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Double-Layer Superlattice Structure Built Up of $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}·4H_2O$ Clusters

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During the last decade the physical and chemical properties of semiconductor nanoclusters have been intensively investigated.[1−4] Thereby the advances in this research field were strongly determined by the progress in the synthesis of monodisperse and well-characterized samples. Undoubtedly the most remarkable results in this context have been the crystallization of single-sized nanoclusters in three-dimensional superlattices which, however, succeeded only in a very few extraordinary cases like $[Cd_{10}S_4(SPh)_{16}]^{4-}$,[5] $[Cd_{17}S_4(SPh)_{28}]^{2-}$,[6] $Cd_{17}S_4(SCH_2CH_2OH)_{26}$,[7] and $Cd_{32}S_{14}(SPh)_{36}·4DMF$.[8]

It is, therefore, a major goal to find new synthetic routes to enlarge the number of species in this novel class of materials. Especially the variation of cluster ligands and cluster sizes makes possible the control of the superlattice parameters and should give access to explanations of how collective phenomena arise by cluster−cluster interaction.

We describe here the crystallization of $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}·4H_2O$ clusters and will discuss structural and optical properties. The preparation of the raw cluster sample was carried out analogously to sample d in ref 9 except using 1-mercapto-2-propanol instead of 1-thioglycerol.[10] During dialysis precipitation occurred as the pH value of the alkaline cluster solution decreased and colorless prismatic crystals of approximately 150 μm edge length were obtained. These crystals were no longer soluble in water, but dissolved readily in *N,N*-dimethylformamide (DMF). For X-ray analysis one single crystal was encapsulated in a capillary containing a few microliters of mother liquor because the crystals were found to crack during drying. Cracking also occurred below 0 °C, making low-temperature measurements impossible. Due to these difficulties, the small crystal sizes, and disorder phenomena, the obtained data set did not allow the determination of accurate atomic parameters of the light ligand atoms. The CdS cluster core structure as well as the superlattice geometry, however, could be reliably determined.[11] The elemental analysis of a vacuum-dried sample was in good agreement with the formula $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}·4H_2O$.[12]

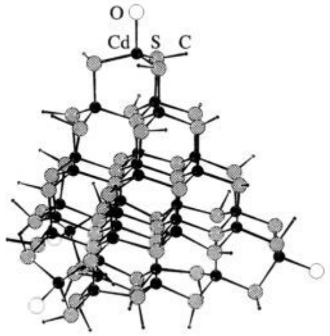

Figure 1. Structure of a $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}·4H_2O$ cluster. For clarity the organic residues have been omitted, but their orientations are indicated by the bonds that protrude from the thiolate S atoms to the corresponding first C atom. The four O atoms at the vertices form a slightly distorted tetrahedron (edge lengths, approximately 18.5 Å). Bond lengths in Å: Cd−S, 2.49(1)−2.54(1); Cd−SR, 2.46(2)−2.55(1); Cd−O, 2.32(1)−2.33(1). The cluster contains a 3-fold axis which coincides with that of the space group $R\bar{3}$.

Figure 1 shows the structure of a single cluster. The cluster is a larger homologue of $Cd_{17}S_4(SCH_2CH_2OH)_{26}$, and its core structure is identical with the thiophenol-capped $Cd_{32}S_{14}(SPh)_{36}·4DMF$ cluster reported by Herron et al.[8] The cluster framework is built up of 13 fused CdS adamantanoid cages, and the cluster is thus best described as a tetrahedral fragment of the cubic CdS phase (zinc blende) with open clefts running along the tetrahedral edges of the cluster. Cd is coordinated by oxygen at the cluster corners, most probably in the form of H_2O.[13] These tripus-like $(\mu\text{-}SR)_3Cd(H_2O)$ structures at the corners resemble the hexagonal CdS phase (wurtzite). The CdS bond lengths vary between 2.45 and 2.55 Å and are, thus, similar to those of bulk CdS (2.519 Å). In contrast to $Cd_{17}S_4(SCH_2CH_2OH)_{26}$ the center of the cluster is not formed by a single Cd atom but by a whole adamantanoid-like cage.

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(10) Briefly, a solution of 1.97 g (4.70 mmol) of $Cd(ClO_4)_2·6H_2O$ and 1.0 mL (11.39 mmol) of 1-mercapto-2-propanol in 250 mL of water was adjusted to pH 11.2 with 1 M NaOH before the addition of 50 mL (2.04 mmol) of H_2S with vigorous stirring. The transparent solution was heated to 100 °C until the UV/vis absorption spectrum displayed a transition at about 325 nm, similar to that shown in Figure 3. After cooling to room temperature, the crude cluster solution was dialyzed exhaustively against deionized water (using Spectra/Por MWCO 6-8000 dialysis tubings).

(11) Diffraction data were collected on an Enraf-Nonius (Delft, Netherlands) CAD4 diffractometer (graphite-monochromized Mo Kα radiation, wavelength of 0.7107 Å). Formula $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}·4H_2O(·xH_2O)$ (with x approximately 66), rhombohedral space group $R\bar{3}$ (No. 148), cell parameters (hexagonal axis) $a = 21.536(3)$ Å, $c = 95.857(10)$ Å, $V = 38851(9)$ Å^3, $Z = 6$, $D_{calcd} > 1.915$ g cm^{-3}, $\mu > 30.4$ cm^{-1}. Because of the instability of the crystals and the weak diffraction power of the nonperfect crystals, only 2403 unique reflections with $I \geq 2\sigma(I)$ were measured in the range $1.5° \leq 2\theta \leq 40°$. The structure was solved by combination of direct methods, molecular modeling, molecular replacement method, and a special *R*-value analysis. Despite the poor quality of the available reflections, all C and O atoms could be located by difference Fourier synthesis. The final refinement of 396 parameters (Cd and S anisotropically, O and C isotropically) by using weighted restraints for the bond lengths and angles of the organic residues converged at $R = 0.126$. This relatively high value is explained by the high mobility of the clusters (caused by the extremely high amount of water within the structure), the instability of the crystals, probably small structural changes during the X-ray exposure, and rotational and stereochemical disorders of most of the organic residues indicated by extremely high thermal parameters of some C and all O atoms. Additional data for this material can be ordered by referring to No. CSD-404300, the names of the authors, and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

(12) Anal. Calcd for $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}·4H_2O$: C, 17.53; H, 3.54; O, 8.65; S, 21.67; Cd, 48.61. Found: C, 17.55; H, 3.45; O, 8.30; S, 21.4; Cd, 48.6.

(13) We do not believe that the O atoms are present in the form of OH^-. In this case the cluster should be 4-fold negatively charged and the structure had to contain counterions. Those counterions, however, could not be detected by the structure analysis.

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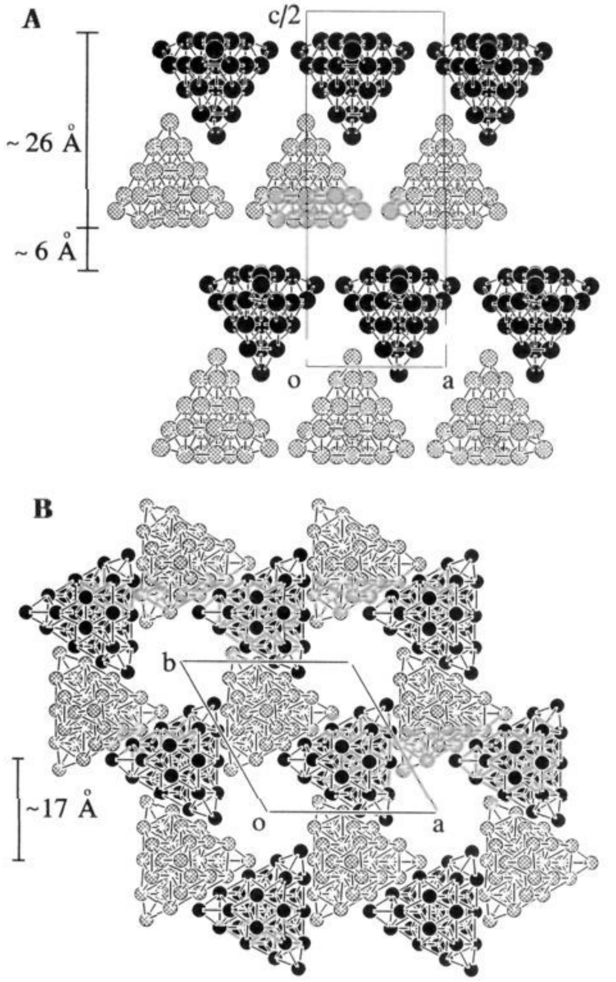

Figure 2. The double-layer superlattice built up of the $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}\cdot 4H_2O$ clusters. (A) Two double layers projected in the *Y* direction. The double-layer thickness is approximately 26 Å, and the spacing between neighboring double layers is approximately 6 Å. (B) A double layer projected in the *Z* direction. The channel-like cages which interdisperse the double layers have a diameter of about 17 Å. Only the Cd atoms of each cluster are shown. For clarity the clusters of adjacent monolayers are graphically distinguished, although they are chemically equivalent. The cell parameters are given in ref 10.

The superlattice formed by the clusters is shown in Figure 2 in *Y* and *Z* projection. It is readily seen from part A of the figure that the clusters crystallize in a double-layer structure. Each double layer has a thickness of about 26 Å and is interdispersed with channel-like cages of approximately 17 Å in diameter, as shown in part B. The distance between neighboring double layers is about 6 Å (neglecting the organic residues of the thiolate ligands). Since the double layers form A−B−C sequences, the channel-like cages get partially closed by neighboring double layers, resulting in a total cavity length of $26\ \text{Å} + 2 \times 6\ \text{Å} = 38\ \text{Å}$. We presume that these cavities are filled with numerous water molecules.[14] Thus, crystal cracking below 0 °C is explained by the formation of an ice-like structure within the cavities. It shall be pointed out that the superlattice structure is entirely different from that of the smaller $Cd_{17}S_4(SCH_2CH_2OH)_{26}$ clusters which were found to crystallize in a covalent double-diamond structure.[7] It is also different from the superlattice built up of the $Cd_{32}S_{14}(SPh)_{36}\cdot 4DMF$ clusters,[8] showing that the organic residue of the capping thiolate ligand has a decisive influence on the superlattice architecture.

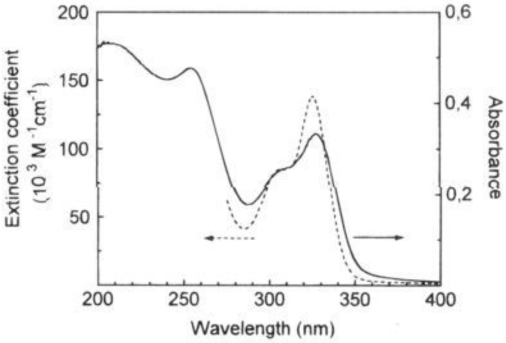

Figure 3. UV/vis spectra of $Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}\cdot 4H_2O$ dissolved in DMF (dashed line) and as a film deposited on a quartz substrate (solid line).

The absorption spectra of the clusters dissolved in DMF and in the form of a thin film deposited on a quartz substrate are shown in Figure 3. Both spectra show a strong absorption maximum at around 325 nm (the extinction coefficient in DMF is $\sim 138\,000\ M^{-1}\ cm^{-1}$) and another transition around 305 nm. In the case of the deposited clusters a third transition is observed at 255 nm (not visible in solution due to absorption of DMF). The absorption bands are broadened in the case of the film, which might be due to cluster−cluster interaction. The optical properties, however, have to be examined in more detail in order to obtain clear evidence for such an interaction. Herron et al. found a strongly red shifted absorption for their $Cd_{32}S_{14}(SPh)_{36}\cdot 4DMF$ cluster ($\lambda_{max} = 358$ nm). This result appears highly remarkable since both cluster cores are entirely identical. At the present state of the experimental results the difference in the optical spectra is most probably due to the different ligands; i.e., the red shift is understood as a contribution of the aromatic rings of the thiophenol ligands in the case of Herron's clusters.

Supporting Information Available: Complete crystallographic details, atomic coordinates, bond lengths and angles, and isotropic and anisotropic displacement parameters (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) As estimated by structure modeling we expect approximately 66 water molecules/cluster. This is indicated by difference electron density calculations. As a criterion for the assignment, the potentiality for the formation of hydrogen bondings within the cavities was used. Details of the hydrate structure will be described in a forthcoming paper.