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Heteroatomic Deltahedral Clusters of Main-Group Elements: Synthesis and Structure of the Zintl Ions $[In_4Bi_5]^{3-}$, $[InBi_3]^{2-}$, and $[GaBi_3]^{2-}$

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Reported are the first heteroatomic deltahedral Zintl ions made of elements differing by more than one group, indium or gallium and bismuth. Nine-atom clusters $[In_4Bi_5]^{3-}$ are characterized in two different compounds, $(Na\text{-crypt})_3[In_4Bi_5]$ (**4**, $P2_1/n$, $a = 23.572(6)$ Å, $b = 15.042(4)$ Å, $c = 24.071(4)$ Å, $\beta = 106.00(3)°$, $Z = 4$) and $(K\text{-crypt})_6[In_4Bi_5][In_4Bi_5]\cdot 1.5en\cdot 0.5tol$ (**5**, $P2_1/c$, $a = 28.532(2)$ Å, $b = 23.707(2)$ Å, $c = 28.021(2)$ Å, $\beta = 93.274(4)°$, $Z = 4$). Tetrahedra of $[InBi_3]^{2-}$ or $[GaBi_3]^{2-}$ are found in $(K\text{-crypt})_2[InBi_3]\cdot en$ (**1**, $P2_1$, $a = 12.347(4)$ Å, $b = 20.884(4)$ Å, $c = 12.619(7)$ Å, $\beta = 119.02(4)°$, $Z = 2$) and in the isostructural $(Rb\text{-crypt})_2[InBi_3]\cdot en$ (**2**, $a = 12.403(8)$ Å, $b = 20.99(1)$ Å, $c = 12.617(9)$ Å, $\beta = 118.83(4)°$) and $(K\text{-crypt})_2[GaBi_3]\cdot en$ (**3**, $a = 12.324(5)$ Å, $b = 20.890(8)$ Å, $c = 12.629(5)$ Å, $\beta = 118.91(3)°$). All compounds are crystallized from ethylenediamine/crypt solutions of precursors with nominal composition "$A_5E_2Bi_4$" where A = Na, K, or Rb and E = Ga or In. The cluster in **4** is a well-ordered monocapped square antiprism with the four indium atoms occupying the five-bonded positions. Compound **5** contains two independent $[In_4Bi_5]^{3-}$ clusters; one is the same as the cluster in **4**, while the other is a tricapped trigonal prism with two elongated prismatic edges. All compounds are EPR-silent and therefore diamagnetic.

Introduction

Zintl ions made from solutions have been known for more than a century, since 1891 when Johannis reported the first reduction of lead by sodium in liquid ammonia.[1] Studies carried out in the following 40 years suggested that the green sodium−lead solution contained polyanions of nine lead atoms, i.e., $4Na^+ + [Pb_9]^{4-}$.[2,3] During that time anions of other groups such as Sb_7^{3-} and Te_4^{2-} were also proposed.[3] More systematic studies by E. Zintl in the 1930s suggested even more polyanions such as Sn_9^{4-}, As_7^{3-}, Bi_7^{3-}, and Se_4^{2-}, all deduced from results of potentiometric titration of liquid ammonia solutions of the corresponding elements and alkali metals.[4,5] Later, dissolution of precursor alloys of the latter was also employed. Also, ethylenediamine (en) was often used as a solvent instead of liquid ammonia. Thus, in 1970 using ethylenediamine, Kummer and Diehl isolated and structurally characterized the first example of a deltahedral Zintl ion, Sn_9^{4-} in $(Na_4\cdot 7en)Sn_9$.[6] Several years later, a much better approach for the stabilization of Zintl ions was developed by Corbett.[7] It involves the use of the cagelike complexing reagent 4,7,13,16,21,24-hexaoxa-1,-10-diazabicyclo-[8,8,8]-hexacosane, abbreviated as *crypt*. It effectively sequesters cations such as Na^+, K^+, and to some extent Rb^+ and therefore prevents back-donation of electrons from the anion to the cation. A variety of homoatomic and a few heteroatomic deltahedral Zintl ions have been synthesized from such mixed ethylenediamine/crypt solutions of dissolved solid-state precursors.[8−30] Until recently these precursors were thought to be alloys without structural features and definitely without clusters. Only recently it was discovered that some of the cluster ions found in solutions actually exist in the precursor solids as well.[31−35] They are characterized in the Zintl (valence)

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compounds $Rb_{12}Si_{17}$, $K_{12}Sn_{17}$, Cs_4Ge_9, K_4Pb_9, Cs_4Pb_9, etc. These compounds established, for the first time, relations between Zintl phases and Zintl ions.

Only four heteroatomic deltahedral Zintl ions have been reported before. These include the tetrahedral $[Sn_2Bi_2]^{2-}$ and $[Pb_2Sb_2]^{2-}$ [26,27] and the mono- and bicapped square antiprismatic $[TlSn_8]^{3-}$ and $[TlSn_9]^{3-}$,[28] respectively, all refined with statistically disordered heteroatoms. The species $[Tl_2Te_2]^{2-}$, on the other hand, has a butterfly shape despite being isoelectronic with the tetrahedral clusters (above).[29,30] There are a number of advantages that heteroatomic clusters with elements of different groups may have over homoatomic species. These possibilities are (a) different reactivity at different vertexes because of the occupation by different elements, (b) ability to increase or reduce the charge of the cluster by simply changing the ratio between the two elements, (c) better potential for interconnecting clusters via bonds between two vertexes of different kinds from each cluster, and (d) opportunity to study the cluster chemistry of elements that may not be able to form such deltahedral clusters on their own. The difficulties associated with the formation of heteroatomic deltahedral clusters stem from the fact that atoms of different groups have, of course, different sizes, electronegativities, number of valence electrons, different stability of the s pair of electrons, etc. and at the same time are required to participate more or less equally in the delocalized bonding of the deltahedral cluster. Thus, deltahedra with positions that differ sufficiently in coordination numbers, distances, charges, geometry, etc., such as mono- or bicapped square antiprism, tricapped trigonal prism, trigonal bipyramid, etc., are more likely candidates for heteroatomic species than deltahedra with equivalent positions such as tetrahedra, octahedra, and icosahedra. Thus, in the former group of shapes different atoms will be able to occupy positions of their "choice" and form an "ordered" cluster. This understanding and the fact that nine-atom homoatomic clusters are already known both in solid state and in solution suggest that the same types of clusters have the best chance for existence as heteroatomic species as well. The choice of groups and elements in them can be based on isoelectronic analogy with the existing nine-atom species of group 14, *nido*-E_9^{4-}. Some important additional requirements are (a) sufficient difference in their X-ray scattering in order to be able to distinguish them in the clusters, (b) known capabilities for formation of isolated clusters, (c) stable s pairs of electrons, (d) similar sizes, and (e) similar electronegativities. Thus, In/Bi is the most promising pair along these lines while Tl/Sb comes next. These pairs have relatively similar electronegativities (Pauling's), 1.78/2.02 for In/Bi and 2.04/2.05 for Tl/Sb, and similar covalent radii, 1.44/1.46 Å for In/Bi and 1.48/1.40 for Tl/Sb. There are a number of isolated clusters of indium and thallium known,[10] and antimony and bismuth are often found with a stable lone pair of electrons. The elements are from different periods and differ substantially in total numbers of electrons and therefore are easily distinguishable by X-ray diffraction. In addition, on the basis of lessons from group 13, it seems that isolated clusters are more abundant for the heavier analogues,[10] and therefore, it is desired to have heavy elements in the heteroatomic species as well. Thus, the following heteroatomic *nido*-clusters isoelectronic with the homoatomic *nido*-E_9^{4-} (E = element of group 14) can be proposed for synthesis: $[In_4Bi_5]^{3-}$, $[Tl_4Sb_5]^{3-}$, $[In_5Bi_4]^{5-}$, and $[Tl_5Sb_4]^{5-}$. Furthermore, *closo*-clusters such as $[In_5Bi_4]^{3-}$, $[In_6Bi_3]$,$^{5-}$ $[Tl_5Sb_4]^{3-}$, and $[Tl_6Sb_3]^{5-}$ isoelectronic with *closo*-E_9^{2-} are good candidates. We have explored these systems as well as the Ga/Bi system (electronegativities of 1.81 and 2.02 for Ga and Bi, respectively). Our initial goal was the synthesis of these clusters in the solid state, in compounds similar to the known A_4E_9 (A = alkali metal) with the E_9^{4-} clusters.[31−35] This, however, has not been achieved so far. All reactions resulted in Zintl phases with extended structures and with rather localized "normal" two-center-two-electron bonding between indium or gallium and the bismuth. Nevertheless, using these and similar Zintl phases as precursors for solution studies, we were able to synthesize deltahedral clusters in solids crystallized from such solutions. Here we report the syntheses and structures of (K-crypt)$_2$[InBi$_3$]·en (**1**), (Rb-crypt)$_2$[InBi$_3$]·en (**2**), and (K-crypt)$_2$[GaBi$_3$]·en (**3**)) with tetrahedra of $[InBi_3]^{2-}$ or $[GaBi_3]^{2-}$, and (Na-crypt)$_3$[In$_4$Bi$_5$] (**4**) and (K-crypt)$_6$[In$_4$Bi$_5$][In$_4$Bi$_5$]·1.5en·0.5tol (**5**) with nine-atom deltahedral clusters of $[In_4Bi_5]^{3-}$. Compound **1** is isostructural with (K-crypt)$_2$[Sn$_2$Bi$_2$] and (K-crypt)$_2$[Pb$_2$Sb$_2$] (**6**),[26,27] compound **5** is isostructural with (K-crypt)$_6$E$_9$E$_9$·1.5en·0.5tol (E = Sn, Pb) (**7**),[25] while **4** crystallizes in a new structural type. The cluster in **4** and one of the clusters in **5** are the first examples of ordered heteroatomic deltahedral Zintl ions.

Experimental Section

Materials and Precursors Syntheses. Redistilled ethylenediamine packaged under nitrogen (99.5+%, Aldrich) and Kryptofix 222 (98%, Acros) was used as received. Toluene (99.5%, Fisher) was dried and kept over sodium. All operations were carried out in nitrogen- or argon-filled gloveboxes. The precursors were made from mixtures of the elements (all from Alfa-Aesar) enclosed in sealed (by arc-welding) niobium containers, the latter jacketed in evacuated quartz ampules. The mixtures were heated at 600 °C for a week. More details on the synthesis of the precursors can be found elsewhere.[36]

1. (K-crypt)$_2$[InBi$_3$]·en (1) and (K-crypt)$_6$[In$_4$Bi$_5$][In$_4$Bi$_5$]·1.5en·0.5tol (5). Powder of a precursor with nominal composition "K$_5$In$_2$Bi$_4$" (40 mg) was placed in a test tube containing crypt (56 mg) and ethylenediamine (8 mL). A blue-green solution formed immediately. It was allowed to stand with occasional shaking for 2 h. The solution was then filtered, and the filtrate was carefully layered with toluene (volume ratio of 1:3). Crystals grew on the walls after several days. The resulting colorless solution was decanted, and the crystals were washed with toluene and dried under vacuum. About 80% of the crystals were of **1** (black blocks), and only 10% were of **5** (black rods). The remaining 10% were crystals (brown-red hexagonal plates) of the compound (K-crypt)$_2$Bi$_2$ containing the molecule $[Bi{=}Bi]^{2-}$ with a double bond between the bismuth atoms.[37]

2. (Rb-crypt)$_2$[InBi$_3$]·en (2), (K-crypt)$_2$[GaBi$_3$]·en (3), and (Na-crypt)$_3$[In$_4$Bi$_5$] (4). The syntheses of **2**, **3**, and **4** precursors with nominal compositions "Rb$_5$In$_2$Bi$_4$", "K$_5$Ga$_2$Bi$_4$", and "Na$_5$In$_2$Bi$_4$", respectively, were treated in the same way as the syntheses of **1** and **5** (above). The solutions that formed were brown-green for **2** and **4** and green for **3**. In the case of **4** the dissolution proceeded very slowly at room temperature, and in order to accelerate the process, the mixture was heated at 80 °C for 5 h. Brown-black rectangular rods of **4** and black blocks of **2** and **3** precipitated on the walls after several days. They were separated from the solution, washed with toluene, and dried under vacuum.

Heated solutions of Rb$_5$In$_2$Bi$_4$ provide hexagonal plates that look similar to those of (K-crypt)$_2$Bi$_2$,[37] the third phase in the synthesis of **1** and **5**. They are most likely of the analogous rubidium compound. Crystallized from the same solution were also black rods (orthorhombic,

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Table 1. Crystallographic Data for Compounds **1**, **4**, and **5**

compound	**1**	**4**	**5**
empirical formula	$C_{38}H_{80}N_6O_{12}K_2InBi_3$	$C_{54}H_{108}N_6O_{18}Na_3In_4Bi_5$	$C_{114.5}H_{232}N_{15}O_{36}K_6In_8Bi_{10}$
fw	1625	2703	5638
space group, *Z*	$P2_1$, 2	$P2_1/n$, 4	$P2_1/c$, 4
a, Å	12.347(4)[a]	23.572(6)	28.532(2)
b, Å	20.884(4)	15.042(4)	23.707(2)
c, Å	12.619(7)	24.071(4)	28.021(2)
β, deg	119.02(4)	106.00(3)	93.274(4)
V, $Å^3$	2845.5(2)	8204(3)	18923(3)
temp, °C	20	20	20
cryst size, mm	0.4 × 0.3 × 0.3	0.40 × 0.15 × 0.10	0.5 × 0.1 × 0.1
μ (Mo Kα), mm^{-1}	9.848	11.860	10.406
density (calcd), g/cm^3	1.897	2.188	1.973
R1/wR2 ($I \geq \sigma_I$), %	6.05/14.44	10.29/23.13	11.28/26.28

[a] The unit cell parameters for the isostructural **2** and **3** are $a = 12.403(8)$ Å, $b = 20.99(1)$ Å, $c = 12.617(9)$ Å, $\beta = 118.83(4)°$ and $a = 12.324(5)$ Å, $b = 20.890(8)$ Å, $c = 12.629(5)$ Å, $\beta = 118.91(3)°$, respectively.

$a \approx 18.011$ Å, $b \approx 22.102$ Å, $c \approx 47.008$ Å, and $V = 18\,713$ $Å^3$) containing very likely clusters of $[In_4Bi_5]^{3-}$ (based on volume estimations).

Structure Determinations. Single crystals of the compounds were mounted in glass capillaries using a drybox equipped with a microscope. Inspection of the unit cell parameters of compounds **1**−**3** indicated that they are isostructural (monoclinic, $a = 12.347(4)$ Å, $b = 20.884(4)$ Å, $c = 12.619(7)$ Å, $\beta = 119.02(4)°$, $V = 2845.5(2)$ $Å^3$ for **1**, $a = 12.403(8)$ Å, $b = 20.99(1)$ Å, $c = 12.617(9)$ Å, $\beta = 118.83(4)°$, $V = 2891(5)$ $Å^3$ for **2**, and $a = 12.324(5)$ Å, $b = 20.890(8)$ Å, $c = 12.629(5)$ Å, $\beta = 118.91(3)°$, $V = 2846(2)$ $Å^3$ for **3**). Data for this structure type were collected on an Enraf-Nonius CAD4 diffractometer only from a crystal of **1** (0.4 mm × 0.3 mm × 0.3 mm). Data of a crystal of **4** (0.40 mm × 0.15 mm × 0.10 mm) were collected on the same diffractometer, while data of a crystal of **5** (0.5 mm × 0.1 mm × 0.1 mm) were collected on a Siemens SMART system with a CCD detector. All data sets were collected with monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at room temperature and were corrected for absorption using the average of three and four ψ scans at different θ angles for **1** and **4**, respectively, and the Xabs (DFABS) program for **5**. The crystals of **1** and **4** diffracted extremely poorly, and even worse, the crystal of **4** decayed more than 50% during the exposure. A second data set collected on another crystal of **4** showed the same decay and similarly weak diffraction, and the structure was refined with relatively high *R* factors. All structures were solved and refined on F^2 using the SHELXTL, version 5.1, package. Important data collection and refinement parameters are given in Table 1, while important intracluster distances for **4** and **5** are listed in Table 2.

Table 2. Intracluster Distances in **4** and **5** (See Figures 2 and 3 for Atom Numbers)

atom no.−atom no.	**4**	**5** (cluster **A**)	**5** (cluster **B**)
1−2	3.022(4)	3.031(2)	3.013(2)
−3	3.016(4)	2.998(3)	2.875(4)
−4	3.014(4)	3.010(2)	3.089(3)
−5	3.008(4)	2.995(3)	2.939(3)
−9			4.489(2)
2−3	3.818(4)	3.613(4)	3.146(3)
−5	3.294(5)	3.425(3)	4.020(3)
−6	3.121(4)	3.039(2)	2.984(3)
−9	3.020(4)	2.985(3)	3.050(3)
3−4	3.360(5)	3.507(3)	3.400(3)
−6	3.108(4)	3.009(2)	3.433(3)
−7	3.048(4)	2.945(3)	2.915(4)
4−5	3.668(5)	3.440(3)	3.167(2)
−7	3.070(4)	3.124(2)	2.988(2)
−8	3.102(4)	3.046(2)	3.155(3)
5−8	3.099(4)	3.109(3)	2.717(5)
−9	3.082(4)	3.174(3)	3.086(2)
6−7	3.092(3)	3.103(2)	3.022(2)
−9	3.045(3)	3.086(2)	3.091(2)
−8	4.414(5)	4.398(2)	4.196(4)
7−8	3.035(3)	3.055(2)	3.394(5)
−9	4.254(5)	4.297(2)	4.638(2)
8−9	3.021(3)	3.056(2)	3.105(3)

For compound **4**, direct methods revealed initially nine heavy atoms forming a monocapped square antiprism. The three sodium atoms and all carbon, nitrogen, and oxygen atoms of the three cryptand molecules were located from subsequent least-squares refinements of the heavy atoms and difference Fourier maps. All cluster atoms were initially treated as bismuth with occupancies that were free to vary. The cap of the antiprism and the four positions of the open square base refined as fully occupied by bismuth within 1σ. The four positions of the capped square base, on the other hand, refined with occupancies of ca. 0.64−0.66, and this clearly suggested indium atoms at these vertexes. They were so assigned, and when refined with variable occupancies, they indicated full occupation. Thus, in the final refinement the cluster was refined as $[In_4Bi_5]$ with fixed full occupancies for all positions, the hydrogen atoms were generated from idealized positions and refined as riding atoms, and all indium, bismuth, potassium, oxygen, and nitrogen atoms were refined anisotropically. No solvent molecules were found in the structure. Elemental analysis (ICP) for indium and bismuth on the single crystal used for the structure determination confirmed the ratio of the two elements.

Compound **5** was identified as isostructural with the known compounds **7** according to its lattice parameters and space group assignment.[25] Nevertheless, the structure was solved by direct methods, and 18 heavy atoms forming two crystallographically different 9-atom clusters and 6 potassium atoms were readily located. The carbon, nitrogen, and oxygen atoms of the cryptand molecules were found from subsequent difference Fourier syntheses. Three ethylenediamine and one toluene molecules were also found and were refined with half occupancies as in **7**. The phenyl ring of the toluene was fixed as a regular hexagon, and all hydrogen atoms were located from calculated positions and refined as riding atoms. All cluster atoms were initially refined as bismuth atoms with variable occupancies. Clearly the two clusters behaved differently. Cluster **A**, a monocapped square antiprism ($\sim C_{4v}$), showed similar occupancies as the cluster in compound **4**, i.e., lower than full occupancies for the sites of the capped square base and full occupancies for the rest. This indicated that four indium atoms fully occupy the capped square sites, and the cluster was refined as ordered $[In_4Bi_5]$ species. The second nine-atom cluster, cluster **B**, however, was found to be significantly distorted from C_{4v} symmetry, very much like the corresponding cluster in the parent compound **7**.[25] The refinement of all positions as bismuth atoms with variable occupancies suggested four positions with mixed indium/bismuth occupancies, two positions with indium only, and the remaining three positions occupied by bismuth. Also, as in the parent structure of **7**, two cluster sites, one of Bi and one of In/Bi in our case, were refined with very elongated thermal ellipsoids. These were refined as two split positions in **7**, but they were kept as single positions in this refinement. The final refinement was done with anisotropic thermal parameters for the non-hydrogen atoms except carbon.

EPR Measurements. EPR spectra of two samples sealed in 3 mm quartz tubes were recorded on a Varian EC-1365E spectrometer at room temperature. One sample was a multiphase crystalline product containing compounds **5**, **1**, and $(K\text{-crypt})_2Bi_2$, and the second sample was pure compound **4.** Both samples were EPR-silent, an indication of no unpaired electrons.

Results and Discussion

Ternary solids of alkali metals combined with an element of group 13 and an element of group 15 have been studied quite extensively before.[38] Nevertheless, nothing has been reported on the systems with indium and bismuth. Our initial goal, as already discussed, was heteroatomic nine-atom deltahedral clusters in this system. The reactions produced compounds with extended structures of edge-sharing tetrahedra of bismuth centered by indium. Among these new phases are $Cs_7In_4Bi_6$,[36] $K_{11}In_5Bi_9$, $A_5In_2Bi_4$ (A = K, Rb), Na_3InBi_2, and $K_{20}Ga_7Bi_{13}$.[39] Common in these structures (figure in Supporting Information) are bismuth atoms in three different coordinations and formal charges, i.e., one-bonded Bi^{2-} (terminal), two-bonded Bi^{1-} (bridging), and three-bonded Bi^0 (capping). All precursors were later prepared with the same nominal composition of $A_5E_2Bi_4$ (A = alkali metal, E = In or Ga) for the starting mixtures. Despite the fact that the compounds do not contain clusters, all but the one with cesium are soluble in the ethylenediamine/crypt solvent mixture. Cesium does not fit at all in the cryptand's cavity, making insoluble the corresponding compounds. Similarly, rubidium fits very poorly and its compounds take longer to dissolve. The sodium analogues usually need heating in order to dissolve because sodium, on the other hand, is too small for that cavity.

Compounds **1**−**3** are isostructural with the known compounds **6** containing the tetrahedral Zintl dianions $[Sn_2Bi_2]^{2-}$ or $[Pb_2Sb_2]^{2-}$.[26,27] Similarly to these known compounds, the isoelectronic tetrahedron $[InBi_3]^{2-}$ was refined with complete disorder with $[^1/_4In + {}^3/_4Bi]$ per position. The stoichiometry of the cluster was deduced solely from charge considerations and the isostructural relationship with **6**; i.e., the only possible combination of indium and bismuth in a cluster isoelectronic with $[Sn_2Bi_2]^{2-}$ and $[Pb_2Sb_2]^{2-}$ is $[InBi_3]^{2-}$. Furthermore, the complete disorder in this case is quite logical because all four positions of a tetrahedron are equivalent. There are no significant interactions between the tetrahedron and the solvent or the cations; the shortest distances from the tetrahedron to a non-hydrogen atom is 4.01 Å. The six distances in the tetrahedron are in the range 2.989(3)−3.035(2) Å.

There is no reason to expect that the cluster $[GaBi_3]^{2-}$ in the isostructural $(K\text{-crypt})_2[GaBi_3]\cdot en$ will be any different. It is quite unexpected that such very different elements, two groups and two periods apart (covalent radii for Ga and Bi are 1.26 and 1.46 Å, respectively), can form clusters with a degree of delocalized bonding. It is interesting to note that the isoelectronic heteroatomic $[Tl_2Te_2]^{2-}$ of elements differing by only one period but by three groups has the shape of a butterfly rather than a tetrahedron.[29,30] Also, reported In−Te Zintl ions are dominated by In-centered tellurium tetrahedra, i.e., with the two elements occupying two very different positions.[40,41]

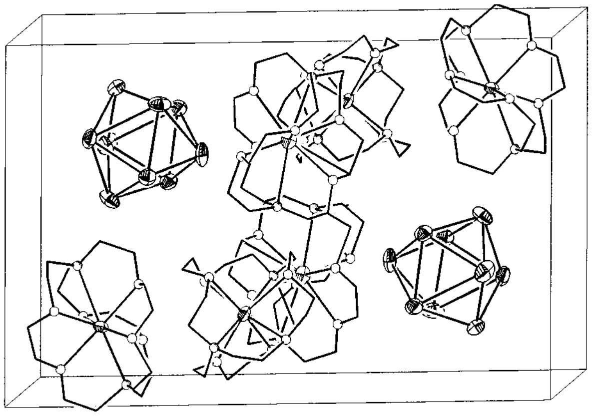

Figure 1. Shown along the *c* axis (*a* horizontal) is the unit cell of compound **4**, $(Na\text{-crypt})_3[In_4Bi_5]$, and its contents of six cations (thermal ellipsoids for the central sodium atoms and open circles for the oxygen and nitrogen atoms of the crypt) and two anions of $[In_4Bi_5]^{3-}$, monocapped square antiprisms, with indium and bismuth shown with thermal ellipsoids at 30% probability level.

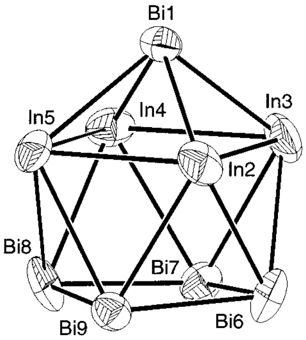

Figure 2. Closer view of the cluster in **4** (30% thermal ellipsoids). The four atoms of the capped square of the monocapped square antiprism are indium and are five-bonded, while the other five atoms are bismuth and are four-bonded.

Compound **4**, $(Na\text{-crypt})_3[In_4Bi_5]$ (a rare case with no solvent molecules), crystallizes in a new structure type; i.e., the packing of the nine-atom clusters and the sodium-filled crypt molecules is different in other compounds (Figure 1). Nevertheless, the geometry of the nine-atom deltahedron is the well-known monocapped square antiprism (Figure 2). The shape has been seen for other E_9^{3-} and E_9^{4-} clusters (E = group 14)[10] and therefore suggests 21 or 22 electrons for cluster bonding. The odd number of electrons is ruled out in our case, however, because the EPR measurements showed diamagnetic behavior. The model with 22 electrons is in agreement with the refined stoichiometry as well as with the charge of the cluster, $[In_4Bi_5]^{3-}$. The fact that the four indium and five bismuth atoms occupy specific positions in the cluster is not surprising because this geometry has vertexes of two types, four- and five-bonded. According to several theoretical calculations on E_9^{4-} and E_9^{3-} clusters utilizing a variety of methods, the five-bonded positions carry much lower negative charges than the four-bonded ones. Thus, extended Hückel calculations on Pb_9^{4-} give charges of −0.46, −0.57, and −0.31 for the capping atom, the open-square base, and the capped-square base, respectively.[42] The corresponding numbers from DFT calculation of the same cluster and for Pb_9^{3-} are −0.57, −0.49, and −0.37, and −0.42, −0.36, and −0.28, respectively.[16] SCF-MO-CNDO calculations on Sn_9^{4-} provide −0.77, −0.55, and −0.25, respectively, for the same three position types.[17] Despite the differences in the values, all four calculations consistently find the lowest negative charges at the five-bonded vertexes. It is quite logical, therefore, to find the electron-poorer indium at these same positions.

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(38) Eisenmann, B.; Cordier, G. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S. M., Ed.; VCH Publishers: New York, 1996; p 62 and references therein.

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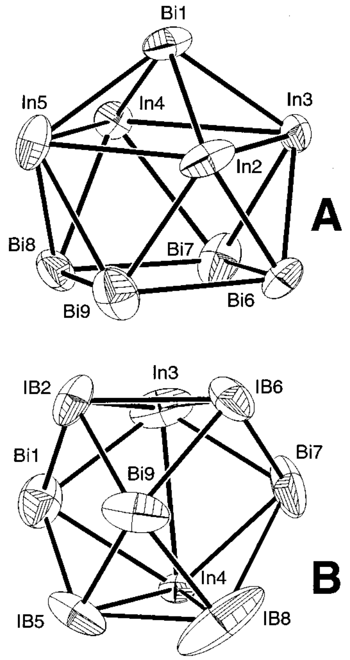

Figure 3. Two clusters of $[In_4Bi_5]^{3-}$ (30% thermal ellipsoids; IB indicates positions refined as 0.5In + 0.5Bi) in compound **5**, $(K\text{-crypt})_6[In_4Bi_5][In_4Bi_5]\cdot 1.5tol\cdot 0.5en$. Cluster **A** (top) is a monocapped square antiprism similar to the clusters in **4** (Figure 2) with four indium atoms at the five-bonded vertexes and five bismuth atoms at the four-bonded vertexes. Cluster **B** (bottom) has two open faces, those made of atom numbers 1, 2, 9, 5 and 6, 7, 8, 9. The atoms at vertexes 7 and 8 were refined as split positions in the parent compounds $(K\text{-crypt})_6[E_9][E_9]\cdot 1.5tol\cdot 0.5en$ (**7**) where E = Sn or Pb [25] but were kept as single positions in this cluster.

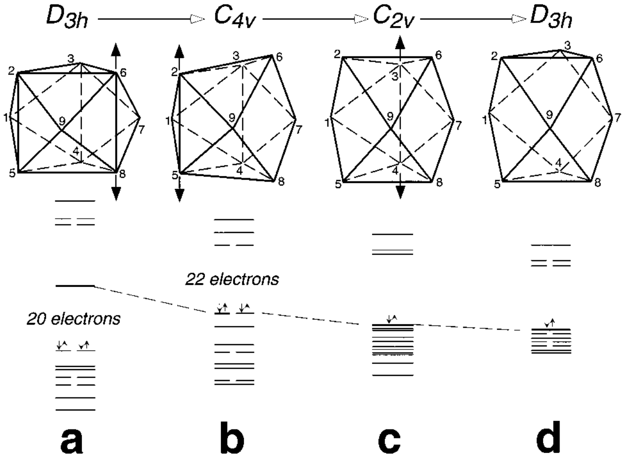

Figure 4. Schematic representation of the successive opening of the three vertical edges of a tricapped trigonal prism (a). The elongation of one edge, 6−8, leads to a monocapped square antiprism (b) shown lying on its side (1, capping atom; 2, 3, 4, 5, capped square base; 6, 7, 8, 9, open square base). Next step, the elongation of one more edge, 2−5, leads to a cluster with symmetry C_{2v} and two open faces (c) similar to cluster **B** in compounds **5**. Last, the elongation of the third edge, 3−4, results in an elongated tricapped trigonal prism (d) with three open faces. Schematic MO diagrams for each geometry are shown under the corresponding cluster.

Compound **5**, $(K\text{-crypt})_6[In_4Bi_5][In_4Bi_5]\cdot 1.5en\cdot 0.5tol$, is isostructural with the reported compounds **7**, $(K\text{-crypt})_6[E_9][E_9]\cdot 1.5en\cdot 0.5tol$ for E = Sn and Pb,[25] and contains two different clusters (Figure 3). Both clusters carry the same charge of −3 as in the parent compounds. Nevertheless, the clusters in **5** are not isoelectronic with those in **7**. The species Sn_9^{3-} and Pb_9^{3-} carry odd number of electrons, 9 (atoms) × 4 (electrons per atom of group 14) + 3 (charge) = 39 electrons, which equals the sum of the 21 skeletal and 18 lone-pair electrons and are paramagnetic. The clusters in **5**, on the other hand, are with even number of electrons, 4 (In atoms) × 3 (electrons per In) + 5 (Bi atoms) × 5 (electrons per Bi) + 3 (charge) = 40 electrons (22 skeletal and 18 lone-pair electrons) and are diamagnetic and EPR-silent. Perhaps as a result of these differences, the shapes of the clusters in **5** are also somewhat different from those in the parent compounds. Thus, the geometry of cluster **A** in **7** is very close to a tricapped trigonal prism (20-electron species) evidenced by the similar three prism heights with ratios 1.10:1.02:1.00 in Sn_9^{3-} and 1.07:1.02:1.00 in Pb_9^{3-}.[25] These numbers for the **A** species in **5** are 1.23:1.08:1.00 and clearly indicate one very long and two much shorter distances. This is typical for monocapped square antiprisms (22-electron species) such as Ge_9^{4-} in Cs_4Ge_9 with ratio 1.25:1.05:1.00,[31] Pb_9^{4-} in K_4Pb_9,[32] Cs_4Pb_9,[34] $K(K\text{-crypt})_3Pb_9$,[16] and $(K\text{-crown})_4Pb_9$ (crown = 18-crown-6 ether = 1,4,7,10,13,16-hexaoxacyclooctadecane)[43] with ratios 1.28:1.04:1.00, 1.28:1.05:1.00, 1:30:1.02:1.00, and 1.33:1.05:1.00, respectively, Sn_9^{4-} in $(Na\text{-crypt})_4Sn_9$ and $K(K\text{-crypt})_3Sn_9$ with ratios 1.32:1.04:1.00 and 1.29:1.03:1.00, respectively,[17,18] and $[In_4Bi_5]^{3-}$ in **4** with ratio 1.16:1.04:1.00. Furthermore, as in a square prism, the open-square base of **5A** (Figure 3A) is virtually planar with dihedral angle of only 2.51(7)° and nearly rectangular with very similar diagonals of 4.398(2) and 4.297(2) Å (Table 2). For comparison, the corresponding dihedral angle and two diagonals in the cluster of **4** are 7.8(2)° and 4.414(5) and 4.254(5) Å, respectively. The distances in the cluster in **4** and the cluster **A** in **5** follow the same pattern as in all other 22-electron 9-atom *nido*-clusters with the shape of a monocapped square antiprism. Thus, the distances from the four-bonded atoms, i.e., the capping and the open square atoms, are generally shorter than the distances between the five-bonded atoms, i.e., the atoms of the capped square. Typically, the average distance of the capped square is longer by up to 15% than that of the open square. This is true for the clusters in **4** with average distances of 3.529 and 3.049 Å for the capped and open squares, respectively, or close to 16% difference, and clusters **A** in **5** with corresponding numbers of 3.496 and 3.080 Å, or about 14% difference. One should keep in mind that the covalent radii of In and Bi, 1.44 and 1.46 Å, respectively, are similar, and therefore, such comparisons are "valid" even for these heteroatomic clusters.

The geometry of the **B** cluster in compound **5** is more complicated to describe (Figure 3B). It has two open and relatively flat square faces (largest dihedral angles of 19.6(1) and 11.9(1)° for the faces of atom numbers 6, 7, 8, 9 and 1, 2, 5, 9, respectively), and therefore, it is not possible to classify it either as a monocapped square antiprism (C_{4v}) or as a tricapped trigonal prism (D_{3h}). To understand its geometry, it is useful to discuss in more detail the relationships between possible shapes for nine-atom clusters and the electronic requirements for bonding. Presented in Figure 4 are four idealized shapes for such clusters and the corresponding schematic molecular orbital diagrams. The cluster to the left, cluster **a**, is the classical tricapped trigonal prism. The capping vertexes, 1, 7, and 9, are four-bonded while the vertexes forming the prism, 2, 3, 4, 5, 6, and 8, are five-bonded. Notice that the vertical prismatic edges are the same as or slightly longer than the edges of the triangular bases. The corresponding MO diagram has a HOMO−LUMO gap at 20 electrons, in agreement with the Wade's rules for

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closo-species such as E_9^{2-} (E = group 14),[44] $2n + 2 = 20$ for $n = 9$. For this particular geometry there is also a relatively large gap above the LUMO, a_2'' in D_{3h} (shown with thicker line), that makes the orbital quite attractive for additional electrons. Thus, the known paramagnetic Ge_9^{3-}, Sn_9^{3-}, and Pb_9^{3-} clusters have 21 electrons and the extra electron occupies that orbital.[11,16,25] This orbital involves only the atoms forming the trigonal prism and is bonding within each of the triangular bases of the prism but is antibonding between them. Its position in the MO diagram is very sensitive to the height of the prism. The result of the elongation of one prism height, the edge 6−8, is shown at the right in cluster **b** ("two short and one long" edges). This cluster is actually the classical monocapped square antiprism, C_{4v}, shown lying on its side. The capping atom, 1, and the four atoms of the open square base, 6, 7, 8, and 9, are four-bonded, while the vertexes of the capped square, 2, 3, 4, and 5, are five-bonded. As a result of the elongation of just one edge of the tricapped trigonal prism in **a**, the antibonding interactions in the former LUMO, a_2'', are relieved, and it drops in energy to become a part of the doubly degenerate HOMO for 22 electrons in **b**. This cluster, of course, is the *nido*-species, and the 22 electrons are in agreement with Wade's rules,[44] $2n + 4 = 22$ for $n = 9$. Shown at the right in cluster **c** is the result of elongation of one more height, the edge 2−5, of the former tricapped trigonal prism. The orbital in question, shown as a thicker line in the figure, drops further in energy because the antibonding interactions are lowered even more, but the HOMO−LUMO gap is still at 22 electrons. This cluster ("two long and one short" edges) is of C_{2v} symmetry, has two open square faces, and represents cluster **B** of compound **5** (Figures 3B and 4). It should be pointed out that the elongation of the two edges 2−5 and 6−8 as in **c** is typically smaller than the elongation of only one edge 6−8 as in **b**. For example, the distance 6−8 in type **b** cluster of Pb_9^{4-} in K_4Pb_9 is 4.376 Å while the two distances 2−5 and 6−8 in type **c** cluster Pb_9^{4-} in the same compound are both 3.895 Å.[32] Similarly, type **b** cluster of Si_9^{4-} in $Rb_{12}Si_{17}$ has $d_{6-8} = 3.206$ Å, while type **c** cluster of Si_9^{4-} in the same compound has d_{2-5} and d_{6-8} of 3.083 and 3.007 Å, respectively.[33] These shorter distances in clusters **c** are not long enough to be considered completely nonbonding. As a result, the corresponding vertexes 2, 5, 6, and 8 should be considered more than four-bonded, while 1, 7, and 9 are just four-bonded and 3 and 4 are five-bonded. This, combined with the relative "weight" of each site in the refinement of cluster **B** (see Structure Determinations in the Experimental Section) and with the observation that indium preferably occupies five-bonded positions in the cluster in **4** as well as cluster **A** in **5**, led to the decision to refine vertexes 3 and 4 as indium, 1, 7, and 9 as bismuth, and 2, 5, 6, and 8 with mixed occupancy of half bismuth and half indium. This would give again total of four indium and five bismuth atoms, and because the geometry requires 22 electrons, just like in the monocapped square antiprisms of compound **4** and cluster **A** in **5**, this cluster would have charge of −3, i.e., also $[In_4Bi_5]^{3-}$.

Next, after elongation of one more edge of the original tricapped trigonal prism **a** (Figure 4), i.e., after elongation of all three edges of that prism, we get cluster **d** ("three long" edges), which is again a tricapped trigonal prism, D_{3h}, but with longer heights. The molecular diagram does not change much on moving from **c** to **d**, and the cluster is stable with 22 electrons. An example of this geometry with three long heights is Bi_9^{5+} found in $Bi[Bi_9](HfCl_6)_3$ with lengths of 3.737 Å for all three edges and in $[Bi_9](Bi_3Cl_{14})$ with lengths of 3.979, 3.704, and 3.704 Å.[19,45] These distances are quite longer, about 1.15−1.20 times, than the distances within the triangular faces of the corresponding trigonal prisms, averages of 3.241 and 3.201 Å for the two compounds, respectively. The heights in a "normal" tricapped trigonal prism are expected to be within 1.00−1.05 times the distances in the bases.

Often the discussion of the type of a particular nine-atom cluster is reduced to whether it is a tricapped trigonal prism or a monocapped square antiprism. Figure 4 shows that clearly the overall shape does not unequivocally define the electronic state of the cluster. Thus, clusters **a** and **d** are both tricapped trigonal prisms but have different electronic requirements because of the relative position of the a_2'' orbital. Clusters **b**−**d**, on the other hand, look quite different but have the same numbers of electrons. Therefore, the usual simple classification of nine-atom clusters into just the two geometrical classes **a** and **b** is not sufficient for an accurate description. Even the edge ratios and dihedral angles often reported for these clusters are not easy to compare because (a) there are too many of them per cluster and (b) there is no clear cut-off line between the two categories. It is perhaps better to discuss each particular cluster more in the context of the stoichiometry of the host compound, the possible charges based on this stoichiometry, and the corresponding molecular orbital diagram. Most importantly, measurements of physical properties such as magnetization, EPR, and conductivity should be available before any conclusions are drawn. Compounds containing clusters or molecules with a seemingly odd number of electrons and that are seemingly paramagnetic may end up being metallic and Pauli-paramagnetic because of delocalization of the odd electron over the structure, as has been seen before.[10]

Finally, some discussion of the mechanism of cluster formation is appropriate at this stage. The presence of negatively charged main group clusters in solution was suggested by Zintl's potentiometric titration of a liquid ammonia solution of sodium with lead iodide.[4] Much later, many of the originally proposed clusters as well as some new ones were confirmed in ethylenediamine solutions by NMR.[46] Likewise, by that time, many of the clusters were observed in solids crystallized from such solutions, and their shapes in these solids were known. During this time, prior to the discovery of Zintl phases containing the same deltahedral Zintl ions as the ones crystallized from solutions, the view on the formation of the clusters was that they assemble only during the dissolution process. The mechanism was unclear, but "known" were the starting materials, which were thought to always contain just isolated and perhaps reduced atoms of the post-transition element, and known was the end result, solvated and charged assemblies of atoms bonded by delocalized electrons. This view, based on the assumption that all precursors were simply "melts" or featureless alloys, can now be amended to accommodate the solid-state precursors that already contain soluble deltahedral clusters. The ionic "salts" K_4Pb_9, Cs_4Pb_9, and Cs_4Ge_9 with clusters of E_9^{4-} easily dissolve in ethylenediamine to $4A^+ + E_9^{4-}$, just in the same way as NaCl, for example, would dissolve to $Na^+ + Cl^-$ in water. The mechanism is clear; it is simple solvation of the ions in the

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(46) (a) Rudolf, R. W.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4629. (b) Rudolf, R. W.; Wilson, W. L.; Taylor, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 2480. (c) Rudolf, R. W.; Taylor, R. C.; Young, D. C. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum Press: New York, 1979; p 997.

same way as ionic salts dissolve because of the greater solvation energy compared with the crystal lattice energy. The heteroatomic clusters discussed here bring perhaps yet another slight variation to these views because their precursor is not a melt or an alloy but rather has a structure and at the same time it does not contain clusters either. The precursor phases in this case, usually chains of indium-centered tetrahedra of bismuth, already contain Bi and In in some negative oxidation states, and also bonds between the heteroatoms are already established. The formation of the clusters in this case is more likely the result of rearrangements of the already bonded atoms accompanied by breakage and creation of only a few bonds, not all of them. This suggests that perhaps many of the known neat solids (as well as some of those yet to be discovered) are potential precursors for such and other clusters or simpler molecules and that the lack of clusters in a solid should not discourage exploration of clusters in solutions made from it.

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Supporting Information Available: A figure showing a part of a typical structure of the compounds found in the precursors with nominal composition “$A_5In_2Bi_4$” and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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