

Three-Dimensional Superlattices Built from $(M_4In_{16}S_{33})^{10-}$ ($M = Mn, Co, Zn, Cd$) Supertetrahedral Clusters

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Semiconducting nanoparticles have been undergoing rapid development because of the feasibility for property engineering based on the particle size. These nanoparticles have properties intermediate between bulk materials and individual molecules and can serve as artificial atoms for constructing a variety of functional materials.

Nanoparticles can crystallize into colloidal or molecular crystals in which they are generally held together via weak van der Waals interactions.¹ In molecular crystals, nanoclusters have well-defined chemical compositions and are free from size dispersion.² These materials may therefore be useful for size-dependent property measurements that are free from the ambiguity due to size dispersion or surface irregularity.

For some applications (e.g., as porous hosts), a covalent network of nanoclusters is preferable.³ By variation of the cluster size, it should be possible to generate extended frameworks with tailored pore sizes and topological features. Unfortunately, most nanoparticles are unsuitable for such a purpose because of irregularity in size and surface features. One family of clusters suitable for constructing covalent frameworks are denoted as T2 (M_4X_{10}), T3 ($M_{10}X_{20}$), T4 ($M_{20}X_{35}$), and so on, where M is a metal cation such as In^{3+} and X is generally a chalcogen such as S^{2-} . These clusters are in fact nanosized fragments of the cubic CdS phase. For a T_n supertetrahedron, n is the number of layers for metal atoms. The structure of a T4 cluster is illustrated in Figure 1.

Supertetrahedral cluster can behave like artificial tetrahedral atoms and form extended frameworks similar to zeolites.^{4,5} For example, from T3 clusters, open-framework sulfides based on diamond, double diamond, sodalite, and CrB_4 lattices have been reported.^{6–11} In these T3 structures, the maximum ring size in terms of the number of supertetrahedral clusters is thus far limited to six.

To generate large pores and to investigate size-dependent properties of nanoclusters, the creation of frameworks from larger

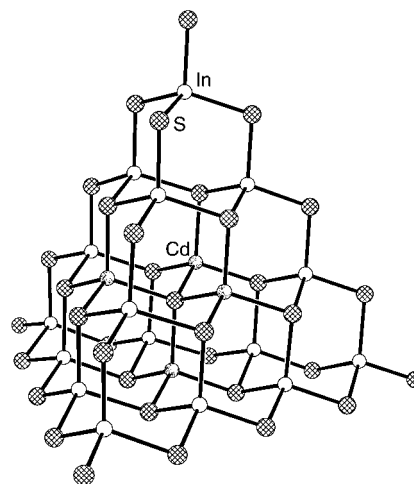


Figure 1. Structural diagram of a T4 cluster, $Cd_4In_{16}S_{35}$, in UCR-1CdInS. The framework formula is $Cd_4In_{16}S_{33}$ because each terminal S^{2-} is shared between two clusters.

clusters such as T4 or higher is desirable. Prior to this work, the only framework structure built from T4 clusters (i.e., CdInS-44) consists of two interpenetrating cristobalite lattices.⁸ Here, we report a family of T4-based noncentrosymmetric three-dimensional sulfides (denoted as UCR-1MInS, $M = Mn^{2+}, Co^{2+}, Zn^{2+}$, or Cd^{2+} , collectively called UCR-1) with a maximum ring size of eight. The four-connected topology in UCR-1 has not been found in known zeolite topologies. Several related compounds (collectively called UCR-5) constructed from $[M_4In_{16}S_{35}]^{14-}$ ($M = Zn^{2+}, Mn^{2+}$, or Co^{2+}) supertetrahedral clusters are also presented here. The framework type of UCR-5 is the same as that of CdInS-44.⁸ In both UCR-1 and UCR-5, the incorporation of the first-row transition metals into the core of T4 clusters makes it possible to obtain the first direct evidence about the preferential distribution of divalent and trivalent cations in T4 clusters.

To prepare crystals of UCR-1CdInS, indium metal (85 mg), sulfur (68 mg), $CdCl_2 \cdot 2.5H_2O$ (46 mg) and 4,4'-trimethylenedipiperidine (TMDP) (608 mg) were mixed in a 23 mL Teflon-lined stainless steel autoclave. After addition of distilled water (4.231 g), the mixture was stirred for 10 min. The vessel was then sealed and heated at 190 °C for 10d. The autoclave was subsequently allowed to cool to room temperature. Light-yellow prismatic crystals were obtained in 79% yield. UCR-1CdInS can also be synthesized under similar conditions with ethylene glycol as a cosolvent (up to 80 wt %). Crystals of other phases (Table 1) were synthesized under similar conditions. Starting materials included $Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Mn(CH_3COO)_2 \cdot 4H_2O$.

Crystal structures were solved from single-crystal data collected at room temperature on a SMART CCD diffractometer (Table 1). While all framework atoms can be determined, the guest molecules are disordered inside large cavities. In UCR-1, one-half of the T4 cluster is crystallographically unique because it is located on a two-fold rotation axis. Using UCR-1CdInS as an example, the dimensions of six edges of the T4 cluster are 15.47 Å ($\times 2$), 15.66 Å, 15.71 Å ($\times 2$), and 16.06 Å. Taking into account of van der Waals radius of the sulfur atom (1.8 Å), each edge of the supertetrahedron is about 20 Å long.

In UCR-1CdInS, each T4 cluster is connected by S^{2-} to four other T4 clusters with a center-to-center distance of 15.84 Å, comparable to the dimension of the supertetrahedral edge (Figure 2). A four-connected three-dimensional net is obtained by considering each T4 cluster as an artificial tetrahedral atom (T-atom). This net consists of only four- and eight-rings. Each T-atom

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(1) Collier, C. P.; Vossmeier, T.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371–404.

(2) Soloviev, V. N.; Eichhofer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2001**, *123*, 2354–2364.

(3) Vossmeier, T.; Reck, G.; Katsikas, L.; Haupt, E. T. K.; Schulz, B.; Weller, H. *Science* **1995**, *267*, 1476–1479.

(4) Bedard, R. L.; Wilson, S. T.; Vail, L. D.; Bennett, J. M.; Flanigen, E. M. In *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference*; Jacobs, P. A., van Santen, R. A., Eds.; Elsevier: Amsterdam 1989; p 375.

(5) Rangan, K. K.; Trikalitis, P. N.; Bakas, T.; Kanatzidis, M. G. *Chem. Commun.* **2001**, 809–810.

(6) Cheetham, A. K.; Ferey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.

(7) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145–1147.

(8) Li, H.; Kim, J.; Groy, T. L.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4867–4868.

(9) Cahill, C. L.; Ko, Y.; Parise, J. B. *Chem Mater.* **1998**, *10*, 19–21.

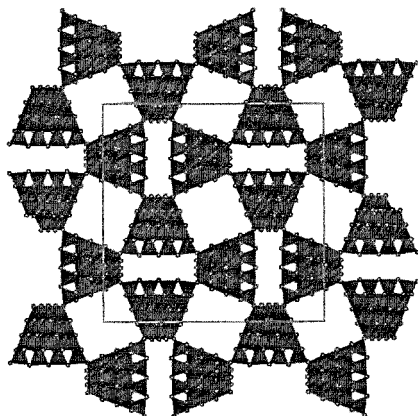
(10) Cahill, C. L.; Parise, J. B. *J. Chem. Soc., Dalton Trans.* **2000**, 1475–1482.

(11) Li, H.; Eddaouli, M.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 6096–6097.

Table 1. A Summary of Crystallographic Data for New T4 Framework Structures Synthesized in This Study

name	T4 cluster	amine ^a	sp. gr.	<i>a</i> (Å)	<i>c</i> (Å)	<i>R</i> (<i>F</i>) ^b	2 <i>q</i> _{max}	M–S (Å) ^c
UCR-1CdInS	[Cd ₄ In ₁₆ S ₃₃] ¹⁰⁻	TMDP	I-42d	42.105(3)	16.700(2)	6.72	45	2.503(6)
UCR-1ZnInS	[Zn ₄ In ₁₆ S ₃₃] ¹⁰⁻	TMDP	I-42d	41.811(8)	16.685(4)	7.93	45	2.384(6)
UCR-1MnInS	[Mn ₄ In ₁₆ S ₃₃] ¹⁰⁻	TMDP	I-42d	41.974(5)	16.727(3)	6.52	45	2.417(6)
UCR-1CoInS	[Co ₄ In ₁₆ S ₃₃] ¹⁰⁻	TMDP	I-42d	41.698(8)	16.673(5)	8.32	45	2.344(7)
UCR-5ZnInS-1	[Zn ₄ In ₁₆ S ₃₃] ¹⁰⁻	BAPP	I4 ₁ /acd	23.580(8)	43.92(1)	8.51	40	2.401(3)
UCR-5ZnInS-2	[Zn ₄ In ₁₆ S ₃₃] ¹⁰⁻	AEPP	I4 ₁ /acd	23.396(8)	43.44(2)	9.87	40	2.381(4)
UCR-5ZnInS-3	[Zn ₄ In ₁₆ S ₃₃] ¹⁰⁻	ATMP	I4 ₁ /acd	23.88(2)	43.69(2)			
UCR-5MnInS	[Mn ₄ In ₁₆ S ₃₃] ¹⁰⁻	BAPP	I4 ₁ /acd	23.45(2)	43.60(5)			
UCR-5CoInS	[Co ₄ In ₁₆ S ₃₃] ¹⁰⁻	BAPP	I4 ₁ /acd	23.29(4)	43.44(6)			

^a TMDP = 4,4'-trimethylenedipiperidine; BAPP = 1,4-bis(3-aminopropyl)piperazine; AEPP = 1-(2-aminoethyl)piperazine; ATMP = 4-amino-2,2,6,6-tetramethylpiperidine. ^b *R*(*F*) = $\sum||F_o| - |F_c|| / \sum|F_o|$ with $F_o > 4.0\sigma(F)$. Single-crystal data with Mo K α . (c) The M–S distance is the average bond distance in the tetrahedral SM₄ unit.

**Figure 2.** Three-dimensional framework projected down the *c* axis showing the connectivity among T4 supertetrahedra in UCR-1CdInS.

is involved with two four-rings sharing a common corner as in sodalite. Such structural feature is called the T-atom loop configuration in zeolites.¹² In addition, each T-atom is also associated with four eight-rings, and thus the vertex symbol for this net is 4.4.8.8.8.8. No four-connected net in known zeolite structures is identical to the net in UCR-1 in both T-atom loop configuration and vertex symbol.¹³

In a T4 cluster, only one S²⁻ is tetraordinated. This sulfur anion is located at the center of the T4 cluster. Sulfur anions located on the vertexes and edges of the supertetrahedra are bicoordinated, whereas those located on the faces of the supertetrahedra are tricoordinated. While the M/X ratio in uninterrupted zeolite frameworks is 2, the M/X ratio in four-connected supertetrahedral T_n structures (*n* > 2) is always less than 2 because of the presence of tricoordinated sulfur sites for clusters T3 or larger and tetrahedral sulfur sites for clusters T4 or larger.

It is worth noting that the framework structure of UCR-1 is noncentrosymmetric. It is also observed that three-dimensional frameworks built from smaller clusters such as T3 are also noncentrosymmetric when the intergrowth of two lattices is avoided.¹¹ This ability to form noncentrosymmetric structures from clusters such as T4 and T3 is in contrast with conventional zeolites that typically crystallize into centrosymmetric structures.¹² It may be related to the fact that the T_n supertetrahedraon itself is noncentrosymmetric. It is anticipated that the continued development of supertetrahedra-based framework materials might have implications as nonlinear optical materials or in their potential use as noncentrosymmetric host.

The presence of divalent cations (i.e., Mn, Co, Zn, or Cd) in T4 clusters (Table 1) is confirmed by energy dispersive spectra.

(12) Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*; Elsevier: Amsterdam, 1996.

(13) O'Keeffe, M.; Hyde, S. T. *Zeolites* **1997**, *19*, 370–374.

In UCR-1CdInS, Cd²⁺ and In³⁺ sites could not be distinguished from single-crystal structure refinement because Cd²⁺ and In³⁺ are isoelectronic. The Cd²⁺ sites are assigned to four metal sites (only two are unique in UCR-1) surrounding the tetrahedral S²⁻ site according to the Brown's bond valence model.¹⁴ Valence sums for two Cd²⁺ sites are 2.23 and 2.27, respectively, whereas valence sums for eight In³⁺ sites range from 2.92 to 3.06.

To obtain more direct information about the distribution of divalent and trivalent cations in a T4 cluster, we prepared a series of structures in which the first-row transition metals are incorporated into [M₄In₁₆S₃₃]¹⁴⁻ clusters. In these clusters, both the electron density and the bond distance indicate that four metal sites surrounding the tetrahedral sulfur atom are predominantly occupied by divalent cations such as Zn²⁺ or Mn²⁺ (Table 1).

Fluorescent spectra of UCR-1CdInS showed a broad emission centered at 521 nm. The excitation spectra showed an absorption onset of 350 nm and the maximum absorption at 401 nm.¹⁵ The fit to a triexponential equation gives $\tau = 1.1, 4.6,$ and 23.2 ns. In comparison, open framework oxides were previously found to display photoluminescence with the emission maximum between 400 and 430 nm.¹⁶ It appears that by varying the composition of open-framework materials, it is possible to develop a family of inorganic–organic phosphors with a broad range of emission characteristics.

UCR-1CdInS can undergo a partial ion exchange. In one experiment, about 0.08 g of crystals of UCR-1CdInS was added to a KCl solution (50.09 g, 1.09M). After standing at room temperature for 24 h, the mixture was filtered, washed with ethanol, and dried at 110°C for 12 h. The crystallinity of the sample was confirmed by X-ray powder diffraction before and after the ion-exchange. The elemental analysis shows a significant decrease in the C, H, and N content.¹⁷

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA011739R

(14) Slupecki, O.; Brown, I. D. *Acta Crystallogr.* **B38**, 1078–1079.

(15) Fluorescent spectra were measured on a SPEX Fluorolog-3 Tau3 system equipped with a 450 W xenon lamp.

(16) Feng, P. *Chem. Commun.* **2001**, 1668–1669.

(17) Results of the elemental analysis (in wt %) for UCR-1CdInS are 16.84 (calcd 16.82) for C, 3.09 (calcd 3.61) for H, and 2.81 (calcd 3.02) for N before the ion exchange and 12.88 for C, 2.11 for H, and 2.12 for N after the exchange. The calculated values are based on the formula [Cd₄In₁₆S₃₃](C₁₃H₂₈N₅)(H₂O)_x (*x* ≈ 13).