lonate pathways in *H. halobium* are identical with those in other organisms.

As discussed above, the cryptic stereochemistry involved in the incorporation of glycerol into the membrane lipid of *H. halobium* was firmly established. In contrast to eubacteria and eukaryotes, it is the *sn*-C-1 methylene group of 2,3-di-*O*-phytanyl glycerol that is derived from the *sn*-C-3 carbon of glycerol and the C-6 carbon of D-glucose. Although stereochemically feasible, a pathway including reduction of D-glyceraldehyde-3-phosphate can be ruled out, since the present as well as previous studies clearly showed that no hydrogen was lost from either hydroxymethyl group of glycerol.[3,4] Furthermore, the ether-forming reaction is also different from that of *O*-alkyl dihydroxyacetone phosphate in mammalian cells,[9,10] in which a hydrogen of the *sn*-C-1 methylene group is stereospecifically replaced. Consequently, the most likely mechanism of formation of *sn*-2,3-*O*-diphytanyl glycerol in *H. halobium* apparently includes a unique stereochemical inversion at the C-2 carbon of glycerol as shown in Scheme I.

Acknowledgment. Proton and deuterium NMR spectra were recorded through the courtesy of Dr. M. Uramoto, Institute of Physical and Chemical Research, and Professor H. Seto and Dr. K. Furihata, the University of Tokyo, to whom we are grateful.

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$[S_4Cd_{17}(SPh)_{28}]^{2-}$, the First Member of a Third Series of Tetrahedral $[S_wM_x(SR)_y]^{z-}$ Clusters

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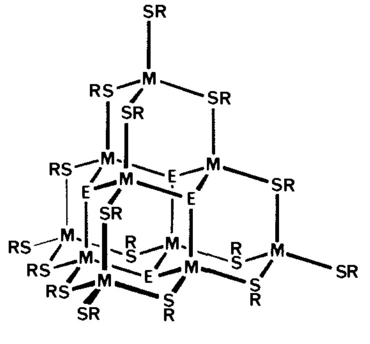
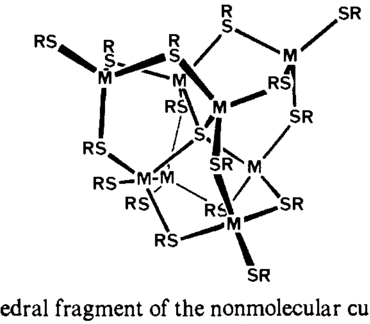
The largest $[S_wM_x(SR)_y]^{z-}$ molecular aggregate structure reported to date is $[E_4M_{10}(SPh)_{16}]^{4-}$ (E = S, Se; M = Zn, Cd) (**1**).[1] With four fused adamantanoid cages, **1** is structurally congruent with a tetrahedral fragment of the nonmolecular cubic (sphalerite) metal chalcogenide lattice, and therefore it is possible to conceive from **1** an infinite series of stereochemically legitimate (but still hypothetical) macromolecules, based on enlarged tetrahedral cores.[2] Subsequent members of this infinite series, denoted $\mathbf{2}^{\{n\}}$ (where *n* is the number of layers of M atoms), are $[E_{13}M_{20}(SR)_{22}]^{8-}$ ($\mathbf{2}^{\{4\}}$) and $[E_{28}M_{35}(SR)_{28}]^{14-}$ ($\mathbf{2}^{\{5\}}$). At $n = 7$, $[E_{80}M_{84}(SR)_{40}]^{32-}$, the size (edge length of tetrahedral core ≈ 28 Å) reaches that of the smallest characterized colloidal particles of CdS, which appear to be an irregular fragment of the cubic lattice.[3] The size regime in which the electronic characteristics of CdS change from bonds to bands is 20–100 Å.[3a] We report here the formation and structures of additional and larger $[S_wM_x(SR)_y]^{z-}$ macromolecules, which are the prototypes of two additional extended series of aggregates which could also intersect the size regime of colloidal metal chalcogenides and relate to their geometrical and electronic structures and reactivities.





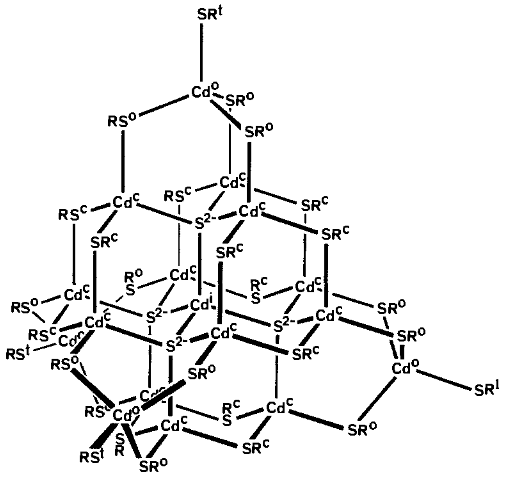


Figure 1. The idealized structure of **6**. The $Cd^i(S^{2-})_4$ center is connected to the $(Cd^c)_{12}$ cuboctahedron, bridged by a $(\mu\text{-}SR^c)_{12}$ tetratruncated tetrahedron, and with four tripodal $(\mu\text{-}SR^o)_3Cd^o(SR^t)$ caps.

A distinctly different macromolecular structure, **3**, is also known. The connectivity pattern comprised of a central ligand, a bitetrahedron of four inner and four outer metal atoms, and 12 doubly bridging thiolate ligands, occurs in $[ClZn_8(SPh)_{16}]^{-4}$ and in $\{SCd_8(SBu^s)_{12}\}(CN)_{4/2}$, **4**, where the aggregates are linked three dimensionally in the crystal by CN ligands as interaggregate bridges between outer metal atoms.[5,6] A second infinite series of macromolecules, $\mathbf{5}^{\{n\}}$,[7] can be conceived with **4** as the first member. These have tetracapped tetrahedral-core topology, with barrelanoid cages at the core/cap interfaces: the compositions of the next two members of the series are $[S_{16}M_{26}(SR)_{28}]^{8-}$ ($\mathbf{5}^{\{2\}}$) and $[S_{50}M_{60}(SR)_{40}]^{20-}$ ($\mathbf{5}^{\{3\}}$).

The ^{113}Cd NMR spectra of various reaction mixtures designed to synthesize cadmium complexes in series **2** and **5** have revealed the formation of at least three new polycadmium products. Recrystallization of the mixed products of reaction of PhSH, Et_3N, Cd^{2+}, Na_2S, and Me_4NCl in methanol/acetonitrile[8] yields

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(6) Cubic space group *Pn*3, $a = 15.928$ (2) Å, 1196 unique reflections (Mo Kα), $R = 0.033$. The crystal structure is the Cu_2O (or $Cd(CN)_2$) type, with interpenetrating unconnected lattices each composed of tetrahedral $\{SCd_8(SBu^s)_{12}\}$ clusters linked at the four outer Cd atoms by linear CN ligands.

(7) The size index *n* is here the number of layers of MS_4 tetrahedra in the core: the total number of M atoms is $(n + 1)(n + 2)(5n + 3)/6$.

(8) Preparation of **6** was by treatment of a solution of PhSH (80 mmol) and Et_3N (80 mmol) in acetonitrile with $Cd(NO_3)_2$ (50 mmol) in acetonitrile and Na_2S (20 mmol) in methanol, with alternating additions of the latter two reagents, followed by addition of Me_4NCl (18 mmol) in methanol. The colorless crystalline precipitate was recrystallized from hot CH_3CN to yield **6** as colorless block crystals, which gave satisfactory elemental analysis: yield ≈ 20%.

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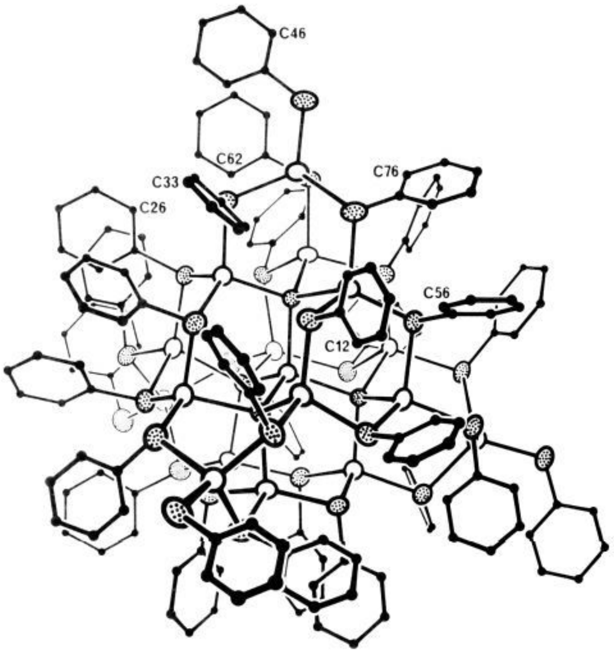

Figure 2. The actual structure of **6**. All S atoms are marked as dotted ellipsoids, all Cd atoms as open ellipsoids, and all phenyl carbon atoms drawn as small circles. Mean values of bond lengths (Å, [sample standard deviations]) are as follows: $\mathrm{Cd^i{-}S^{2-}}$, 2.497; $\mathrm{S^{2-}{-}Cd^c}$, 2.53 [2]; $\mathrm{Cd^c{-}S^c}$, 2.52 [4]; $\mathrm{Cd^c{-}S^o}$, 2.52 [2]; $\mathrm{Cd^o{-}S^o}$, 2.556 [9]; $\mathrm{Cd^o{-}S^t}$, 2.482.

$[\mathrm{S_4Cd_{17}(SPh)_{28}}]^{2-}$, **6**, as its $\mathrm{Me_4N^+}$ salt which has been characterized crystallographically.[9] Figure 1 is an idealized structural diagram of **6**, defining atom types: the actual molecular structure of **6**, with exact symmetry D_2, is shown in Figure 2. A central cadmium atom, $\mathrm{Cd^i}$, is connected to four quadruply bridging $\mathrm{S^{2-}}$ ions, each of which is connected to three cadmium atoms, $\mathrm{Cd^c}$, which are part of a cuboctahedron, $(\mathrm{Cd^c})_{12}$. Four of the eight faces of the $(\mathrm{Cd^c})_{12}$ cuboctahedron, and 12 of its 24 edges, are internally spanned by μ_4-$\mathrm{S^{2-}}$ ligands. The 12 edges which are not so spanned are doubly bridged by thiolate ligands $\mathrm{SPh^c}$, and these 12 μ-$\mathrm{SPh^c}$ ligands constitute a tetratruncated tetrahedron. The four triangular faces of the $\mathrm{Cd_{12}}$ cuboctahedron which are internally bridged by the μ_4-$\mathrm{S^{2-}}$ ligands are also linked to external cadmium atoms $\mathrm{Cd^o}$ by tripodal $(\mu\text{-}\mathrm{SPh^o})_3\mathrm{Cd^o}(\mathrm{SPh^t})$ caps. The 17 cadmium atoms occur as three types: one $\mathrm{Cd^i}$ with tetrahedral $(\mu_4\text{-S})_4$ coordination; 12 $\mathrm{Cd^c}$, each with tetrahedral $(\mu_4\text{-S})(\mu\text{-}\mathrm{SPh^c})_2(\mu\text{-}\mathrm{SPh^o})$ coordination; and four $\mathrm{Cd^o}$ each with tetrahedral $(\mu\text{-}\mathrm{SPh^o})_3(\mathrm{SPh^t})$ coordination. With Cd–Cd distances ranging from 4.07 to 4.20 Å, **6** is the largest metal chalcogenide molecular aggregate not dependent on the substantial M–M bonding which occurs in $[\mathrm{Se_{22}Ni_{34}(PPh_3)_{10}}]$[10] and congeners.[10,11]

Although the structure of **6** is unique, its central $\mathrm{Cd^i}(\mu_4\text{-S})_4(\mathrm{Cd^c})_{12}$ core reciprocates (by Cd/S interchange) the core of **4**. Four adamantanoid cages occur in both **1** and **6**, sharing edges and one vertex in **6** but fused in **1**. The capping cages $\{\mathrm{S}(\mathrm{Cd^c})_3(\mu\text{-}\mathrm{SPh^o})_3\mathrm{Cd^o}\}$ of **6** are barrelanoid rather than adamantanoid and thus are similar to the hexagonal (wurtzite) lattice of metal chalcogenides. Two new structural features in **6** are (a) the open cleft which occurs along each of the edges of the approximately tetrahedral molecule, with the cyclic atom sequence $\overline{\mathrm{Cd^oSR^oCd^cSR^cCd^cSR^oCd^oSR^oCd^cSR^cCd^c}}\mathrm{SR^o}$, and arising as a consequence of the microhexagonal topology of the cap and (b) facial $\overline{\mathrm{Cd^cSR^cCd^cSR^cCd^c}}\mathrm{SR^c}$ triangles in chair conformation with $(\text{axial})_3$ substituent configuration.

The molecule **6** is the prototype of another infinite series of molecular aggregates, $\mathbf{7}^{|n|}$.[12] The next two members are $[\mathrm{S_{14}M_{32}(SR)_{40}}]^{4-}$ ($\mathbf{7}^{|4|}$) and $[\mathrm{S_{32}M_{54}(SR)_{52}}]^{8-}$ ($\mathbf{7}^{|5|}$). The structural principles which generate and differentiate the series $\mathbf{2}^{|n|}$, $\mathbf{5}^{|n|}$, and $\mathbf{7}^{|n|}$ will be elaborated[13] in the context of the questions of (i) possible additional structural types for molecular aggregates and (ii) the structures of colloids and of fragments of nonmolecular metal chalcogenides.

The ^{113}Cd NMR spectrum of **6** redissolved in DMF is temperature and time dependent and indicates the presence of both fast and slow rearrangement processes. Laser desorption FT-ICR mass spectra of **6** contain negative and positive ions of m/z ca. 4900.[14]

Acknowledgment. The support of this research by the Australian Research Grants Scheme is gratefully acknowledged. Dr A. D. Rae assisted with the program RAELS, and Dr. G. D. Willett obtained the FT-ICR spectra.

Supplementary Material Available: Atomic positional and thermal parameters, bond lengths, bond angles, and the polycrystalline diffraction pattern (i.e., d-spacings (Å) and relative intensities) for **6** (6 pages). Ordering information is given on any current masthead page.

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(9) Crystallography: $\mathrm{Cd_{17}S_{32}N_2C_{176}H_{164}}$, $M = 5244.0$, orthorhombic space group *Ccca*, $a = 30.930$ (5) Å, $b = 32.772$ (5) Å, $c = 19.997$ (2) Å, $V = 20270$ (5) Å^3, $Z = 4$, $d_{\text{obsd}} = 1.76$ (2), $d_{\text{calcd}} = 1.73$ g cm^{-3}; 4712 unique reflections (using two crystals, to compenstate for radiation damage), Mo Kα radiation, to $\theta = 20°$; solution by direct methods, least-squares refinement with Cd and S anisotropic, the Ph substituents as constrained planar groups, and spherically disordered $\mathrm{Me_4N}$ groups; $R = 0.059$, $R_w = 0.079$ for 2187 observed reflections. Full details of this structure will be published separately.

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(12) n is the number of layers of M atoms in the core, and thus **6** is $\mathbf{7}^{|3|}$. Structural isomerism can arise in larger members of the series by alternative core truncations and alternative cap rotations.

(13) Dance, I. G., in preparation.

(14) NMR and mass spectroscopic data for **6** will be reported separately.

A Novel Mechanism of Glycoside Anomerization

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Mechanisms of acid-catalyzed glycoside anomerization are reasonably well understood,[1] but base-catalyzed anomerizations are not.[2] We have investigated the carbonate-catalyzed anomerization of protected 2,4-dinitrophenyl β-D-glucopyranosides[3] by using a variety of techniques and have shown the reaction to proceed via a novel mechanism involving nucleophilic aromatic substitution (Scheme I). A similar mechanism probably obtains for the previously reported[4] base-catalyzed anomerization of penta-*O*-acetyl-β-D-glucopyranose.

Treatment of 2,4-dinitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**1**) (β-2,4-DNPG) with $\mathrm{K_2CO_3}$ or dimethylsulfinyl anion in DMSO affords an equilibrium mixture of the α and β anomers (80:20, respectively).[5] We have considered four possible mechanisms for this transformation. These involve (i) base-catalyzed proton abstraction at C(1) forming a carbanion intermediate; (ii) phenolate departure forming an oxocarbonium ion intermediate, with possible participation of the C(2)-acetoxy

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(5) 2,4-Dinitrophenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside also undergoes anomerization but more slowly.

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