20 Å Cd$_4$In$_{16}$S$_{35}$$^{14-}$ Supertetrahedral T4 Clusters as Building Units in Decorated Cristobalite Frameworks

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The process of replacing a vertex in a network by a group of vertexes—termed decoration—has been recognized as an important strategy for designing low-density (porous) metal−organic frameworks.[1] We and others have recently employed this strategy in the synthesis of inorganic frameworks based on TX$_4$ (T1) tetrahedra by using Tn supertetrahedral clusters in which n tetrahedra are linked along each edge as illustrated in Figure 1.[2,3] Ge$_4$S$_{10}$$^{4-}$ (T2) and In$_{10}$S$_{20}$$^{10-}$ and B$_{10}$S$_{20}$$^{10-}$ (T3) supertetrahedra have been linked into the cristobalite framework of SiO$_2$ (Si atoms on a diamond network), in which SiO$_4$ tetrahedra are replaced by T2 or T3 clusters to produce large-pore structures. However, structures with larger Tn supertetrahedral units remain unknown,[4] although they have the potential of creating novel low-density nanoporous crystalline solids as well as yielding ordered and regular arrays of clusters that are comparable in size to individual nanocrystallites of tetrahedral quantum dots of CdS and other group 12 chalcogenides.[4,5] Here we report the preparation of T4 clusters of 20 Å dimension[6] in a Cd$_4$In$_{16}$S$_{33}$$^{10-}$ cristobalite framework, and discuss the essential role Cd^{2+} plays in facilitating the realization of such structures.

Yellow octahedral crystals of Cd$_4$In$_{16}$S$_{33}$·(H$_2$O)$_{20}$(C$_{10}$H$_{28}$N$_4$)$_{2.5}$ (hereafter CdInS-44) were prepared by reacting a water (1.0 mL) and ethylene glycol (0.5 mL) solution mixture of In (65.0 mg, 0.57 mmol), S (45.0 mg, 1.40 mmol), Cd(CH$_3$CO$_2$)$_2$·2H$_2$O (40.0 mg, 0.15 mmol), and 1,4-bis(3-aminopropyl)piperazine (BAPP)
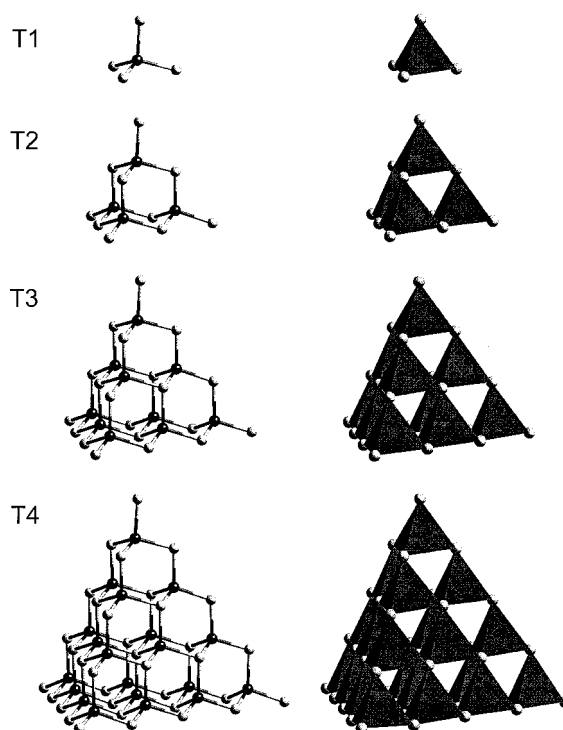

Figure 1. Construction of supertetrahedra from a single tetrahedron (T1, MX$_4$) shown in progression of size from T2 (M$_4$X$_{10}$) to T3 (M$_{10}$X$_{20}$) to T4 (M$_{20}$X$_{35}$). Here M is a metal cation and X is anion such as sulfide.

(0.50 mL, 2.43 mmol) at 145 °C in a Teflon-lined vessel for 4 days. This phase is insoluble in water and organic polar and nonpolar solvents.

A single-crystal X-ray diffraction study[7] on CdInS-44 showed that its structure is composed of two intergrown networks each constructed from T4 units that are linked together by doubly bridging sulfide atoms to produce a cristobalite (SiO$_2$) topology: each T4 supertetrahedron decorates the vertexes occupied by Si and the sulfides bridging the T4 units replace the −O− links (Figure 2a). Each T4 supertetrahedron is nearly regular with edge lengths (S···S distances) of 15.69 and 15.85 Å. However, since the T−S−T angle (106.9 (3)°) is significantly less than the typical T−O−T angle (145° in cristobalite), the resulting network is relatively contracted. As In^{3+} and Cd^{2+} are isoelectronic they cannot be distinguished directly by X-ray diffraction; however, the Cd/In ratio was determined by elemental microanalysis[8] and verified by analysis of the bond lengths. The bonds to S from the inner metal sites in each T4 range from 2.502(2) to 2.516(7) Å (average 2.507(4) Å), which can be compared with the Cd−S distance of 2.525 Å in the sphalerite structure of CdS and 2.55 Å

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(7) Single crystals of CdInS-44 are, at 298°K, tetragonal, space group *I*4$_1$/*acd* with *a* = 23.580 (8) Å, *c* = 43.92 (1) Å, *V* = 24422 (14) Å^3, and *Z* = 16 formula units {based on CdInS framework, d_{calcd} = 1.825 g cm^{-3}; μ_a(Mo Kα) = 4.264 mm^{-1}}. A total of 15484 integrated reflection intensities having 2Θ-(Mo Kα) < 49.96° were produced using the Bruker program SAINT version 6.02A. A total of 5027 of these were independent and gave R_{int} = 0.1102. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL-97 software package and converged to give R_1 (unweighted, based on F) = 0.1138, wR_2 (weighted, based on F^2) = 0.2664, and goodness of fit (S) = 1.114. Sulfur and indium were refined with anisotropic displacement parameters. All metal positions were refined as indium atoms. Although water and BAPP cation molecules were not included in the model due to major disorder problems and diffuse electron density, the residual electron density indicates their presence in the pores. However, attempts to include the guests in the model did not improve the refinement.

(8) (a) Anal. Calcd for CdInS-44 or Cd$_4$In$_{16}$S$_{33}$·(H$_2$O)$_{20}$(C$_{10}$H$_{28}$N$_4$)$_{2.5}$: C, 7.12; H, 2.63; N, 3.32; S, 25.09; Cd, 10.67; In, 43.58. Found: C, 7.10; H, 2.49; N, 3.37; S, 24.61; Cd, 10.56; In, 42.60. (b) FT-IR (KBr, BAPP range, 1500−700 cm^{-1}): 1466.2 (m), 1150.3 (b), 1005.5 (w), 755.4 (s).
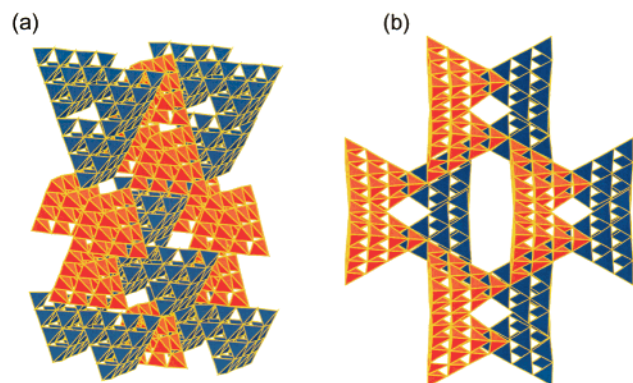
Figure 2. The crystal structure of CdInS-44 containing two interpenetrating cristobalite-like networks (a) (blue and red) and large channels shown in the [111] projection (b).

Table 1. Composition and Charge per Supertetrahedon for Condensed Supertetrahedral Structures[a]

	binary composition	charge	ternary composition	charge	S coordination		
					4	3	2
T1	InS_2	-1			0	0	2
T2	In_4S_8	-4			0	0	8
T3	$In_{10}S_{18}$	-6			0	4	14
T4	$In_{20}S_{33}$	-6	$Cd_4In_{16}S_{33}$	-10	1	12	20
T5	$In_{35}S_{54}$	-3	$Cd_{13}In_{22}S_{54}$	-16	4	24	26
T6	$In_{56}S_{82}$	$+4$	$Cd_{28}In_{28}S_{82}$	-24	10	40	32
T7	$In_{84}S_{118}$	$+16$	$Cd_{50}In_{34}S_{118}$	-34	20	60	38
T8	$In_{120}S_{163}$	$+34$	$Cd_{80}In_{40}S_{163}$	-46	35	84	44

[a] Cd and In are used generically for divalent and trivalent cations, and S for a divalent anion.

expected from bond valence parameters.[9] For the remaining sites, the T–S bond lengths are significantly shorter: 2.403(6)–2.487-(7) Å (average 2.451(6) Å), a value that is typical for a tetrahedral In–S bond length (2.47 Å).[9]

The number of tetrahedra (T atoms) in a Tn supertetrahedron is the nth tetrahedral number $t_n = n(n + 1)(n + 2)/6$. The number of distinct vertexes (X atoms) in one supertetrahedron is t_{n+1}. In a continuous framework, each of the four outermost vertexes of a supertetrahedron is shared with another supertetrahedron so the overall composition is T_xX_y with $x = t_n$ and $y = t_{n+1} - 2$. Table 1 lists compositions for some small values of n and also the formal charge per cluster assuming T is trivalent (e.g. B or In) and X is divalent (e.g. S). Notice that the charge changes sign between T5 and T6. However, as we next discuss, we feel it is less likely that binary clusters larger than T3 will be stable for trivalent cations, and that the use of divalent ions such as Cd^{2+} is essential in accessing larger clusters.

Although all the T atoms are 4-coordinated, the X atoms have 2-coordination (on the supertetrahedron edges and the outermost vertexes), 3-coordination (in the supertetrahedron faces), and 4-coordination (inside the cluster). Per Tn cluster in a corner-linked framework, the number of 2-coordinated S atoms is $6n - 4$, the number of 3-coordinated S atoms is $2(n - 1)(n - 2)$ and when $n = 4$, the number of 4-coordinated S atoms is t_{n-3} (zero

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for $n < 4$). In the limit of large n the structure approaches that of sphalerite ZnS, and in this limit the T atoms must be divalent as the whole (neutral) crystal is one giant cluster. We suppose that in accord with Pauling's electrostatic valence rule, or better, in accordance with Brown's equal valence rule,[10] the 4-coordinated divalent X atoms (e.g. S atoms) will be bonded only to divalent tetrahedral (T) atoms (such as Cd) so that each of these X atoms forms four bonds with bond valence 1/2. For this to be the case the number of trivalent T atoms will be $6n - 8$, and the number of divalent atoms is accordingly $t_n - 6n + 8$, thus progressively larger Tn supertetrahedra will have an increasing ratio of divalent to trivalent cation and the charge per cluster remains negative (Table 1). Note that the hypothesis that the four-connected S atoms in CdInS-44 are bonded to Cd is confirmed both by the chemical analysis and by the bond length analysis given above.

Despite being contracted and 2-fold intergrown (interpenetrated), the structure of CdInS-44 contains large cavities: in particular there are 20×6 Å^2 rectangular channels in the [111] projection (Figure 2b).[6] Although the positions of the framework atoms were determined accurately, the guest atoms filling the pores were not located due to the disorder problems usually encountered in this kind of structure. Nevertheless, elemental microanalysis and FTIR confirmed the presence of 20 water and 2.5 BAPP guests for each T4 cluster or 160 water and 20 BAPP molecules per unit cell.[7,8] These guests fill a calculated nonframework void space that is 53% of the crystal volume.[6,11] Thermal gravimetric measurements on CdInS-44 showed two major weight loss steps in two temperature ranges indicating the removal of guests from the voids: (a) 8.4% between 23 and 180 °C associated with the removal of 20 water molecules per formula unit (calcd: 8.5%), and (b) 14.0% between 230 and 430 °C attributed to the decomposition of 2.5 BAPP guests (calcd: 12.1%) and the loss of 1.9% of S. At 600 °C, this material is converted to $CdIn_2S_4$ and In_2S_3 as evidenced by X-ray powder diffraction. In contrast to the behavior of the T3 analogue (ASU-34),[3e] preliminary attempts to exchange BAPP guests with small inorganic cations by exposing solids of CdInS-44 to concentrated solutions of simple inorganic salts showed very little to no exchange. We believe that the rectangular nature of the void openings hinder the facile diffusion of large guests such as BAPP from the structure.

Supporting Information Available: Crystallographic data, bond lengths, and angles for CdInS-44 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Cerius2.0 was used to calculate the volume occupied by interpenetrating frameworks which is then subtracted from the crystal volume to give the total volume of voids. Crevices below 1.0 Å in diameter were included in the space occupied by the frameworks and thus not included in the void volume.