

[Cd₁₆In₆₄S₁₃₄]⁴⁴⁻: 31-Å Tetrahedron with a Large Cavity***Hailian Li, Jaheon Kim, Michael O'Keeffe, and Omar M. Yaghi***Dedicated to Professor Gérard Férey on the occasion of his 60th birthday*

Structures constructed from supertetrahedral clusters of TX₄ tetrahedra may have giant pores representing more than 80 % of their crystal volume and cation-exchange properties.^[1] As well as creating porous materials we note that larger clusters are comparable in size with the individual nanocrystallites of tetrahedral sulfide (e.g. CdS) “quantum dots” which show great promise and are currently being investigated as quantum-dot lasers and other optical devices.^[2] Similarly, interesting optical properties might be expected in supertetrahedral crystals of semiconducting sulfides.^[2h] Clusters labeled T_n have *n* tetrahedra along each edge.^[1] Isolated T₂ units are very familiar in chemistry, in molecules such as P₄O₁₀, Ge₄S₆Br₄, anions such as [Ge₄S₁₀]⁴⁻, and condensed (corner-sharing) in framework crystals particularly of halides,^[3] but also of sulfides^[4] and of nitrides.^[5] A number of extended tetrahedral frameworks based on T₃ sulfides, mostly of B^[6] or In,^[1,7] with a variety of frameworks have been prepared.

To prepare the T₄ generation of the indium sulfide clusters, we and others have recently shown that in addition to In³⁺, it is necessary to have divalent metal ions, such as Cd²⁺.^[8,9] The likely distribution of different valence cations in larger T_n clusters was also delineated.^[8] A number of compounds with frameworks of alternating T₁ and T₂ units^[10] and recently containing T₃ and T₅ units^[11] have also been described. Other even larger (not supertetrahedral) chalcogenide clusters are known.^[12]

Herein we report the preparation of the first compound representing the next stage of a structural hierarchy, that is, supertetrahedra of supertetrahedra; specifically a T₂ supertetrahedron of T₄, a discrete anionic cluster of 214 atoms and 80 tetrahedral centers.

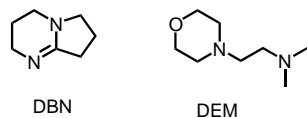
This material was synthesized by combining an aqueous mixture (2.2 mL) of In (50.0 mg, 0.44 mmol), S (70.0 mg, 2.18 mmol), Cd(CH₃CO₂)₂·2H₂O (200 mg, 0.75 mmol), DBN

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(1,5-diazabicyclo[4,3,0]-non-5-ene) (0.40 mL, 3.24 mmol), and DEM (4-[2-(dimethylamino)ethyl]morpholine) (0.75 mL, 4.38 mmol), which was heated at 138 °C in a 23-mL teflon-lined vessel for 5 days.



The resulting yellow octahedral crystals (12.8% yield based on In) were isolated by density-difference separation and washed with several aliquots of water, ethanol, and acetone, and formulated as $\text{Cd}_{16}\text{In}_{64}\text{S}_{134} \cdot (\text{DBNH}_2)_{11}(\text{DEMH}_2)_{11}(\text{H}_2\text{O})_{50}$ (hereafter CdInS-420) from elemental microanalysis and single-crystal X-ray diffraction results.^[13,14]

The crystal structure revealed the presence of finite tetrahedral anionic units of $[\text{Cd}_{16}\text{In}_{64}\text{S}_{134}]^{44-}$ that have an underlying T2 type of structure in which the individual tetrahedra have each been replaced by a T4 supertetrahedron (Figure 1) forming a super-supertetrahedron. Since In^{3+} and Cd^{2+} centers are isoelectronic they cannot be distinguished directly by X-ray diffraction. However, the Cd/In ratio was determined by elemental microanalysis^[13] and verified by analysis of the bond lengths. The bonds to S atoms from the four inner metal sites in each T4 unit range from 2.502(11)–2.532(11) Å (average 2.516(11) Å). This value can be compared with the Cd–S separation of 2.525 Å in the sphalerite structure of CdS and the 2.55 Å expected from bond valence parameters.^[15] For the remaining sites, the T–S bond lengths are significantly shorter: 2.382(10)–2.520(11) Å (average 2.453(11) Å), a value that is typical for a tetrahedral In–S bond length (expected^[15] 2.47 Å).

The clusters (with S_4 symmetry) are nearly regular tetrahedra with edge lengths (S··S separations) of 31.06 and 31.07 Å, and with an overall volume of 3531 Å³. Each has a large octahedral cavity of diameter of 22.3 Å (S··S distance between opposing vertices), which can be accessed through open triangular faces of edge 15.8 Å.

Although the positions of Cd, In, and S of the cluster were determined accurately, the guest molecules and organic ammonium counterions filling the pores and residing between

the anions in the crystal were not all located because of the disorder problems usually encountered in this kind of structure. Nevertheless, ¹³C cross-polarization magic-angle spinning (CPMAS) NMR spectroscopy measurements showed resonance signals for all the anticipated types of C atoms, which appeared in their respective chemical shift regions.^[16] Furthermore, elemental microanalysis and FTIR^[17] confirmed the presence of 50 water molecules plus 11 DBNH_2^{2+} and 11 DEMH_2^{2+} ions. There are four clusters per unit cell, packed around 4₁ and 4₃ axes (Figure 1). The unit cell also contains 200 water molecules, and 88 organic ammonium dications. These guests fill an otherwise void space calculated to be 55% of the crystal volume.

Thermogravimetric measurements on CdInS-420 showed two major weight-loss steps in two temperature ranges indicating the removal of water guests and decomposition of the cations: a) 5.16% between 25 °C and 150 °C associated with the removal of 50 water molecules per formula unit (calcd: 5.14%), and b) 20.73% between 170 °C and 440 °C attributed to the decomposition of 11 DBNH_2^{2+} and 11 DEMH_2^{2+} counterions (calcd: 18.1%) and the loss of 2.72% of the S atoms. Preliminary attempts to exchange the organic counterions with small inorganic cations by exposing solids of CdInS-420 to concentrated solutions of simple inorganic salts showed no exchange, which points to the strong ionic forces existing between the ions in the crystal.

The structure of this anion is intriguing since it represents a new level of complexity in the structures of tetrahedra. At the outset of this study all tetrahedral units of TX_4 tetrahedra have been limited to the simple T_n ($n = 1-5$) series in which the resulting units are composed entirely of condensed tetrahedra. The present compound shows how open tetrahedra can be prepared using those T4 condensed clusters as building blocks. Thus, we propose to extend the notation for supertetrahedra^[1] to include this first member of what we believe will be an extensive series. Specifically, $T_{p,q}$ will be used to describe a T_q supertetrahedron of T_p supertetrahedra. The number of tetrahedra (T atoms) in a T_p supertetrahedron is the p th tetrahedral number, $t_p = p(p+1)(p+2)/6$, and the number of X atoms is t_{p+1} . In a $T_{p,q}$ super-supertetrahedron the number of T atoms is $t_q t_p$ and the number of X atoms is $t_q(t_{p+1}-2)+2$. In this notation the cluster in CdInS-420 is T4,2.

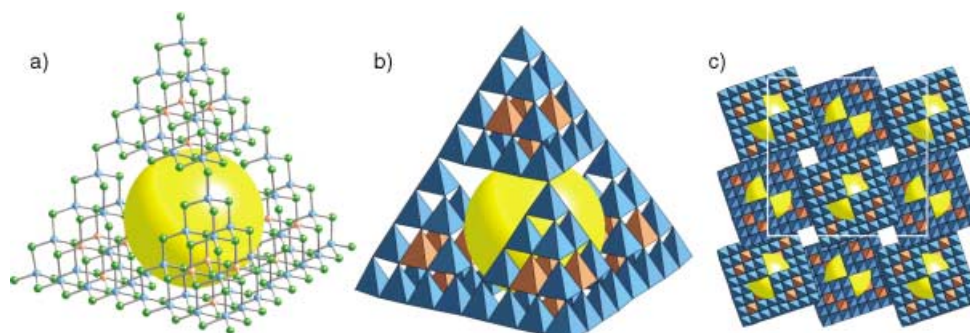


Figure 1. a) The CdInS-420 cluster as a ball and stick model. In blue; Cd orange; S green. The large yellow sphere indicates the central cavity. b) The same view as (a) shown as metal-centered tetrahedra. c) Crystal packing of the clusters illustrated as metal-centered tetrahedra, view down the c axis with the unit cell outlined in white.

An obvious extension of the notation is to structures Tp,q,r which are Tr supertetrahedra of Tp,q super-supertetrahedra. We note (Figure 1) that the In-S structure of CdInS-420 alone is a $T2,2,2$ structure which we may also write $T2^3$. The infinite sequence $T2^\infty$ describes the structure of the famous self-similar fractal structure known as the Sierpinski tetrahedron.^[18] In condensed frameworks (e.g. diamond-like) of $T2^n$ units the overall composition is always TX_2 , and their realization in a compound such as GeS_2 (already known as $n = 0$ and 1 structures^[4a]) is an interesting synthetic challenge.^[19]

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- [13] Elemental microanalysis calcd (%) for $C_{165}H_{474}N_{44}O_{61}S_{134}Cd_{16}In_{64} = Cd_{16}In_{64}S_{134}(DBNH_2)_{11}(DEM H_2)_{11}(H_2O)_{50}$: C 11.33, H 2.73, N 3.52, S 24.56, Cd 10.28, In 42.00; found C 11.28, H 2.35, N 3.61, S 22.94, Cd 10.56, In 41.82.
- [14] Crystal data for CdInS-420: A yellow octahedral crystal ($0.16 \times 0.16 \times 0.16 \text{ mm}^3$) of CdInS-420 was analyzed: Siemens SMART CCD diffractometer, ω scans, graphite-monochromated $Mo_{K\alpha}$ radiation, $T = 158(2) \text{ K}$, tetragonal, space group $I4_1/a$ (No. 88) with $a = 43.297(2)$, $c = 27.7067(14) \text{ \AA}$, $V = 51940(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.237 \text{ g cm}^{-3}$, and $\mu(Mo_{K\alpha}) = 40.01 \text{ cm}^{-1}$. Total 184910 reflections were collected within $2\theta_{\text{max}} = 41.36^\circ$ with a ω scan width of 0.3° ; 18710 independent reflections, 7385 with $I > 2\sigma(I)$. Absorption correction with SADABS $T_{\text{min}} = 0.2799$, $T_{\text{max}} = 0.8369$. All Cd, In, and S atoms were located on the general positions except for the S(21) atom that sits on the twofold crystallographic axis with occupancy a half. Because of the severe disorder of the guest molecules, it was difficult to locate the counterions; only two DBN units were found in the asymmetric unit and fifty randomly distributed peaks were considered and included as part of guest molecules in the refinement process. All the atoms in the cluster were refined anisotropically, but the disordered guest molecules were treated isotropically. Final full-matrix least-squares refinement on F^2 converged to $R1 = 0.1247$ ($I > 2\sigma(I)$) and $wR2 = 0.2959$ (all data) with $GOF = 1.082$. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.48 and -1.92 e \AA^{-3} , respectively. CCDC-197754 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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