(12.8), and SBS(12.1), the framework density of NKX-6 is the lowest. It can also be found that structures formed by the cubic stacking of cages with small windows, such as DFO(14.1), KFI(14.6), LTA-(12.9), RHO(14.1), and SAS(15.3), may have a much higher framework density. On the contrary, frameworks built up of the cage units with large windows such as 12-ring may have a lower density.

Thermogravimetric (TG) analysis (Figure S3, Supporting Information) of NKX-6 with two morphologies (truncated tetrahedron and octahedron) has shown that the weight losses between 100 °C and 395.8 °C are 29.20% and 30.15%, respectively, which is attributed to desorption of water in the structure and the decomposition of the 1,6-hexanediammonium cations (calcd 28%). An XRD study showed that the structure collapses after heating at 350 °C for 2 h, which suggests that the inorganic framework structure is unstable upon removal of the organic molecules.

Conclusion

An aluminophosphite open framework with large cavities and channel structure has been obtained in two different morphologies by the usage of two different aluminum sources. Two novel super-AlHPO-cages (type A cage and type B cage) have been found in the structure of NKX-6. The super-type A cage is located on the center of the unit cell and constructed from the crown-shaped clusters and turtleback-shaped clusters. It is reminiscent of an extended truncated octahedron with each of the six corners of the super-octahedron occupied by a crown unit of eight Al octahedral alternatively linked with each other through corners or edges. The facets of the super-truncated octahedron cage are occupied by four 12-ring windows and four turtleback-shaped clusters. The super-type B cage is formed by the stacking of eight super-truncated octahedron A cages. It sits on the corners of the unit cell and is also constructed from four turtleback-shaped clusters arranged tetrahedrally. The super-type B cage has 10 12-ring windows, four being arranged tetrahedrally (connected to four adjacent type A cages) and six being arranged octahedrally (connected to the six adjacent type B cages). The open framework of NKX-6 with multidimensional large 12-ring channels extending along the crystallographic *a*-, *b*-, and *c*-axes and [101], [110], and [011] directions, respectively, is built up from the stacking of the type A super-cages.

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Supporting Information Available: Additional figure, XRD patterns, TG and DSC curves, atomic coordinates and equivalent isotropic displacement parameters, and selected bond lengths and angles (PDF) and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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