Cluster Synthesis via Ligand-Arrested Solid Growth: Triethylphosphine-Capped Fragments of Binary Metal Chalcogenides

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In work emulating the initial observations of fullerenes, extraordinarily broad classes of metal-nonmetal clusters have been generated in the gas phase by laser ablation.[1] Typically, these clusters are produced only in very small quantities and are photoionized prior to identification by mass spectrometry. With sizes ranging from a few atoms to hundreds of atoms, they can generally be viewed as fragments of a binary parent solid, and their structures and reactivity stand to lend insight into solid nucleation and growth processes. Such species are of additional interest to us as building units for constructing microporous coordination solids, and as potential components in future molecular electronics devices.[2] Unfortunately, however, in the absence of bulk preparative techniques, even experimental verification of proposed cluster structures remains elusive.[3] Herein, we report the results of our initial efforts to develop a general method for synthesizing ligand-stabilized fragments of binary solids. The approach taken uses resistive heating to evaporate bulk quantities of the solid, and then co-condenses the resulting vapor with a volatile ligand.

A metal atom reactor[4] was purchased from H. S. Martin and adapted for this purpose. The reactor consists of a heating boat clamped between two water-cooled copper electrodes and suspended below a ligand inlet tube, all enclosed within a Pyrex chamber. Connection to a high vacuum line—comprising a roughing pump, an oil diffusion pump (Edwards Diffstak 63), and a turbomolecular pump (Edwards ETP63/80)—allows the reactor to be maintained under a dynamic vacuum of $<10^{-4}$ Torr. During operation, the reaction vessel is immersed in a bath of liquid nitrogen, such that the evaporated solid and the vacuum-transferred ligand condense simultaneously on the chamber walls.

Tungsten heating boats employed in the reactor operate reliably at temperatures of up to $\sim$2000 °C and are therefore suited for evaporating a range of transition metal chalcogenides.[5] With the exception of V_2S_3, compressed powder samples of the solids listed in Table 1 were all found to evaporate cleanly under the specified operating conditions. In each case, 100–800 mg of solid could be evaporated over the course of 8 h. On the basis of X-ray powder diffraction patterns of films deposited onto Si substrates, the condensate resulting without introduction of a coordinating ligand generally contained the original metal chalcogenide in crystalline form.

Simultaneous deposition of a coordinating ligand disrupts growth of the solid, permitting isolation of molecular intermediates. Triethylphosphine was selected as a volatile ligand expected to have an affinity for the soft chalcogenide-bound metal centers and to be capable of providing solubility to a high-nuclearity cluster product. After deposition, the reactor was allowed to warm gradually, until the frozen solid coating the chamber walls melted to give a darkly colored solution. Unreacted triethylphosphine was then removed by vacuum-transfer, and the products were extracted via cannula

Table 1. Cluster Products Observed from Co-depositing a Binary Metal Chalcogenide and Triethylphosphine

solid	evaporation conditions[a]	major products identified
V_2S_3	none suitable	
Cr_2S_3	w: 103 A, 3.2 VAC	$Cr_6S_8(PEt_3)_6$
MnS	n: 78 A, 2.3 VAC	insoluble
FeS	w: 100 A, 1.4 VAC	$Fe_4S_4(PBu^n_3)_4$[b]
CoS	w: 85 A, 1.6 VAC	$Co_6S_8(PEt_3)_6$
NiS	w: 90 A, 1.0 VAC	$Ni_4S_4(PEt_3)_8$
Cu_2S	t: 95 A, 1.9 VAC	$Cu_6S_4(PEt_3)_4$, $Cu_{12}S_6(PEt_3)_8$
Cu_2Se	t: 85 A, 2.1 VAC	$Cu_{26}Se_{13}(PEt_3)_{14}$, $Cu_{70}Se_{35}(PEt_3)_{21}$

[a] Solids were evaporated using a narrow ribbon (n), wide ribbon (w), or trough-shaped (t) tungsten heating boat, operating at the specified current and voltage.[5] [b] NEt_3 was employed instead of PEt_3 and was subsequently substituted by PBu^n_3 in acetonitrile solution.

as a chilled solution in ether or toluene. All of the cluster-containing solutions proved air-sensitive and were therefore stored and manipulated under a dinitrogen atmosphere.

Table 1 lists the clusters predominantly obtained from our survey of first-row transition metal sulfides using this method.[6] In several instances, a known species constituted the major product. The face-capped octahedral clusters $M_6S_8(PEt_3)_6$ (M = Cr, Co) were readily identified by mass spectrometry and NMR spectroscopy.[7] In a reaction employing Cu_2S, simply warming the reactor to room temperature afforded ca. 300 mg of large violet crystals of $Cu_{12}S_6(PEt_3)_8$.[8] Other cluster products recognizable by mass spectrometry, $Fe_4S_4(PBu^n_3)_4$, $Ni_4S_4(PEt_3)_8$, and $Cu_6S_4(PEt_3)_4$, seem to be without precedent.[9] Efforts to isolate and characterize these species are ongoing.

Larger clusters resulted from test reactions employing Cu_2Se. The 40 mL of dark brown ether solution extracted from the reactor was filtered and then reduced to dryness in vacuo. The resulting residue was dissolved in 10 mL of ether and allowed to stand at −25 °C for 12 h. The supernatant solution was then decanted to yield 217 mg (17% based on 780 mg of evaporated Cu_2Se) of red block-shaped crystals of $Cu_{26}Se_{13}(PEt_3)_{14}$ (**1**).[10] Three additional crops were obtained similarly upon further storage of the supernatant solution at −25 °C. These combined to give 147 mg of solid, which we estimate to contain 97% **1** and 3% Et_3PSe by mass. After 2 months at −25 °C, the remaining solution ultimately produced additional **1**, along with black needle-shaped crystals of $Cu_{70}Se_{35}(PEt_3)_{21}$·$Et_2O$ (**2**).

X-ray analysis[11] of a single crystal of **1** revealed the highly symmetric $Cu_{26}Se_{13}(PEt_3)_{14}$ cluster depicted in Figure 1. Its structure features a central Se^{2-} anion surrounded by 12 Cu^+ cations arranged in a slightly distorted icosahedron with a mean Cu···Cu edge distance of 2.86 Å. This is enclosed within an icosahedron of 12 Se^{2-} ions, which is, in turn, surrounded by a rhombic dodecahedron of 14 Cu^+ ions, each capped by a triethylphosphine ligand. Although the body-centered icosahedron of anions represents a closest packed arrangement, it obviously bears no relationship to the face-centered

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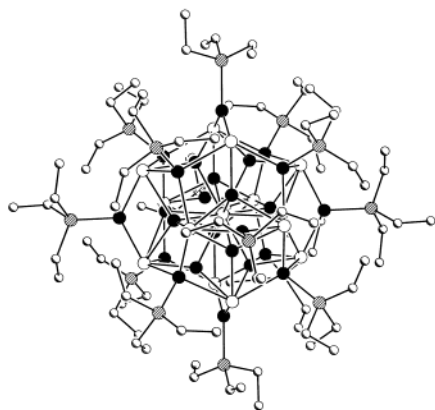
Figure 1. Structure of the $Cu_{26}Se_{13}(PEt_3)_{14}$ cluster (**1**). Black, white, hatched, and shaded spheres represent Cu, Se, P, and C atoms, respectively; H atoms are omitted for clarity. The cluster resides on a $2/m$ symmetry site in the crystal and possesses a core that closely approaches its maximal point group symmetry of T_h. Ranges for selected interatomic distances (Å) and angles (deg): Cu−Se 2.346(4)−2.743(4), Cu···Cu 2.484(5)−2.986(5), Cu−P 2.168(7)−2.26(1), Se−Cu−Se 99.3(1)−125.9(2), Se−Cu−P 102.8-(3)−121.2(3), Cu−Se−Cu 54.1(1)−180.0.
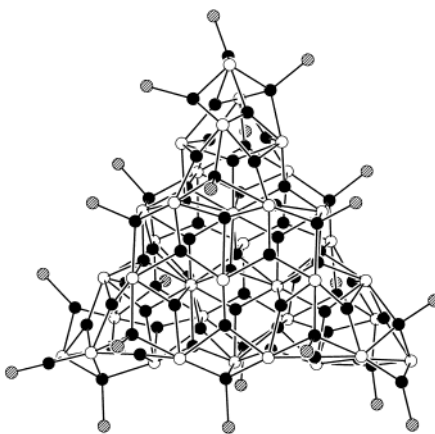
Figure 2. Core structure of the triangular $Cu_{70}Se_{35}(PEt_3)_{21}$ cluster, as observed in **2**. Black, white, and hatched spheres represent Cu, Se, and P atoms, respectively. Ranges for selected interatomic distances (Å) and angles (deg): Cu−Se 2.20(3)−2.95(2), Cu···Cu 2.39(3)−3.05(3), Se−Cu−Se 88.4-(7)−140(1), Cu−Se−Cu 52.8(7)−178.7(9).

cubic lattice of Cu_2Se.[12] We note, however, that the distorted tetrahedral coordination environment of the 12 innermost Cu^+ ions is comparable to that suggested by the disorder in the bulk, antifluorite-type solid.[12] A previously reported cluster, $Cu_{26}Se_{13}$-$(PEt_2Ph)_{14}$,[13] exhibits a deformed variant of the structure of **1**, highlighting the influence of the outer phosphine ligands on the core geometry.

As depicted in Figure 2, crystals[11] of **2** contain a higher-nuclearity $Cu_{70}Se_{35}(PEt_3)_{21}$ cluster with an unrelated core structure. Here, the Se^{2-} anions form a hexagonal closest packing, with an ABA stacking of triangular Se_{10}, Se_{15}, and Se_{10} layers. Copper cations are associated with 20 of the 26 tetrahedral holes created by this packing, but stray considerably from the hole centers. The remaining 29 interior Cu^+ ions lie near trigonal planar sites within and between the selenium layers. Significantly, although the central portion of the core structure is now consistent with the three-dimensional periodicity of a crystal, its hexagonal anion packing still deviates from the cubic closest packing found in Cu_2Se.[11] The surface of the core features 21 Cu^+ centers, displaying a mix of distorted tetrahedral and trigonal planar coordination geometries, each with a single triethylphosphine ligand. The disposition of these surface moieties confers a handedness to the corners of the triangular cluster

that differs at the uppermost vertex in Figure 2, thereby destroying the potential three-fold symmetry. At one such corner, the structure differs substantially from that reported for the related cluster in $Cu_{70}Se_{35}(PEt_3)_{22}\cdot5Et_2O$;[14] however, this could possibly be a consequence of disorder imposed by the higher crystal site-symmetry of the latter species.

The foregoing results establish the effectiveness of a potentially highly generalizable method for synthesizing molecular fragments of binary solids. Thus far, the species isolated have not yet reached a size regime at which surface reorganization is overridden by emergence of the original bulk crystal structure. Future work will endeavor to extend the applicability of this technique to more refractory solids, such as metal carbides, nitrides, and oxides, through the design of a related reactor system based upon laser ablation.

Supporting Information Available: Tables for the structures of **1** and **2** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The solutions obtained were analyzed by FAB^+ mass spectrometry and ^{31}P NMR spectroscopy, which in most instances indicated the presence of a mixture of clusters. On the basis of comparisons of peak intensities, the species in Table 1 are estimated to represent 60−100% of the observable products.

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(10) Characterization of **1**: ^{31}P NMR (d_8-toluene): δ −12.3, −15.5, −22.1 ppm. Anal. Calcd for $C_{84}H_{210}Cu_{26}P_{14}Se_{13}$: C, 23.29; H, 4.89. Found: C, 23.38; H, 4.92.

(11) Crystal and structure refinement parameters, **1**: $C_{84}H_{210}Cu_{26}P_{14}Se_{13}$, $T =$ 130 K, $I2/m$, $Z = 2$, $a = 17.2391(7)$, $b = 23.491(1)$, $c = 17.303(1)$ Å, $\beta = 90.305(2)°$, $V = 7006.9(6)$ Å^3, $R_1 = 0.0925$, w$R_2 = 0.2391$. **2**: $C_{130}H_{325}Cu_{70}OP_{21}Se_{35}$, $T = 147$ K, Pc, $Z = 4$, $a = 25.699(2)$, $b = 35.504-(3)$, $c = 29.214(2)$ Å, $\beta = 100.573(3)°$, $V = 26202(3)$ Å^3, $R_1 = 0.1581$, w$R_2 = 0.3400$. Data were collected on a Siemens SMART diffractometer using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Structures were solved by direct methods and refined against all data using SHELXTL 5.0. In both cases, ethyl groups on several of the PEt_3 ligands are severely disordered, leading to poor data quality and high final agreement factors.

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