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Synthesis and Characterization of the First Neutral Zinc−Sulfur Cluster: $Zn_{10}S_4(SEt)_{12}L_4$

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Synthesis of solid-state materials from molecular building blocks is a field of considerable interest from both academic and technological standpoints.[1−9] The molecular building block approach can provide strategies to assemble novel materials which cannot be prepared by traditional, nonmolecular synthesis techniques. However, inorganic systems in which an extended solid is assembled from molecular clusters in a stepwise and controlled fashion where the structure of the precursor directs the structure of the resulting material are relatively few. The first step in this strategy is to develop a systematic route to molecular clusters.

We are interested in molecular routes to group 12 metal−chalcogen clusters and their use as precursors to metal chalcogenide materials where the ability to influence material properties through cluster design can be investigated. This approach to these materials is technologically motivated by their properties, including conductivity, UV−visible absorption properties, and phosphoresence,[5] which depend on composition, purity, stoichiometry, phase purity (cubic or hexagonal), and dopant distribution. In addition, molecular metal−chalcogenide semiconductor nanoclusters themselves are of interest because their properties such as bandgap vary with cluster radius in the quantum-confinement size regime (≈10−100 Å).[10−12]

Several literature reports demonstrate that nonmolecular routes to these materials[13−16] do not offer adequate control over material properties. On the other hand, molecular routes to these materials can potentially offer control over any or all of these properties. For example, it has been demonstrated that chemical vapor deposition (CVD) using the cubane gallium−sulfide cluster (t-BuGaS)$_4$ as a precursor results in formation of a new cubic phase of GaS.[17] It has also been demonstrated that CVD using the wurtzite core cluster $[Zn(SEt)(Et)]_{10}$[18] results in formation of preferentially oriented wurtzite phase ZnS films at low temperatures.[19] In order to examine the connection between cluster structure and film properties in the deposition of sphalerite phase ZnS films, it is necessary to prepare neutral, sphalerite-core zinc−sulfur clusters. However, while many sphalerite-core clusters have been prepared, to our knowledge, there are no examples of such neutral clusters in the literature.[20] In this report, we describe the synthesis and characterization of $Zn_{10}S_4(SEt)_{12}L_4$ (L = 3,5-lutidine) (**1**), a neutral, sphalerite-core zinc−sulfur cluster which is potentially useful for molecular synthesis of metal−chalcogen materials.

The $Zn_{10}S_4(SEt)_{12}L_4$ (L = 3,5-lutidine (**1**), pyridine (**2**)) clusters were synthesized[21] by first reacting $ZnEt_2$ with 2 equiv of S^0 (as S_8) in toluene at room temperature followed by removal of the volatile components *in vacuo* and addition of an excess of either 3,5-lutidine or pyridine. This gave a yellow solution and a white crystalline precipitate, which was characterized by elemental analysis and NMR spectroscopy and shown to be $Zn_{10}S_4(SEt)_{12}L_4$ by single-crystal X-ray diffraction. The yellow solution was isolated and dried *in vacuo* to give a glassy orange solid. Proton NMR and elemental analysis of this solid were consistent with the empirical formula $[Zn_2S(SEt)(Et)L]_n$.

Single crystals of **1** were grown by slow evaporation of a dilute lutidine solution to yield small colorless blocks, and **1** was structurally characterized in the solid state by single-crystal X-ray diffraction.[22] The core structure of **1** is similar to that of $[S_4M_{10}(SPh)_{16}](Me_4N)_4$ (M = Cd (**3**), Zn (**4**)) described previously by Dance et al.,[23] with the major difference that **1** contains four neutral lutidine ligands in place of the four terminal SR$^-$

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(21) Synthesis of $Zn_{10}S_4(SEt)_{12}L_4$ (L = 3,5-lutidine (**1**)): In an inert-atmosphere box, 5 mL (48.6 mmol) of diethylzinc and 75 mL of dry toluene were syringed into a 250 mL Schlenk flask. In three equal portions over 2 h, 3.1 g of S_8 (12.1 mmol) was added to the stirring solution of diethylzinc and toluene at room temperature. The solution was stirred for 15 min more, and a pale yellow solution remained when the reaction was complete. The volatile components were removed *in vacuo*, leaving a glassy, cream-colored solid. Approximately 8.5 g of this crude mixture of products was collected and redissolved in 100 mL of 3,5-lutidine to give a yellow solution, and **1** crystallized as a white, crystalline solid. Yield: 2.5 g (approximately 25% based on zinc). ^1H NMR for **1** (C_7D_8): $\delta = 3.35$ (q, 24H, SCH_2CH_3), $\delta = 1.60$ (t, 36H, SCH_2CH_3), $\delta = 1.85$ (s, 24H, $(CH_3)C_5H_3N$), $\delta = 7.09$ (s, 4H, 4-lutidine position), $\delta = 8.39$ (s, 8H, 2,6-lutidine position). Anal. Calcd for $Zn_{10}S_4(SEt)_{12}(C_5H_3(Me)_3N)_4$: 32.13% C, 4.9% H, 2.9% N. Found: 34.90% C, 5.1% H, 3.5% N. The analytical data better fits the empirical formula $Zn_{10}S_4(SEt)_{12}(C_5H_3(Me)_3N)_5$. Calcd for $Zn_{10}S_4(SEt)_{12}(C_5H_3(Me)_3N)_5$: 34.55% C, 5.12% H, 3.42% N. However, powder X-ray diffraction analysis of the bulk product matches the powder pattern calculated from the single-crystal data obtained for $Zn_{10}S_4(SEt)_{12}(C_5H_3(Me)_3N)_4$ and shows that this is the only *crystalline* phase present.

(22) Crystal data for **1**: $Zn_5S_8C_{26}H_{48}N_2$, monoclinic, $C2/c$, $a = 25.797(2)$ Å, $b = 17.773(2)$ Å, $c = 21.655(2)$ Å, $\beta = 112.00(1)°$, $V = 9208.6(15)$ Å^3, $Z = 8$, $D_c = 1.402$ g cm^{-3}, μ(Mo Kα) = 2.947 mm^{-1}, $T = 20$ °C, Siemens R3m/v, Mo Kα. Of 6803 data ($3 \leq 2\theta \leq 37$), 3418 were independent and 1611 were observed [$2\sigma(F_o)$]. The structure was solved by direct methods. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized, $R(F) = 6.98\%$, $R_w(F) = 9.83\%$, GOF = 1.32, $N_o/N_v = 8.9$, $\Delta(r) = 1.00$ e Å^{-3}, $\Delta/\sigma(\max) = 0.005$. SHELXL software was used for all computations (G. Sheldrick, Siemens XRD, Madison, WI).

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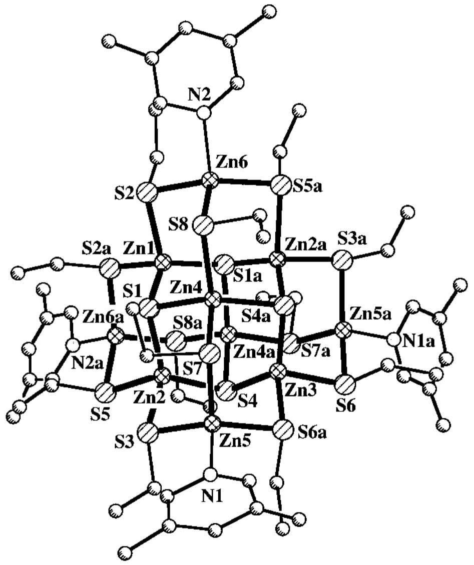

Figure 1. Molecular structure of $Zn_{10}S_4(SEt)_{12}(C_5H_3(Me)_3N)_4$. Relevant bond lengths (Å): Zn(1)−S(1) = 2.287(12); Zn(1)−S(2) = 2.397(11); Zn(2)−S(1) = 2.314(12); Zn(2)−S(4) = 2.310(12); Zn(2)−S(3) = 2.433(13); Zn(2)−S(5) = 2.460(12); Zn(6)−N(2) = 2.161(29). Relevant bond angles (deg): S(1)−Zn(1)−S(2) = 104.1(4); S(1)−Zn(1)−S(1A) = 123.8(6); S(2)−Zn(1)−S(2A) = 99.5(5); Zn(1)−S(1)−Zn(2) = 102.5(4); Zn(1)−S(1)−Zn(4) = 100.4(4).

ligands to afford a neutral cluster. Cluster **1** contains an adamantane core with four μ_3-S^{2-} ligands, twelve μ_2-SEt^- ligands, and four neutral lutidine ligands. Species **1** exhibits approximately tetrahedral symmetry with a lutidine on each corner of the tetrahedron. All the zinc atoms are in a tetrahedral coordination environment; six zinc atoms are bonded to two S^{2-} and two SEt^-, four zinc atoms are bonded to one lutidine and three SEt^-. The zinc atoms bonded to two S^{2-} and two SEt^- have zinc−sulfur bond lengths comparable to the analogous bond lengths in **4** [Zn−S = 2.30(1) Å (**1**), 2.303(3) Å (**4**); Zn−SR (R = Et, Ph) = 2.42(3) Å (**1**), 2.404(3) Å (**4**)]. The Zn−SR (R = Et, Ph) bond lengths of the outer zinc coordinated to three μ_2-SEt^- and one lutidine in **1** or three μ_2-SPh^- and one terminal SPh− in **4** are slightly different [2.32(1) Å (**1**); 2.373(3) Å (**4**)], as might be expected. In both **1** and **2**, all SEt^- ligands are equivalent on the ^1H NMR time scale in pyridine-d_5 and toluene-d_8 solution.

Proton NMR in pyridine-d_5 of the crude mixture of products isolated from the reaction of $ZnEt_2$ with 2 equiv of S^0 in toluene shows the presence of two products, $Zn_{10}S_4(SEt)_{12}L_4$ and $Zn_2S(SEt)(Et)L$, formed in a 1:12 ratio based on integration of the methylene quartets of the ethyl sulfide ligands (1:1, respectively). Volatile byproducts of this reaction, SEt_2 and S_2Et_2, were observed by proton NMR in pyridine-d_5 and toluene-d_8, and their presence was confirmed by GC-MS. On the basis of yield, ^1H NMR integration, and elemental analysis of the reaction mixture isolated from toluene[24] and zinc−sulfur products[25] separated from **1** by precipitation of **1** in lutidine, the following reaction stoichiometry is proposed:

$$34ZnEt_2 + 68S^0 \rightarrow$$
$$\text{“}Zn_{10}S_4(SEt)_{12}\text{”} + 12\text{“}Zn_2S(SEt)(Et)\text{”} + 4SEt_2 + 12S_2Et_2$$

In previous work, we have shown that the reaction between $ZnEt_2$ and S_8 in a 1:1 $ZnEt_2$:S^0 ratio produces $[Zn(SEt)(Et)]_{10}$ (**5**) in high yield.[18] The reaction of **5** with 1 equiv of sulfur per Zn in toluene followed by solvation of solid product in pyridine or lutidine also results in a ~25% yield of $Zn_{10}S_4(SEt)_{12}L_4$, suggesting that $[Zn(SEt)(Et)]_{10}$ may be an intermediate in the formation of “$Zn_{10}S_4(SEt)_{12}$”. We conclude that sulfido ligands are formed by further reaction of “Zn(SEt)(Et)” with S^0, and diethyl sulfides are evolved as byproducts, by SEt_2 or S_2Et_2 elimination. In contrast, when $[Zn(SEt)(Et)]_{10}$ is reacted with 1 equiv of S^0 in pyridine, or $ZnEt_2$ with 2 equiv of S^0 in pyridine; there is no evidence for formation of **2**. It is likely the sulfur insertion and diethyl sulfide elimination reactions are altered by the presence of a coordinating solvent.

The UV−vis spectrum of **1** in acetonitrile exhibits a strong absorption at 280 nm and a weaker absorption at 320 nm. This spectrum is similar to the spectrum of the analogous “$Cd_{10}S_{16}Ph_{12}$” dissolved in pyridine reported by Farneth et al.,[26] where the stronger, higher energy absorption (300 nm) was attributed to “$Cd_{10}S_{16}Ph_{12}$” and the weaker, lower energy absorption (346 nm) was attributed to aggregation of the cluster in solution.

Finally, attempts to deposit ZnS films by CVD from **1** or **2** have been thwarted thus far as a result of high lability of the Lewis base ligands. We hope to solve this problem by synthesizing less labile derivatives. However, prolonged stirring of **1** or **2** in toluene solution results in further reaction to produce nanocrystalline cubic ZnS (approximately 10 Å), and reactions of diethylzinc with >2 equiv of S result in formation of nanocrystalline cubic ZnS with 10−60 Å crystallite size as determined by transmission electron microscopy and electron diffraction. We note that a pyridine adduct of “$Cd_{10}S_4(SPh)_{12}$” has also been proposed as an intermediate in the thermal decomposition of **4** to form CdS at 500 °C via elimination of $4[NR]^+[SR]^-$.[14,26]

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Supporting Information Available: For $Zn_{10}S_4(SEt)_{12}(lutidine)_4$, tables giving a structure determination summary, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients and a textual summary of the refinement (14 pages). Ordering information is given on any current masthead page.

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(24) Characterization of crude product mixture isolated from toluene is as follows. Ratio of $Zn_{10}S_4SEt_{12}L_4$:“$Zn_2S(SEt)(Et)L$ (L = C_5D_5N) in pyridine-d_5: 1:12 based on integration of methylene quartets of the ethyl sulfide ligands (1:1). Elemental analysis of the product mixture: 22.71% C and 4.76% H, which is consistent with “$Zn_{10}S_4(SEt)_{12}$” + 12“$Zn_2S(SEt)(Et)$” + $9S_2Et_2$ (22.9% C, 4.78% H) and assumes that the more volatile SEt_2 (90 °C) was removed on evacuation. The presence of S_2Et_2 is confirmed by ^1H NMR. Incomplete removal of the S_2Et_2 byproduct might be due to coordination of sulfur lone pairs of S_2Et_2 to low-coordinate zinc atoms. Longer reaction time results in lower yield of $Zn_{10}S_4(SEt)_{12}$ and formation of colloidal zinc sulfide.

(25) Characterization of $[Zn_2S(SEt)(Et)L]_n$ (L = 3,5-lutidine) is as follows. Yield: approximately 6 g. ^1H NMR (C_5D_5N): δ = 0.74 (q, Zn−CH_2-CH_3), δ = 1.56 (t, Zn−SCH_2CH_3), δ = 1.63 (t, Zn−CH_2CH_3), δ = 3.00 (q, Zn−SC$H_2$$CH_3$). Lutidine ligands are displaced by pyridine solvent, but are present in a 1:1 ratio with Zn−SEt and Zn−Et. Anal. Calc: 36.7% C, 5.2% H, 3.89% N. Found: 34.2% C, 4.41% H, 3.17% N. We believe the elemental analysis data are low due to loss of lutidine.

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