Crystal Structure and Optical Properties of $Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4$, a Cluster with a 15 Angstrom CdS Core

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Recrystallization of the solid $Cd_{10}S_4(SC_6H_5)_{12}$ from a solution of pyridine and *N,N*-dimethylformamide (DMF) results in the formation of the cluster $Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4$ as pale yellow cubes. The structure consists of an 82-atom CdS core that is a roughly spherical piece of the cubic sphalerite lattice ~12 angstroms in diameter. The four corners of the lattice are capped by hexagonal wurtzite-like CdS units, which results in an overall tetrahedral cluster ~15 angstroms in diameter. This cluster dissolves intact in tetrahydrofuran where its absorption spectrum reveals a sharp peak at 358 nanometers at room temperature and its emission spectra show a strong broad band at 500 nanometers.

The use of very small molecular clusters as synthetic precursors to bulk, extended solids interests both the physics (*1*) and chemistry (*2*) communities. In the particular case of semiconductor materials, the small clusters themselves are of interest, given that the transport and optical behaviors vary as a function of crystallitic size. These phenomena have led to a whole area of research into so-called nanoclusters or quantum dots (*3*). In this size regime (ten to a few hundred angstroms in particle diameter), quantum effects lead to severe perturbations in electronic properties. The clusters act as examples of the quantum mechanical particle in a box (*4*). Although research in this area has been intense, almost all efforts have suffered from the same problem: attempts are made to relate properties to cluster size, but cluster size is crudely defined. In most cases, only a distribution of sizes is accessible because of the synthetic routes that are used to prepare such clusters (*4*). Although a few well-defined molecular clusters of this type do exist (*5, 6*), these tend to be on the small end of the size spectrum where the properties are more like those of the molecules than like those of the bulk.

We report the single-crystal structure and optical properties of a large, well-characterized semiconductor molecular cluster. It is a 15 Å diameter crystalline fragment of bulk cubic CdS with an 82-atom core. This cluster contains all of the structural features of the bulk extended solid, yet it remains soluble in organic solvents and so retains many of the attractive properties (from a characterizational and processing viewpoint) of a discrete molecule.

We reported previously (*7*) that when the discrete molecular species $(NMe_4)_4Cd_{10}S_4(SC_6H_5)_{16}$ (*5*) (Me, methyl) is heated under carefully controlled conditions, the material converts to bulk crystalline CdS. It does so in two distinct steps. First, at 250°C, it loses the tetramethylammonium cations and four of the thiophenolate "caps," which generates a solid, $Cd_{10}S_4(SC_6H_5)_{12}$. This step is followed by the loss, at 500°C, of the remaining phenyl groups in the form of diphenyl sulfide which leaves behind crystalline CdS. The intermediate composition, $Cd_{10}S_4(SC_6H_5)_{12}$, is a pale-yellow solid with a broad x-ray diffraction pattern that indicates very small (<25 Å) sphalerite-phase (cubic) crystallites of CdS. However, this solid is very soluble in pyridine, and such solutions can be recrystallized by the addition of DMF to the point of incipient precipitation. Large, clear-yellow, cubic crystals formed (along with a small amount of yellow powder) during a period of several days at room temperature. The larger crystals appear to fracture when exposed to strong visible or ultraviolet (UV) light. The crystals are, therefore, routinely grown and handled under subdued lighting conditions. One such crystal was suitable for x-ray diffraction analysis.

The solution of its structure (Fig. 1A) reveals that recrystallization has led to the nucleation of a cluster with a stoichiometry of $Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4$ (*8*). This molecule is much larger than the original Cd_{10} cluster from which it was prepared. It appears that this cluster assembled itself from CdS/SC_6H_5 species of various nuclearities that are in rapid exchange in the pyridine solution [^{113}Cd nuclear magnetic resonance shows broad resonances in pyridine at all of the temperatures that we measured (*7*)]. This cluster was apparently the least soluble species and therefore the one that preferentially crystallized. The structural details reveal that the 82-atom core is constructed from a large (~12 Å diameter), roughly spherical chunk of the sphalerite form of bulk CdS whose requisite "dangling" surface bonds have been terminated by wurtzite-like (hexagonal) CdS units at four tetrahedral corners. Thus, the cluster looks like a large tetrahedron whose points have been capped by DMF solvent molecules and is neutral in charge. The cluster core is ~15 Å across (from the Cd atom at the vertex of the tetrahedron to the center of the opposite tetrahedral face). All of the edges of the core are covered with phenyl rings of bridging and capping thiophenolate ligands. The structure is, in fact, a larger homolog of the large CdS cluster, $Cd_{17}S_4(SC_6H_5)_{28}{}^{2-}$, which was prepared by Dance and co-workers (*6*). It has all of the same structural features that are noted for that material (including the open clefts that run along each of the tetrahedral edges) except for (i) the capping of the Cd atoms that are at the vertices of the tetrahedron, which, in our case, is performed by DMF solvent but, in the structure of Dance and co-workers, is done by $SC_6H_5{}^-$ units and (ii) the appearance of four triply bridging sulfide ions in the centers of the tetrahedral faces. At the very center of the cluster is a ten-atom fragment with the same connectivity as bulk sphalerite-phase CdS with four tetracoordinated cadmium and six tetracoordinated sulfide ions in an adamantyl arrangement.

The Cd–S bond length in this core is 2.503(4) Å (where the number in parenthesis is the error in the last digit), which is significantly less than that found for bulk CdS (2.519 Å). The individual clusters of the crystal structure interact only by means of nonbonded contact of the phenyl groups of the capping thiophenolate ligands, as depicted in the packing diagram (Fig. 1B). One fascinating aspect of the packing structure is the presence of very large intercluster voids, which is similar to what is found in zeolites. Channels ~8 Å in diameter provide access to large spherical cavities ~16 Å in diameter between the individual clusters. These spaces appear to be essentially free of adsorbed solvent molecules.

With such a well-defined molecular cluster, we examined the intrinsic optical properties of a single-sized, 15 Å quantum dot without ambiguities from size dispersion or poorly defined surfaces. On photoexcitation, the crystals emit green light at ~520 nm (Fig. 2A). The excitation spectrum shows absorption bands at 325 and 384 nm with a weak shoulder at 435 nm (Fig. 2A).

In pyridine solution, the optical spectra and emission properties are quite different from those of the solid and revert to the behavior of the precursor material, $Cd_{10}S_4(SC_6H_5)_{12}$, in pyridine (*7*); this result is consistent with the view that pyridine causes the rapid fracture of the cluster core into a dynamic mixture of species with lower nuclearities. The instability of clusters of this type in coordinating solvents such as pyridine and DMF has been well documented (*5*). We propose that this is a

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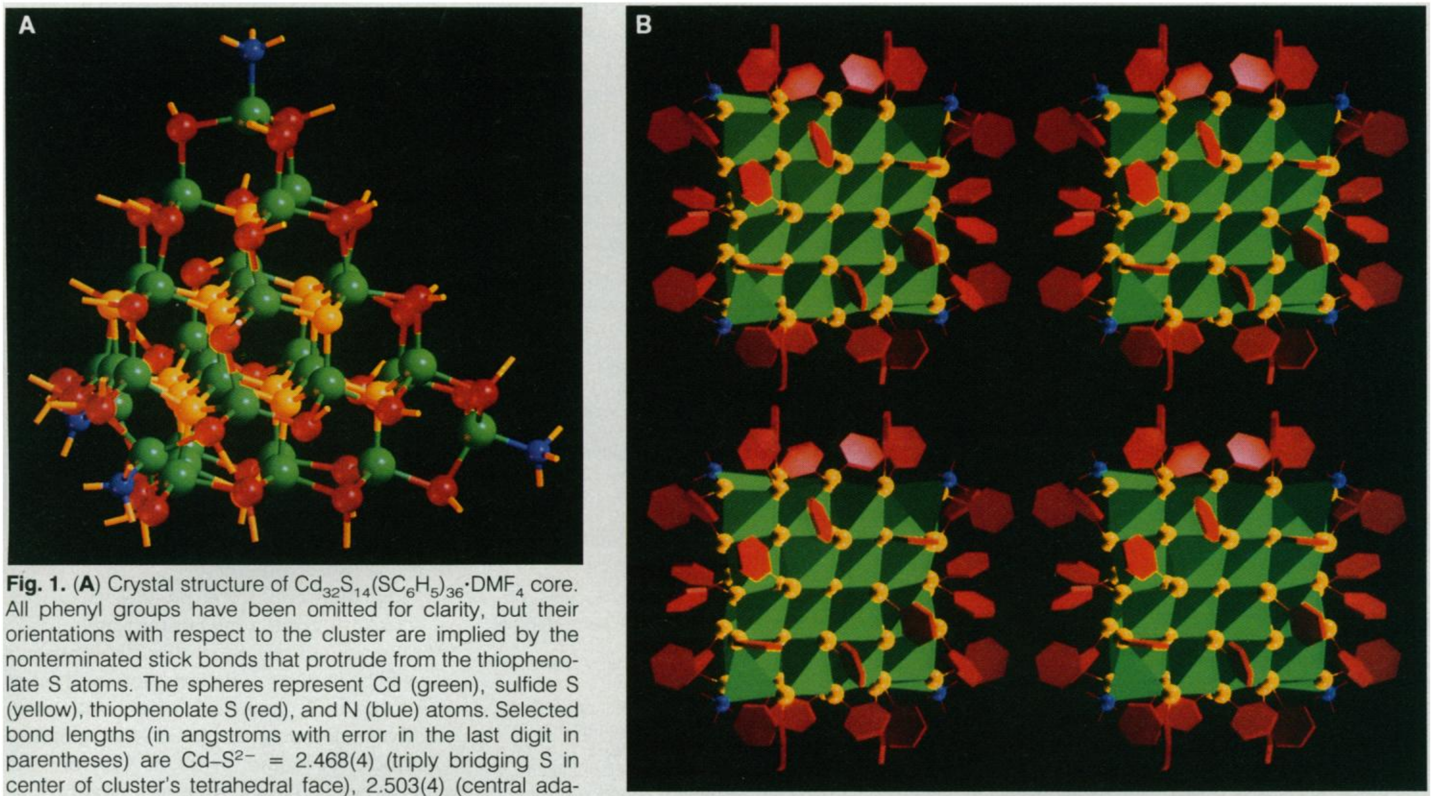

Fig. 1. (**A**) Crystal structure of $\mathrm{Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4}$ core. All phenyl groups have been omitted for clarity, but their orientations with respect to the cluster are implied by the nonterminated stick bonds that protrude from the thiophenolate S atoms. The spheres represent Cd (green), sulfide S (yellow), thiophenolate S (red), and N (blue) atoms. Selected bond lengths (in angstroms with error in the last digit in parentheses) are Cd–S^{2-} = 2.468(4) (triply bridging S in center of cluster's tetrahedral face), 2.503(4) (central adamantyl core), 2.538(8), 2.532(4), and 2.537(5) Å (second shell out from central core); Cd–$\mathrm{SC_6H_5}$ = 2.495(5), 2.569(5), 2.546(5), 2.503(5), 2.554(5), and 2.560(5) Å; Cd–N = 2.33(4) Å. (**B**) Crystal packing diagram of $\mathrm{Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4}$ that shows four molecules at the corners of a face of the unit cell. The phenyl rings have been reduced to red hexagons, and the cores of the clusters are represented by green tetrahedra that are centered on the Cd atoms and defined by the attached S (yellow) and N (blue) atoms.

result of the ability of the coordinating solvent to both compete with the surface-capping thiophenolate ligands for the metal sites and to immediately passivate dangling bonds, which arise as individual cluster bonds break and fragments detach from the cluster surface.

When the crystals are dissolved in tetrahydrofuran (THF), however (they are sparingly soluble in this, as well as DMF and acetonitrile solvents), the solution emits at ~500 nm (Fig. 2B). The excitation spectrum shows sharp absorption bands at 313 and 366 nm, the same as those observed in the solid crystal except that they are shifted to higher energy by ~18 nm. The similarity between the THF-solution and the solid-state spectra indicates that the cluster dissolves intact into this solvent and, furthermore, in the crystal there exist only weak cluster-cluster interactions, which is consistent with the cluster packing that is revealed in Fig. 1B. The $\mathrm{Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4}$ solid should therefore be regarded as a molecular crystal, similar to what has been found in the case of C_{60} fullerene crystals.

The lowest absorption band of $\mathrm{Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4}$ dissolved in THF is located at 358 nm (Fig. 2C). This transition has a large absorption cross section (the extinction coefficient is ~84,500 M^{-1} cm^{-1}). The position of the peak is insensitive to the effect of solvent polarity (from THF to acetonitrile), which indicates that the ground state or the corresponding excited state has a vanishingly small dipole moment. Both the large absorption cross section and the vanishing dipole moment are signatures of an ideal quantum-confined "exciton state" (*4*), to use a bulk semiconductor term. The possibility that this band is a result of charge transfer from cadmium to thiophenolate, which would yield a large excited-state dipole moment, can be eliminated on the basis of these data.

In spite of the large oscillator strength of the 358-nm state, the luminescence spectrum is dominated by a low-lying excited state that emits in the green (Fig. 2B). There is a very efficient relaxation process that leads to the formation of this second, lower lying excited state. Previous research on small CdS particles (*9*) has often revealed such an emission band that is at a much lower energy than the absorption edge. This band has usually been loosely associated with defects largely because the samples have not been sufficiently defined to permit a more definitive description. This defect concept is no longer valid for our well-defined cluster, and such an emission band must be attributable to an intrinsic excited state of the cluster. This excited state has a very low oscillator strength (because it cannot be observed in the absorp-

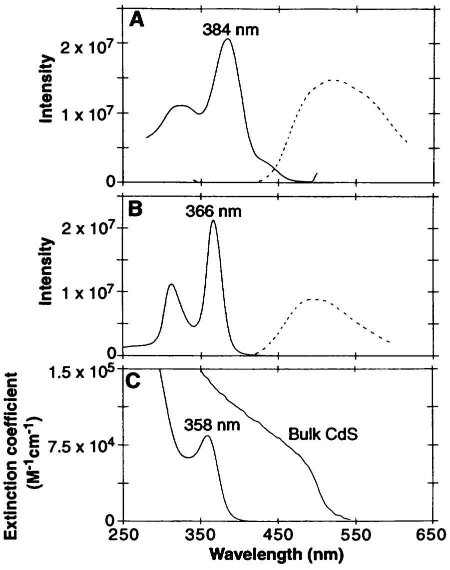

Fig. 2. (**A** and **B**) Excitation (solid line) and luminescence (dotted line) spectra of $\mathrm{Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4}$ cluster (A) as polycrystalline solids at 6.5 K and (B) in THF at 77 K. The spectra were taken with a reflection geometry. The excitation wavelength for the emission spectra was 320 nm, and the monitoring wavelength for the excitation spectra was 520 nm. (**C**) Absorption spectrum of $\mathrm{Cd_{32}S_{14}(SC_6H_5)_{36}\cdot DMF_4}$ in THF at room temperature compared with the bulk CdS absorption spectrum. All three graphs were scaled arbitrarily.

tion spectrum), yet it dominates the excited-state properties. It has a broad emission band without any detectable vibronic structure even at 6 K. All of these properties are characteristic of a charge-transfer state. Questions about the nature of this excited state and how it evolves with increasing cluster size remain to be addressed.

Finally, the solubility of this new crystalline cluster may be used in the production of polymer films, such as polyvinylcarbazole, doped with the CdS cluster simply by spin-coating from a pyridine solution. Such films have been found to exhibit good photoconductive properties (*10*), which points to a real utility for such soluble semiconductor clusters in the preparation of materials that go into electronic devices made for this and other thin-film applications.

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8. A light-yellow, clear cubic block, 0.39 mm on a side, was mounted on an Enraf-Nonius (Delft, Holland) CAD4 diffractometer (graphite monochromatized MoKα radiation, wavelength of 0.71069 Å) and cooled to −70°C. The cubic unit cell parameter was determined from the Bragg angles of 25 computer-centered reflections as a = 21.856(2) Å. The space group was assigned as $P23$ (No. 195), and the structure later confirmed this assignment. We collected 12,924 data points, of which 1,672 were unique with $I \geq 3.0\sigma(I)$, where I is intensity. The structure was solved by direct methods and was refined by full-matrix least-squares techniques with scattering factors from *International Tables for X-ray Crystallography* (Mathematical Tables Series, Kluwer Academic, Norwell, MA, 1974), vol. IV, including the anomalous terms for Cd and S. The final refinement of 239 parameters (data to parameter ratio = 6.91), in which Cd, S, N, and C were anisotropic and H was fixed, converged at R = 0.042 and R_w = 0.039. The single molecule for each unit cell resides on a site of T symmetry.
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11. DuPont Contribution 6304. Supplementary data (atomic coordinates, bond lengths, and angles) are available on request. Atomic coordinates will also be deposited with the Cambridge crystallographic data files. We thank J. B. Jensen and S. J. Harvey for technical assistance and W. J. Marshall for x-ray manipulations.

31 August 1992; accepted 4 December 1992

Stable Compounds of Helium and Neon: He@C_{60} and Ne@C_{60}

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It is demonstrated that fullerenes, prepared via the standard method (an arc between graphite electrodes in a partial pressure of helium), on heating to high temperatures release ^{4}He and ^{3}He. The amount corresponds to one ^{4}He for every 880,000 fullerene molecules. The ^{3}He/^{4}He isotopic ratio is that of tank helium rather than that of atmospheric helium. These results convincingly show that the helium is inside and that there is no exchange with the atmosphere. The amount found corresponds with a prediction from a simple model based on the expected volume of the cavity. In addition, the temperature dependence for the release of helium implies a barrier about 80 kilocalories per mole. This is much lower than the barrier expected from theory for helium passing through one of the rings in the intact structure. A mechanism involving reversibly breaking one or more bonds to temporarily open a "window" in the cage is proposed. A predicted consequence of this mechanism is the incorporation of other gases while the "window" is open. This was demonstrated through the incorporation of ^{3}He and neon by heating fullerene in their presence.

An intriging feature of buckminsterfullerene is the hollow interior, which is large enough to enclose atoms. In contrast with other molecules that bind ligands through noncovalent forces, buckminsterfullerene and its higher homologs are like closed bottles. Atoms or small molecules can be contained and held without need for binding interactions. Smalley *et al.* have reported the preparation of metallofullerenes (*1*). Although there was early discussion about whether the metals might be covalently attached to the outside (*2*), the present evidence indicates that there are metal atoms inside the carbon cages (*3–6*). Cram *et al.* (*7*) have suggested the name carcerands for closed-surface compounds that trap atoms and molecules inside. Schwarz *et al.* have reported that collisions of C_{60} cations with ^{4}He and ^{3}He in a mass spectrometer produce ions which have the additional mass of helium (*8, 9*). In order to provide evidence that the helium is inside, the ions were neutralized and then reionized with a four-sector tandem mass spectrometer. Helium retention was interpreted as indicating that the helium was inside (*10*). It would be extremely difficult to recover macroscopic quantities of fullerenes containing helium or other rare gas atoms after formation of such ions in a mass spectrometer.

How then could one prepare quantities of buckminsterfullerene containing helium? We considered the possibility that this had already been done. The common method of preparing bulk quantities of the fullerenes involves operating an arc between graphite electrodes in helium at about 150 torr. As each molecule closes, there is a chance that a helium atom will end up inside. How could one detect this helium? If enough were present, one might see it directly in the mass spectrum of buckminsterfullerene. However, the ion with four ^{13}C atoms (and no helium) will generally be present. This ion has a mass so similar to the ion with no ^{13}C but with ^{4}He that only extremely high resolution would resolve them. If only a small quantity were present, it would not be seen.

Helium itself can be detected with extremely high sensitivity in a mass spectrometer. One of us (R.J.P.) has been using an instrument designed to measure helium content in geological samples (*11*). A sample, after evacuation is heated to high temperature in an all-metal furnace and the released gases are analyzed. Helium and neon were measured with a VG 5400 noble gas mass spectrometer fitted with a Johnston electron multiplier with pulse-counting electronics on the axial collector [see (*11*) for details]. A resolution of 550 ($\Delta m/m$) achieved complete baseline separation of ^{3}He$^+$ from HD$^+$. A "high side" Faraday cup with a resolution of 200 was used for the ^{4}He measurement. Absolute abundances of ^{3}He, ^{4}He, and ^{22}Ne were calculated by peak height comparison to an air standard of known size (0.101 cm^3 standard temperature and pressure) and are accurate to ±3%. A split of the gas was also measured for ^{40}Ar abundance on a Dycor quadrupole mass spectrometer by peak height comparison with the air standard. The small amount of ^{22}Ne in all tempera-

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