

From Designer Clusters to Synthetic Crystalline Nanoassemblies

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ABSTRACT

Clusters have the potential to serve as building blocks of materials, enabling the tailoring of materials with novel electronic or magnetic properties. Historically, there has been a disconnect between magic clusters found in the gas phase and the synthetic assembly of cluster materials. We approach this challenge through a proposed protocol that combines gas-phase investigations to examine feasible units, theoretical investigations of energetic compositional diagrams and geometrical shapes to identify potential motifs, and synthetic chemical approaches to identify and characterize cluster assemblies in the solid state. Through this approach, we established As_7^{3-} as a potential stable species via gas-phase molecular beam experiments consistent with its known existence in molecular crystals with As to K ratios of 7:3. Our protocol also suggests another variant of this material. We report the synthesis of a cluster compound, $\text{As}_7\text{K}_{1.5}(\text{crypt222-K})_{1.5}$, composed of a lattice of As_7 clusters stabilized by charge donation from cryptated K atoms and bound by sharing K atoms. The bond dimensions of this supercluster assembled material deduced by X-ray analysis are found to be in excellent agreement with the theoretical calculations. The new compound has a significantly larger band gap than the hitherto known solid. Thus, our approach allows the tuning of the electronic properties of solid cluster assemblies.

One of the most promising prospects in the field of clusters and nanoscience is the possibility of synthesizing nanoscale materials^{1–5} where size-specific clusters serve as the elementary molecular building units. As the physical, chemical, electronic, optical, or magnetic properties of clusters are controllable by size and composition,⁶ this approach may provide an unprecedented ability for synthesizing customized materials. In addition, the cluster materials would generally possess differing intracuster and intercluster length scales, leading to novel functionalities not available in conventional solids.⁷ While clusters are stable, the cluster materials are a kinetically stable phase of matter and their compositions cannot be predicted through conventional phase diagrams. The realization of this important concept therefore rests on our ability to identify stable motifs and processes that will enable synthesis of cluster assembled materials. We propose that such identifications can be carried out through energetic compositional diagrams showing differences in energy as one varies the number of atoms of various kinds. While these diagrams can be thought of as an analogue of phase diagrams in alloys, unlike alloy phase diagrams which are indicative

of the miscibility and formation of ordered phases, the energetic compositional diagrams demonstrate the ability of specific numbers of atoms joined to form strongly bonded motifs.

In this letter, we present a protocol that provides a pathway to producing such materials more widely and with better control on primary units, thus allowing tunability of electronic properties. Our approach combines three major steps. (1) Identification of potential cluster building blocks produced in molecular beams from bulk starting material. (2) First-principles theoretical investigations to characterize electronic features and the bonding patterns that could guide the nature of assemblies and the conditions that might favor their formation. (3) Synthetic chemical approach designed to facilitate the assemblies of desired cluster building blocks and subsequently materials in macroscopic quantities. In this work, we demonstrate the full potential of the synergistic approach by considering a Zintl phase that has been known to exist for a long time,¹⁴ namely As_7K_3 . We first show how steps (1) and (2) lead to identification of the features and provide an understanding of the interactions that serve to stabilize the existing cluster solid. The knowledge gained is then used to go beyond the existing compound and open the pathway to stabilize a new phase by replacing some of the potassiums in As_7K_3 by cryptated species that serve to

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incorporate some of the potassium atoms in the crypt-222. As the cryptated potassiums are shown to favor potassium cations, the energy to remove an electron from K is significantly reduced. In effect, this can be looked upon as leading to a reduction in the ionization potential of K. The incorporation of crypt facilitates the formation of the ionic phase through charge transfer. As opposed to previously known As_7K_3 in which the As_7 motifs arrange in a compact structure with each As_7 surrounded by K atoms, in the new phase, the motifs are linked only via a single K atom while the cryptated K atoms stabilize the solid via charge transfer and as space fillers. Because K atoms are needed to link As_7 motifs, only a limited number of K atoms in As_7K_3 can be cryptated. The new solid is marked by As_7 units assembled into hexagonal rings and helices joined together by sharing K atoms which leads to a $(\text{As}_7\text{K}_{1.5})_\infty$ three-dimensional (3D) structure. The $\text{K}_{1.5}$ stoichiometry arises due to sharing of potassium by adjacent rings in the extended structure; the remainder of the potassium is cryptated and occupies the cavities of the 3D structure. The approach revealed from the work presented here is shown to offer a viable protocol for successful passage from free gas-phase clusters to cluster crystals and also as a guide to search for newer phases through modification of the selected species.

Elements belonging to group VA of the periodic table (N, P, As, Sb, and Bi), though similar in regard to the $ns^2 np^3$ valence shells, exhibit a large variation in properties from the light to the heavy element. For example, N_2 has one of the highest homonuclear dissociation energies, i.e., 9.91 eV. The molecule is so stable that bigger units, e.g., N_4 , would fragment into molecular units. On the other hand, As_2 has a modest dissociation energy of 4.17 eV and favors formation of larger units. For example, previous studies^{8,9} have suggested that As_n ($n = 4, 8, 20, 32, 36$, and 80) cages are quite stable and compound clusters composed of As cages have been synthesized. Note that while an As atom has a partially filled p subshell, bulk As is a semimetal. The possible variations in properties along with the existence of Zintl phases¹⁰ suggest that it may be an ideal system to explore the possibility and properties of cluster-based materials. The combination of As clusters with alkali atoms has also attracted considerable attention because some of the As clusters are stable in ionic form and the alkali atoms can provide the required charge. For example, As_5^- in As_5K is a very stable species due to the π -bonding and aromaticity of the valence electrons.⁹ Indeed, Zintl phases composed of As and alkali metals are known to exist.^{11–15} Some involve the use of As_7K_x as subunits in forming materials, but our protocol for identifying the building blocks and approaching the assembly differs from others. We first seek to identify species that are stable and abundant magic numbers in the gas phase that arise through self-assembly and are thereby viable building blocks for condensed phase nanoclusters of identical composition.

Identification of Stable Cluster in Gas-Phase Experiments. The formation of a cluster solid requires motifs that will maintain their integrity upon assembly. The first step is then to investigate pure As, and As incorporated with alkali

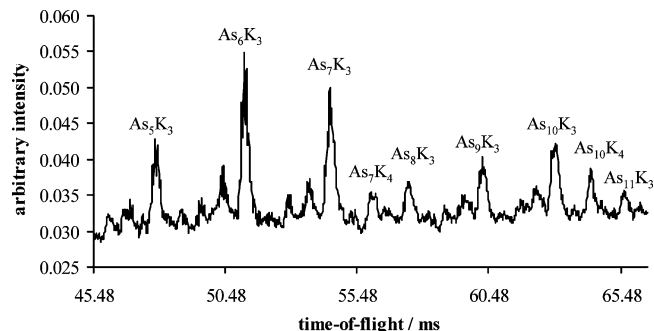


Figure 1. Mass spectra of As_nK_m clusters generated in a molecular beam by the laser vaporization of a dispersed mixture of arsenic and potassium.

metals, to identify stable free species that may serve as building blocks. To accomplish this, we implemented previously developed gas-phase cluster techniques.^{16,17} Specifically, in the present study, we investigated As–K clusters produced by vaporizing with the second harmonic (532 nm) of a Nd:YAG laser, a rotating and translating dispersed mixture of bulk arsenic and potassium, while pulsing a cooling gas (methane seeded in helium) over the ablated region. Clusters were created from the ensuing plasma formed by the laser ablation event and further energetically cooled via a supersonic expansion into vacuum. The consequent pulsed neutral molecular beam of clusters was ionized with a XeCl excimer laser (308 nm) and then analyzed with a time-of-flight mass spectrometer.

Figure 1 shows the mass spectra of $\text{As}_n\text{K}_{3,4}^+$ clusters produced in this manner. A prominent cluster series, with compositions corresponding to known Zintl compounds,¹⁶ is readily formed. The clusters are composed of As_n^{3-} , stabilized by three potassium atoms. Three such species are found with $n = 5, 7, 9$; these are believed to be neutral clusters that are directly ionized in the analysis and associated detection scheme. Other members of the K_3 series, as well as clusters that contain four potassium atoms, may be stable cation fragments of larger arsenic and potassium clusters produced upon ionization. Note the prominent stability of the As_nK_3 cluster when compared to the other potassium-containing compounds. The As_7K_3 is the most prominent “magic cluster” of the Zintl series, which is identified as the building block for condensed-phase materials as discussed below. Our theoretical studies indicate that the ionization potentials of As_7K_3 and other stable Zintl species are higher than the photon energy used to produce cationic species and hence their ionization involves a multiphoton process. On the other hand, the ionization potential of several other species and in particular that of As_6K_3 is less than the photon energy used for ionization. The As_6K_3^+ , seen as the prominent peak in Figure 1 is either a product of a single photon ionization of the neutral or a stable fragment of the larger ionized species. In any event, its cationic character prevents it, as well as any other stable cations, from serving as building blocks for condensed matter.

Energetic Compositional Diagrams to Identify Potential Species. The electronic features leading to the observed stability of As_7K_3 and its viability for cluster assemblies were

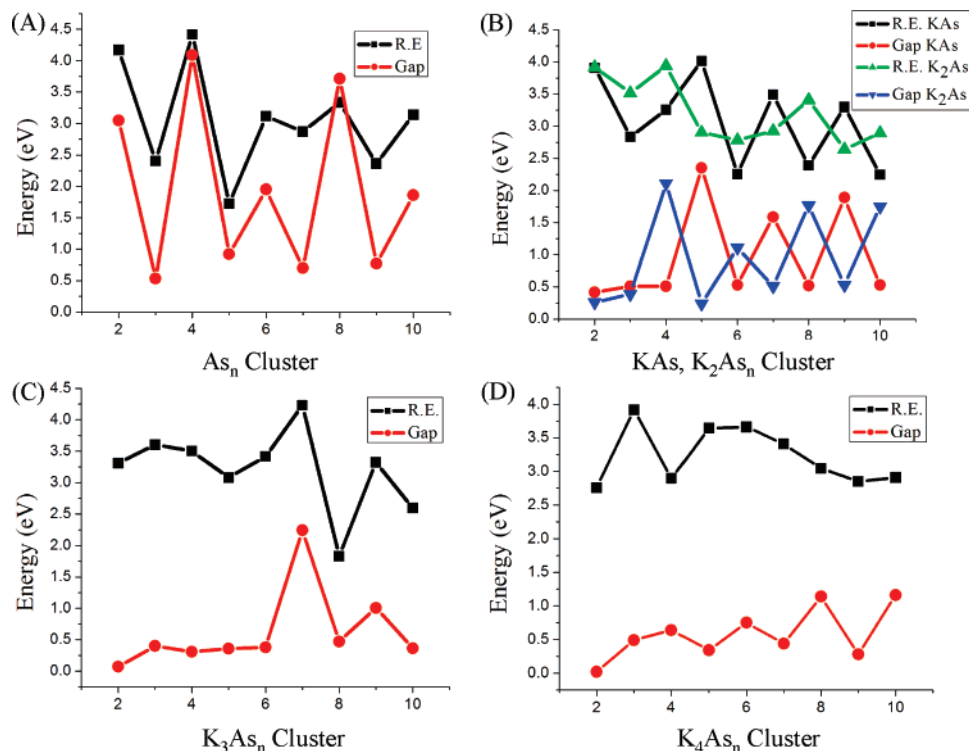


Figure 2. Removal energy (see eq 1) and the HOMO–LUMO gap in the ground-state structures of As_n , As_nK , As_nK_2 , As_nK_3 , and As_nK_4 clusters as a function of the number of As atoms. The energies are in electron volts (eV).

theoretically investigated through electronic structure studies. These studies were based on a first-principles self-consistent molecular orbital approach where the cluster wave function is expressed as a linear combination of atomic orbitals located at the atomic sites. The atomic orbitals were expanded in a sum of Gaussian functions. The exchange and correlation contributions were incorporated via a generalized gradient-corrected density functional.^{18,19} The cluster calculations were carried out using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) set of codes developed by Pederson and co-workers.^{20–22} The cluster assembly calculations were performed using the deMon²³ code developed by Koester and co-workers. Minimum structures were fully optimized in delocalized internal coordinates without constraints using the rational function optimization method and the Broyden, Fletcher, Goldfarb, and Shanno update.²⁴ The double- ζ valence polarized (DZVP) basis set was employed.²⁵ The determination of the ground-state geometry is a complicated task due to directional bonding. Hence, the configuration space was sampled by starting from a large number of initial configurations and optimizing the geometry by moving atoms in the direction of forces until they dropped below a threshold value. Our past experience on a variety of systems indicates that the large number of starting geometries and different optimization methods implemented in NRLMOL or deMON are sufficient to ensure the ground-state geometries.

The stability of clusters was probed through two markers. First, removal energy (RE), defined as the energy required

to remove an As atom from a given cluster, was calculated using the equation:

$$\text{RE} = E(\text{As}_{n-1}\text{K}_m) + E(\text{As}) - E(\text{As}_n\text{K}_m) \quad (1)$$

Here $E(\text{As}_n\text{K}_m)$, $E(\text{As}_{n-1}\text{K}_m)$, and $E(\text{As})$ are, respectively, the total energies of a cluster containing n As and m K atoms, a cluster containing $n - 1$ As and m K atoms, and an isolated As atom. The RE also represents the energy gain in adding an As atom to the preceding cluster. Peaks in RE represent cluster sizes where there is a larger gain in energy in forming the cluster from the preceding size, and smaller energy is required to form it by stripping an atom from the larger size. Both of these are indicative of a stable cluster. A similar RE can be defined for the growth involving K atoms. The second marker relates to the chemical inertness of the cluster. It is known that systems characterized by filled electronic shells and having a large gap between the filled shell and the next available electronic level, exhibit lower reactivity. The inert gas atoms and our earlier results² on Al_{13}^- are some of the classic examples. Consequently, the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO–LUMO) was used as the second marker to find units that interact weakly.

In Figure 2, we show the RE and HOMO–LUMO gap for various clusters. In the case of pure As_n clusters (upper left insert), As_4 appears to be particularly stable.^{9,26} Another cluster that is marked by a sharp drop in RE and HOMO–LUMO gap is As_7K_3 (lower left pane). More quantitatively, while it takes 4.32 eV to remove an As atom from As_7K_3 , it

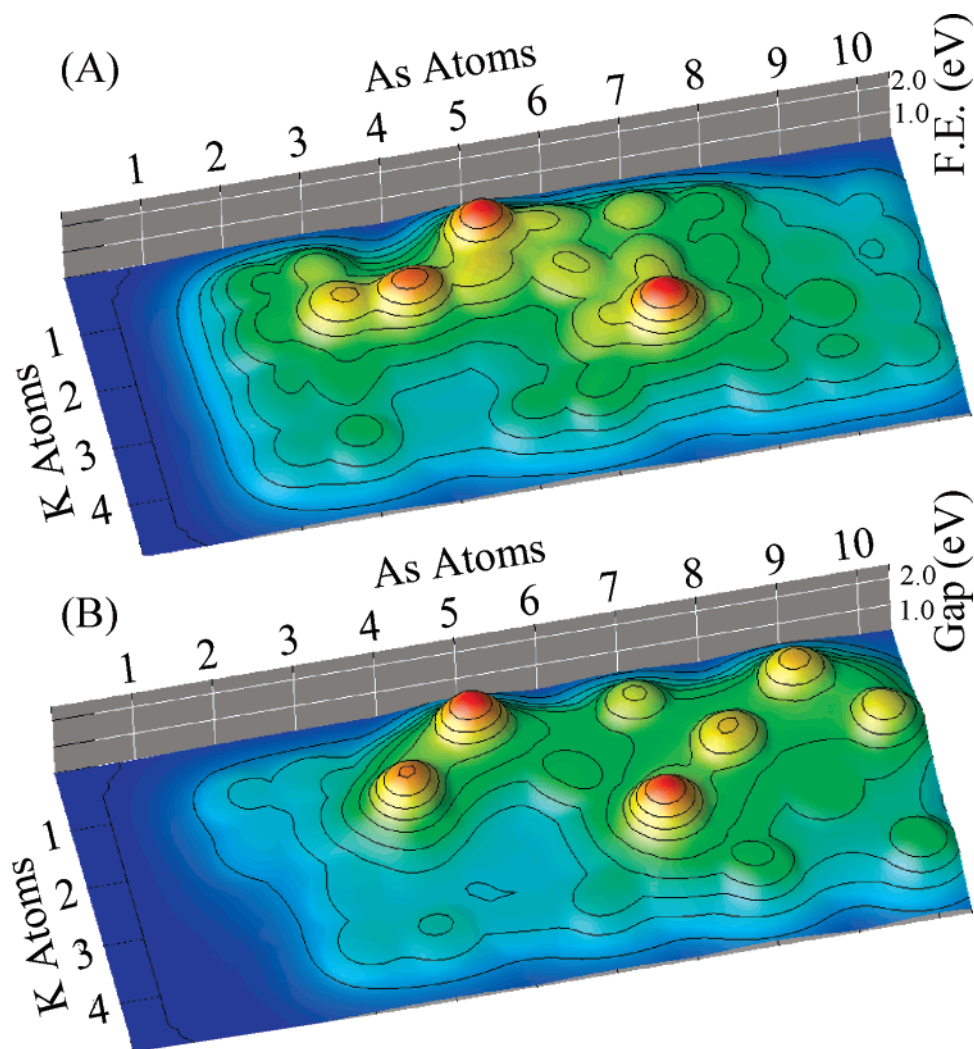


Figure 3. (A) Minimum fragmentation energy, FE, (in eV) of As_nK_m ($n = 2-10$, $m = 1-4$) as a function of composition. See eq 2. (B) HOMO–LUMO gap as a function of composition. The islands of stability are readily discernible.

only takes 1.83 eV to remove an As atom from As_8K_3 , indicating that the fragmentation of larger species could end up enhancing As_7K_3 . The As_7K_3 species is also stable against significant further enrichment of K. While the gain in binding energy is 2.57 eV in going from As_7K_2 to As_7K_3 , the corresponding gain in energy is only 0.43 eV in going from As_7K_3 to As_7K_4 . The unique resistance toward changes in As or K composition is the key to its stability. To further examine the unique nature of As_7K_3 , we investigated the minimum energy required to break the cluster into two fragments.²⁷ To this end, we calculated the fragmentation energy (FE) for all possible fragmentation channels

$$\text{FE} = E(\text{As}_{n-x}\text{K}_{m-y}) + E(\text{As}_x\text{K}_y) - E(\text{As}_n\text{K}_m) \quad (2)$$

and determined the minimum fragmentation energy for each cluster. The minimum fragmentation energy and HOMO–LUMO gap in all the As_nK_m ($n = 1-14$, $m = 1-4$) clusters are shown in Figure 3A,B. Because clusters with high minimum fragmentation energy are particularly stable while large HOMO–LUMO gaps are indicative of chemical inertness, the energetic compositional diagrams marking

variations in fragmentation energy and the HOMO–LUMO graphs characterizing the chemical inertness enable a determination of compositions that lead to islands of stability. Three clusters emerge as having higher values for both the fragmentation energy and HOMO–LUMO gap. These are As_4K_2 , As_5K , and As_7K_3 . As_4K_2 and As_5K have planar As_4 or As_5 rings, with K occupying a hollow sites above (and below for As_4) the ring. The planar structures of As_4 and As_5 make them unsuitable for forming three-dimensional assemblies, particularly those involving Zintl structures as building blocks. Hence the theoretical and gas-phase experimental findings point to As_7K_3 as being the most promising candidate for developing cluster-assembled materials. Its stability is derived from the π -electronic bonding. To illustrate this, Figure 4 shows the ground-state geometry and the HOMO electronic charge density in the cluster. The K sites are seen to lose charge to the As_7 motif (Figure 4B). A Mulliken population analysis of the resulting charge density indicates that each K donates around $0.49 e^-$. A reasonable assignment of the cluster would be the arsenic motif tending toward anionic As_7^{3-} surrounded by K^+ cations. If the primary purpose of K is to donate charge, the stability of

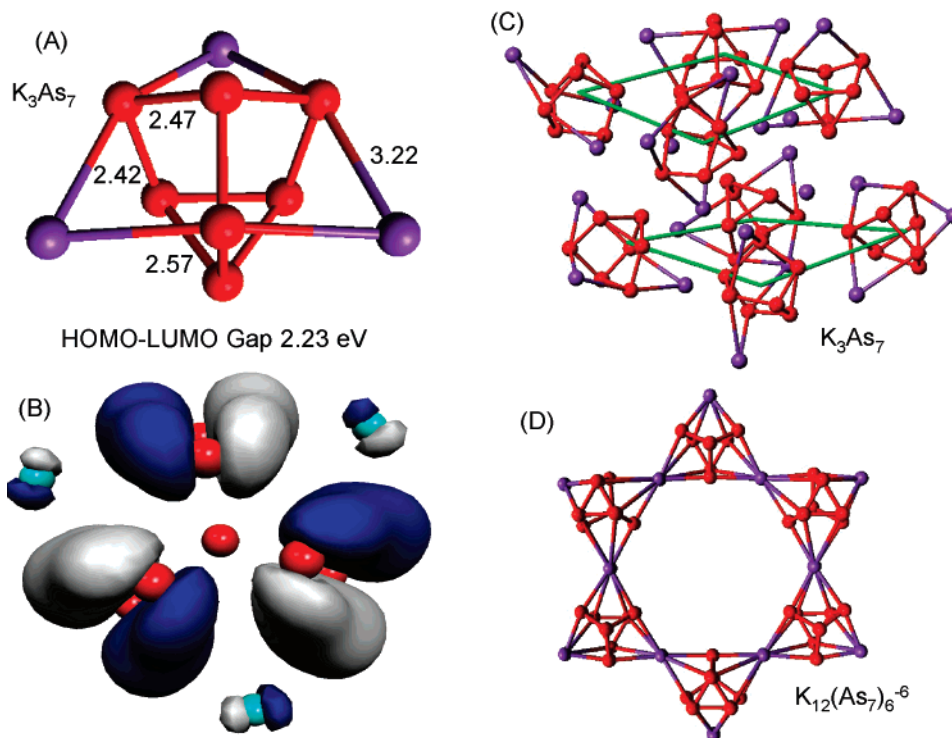


Figure 4. (A) Ground-state geometry of a K_3As_7 cluster (also marked is the HOMO–LUMO gap). (B) Wave function in the HOMO of K_3As_7 . (C) Geometry of the K_3As_7 crystal from ref 12. The green lines are to guide the eye. (D) Optimized geometry of $K_{12}(As_7)_6^{6-}$ with no restraint.

anionic As_7 could be looked upon from the following viewpoint. Assuming that each As contributes three valence electrons (our studies indicate no significant mixing between s and p states), an anionic As_7^{3-} unit would tend toward 24 electrons.

The structure shown in Figure 4A has two kinds of As sites, namely with coordination of 3 (apex As atom and three As forming the hidden triangle at the base) and those that have double coordination. There are nine σ bonds that are occupied by 18 valence electrons. In addition, the sites having double coordination with arsenic form π -bonds with the three base sites that are occupied by six electrons and lead to a very stable structure. It is interesting to note that the ground-state structure can be looked upon as three As_5 pentagons (distorted) decorated by K atoms, and one might think of the stability of As_7K_3 as being related to the stability of As_5K units. While there is similarity, the nonplanar nature of pentagons in As_7K_3 does not lend to aromaticity as in the case of As_5K . The next question is whether the As_7K_3 units will maintain their identity as the individual units are assembled to form cluster assemblies and eventually a cluster solid. To examine this possibility, we looked at the geometry of a lattice of (As_7K_3) clusters¹² (see Figure 4C). In all cases, the individual As_7 units maintained their identity.

Synthesis and Characterization of a New Cluster-Assembled Material. The central issue is whether the stability in free beams and the theoretical prediction of stable rings consisting of As_7 motifs linked by a pair of K atoms does translate to materials in the condensed phase. Indeed, a stable cluster material with As_7K_3 has been known to exist.^{12,14} As suggested by the theoretical studies on rings,

the solid does consist of As_7 motifs linked by two K atoms. The objective of this present study is to determine whether the knowledge gained in the foregoing would allow us to form new phases with different bonding characteristics and consequently novel properties.

As discussed above, the stability of As_7K_3 is linked to the formation of As_7^{3-} motifs through charge transfer from K atoms. As As_7K_3 clusters are assembled, the arrangement develops into a close-packed structure¹² consisting of a central As_7 unit surrounded by six other As_7 units (see Figure 4C). There is no direct interaction between the As_7 motifs as each As_7 is surrounded by a pocket of potassium atoms. As mentioned before, the purpose of K is primarily to donate charge and to link As_7 motifs. This raises an interesting possibility. Consider the energetics of the formation of ionic As_7K_3 . The theoretical studies indicate that the electron affinity of As_7K_2 cluster is 1.73 eV while the ionization potential of K is known to be 4.34 eV. Because the unit is stabilized via charge transfer, the formation of the ionic phase could be facilitated if the ionization potential of K could be reduced. One way to accomplish this is to add a sequestering agent (crypt-222) as also suggested by Corbett.¹¹ It is, however, important to note that the effectiveness of the sequestering agents depends on the competition between the reduction in the energy to remove an electron from the cryptated species and the electron affinity of the remaining species and requires a careful balance. Our calculations reveal that the cryptated K cation is highly stable, leading to an effective ionization potential of only 1.58 eV, which is even lower than the electron affinity of As_7K_2 , 1.73 eV. By limiting the amount of added crypt, only a part of the K

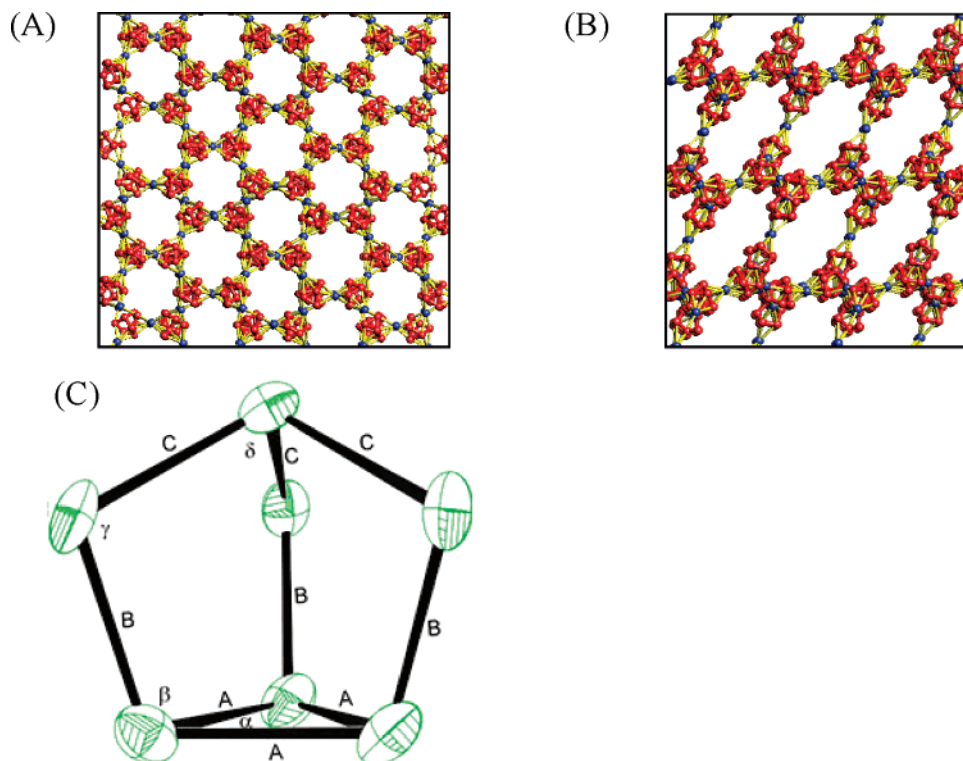


Figure 5. Representation of the 3D structure along: (A) the diagonal between *a* and *b* axes and (B) *c* axis (red: As clusters; blue: K atoms; yellow: bonds between the clusters and K atoms). The cryptated potassium ions are located within the cavity of the 3D network and are not shown for clarity. (C) As₇³⁻ cluster, 50% thermal ellipsoids are used.

ions were cryptated and the remaining K ions then linked the As₇ motifs. To examine this possibility, we carried out calculations on a free supercluster composed of six As₇ units and 12 K atoms. To incorporate the effect of cryptated K atoms in the solid, the resulting supercluster was studied with a net charge of -6 (compensating for the missing potassium atoms). In Figure 4D, we show the ground-state geometry. Note that such a composition has As₇ motifs linked via single K atoms. This also shows that only 1 out of 3 potassium atoms in As₇K₃ can be cryptated because removal of additional K atoms will leave unlinked As₇ motifs. Are these considerations borne out by experiments? Can one really make a different phase of As₇³⁻ cluster materials by adding a crypt-222?

To this end, a synthetic approach that relies on an assembly of clusters in solution was employed in the subsequent phase of this study. More specifically, K, As, and Ph₃SnCH₂SnPh₃ (3:6:1 by weight) were mixed in ethylenediamine. The mixture was stirred overnight at room temperature, and the resulting dark-green solution was filtrated. Crypt-222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]-hexacosane) (1:3 ratio versus K) was added to the solution, and it was layered with toluene. Orange crystals were formed on the wall and on the bottom of the test tube. Mother liquor was decanted and a crystal was used for single-crystal X-ray diffraction.

X-ray diffraction data were collected from one crystal (0.22 mm × 0.21 mm × 0.12 mm) with graphite-monochromatic Mo Kα radiation on a Bruker APEX diffractometer with a CCD area detector at 110 K. The

structure was solved by direct methods in *P*-1 and refined on *F*-2 (full matrix, absorption corrections with SADABS) using the SHELXTL V6.14 package. Crystal data: 24.61 Å, 32.89 Å, 37.21 Å, 89.95°, 89.90°, 81.470°, R1/wR2 = 13.65/34.05% for the observed data ($I \geq 2\sigma_I$). The anionic species, As₇³⁻ (see Figure 5A,B), joined via K atoms, form an infinite 3D structure with very high symmetry and with stoichiometry of As₇K_{1.5}. The distances between the As atoms are as follows: A, 2.50(1)–2.55(1) Å; B, 2.33(1)–2.38(1) Å; C, 2.41(1)–2.42(1) Å. Note that the first principles theoretical calculations on a single As₇K₃ unit shown in Figure 4A predict values of 2.57, 2.42, and 2.47 Å for the three lengths, respectively. The important bond angles (Figure 5C) in all clusters are: α, 59.2(2)–61.04(2)°; β, 104.4(2)–105.4(2)°; γ, 98.7(2)–99.45(2)°; δ, 99.6(2)–102.3(2)°. Arsenic clusters and potassium atoms (Figure 5A) form hexagonal rings that include six Zintl anions and six K atoms (see Figure 5A). The hexagonal rings join together by sharing K atoms and form a three-dimensional network. The distances of the potassium atoms from the two-bonded arsenic atoms (see Figure 5C) are 3.33(1)–3.55(1) Å, and the distances between potassium atoms and the three-bonded arsenic atoms (the atoms in the triangular base) of the clusters are 3.60(1)–3.95(1) Å.

As discussed above, the 3D framework has a negative charge, ((As₇K_{1.5})^{1.5-})_∞. The remaining potassium cations, those necessary to form a neutral compound and not included in the 3D network, are cryptated and located within the cavity of the 3D network. The cryptated potassium ions are necessary for the integrity of the crystals. Without the crypt-

222, the As₇ units are well separated and only a few As₇ clusters share a single potassium atom to form a dimer. The cryptated system reveals a higher degree of order, as all As₇ units are bound together through a network of hexagonal rings and helices.

The unit cell of the X-ray structure contains (K-crypt-222)₈[As₇K_{1.5}]₆•5en with $z = 4$. Assuming complete charge transfer from the potassium atoms, the As₇ clusters have an actual charge of -2.83 rather than -3 . *Because the band gap of the resulting material depends on the charge transfer, the choice of the sequestering agent allows tunability of the electronic behavior. In the present case, the addition of crypt-222 increases the charge transfer as well as opens the structure. Both of these lead to an enhancement of the band gap, and our theoretical calculations predict a band gap of 2.60 eV as opposed to 1.35 eV for the uncryptated solid.*

Because of disorder in the crystal lattice, the crystallographic R-factor is relatively high. Several crystals were screened and three complete data sets were collected from as many crystals. In all three cases, the diffraction images show that reflections at higher 2θ angles were either absent or very weak. Most of the diffraction peaks are broad, i.e., the mosaicity of the crystal is higher than usual. The data was processed using SAINT (Bruker), and the coverage statistics confirmed the absence of higher resolution data. Ninety percent of the reflections above 1.5 Å have their intensities lower than 2σ . While the crystal quality precludes high precision in bond lengths and angles, the overall structure is unambiguously established and shows remarkable agreement with theoretical calculations. It is indeed remarkable that the calculated As–K bond lengths of 3.63 and 4.32 Å in the cluster (As₇K₂)₆⁶⁻ (Figure 4D) are close to the experimentally determined bond lengths in the cryptated crystal we prepared. One must point out that the calculations are on a single ring while the experiments are on a macroscopic solid. Another interesting aspect is that any attempt to rotate the As₇ units brought them back into the symmetric cluster.

Conclusions and Future Prospects. In summary, the results presented here demonstrate the development of a protocol that may allow the production of nanoscale materials through cluster assembly. It involves the synergistic integration of three very different facets of cluster science: first, examining the stability of clusters in an interaction-free environment; second, carrying out theoretical investigations to identify the nature of bonding leading to the stability; and third, chemically synthesizing and structurally elucidating these cluster assemblies in the solid state. We have shown that the passage from stable clusters in molecular beams to cluster assemblies involves going far beyond the conventional wisdom of merely focusing on a single magic peak seen in an experimental mass spectrum. On the contrary, major and minor peaks all need to be examined. To be an effective building block for new materials, the cluster has to be singularly stable toward variations in the composition of all the constituents, exhibiting a large HOMO–LUMO gap and having a geometry that will favor three-dimensional assembly. Indeed, the island of stability shown in Figure 3 is

reminiscent of the eutectic in alloy formations where energetics governs the stable composition of a mixed system. The cluster charge and the use of sequestering agents (such as crypt-222) play an important role in stabilizing the new compound. Our preliminary investigations indicate that, while the existing As₇K₃ phase has a band gap of 1.35 eV, the new cluster solid is a wide band gap semiconductor with a band gap of 2.60 eV. Thus, our approach allows the tuning of the electronic properties of solid cluster assemblies. These are exciting developments and the current emphasis is to explore if the above experience can be extended to other systems and in particular to other metal/metalloid combinations.

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