Noninterpenetrating Indium Sulfide Supertetrahedral Cristobalite Framework

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Realizing the synthesis and crystal structure of microporous materials with pore sizes 10–20 Å has been a formidable challenge in molecular sieve science. Access to such materials, with uniform pore size, is expected to impact the petrochemical and the life-sciences fields by providing opportunities for the size- and shape-selective catalysis/separation of *large* molecules.[1] In this direction, theoretical approaches to decorating specific 4-connected networks have been proposed,[2] whereby replacing each (T1) tetrahedron, TX_4, in a given network by a larger tetrahedron (hereafter referred to as a supertetrahedron), signified T*n*, yields a porous network due to the increased size of the building blocks.[3] With large *n*, frameworks of unprecedented porosity could be achieved. Recognizing the potential of this approach, we have embarked on a program aimed at using inorganic clusters as molecular building blocks in the assembly of extended networks: The copolymerization of Mn(II) with the

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(1) (a) Barrer, R. M.; Villiger, H. *Z. Kristallogr.* **1963**, *128*, 352. (b) Davis, M. E. *Chem.–Eur. J.* **1997**, *3*, 1745.
(2) The production of very open networks by replacing a vertix with a group of vertices (decoration) has been examined. (a) O'Keeffe, M.; Hyde, B. G. *Crystal Structures*; Mineralogical Society of America: Washington, DC, 1996. (b) Hansen, S. *Nature* **1990**, *346*, 799 and references therein.
(3) The formula of an isolated T*n* unit is where $t_n = n(n + 1)(n + 2)/6$ is the *n*th tetrahedral number. The corresponding formula for a corner-connected supertetrahedral framework is $T_{t_m} X_{t_{n+1}-2}$.
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(5) Microporous sulfides have been the subject of intense research, for example, see: (a) Bedard, R. L.; Wilson, S. T.; Vail, L. D.; Bennett, J. M.; Flanigen, E. M. In *Zeolites: Facts, Figures, Future*; Jacobs, P. A., van Santen, R. A., Eds.; Elsevier: Amsterdam, 1989, Vol. 1, pp 375–387. (b) Jiang, T.; Lough, A.; Ozin, G. A.; Bedard, R. L.; Broach, R. *J. Mater. Chem.* **1998**, *8*, 721. (c) Parise, J. B. *Science* **1991**, *251*, 293. (c) Dingra, S.; Kanatzidis, M. G. *Science* **1992**, *258*, 1769.
(6) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145.
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(8) We have independently made this T3 In–S material (ASU-33) with the same topology and verified that its cavities are substantially smaller than those in the new structure of this report.
(9) (a) Anal. Calcd for $C_{42}H_{107}N_7S_{18}O_5In_{10} = In_{10}S_{18}\cdot(C_6H_{12}NH_2)_6(C_6H_{12}$-NH)(H₂O)₅ C, 20.05; H, 4.29; N, 3.90; S, 22.94; In, 45.64%. Found: C, 20.81; H, 3.85; N, 3.89; S, 22.60; In, 44.79%. FT-IR (KBr, 1600–400 cm⁻¹) 1585 (s), 1460 (s), 1216 (w), 1111 (w), 1012 (m), 966 (m), 877 (w), 834 (m), 815 (m), 742 (w), 644 (m), 538 (w), 505 (w).
(10) Single crystals of ASU-34 are, at −109 ± 2 °C, tetragonal, space group *I*4̄2*d* with *a* = 16.6709(7) Å, *c* = 33.5000(2) Å, *V* = 9310.3(8) Å³, and *Z* = 4 formula units {d_{calcd} = 1.961 g cm⁻³; μ_a(Mo Kα) = 2.930 mm⁻¹}. A total of 8260 integrated reflection intensities having 2Θ(Mo Kα) < 16.52° were produced using the Siemens/Bruker program SAINT. A total of 1247 of these were independent and gave R_{int} = 0.1559. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL-PC Version 5 software package and converged to give R1 (unweighted, based on *F*) = 0.0765 and wR2 (weighted, based on *F*²) = 0.1718. Sulfur and indium were refined with anisotropic displacement parameters and the remaining atoms refined with isotropic parameters. Diffuse electron density (solvent and cations) in the large open volumes were modeled by using Babinet's principle (Atomic coordinates for the indium sulfide framework of ASU-34 [atom type (10⁴*x*, 10⁴*y*, 10⁴*z*)]: In1 (−1737, −66, 4); In2 (−1585, −1693, 822); In3 (0, 0, 846); S1 (−2591, 725, −431); S2 (−2532, −896, 416); S3 (−916, 839, 435); S4 (−766, −861, 1257); S5 (−2489, −2500, 1250). Due to the high regularity of the indium sulfide tetrahedra, the framework structure was initially solved from the X-ray powder diffraction pattern and confirmed by the single-crystal X-ray diffraction study.

tetrahedral adamantine $Ge_4S_{10}^{4-}$ (T2) cluster, composed of 4 $GeS_{4/2}$ tetrahedra, yielded $MnGe_4S_{10}\cdot2(CH_3)_4N$ having a porous cristobalite network with the organic cations occupying the void space.[4,5] Recently, we demonstrated that supertetrahedral (T3) clusters, $In_{10}S_{20}^{10-}$, containing 10 $InS_{4/2}$ tetrahedra, can be condensed to form ASU-31 and ASU-32, which have open frameworks possessing unprecedented 80% void space.[6] Although a cristobalite framework based on T3 indium sulfide clusters has been reported, it has an interpenetrating structure, thus precluding the presence of large cavities.[7,8] Here, we describe how the same T3 indium sulfide clusters can be assembled into a cristobalite *noninterpenetrating* structure, $In_{10}S_{18}\cdot(C_6H_{12}NH_2)_6(C_6H_{12}NH)$-$(H_2O)_5$, ($C_6H_{12}NH$:hexamethyleneimine), ASU-34, with 70% of its crystal volume occupied by the hydrated organic guests.

Indium metal (−100 mesh, 99.99%, 65 mg, 0.57 mmol), sulfur (−100 mesh, 41 mg, 1.28 mmol), and distilled water (1.0 mL) were placed into a 23-mL Teflon-lined stainless steel vessel, followed by the addition of $C_6H_{12}NH$ (0.30 mL, 2.662 mmol). The resulting mixture was stirred for 1 min, and the vessel was sealed and then heated to 150 °C at 5°/min for 4 d. After the reaction cooled to room-temperature at 0.1°/min, slightly yellow octahedral-shaped crystals formulated as $In_{10}S_{18}\cdot(C_6H_{12}NH_2)_6$-$(C_6H_{12}NH)(H_2O)_5$, (60 mg, 43% yield based on In) were mechanically separated from a small amount of red-brown solid and then washed with distilled water and dried in air.[9]

An X-ray diffraction study[10] performed on a single-crystal isolated from the reaction product reveals a 3-D $In_{10}S_{18}^{6-}$ structure formed by condensation of $In_{10}S_{20}^{10-}$ clusters to produce a network with the cristobalite topology as shown in Figure 1. The
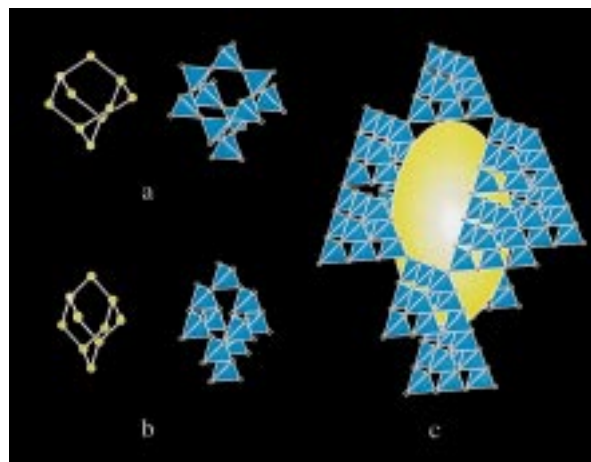

Figure 1. (a) A unit cell of the cubic cristobalite TX_2 framework showing the positions of the T atoms (yellow) and TX_4 tetrahedra. (b) The same framework contracted so that the T–X–T angles are 109°. (c) The contracted framework constructed from T3 supertetrahedra as in ASU-34. The large yellow ellipsoid fits inside one of the cavities in the structure. The fixed- and free-sphere diameters are 10.9 and 7.7 Å, respectively.[6]

cristobalite framework, TX_2, with regular TX_4 tetrahedra can exist with T–X–T angles as large as 180° (at which point the structure is cubic) as shown in Figure 1a; however, this value can be decreased by concerted rotation of the tetrahedra to yield a contracted structure with tetragonal symmetry as shown in Figure 1b for T–X–T = 109°, where the X array is cubic close-packed.[11a,b] When the TX_4 units are really T3 supertetrahedra, as in ASU-34, the decorated structure is very open (Figure 1c and Figure 2). This may be appreciated from the following argument: In the contracted structure with close-packed X (Figure 1b), one-fourth of the tetrahedral sites are filled, and these tetrahedra comprise only $1/12$ of the total volume of the structure.
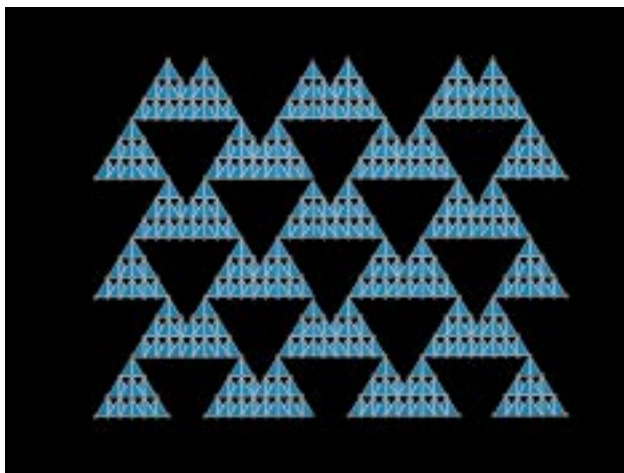
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Figure 2. A projection of the indium sulfide framework of ASU-34 showing the connectivity of supertetrahedra (cf. Figure 1).
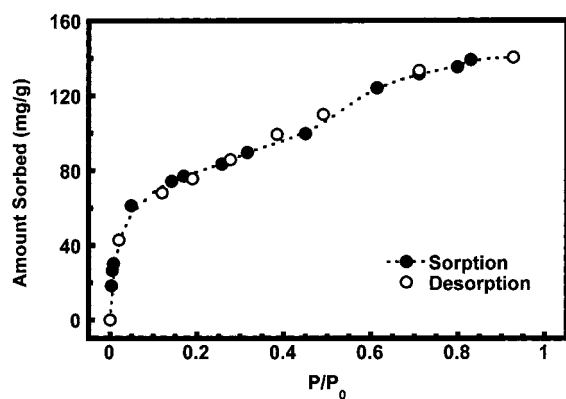

Figure 3. The room-temperature water sorption isotherm for $In_{10}S_{18} \cdot (C_6H_{12}NH)_3Ca_{1.5}$.

Actually, we estimated the porosity to be 70−75% by either centering (possibly overlapping) spheres with van der Waals radii at each atom position and calculating the space not occupied by these spheres (75%)[12] or by using the SOLV facility in PLATON, where the unoccupied space at a distance greater than 1.2 Å from the van der Waals sphere of each atom is considered to be the void space (70%).[13]

The pore structure consists of continuous channels with the large cavities centered at four places in the unit cell. At these points $(0, 0, {}^1/_2$ and their symmetry-related points) the nearest atoms are those of S at a distance of 7.24 Å, thus allowing for the van der Waals radius of S,[12] it can accommodate a sphere of diameter 10.9 Å. Actually, as the site symmetry is tetragonal, neighbors in the $\pm c$ direction are further away, and the cavity is better approximated as a prolate (elongated) ellipsoid with the long axis 1.4 times the shorter one as suggested in Figure 1c. Although the In and S positions were determined accurately, it was not possible to locate the positions of the guests due to their disorder within the large cavities. Nevertheless, the FT-IR spectrum of the as-synthesized material showed the signature peak pattern attributed to the presence of $C_6H_{12}NH$ in the voids, which was also confirmed by elemental microanalysis.[9,14]

The unit cell of ASU-34 ($Z = 4$) contains 28 $C_6H_{12}NH$ and 20 H_2O guests which fill contracted adamantine-like cavities (Figure

1c). Thermal gravimetric analysis showed two consecutive weight loss intervals (total = 4.7%) between 50 and 210 °C. These were due to the loss of 5 water molecules and 0.3 $C_6H_{12}NH$ guests per formula unit (calcd: 4.8%). This was followed at 275 °C with a larger weight loss (20.0%), which may account for the removal of most, but not all, of the organic guests (calcd for 7 $C_6H_{12}NH$: 26.7%). We believe that the framework is thermally unstable in that the TG data showed continuous weight loss pattern from 85 to 430 °C without any clear plateau regions.

However, ion-exchange studies indicate that the guests can be exchanged in solution by inorganic monocations (Li^+, Na^+, K^+, Rb^+, Cs^+) and dications (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). In a typical ion-exchange experiment, a crystalline sample (5 mg) of the as-synthesized material was immersed in a 20 mL (1 M) nitrate (0.3 M for Ba^{2+}) of the inorganic cation for 1 d. The exchanged product was filtered, washed thoroughly with distilled water, ethanol, and acetone and then dried in air. In all experiments, we found that the FT-IR spectrum of the exchanged solid showed a depression of the strong band at 1460 cm^{-1} and the disappearance of all medium and weak bands associated with $C_6H_{12}NH$ cations in the original unexchanged samples.[9] Furthermore, a concomitant decrease in the carbon (from ∼20 to 10%) and nitrogen (from ∼4 to 2%) content in the exchanged solids was observed— corresponding to the exchange of 40−50% of organic guests with inorganic cations.[15,16]

To study the sorption within the pores, we measured the water sorption isotherm for the exchange product, $In_{10}S_{18} \cdot (C_6H_{12}NH_2)_3$-$Ca_{1.5}(H_2O)_{12}$.[17,18] It revealed a type I isotherm in the range $P/P_0 = 0−0.50$, followed by a weak uptake above $P/P_0 > 0.50$ as shown in Figure 3.[19] The observed initial sorption is consistent with favorable H_2O-Ca^{2+} interaction within the pores, and it is equivalent, at the first saturation psuedoplateau, to the sorption of 12 H_2O molecules. The second step is a weak uptake in the range of water capillary condensation; it is equivalent to the sorption of an additional 4 H_2O, which are readily lost upon drying the sample for elemental microanalysis.[17] The fact that no further sorption was observed near saturation pressure (Figure 3) indicates complete filling of the pores; the second step is driven by water−water interactions inside the pores rather than on the crystal surface. Even though most of the fixed pore volume in $In_{10}S_{18} \cdot (C_6H_{12}NH_2)_3Ca_{1.5}$ is occupied by guest cations, the remaining total void space occupied by the 16 water molecules per formula unit is estimated to be 0.14 cm^3/g, which is still as large as the void volume found in most zeolites.[19]

Supporting Information Available: Crystallographic data for ASU-34 including crystal structure analysis report, positional parameters, thermal parameters, and interatomic distances and angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) For expanded and contracted cristobalite frameworks, see: O'Keeffe, M.; Hyde, B. G. *Acta Cryst.* **1976**, *B32*, 2923. (b) Here, the atoms at the vertices of the supertetrahedra are S5,[10] each of which have 12 nearest S5 neighbors at 11.76 to 11.83 Å.

(12) Van der Waals radii of 1.8 and 2.0 Å for S and In, respectively, were employed in the evaluation of empty space, which was done by a Monte Carlo type of integration using Sobol quasi-random numbers. Press, W. H.; Teulolsky, S. A.; Vetterling, W. T.; Flannery, B. P.; *Numerical Recipes*, 2nd ed.; Cambridge University Press: New York, 1993.

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(15) Exposing ASU-34 to a more concentrated solution (5 M) of sodium nitrate over a longer period of time (7 d), gives a total exchange of 70%. Anal. Calcd for $In_{10}S_{18} \cdot (C_6H_{12}NH)_{1.5}(Na)_{4.5}(H_2O)_{20}$ C, 4.62; H, 2.63; N, 0.90; S, 24.67%. Found C, 4.95; H, 1.79; N, 0.86; S, 24.43%.

(16) X-ray powder diffraction data for the as-synthesized ASU-34 and a typical exchanged material (*italics*). The most prominent lines are recorded with *d*-spacings in Å. Observed: 15.49, *15.94*; 9.95, *9.95*; 3.34, *3.34*. Data were collected under saturated water vapor.

(17) Anal. Calcd for $In_{10}S_{18} \cdot (C_6H_{12}NH)_3(Ca)_{1.5}(H_2O)_{12}$ C, 9.18; H, 3.08; N, 1.78; S, 24.50%. Found C, 9.83; H, 2.61; N, 1.30; S, 23.72%.

(18) Attempts to measure N_2 sorption isotherm at 77 K for this material were unsuccessful, possibly due to blockage of the pore aperture by the remaining guests.

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