Ammoniates of Zintl Phases: Similarities and Differences of Binary Phases A₄E₄ and Their Corresponding Solvates

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Received: 20 April 2018; Accepted: 23 June 2018; Published: 29 June 2018

Abstract: The combination of electropositive alkali metals A (A = Na-Cs) and group 14 elements E (E = Si-Pb) in a stoichiometric ratio of 1:1 in solid state reactions results in the formation of polyanionic salts, which belong to a class of intermetallics for which the term Zintl compounds is used. Crystal structure analysis of these intermetallic phases proved the presence of tetrahedral tetrelide tetraanions $[E_4]^{4-}$ precast in solid state, and coulombic interactions account for the formation of a dense, three-dimensional cation-anion network. In addition, it has been shown that $[E_4]^{4-}$ polyanions are also present in solutions of liquid ammonia prepared via different synthetic routes. From these solutions crystallize ammoniates of the alkali metal tetrahedranides, which contain ammonia molecules of crystallization, and which can be characterized by X-ray crystallography despite their low thermal stability. The question to be answered is about the structural relations between the analogous compounds in solid state vs. solvate structures, which all include the tetrahedral $[E_4]^{4-}$ anions. We here investigate the similarities and differences regarding the coordination spheres of these anions and the resulting cation-anion network. The reported solvates Na₄Sn₄·13NH₃, Rb₄Sn₄·2NH₃, Cs₄Sn₄·2NH₃, Rb₄Pb₄·2NH₃ as well as the up to now unpublished crystal structures of the new compounds Cs₄Si₄·7NH₃, Cs₄Ge₄·9NH₃, [Li(NH₃)₄]₄Sn₄·4NH₃, Na₄Sn₄·11.5NH₃ and Cs₄Pb₄·5NH₃ are considered for comparisons. Additionally, the influence of the presence of another anion on the overall crystal structure is discussed by using the example of a hydroxide co-crystal which was observed in the new compound K₄.5Sn₄(OH)₀.5·1.75 NH₃.

Keywords: Zintl compounds; liquid ammonia; crystal structure

1. Introduction

The term “polar intermetallics” applies to a large field of intermetallic compounds, the properties of which range from metallic and superconducting to semiconducting with a real band gap [1–5]. For the compounds showing a real band gap, the Zintl–Klemm concept is applicable by formally transferring the valence electrons of the electropositive element to the electronegative partner, and the resulting salt-like structure allows for the discussion of anionic substructures [1–9]. The combination of electropositive alkali metals A (A = Na-Cs) and group 14 elements E (E = Si-Pb) in a stoichiometric ratio of 1:1 in solid state reactions results in the formation of salt-like, semiconducting intermetallic compounds which show the presence of the tetrahedral $[E_4]^{4-}$ anions precast in solid state. These anions are valence isoelectronic to white phosphorus and can be seen as molecular units. They have been known since the work of Marsh and Shoemaker in 1953 who first reported on the crystal structure of NaPb [10]. Subsequently, the list of the related binary phases of alkali metal and group 14 elements was completed (Table 1, Figure 1). Due to coulombic interactions a dense,
three-dimensional cation-anion network in either the KGe structure type (A = K-Cs; E = Si, Ge) [11–17] or NaPb structure type (A = Na-Cs; E = Sn, Pb) (Figure 1e,f) [18–21] is observed. For sodium and the lighter group 14 elements silicon and germanium, binary compounds lower in symmetry (NaSi: C2/c [14,16,17,22], NaGe: P21/c [14,16]) are formed, which also contain the tetrahedral shaped [E4]4− anions (Figure 1c,d). In the case of lithium, no binary compound with isolated [E4]4− polyanions is reported at ambient conditions: In LiSi [23] and LiGe [24] (LiSi structure type, Figure 1a), threefold bound silicon atoms are observed in a three-dimensionally extended network, which for tetrel atoms with a charge of −1 is an expected topological alternative to tetrahedral molecular units, and which conforms to the Zintl–Klemm concept. If the [E4]4− cages are viewed as approximately spherical, the calculated radius r would be 3.58 Å for silicide, 3.67 Å for germanide, 3.96 Å for stannide and 3.90 Å for plumbide clusters (r = averaged distances of the center of the cages to the vertex atoms + van der Waals radii of the elements, each [25]). The dimensions for silicon and germanium are very similar, as are those for tin and lead. It is worth noticing that there is a significant increase in the size of the tetrahedra, which are considered as spherical, for the transition from germanium to tin, which could explain the change of the structure type KGe to NaPb.

For binary compounds of lithium and tin or lead, the case is different. The Zintl rule is not applicable as LiSn (Figure 1b) [26] includes one-dimensional chains of tin atoms, whereas NaSn [19,27] forms two-dimensional layers as the tin substructure. For LiPb [28] the CsCl structure has been reported, which is up to now unreported.

Table 1. Binary phases of alkali metal (Li-Cs) and group 14 element with 1:1 stoichiometric ratio (ambient conditions).

<table>
<thead>
<tr>
<th>A</th>
<th>Structure Type</th>
<th>Cation-Anion Interaction</th>
<th>Alkali Metal Ammoniate</th>
<th>Group 14 Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>I4/a LiSi [23]</td>
<td>Li1/a LiSi [24]</td>
<td>I4/a/amid [26]</td>
<td>CsCl [7]</td>
</tr>
</tbody>
</table>

Additionally, it has been shown that the tetrelide tetraanions are also present in solutions of liquid ammonia [29], and from these solutions alkali metal cation-[E4]4− compounds that additionally contain ammonia molecules of crystallization can be precipitated. We earlier reported on the crystal structures of Rb4Sn4·2NH3, Cs4Sn4·2NH3, and Rb4Pb4·2NH3, which showed strong relations to the corresponding binaries [30]. In Na4Sn4·13 NH3 [31,32] no such relation is observed. In general, ammonia in solid ammoniates is not only an innocent and largely unconnected solvent molecule but may also act as a ligand towards the alkali metal cations. This leads to a variety of crystal structures, which allows for the investigation of the competing effects of cation-anion-interaction vs. alkali-metal-ammine complex formation in the solid state. We here report on the single crystal X-ray investigations of the new compounds Cs4Sn4·7NH3, Cs4Ge4·9NH3, [Li(NH3)4]4Sn4·4NH3, Na4Sn4·11.5NH3 and Cs4Pb4·5NH3 and compare the previously reported solvates as well as the new ammoniate compounds of tetratetrelide tetraanions to the known binary compounds. It has to be noted that the number of ammoniate structures of tetratetrelide tetraanions is very limited [30–34] as they are easily oxidized in solution by forming less reduced species like [E4]4− [35–40] and [E5]2− [36,41–43]. In Table 2, all hitherto known ammoniates which contain the highly charged [E4]4− (E = Si-Pb) cluster are listed. For [Sn4]4− we could recently show that co-crystallization of hydroxide anions is possible in the compound Cs5Sn4(OH)4·4NH3 [44]. We here present the first crystal structure of the co-crystal of [Sn4]4− and the hydroxide anion in the compound K4.5Sn4(OH)0.5·1.75 NH3 which allows for the discussion of the influence of another anion on the overall crystal structure.
Figure 1. Different structure types for the binary phases of alkali metal (Li-Cs) and group 14 element with 1:1 stoichiometric ratio (ambient conditions) (a–f).

**Table 2.** Hitherto known A₄E₄·ₓNH₃ (A = Li-Cs; E = Si-Pb) solvate structures and selected crystal structure details. The bold marked new compounds are discussed in this article.

<table>
<thead>
<tr>
<th>Compound Chain</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Unit Cell Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Cs₄Si₄·7NH₃</td>
<td>triclinic</td>
<td>P-1</td>
<td>a = 12.3117(6) Å ; b = 13.0731(7) Å ; c = 13.5149(7) Å ; V = 2035.88(19) Å³</td>
</tr>
<tr>
<td>Ge-Cs₄Ge₄·9NH₃</td>
<td>orthorhombic</td>
<td>Ibam</td>
<td>a = 11.295(2) Å ; b = 11.6429(15) Å ; c = 17.237(2) Å ; V = 2266.9(6) Å³</td>
</tr>
<tr>
<td>Sn-[Li(NH₃)₄]₄Sn₄·4NH₃</td>
<td>monoclinic</td>
<td>I2/a</td>
<td>a = 16.272(3) Å ; b = 10.590(2) Å ; c = 20.699(4) Å ; V = 3446.9(13) Å³</td>
</tr>
<tr>
<td>Li-[Li(NH₃)₄][Sn₄Li₃]·11NH₃</td>
<td>monoclinic</td>
<td>P2₁/c</td>
<td>a = 12.4308(7) Å ; b = 9.3539(4) Å ; c = 37.502(2) Å ; V = 4360.4(4) Å³</td>
</tr>
<tr>
<td>Na₄Sn₄·11.5NH₃</td>
<td>monoclinic</td>
<td>P2₁/c</td>
<td>a = 13.100(3) Å ; b = 31.393(6) Å ; c = 12.367(3) Å ; V = 5085.8(18) Å³</td>
</tr>
<tr>
<td>Na₄Sn₄·13NH₃</td>
<td>hexagonal</td>
<td>P6₃/m</td>
<td>a = b = 10.5623(4) Å ; c = 29.6365(16) Å ; V = 2863.35 Å³</td>
</tr>
<tr>
<td>K₄Sn₄·8NH₃</td>
<td>hexagonal</td>
<td>P6₃</td>
<td>a = b = 13.1209(4) Å ; c = 39.285(2) Å ; V = 5857.1(4) Å³</td>
</tr>
</tbody>
</table>
Table 2. Hitherto known $A_4E_4 \cdot xNH_3$ ($A = \text{Li-Cs}; E = \text{Si-Pb}$) solvate structures and selected crystal structure details. The bold marked new compounds are discussed in this article.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Unit Cell Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Cs$_4$Si$_4$·7NH$_3$</td>
<td>triclinic P-1</td>
<td>$a = 12.3117(6) , \text{Å}; b = 13.0731(7) , \text{Å}; c = 13.5149(7) , \text{Å}; V = 2035.88(19) , \text{Å}^3$</td>
</tr>
<tr>
<td>Ge</td>
<td>Cs$_4$Ge$_4$·9NH$_3$</td>
<td>orthorhombic Ibam</td>
<td>$a = 11.295(2) , \text{Å}; b = 11.6429(15) , \text{Å}; c = 17.237(2) , \text{Å}; V = 2266.9(6) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>[Li(NH$_3$)$_4$]$_4$Sn$_4$·4NH$_3$</td>
<td>monoclinic $P2_1/a$</td>
<td>$a = 16.227(3) , \text{Å}; b = 10.590(2) , \text{Å}; c = 20.699(4) , \text{Å}; V = 3446.9(13) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>[Li(NH$_3$)$_4$]$_4$L$_3$(Sn$_4$)$_3$·11NH$_3$</td>
<td>monoclinic $P2_1/c$</td>
<td>$a = 12.4308(7) , \text{Å}; b = 9.353(4) , \text{Å}; c = 37.502(2) , \text{Å}; V = 4360.4(4) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>Na$_4$Sn$_4$·11.5NH$_3$</td>
<td>monoclinic $P2_1/c$</td>
<td>$a = 13.100(3) , \text{Å}; b = 31.393(6) , \text{Å}; c = 12.367(3) , \text{Å}; V = 5085.8(18) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>Na$_4$Sn$_4$·13NH$_3$</td>
<td>hexagonal $P6_3/m$</td>
<td>$a = b = 10.5623(4) , \text{Å}; c = 29.6365(16) , \text{Å}; V = 2863.35 , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>K$_4$Sn$_4$·8NH$_3$</td>
<td>hexagonal $P6_3$</td>
<td>$a = b = 13.1209(4) , \text{Å}; c = 39.285(2) , \text{Å}; V = 5857.1(4) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>Rb$_2$Sn$_4$·2NH$_3$</td>
<td>monoclinic $P2_1/a$</td>
<td>$a = 13.097(4) , \text{Å}; b = 9.335(2) , \text{Å}; c = 15.237(4) , \text{Å}; V = 1542.3(7) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>Cs$_4$Sn$_4$·2NH$_3$</td>
<td>monoclinic $P2_1/a$</td>
<td>$a = 13.669(2) , \text{Å}; b = 9.627(1) , \text{Å}; c = 13.852(2) , \text{Å}; V = 1737.6(4) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>Rb$_2$Pb$_2$·2NH$_3$</td>
<td>monoclinic $P2_1/a$</td>
<td>$a = 13.179(3) , \text{Å}; b = 9.490(2) , \text{Å}; c = 13.410(3) , \text{Å}; V = 1595.2(6) , \text{Å}^3$</td>
</tr>
<tr>
<td></td>
<td>Cs$_4$Pb$_2$·5NH$_3$</td>
<td>orthorhombic $Pbcn$</td>
<td>$a = 9.4149(3) , \text{Å}; b = 27.1889(7) , \text{Å}; c = 8.1435(2) , \text{Å}; V = 2084.63(10) , \text{Å}^3$</td>
</tr>
</tbody>
</table>

2. Materials and Methods

For the preparation of $[E_4]^{4-}$-containing solutions different preparative routes are possible which are described elsewhere [8]. In general, liquid ammonia was stored over sodium metal and was directly condensed on the reaction mixture under inert conditions (see Appendix A). The reaction vessels were stored for at least three months at 235 K or 197 K. For the handling of the very temperature and moisture labile crystals, a technique developed by Kottke and Stalke was used [45,46]. Crystals were isolated directly with a micro spatula from the reaction solutions in a recess of a glass slide containing perfluoroether oil, which was cooled by a steam of liquid nitrogen. By means of a stereo microscope, an appropriate crystal was selected and subsequently attached on a MicroLoop™ and placed on a goniometer head on the diffractometer. For details on the single crystal X-Ray structure analysis, please see Table 3.
Table 3. Crystal structure and structure refinement details for the compounds described above.

| Chemical Formula | CSD No. * | Mr [g mol⁻¹] | Space group | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | V [Å³] | Z | F(000) (e) | ρ calc [g cm⁻³] | µ [mm⁻¹] | Absorption correction | 2θ-range for data collection | Reflections collected/independent | Data/restraints/parameters | Goodness-of-fit on F² | Final R indices [I > 2σ(I)] | R indices (all data) | Δρmax, Δρ min [e Å⁻³] |
|------------------|-----------|--------------|-------------|------|------|------|------|------|------|-------|---|------------|-----------------|----------|---------------------|-----------------------------|-----------------------------|-----------------------------|----------------------|--------------------------|-------------------------|-------------------|-------------------|
| Cs₄Pb₄·5NH₃     | 434173    | 1445.57      | Pbcm        | 9.4149(3) | 11.2956(2) | 8.1435(2) | 90    | 90    | 90    | 2084.63(10) | 4 | 2392.0      | 4.606            | 39.072   | numerical [47]     | 6.24–52.74               | 18834/2274                | 2274/0/72               | 2274/0/72               | 1.086                     | R₁ = 0.0388, wR₂ = 0.0900 | R₁ = 0.0425, wR₂ = 0.0926 | 2.48/−2.32           |
| Cs₄Ge₄·9NH₃     | 434172    | 948.09       | Ibam        | 11.2956(2) | 11.6429(15) | 17.237(2)  | 90    | 90    | 90    | 2294/748    | 4 | 1644.0      | 2.778            | 11.578   | numerical [47]     | 6.9–48.626               | 2294/748                | 748/0/44                | 748/0/44                | 1.043                     | R₁ = 0.0711, wR₂ = 0.1251 | R₁ = 0.1323, wR₂ = 0.1525 | 1.70/−1.24           |
| Cs₄Si₄·7NH₃     | 434176    | 763.24       | P-1         | 12.3117(6) | 13.0731(7) | 85.067(4)  | 90    | 90    | 90    | 2035.88(19) | 4 | 1384.0      | 2.490            | 7.331    | numerical [48]     | 6.3–50.146               | 26514/50.146             | 5085.8(18)              | 5085.8(18)              | 1.384                     | R₁ = 0.1007, wR₂ = 0.1276 | R₁ = 0.1101, wR₂ = 0.1252 | 2.00/−2.22           |
| Na₂Sn₄·11.5NH₃  | 421860    | 1525.25      | P₂₁/c       | 13.100(3)  | 31.393(6)  | 90.03(2)   | 90    | 90    | 90    | 3446.9(13)  | 4 | 1648.0      | 1.968            | 3.953    | numerical [48]     | 13.1–51.078              | 10490/10.590             | 3446.9(13)              | 3446.9(13)              | 1.648                     | R₁ = 0.090(3), wR₂ = 0.1529 | R₁ = 0.0748, wR₂ = 0.0861 | 0.90/−0.90            |
| (Li(NH₃)₄)₄Sn₄·4NH₃ | 421857 | 843.20       | P2₁/a       | 16.272(3)  | 10.590(2)  | 90.0       | 90    | 90    | 90    | 5988(2)     | 4 | 4920.0      | 1.625            | 7.887    | numerical [48]     | 16.775(3)                | 27272/10.460             | 5988(2)                  | 5988(2)                  | 3.057                     | R₁ = 0.0711, wR₂ = 0.1276 | R₁ = 0.1101, wR₂ = 0.1252 | 0.90/−0.90            |
| K₄.5Sn₄(OH)₃·1.75NH₃ | 427472 | 689.03       | P₂₁/c       | 17.237(2)  | 31.393(6)  | 90.03(2)   | 90    | 90    | 90    | 3446.9(13)  | 16 | 4920.0      | 1.625            | 7.887    | numerical [48]     | 17.237(2)                | 27272/10.460             | 5988(2)                  | 5988(2)                  | 3.057                     | R₁ = 0.0711, wR₂ = 0.1276 | R₁ = 0.1101, wR₂ = 0.1252 | 0.90/−0.90            |

* Further details of the crystal structure investigations may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; e-mail: crysdata(at)fiz-karlsruhe(dot)de, on quoting the deposition numbers.
3. Results

In the following, the crystal structures of the new compounds Cs4Pb4·5NH3, Cs4Ge4·9NH3, Cs4Si4·7NH3, Na4Sn4·11.5NH3, [Li(NH3)4]4Sn4·4NH3 and K4Sn4(OH)0.5·1.75NH3 are described independently, their similarities and differences towards the binary materials are discussed subsequently in Section 4 (Discussions).

3.1. Cs4Pb4·5NH3

The reaction of elemental lead with stoichiometric amounts of cesium in liquid ammonia yields shiny metallic, reddish needles of Cs4Pb4·5NH3. The asymmetric unit of the crystal structure of Cs4Pb4·5NH3 consists of three crystallographically independent lead atoms, four cesium cations and four ammonia molecules of crystallization. One of the lead atoms and one of the nitrogen atoms are located on the general Wyckoff position 8e of the orthorhombic space group Pbcm (No. 57). The other two lead atoms, four Cs+ cations and three nitrogen atoms occupy the special Wyckoff positions 4d (mirror plane) and 4c (twofold screw axis) with a site occupancy factor of 0.5 each. The Pb4 cage is generated from the three lead atoms through symmetry operations. As there is no structural indication for the ammonia molecules to be deprotonated, the [Pb4]4– cage is assigned a fourfold negative charge, which is compensated by the four cesium cations. The Pb-Pb distances within the cage range between 3.0523(7) Å and 3.0945(5) Å. They are very similar to those that have been found in the solventless binary structures (3.090(2) Å) [21]. The cluster has a nearly perfect tetrahedral shape with angles close to 60°. The tetrplumbide tetraanion is coordinated by twelve Cs+ cations at distances between 3.9415(1)–5.4997(8) Å. They coordinate edges, faces and vertices of the cage (Figure 2e). The coordination sphere of Cs1 is built up by four ⟨Pb4⟩ cages (3 × η1, 1 × η2) and five ammonia molecules of crystallization. Here, the cesium cation is surrounded by four lead clusters tetrahedrally and thus forms a supertetrahedron. Cs2 and Cs4 are trigonally surrounded by three Pb4 cages (1 × η1, 2 × η2 and 2 × η1, 1 × η3) each. Their coordination spheres are completed by five and four ammonia molecules of crystallization, respectively, as shown for Cs2 in Figure 3b. Cs3 only shows contacts to two Pb4 cages (2 × η2) and six ammonia molecules of crystallization (Figure 3c). Altogether, a two-dimensional network is formed. Along the crystallographic b-axis, corrugated Cs+·NH3 strands are built. The [Pb4]4– cages are situated along the strands and are stacked along the c-axis (Figure 4).

Figure 2. Comparison of the cationic coordination spheres of [E4]4– (E = Sn, Pb) clusters in Na4Sn4·11.5NH3 (a); Rb4Sn4·2NH3 (b); NaPb (c); Rb4Pb4·2NH3 (d) and Cs4Pb4·5NH3 (e); probability factor: 50%; dark grey marked cations occupy special Wyckoff positions.
and thus forms a supertetrahedron (Figure 3a).

respectively, as shown for Cs2 in Figure 3b. Cs3 only shows contacts to two Pb. Their coordination spheres are completed by five and four ammonia molecules of crystallization.

4
2e). The coordination sphere of Cs1 is built up by four \([\text{Pb}^4]^{2-}\) cages and are stacked along the c-axis (Figure 4).

ammonia molecules of crystallization (Figure 3c). Altogether, a two-dimensional network is formed.

cage range between 3.0523(7) \(\text{Å}\) and 3.0945(5) \(\text{Å}\). They are very similar to those that have been found.

molecules of crystallization. Here, the cesium cation is surrounded by four lead clusters tetrahedrally.

indication for the ammonia molecules to be deprotonated, the \([\text{Pb}^4]^{2-}\) generated from the three lead atoms through symmetry operations. As there is no structural.

4
indication for the ammonia molecules to be deprotonated, the \([\text{Pb}^4]^{2-}\) generated from the three lead atoms through symmetry operations. As there is no structural.

4

4

na}\)

the dimensions of the germanium cage (2.525(3)–2.592(3) \(\text{Å}\)) comply with the expected values found in literature (2.59 \(\text{Å}\) [11]). The \([\text{Ge}_4]^{4-}\) anion shows almost perfect tetrahedral symmetry with Ge-Ge-Ge angles between 58.63(10)° and 61.21(11)°. It is surrounded by eight cesium cations. They coordinate \(\eta^1\)-like to edges and \(\eta^3\)-like to triangular faces of the cage (Figure 5e). The coordination sphere of the cesium atom itself is built by two \([\text{Ge}_4]^{4-}\) cages and is completed by eight ammonia molecules of crystallization. Considering the Cs\(^+\)-[Ge\(_4\)]\(^{4-}\) contacts, layers parallel to the crystallographic a- and b-axis are formed, which are separated by ammonia molecules of crystallization.

3.2. Cs\(_4\)Ge\(_4\)-9NH\(_3\)

Deep red needles of Cs\(_4\)Ge\(_4\)-9NH\(_3\) could be obtained by the dissolution of Cs\(_{12}\)Ge\(_{17}\) together with two chelating agents, [18]crown-6 and [2.2.2]cryptand in liquid ammonia. Indexing of the collected reflections leads to the orthorhombic space group \(Ibam\) (No. 72). The asymmetric unit of this compound consists of one germanium atom, one cesium cation and four nitrogen atoms. The anionic part of the compound is represented by a \([\text{Ge}_4]^{4-}\) tetrahedron, which is generated by the germanium position through symmetry operations resulting in the point group \(D_2\) for the molecular unit. The definite number of ammonia molecules of crystallization cannot be determined due to the incomplete data set (78\%), but very likely sums up to four in the asymmetric unit. Cs\(_4\)Ge\(_4\)-9NH\(_3\) is the first ammoniate with a ligand-free tetragermanide tetraanion reported to date. In spite of the incomplete data set, the heavy atoms Cs and Ge could be unambiguously assigned as maxima in the Fourier difference map.

References

Figure 3. Coordination spheres of the cesium cations in Cs\(_4\)Pb\(_4\)-5NH\(_3\); (a) tetrahedral environment of Cs1 by \([\text{Pb}_4]^{2-}\), for reasons of clarity, ammonia molecules are omitted; (b,c) coordination spheres of Cs2 (representative for Cs4) and Cs3; for reasons of clarity, hydrogen atoms are omitted; probability factor: 50%.

Figure 4. Section of the structure of Cs\(_4\)Pb\(_4\)-5NH\(_3\); corrugated Cs\(^+\)-NH\(_3\) strands along the crystallographic b-axis; the chains are emphasized by bold lines; \([\text{Pb}_4]^{2-}\) cages are located along the strands; hydrogen atoms are omitted for clarity; probability factor: 79%.
ali metal cations are completed by four to nine ammonia molecules of crystallization (Figure 6b). Altogether, a two-dimensional network is formed. The anionic cluster and the cations built corrugated waves, comparable to Cs₄Pb₄·5NH₃ (Figure 4). The ammonia molecules of crystallization fill the space between the strands.

3.3. Cs₄Si₄·7NH₃

Dissolving Cs₁₂Si₁₇ together with dicyclohexano[18]crown-6 and [2.2.2]cryptand in liquid ammonia resulted in deep red prismatic crystals of Cs₄Si₄·7NH₃. The asymmetric unit consists of two crystallographically independent [Si₄]⁴⁻ clusters, eight cesium cations and 14 ammonia molecules of crystallization. All atoms are located on the general Wyckoff position 2i of the triclinic space group P-1 (No. 2). [Si₄]⁴⁻ (1) is surrounded by nine, [Si₄]³⁻ (2) by eleven Cs⁺ cations (Figure 5a,b). Here the cations span edges, faces and vertices of the clusters in a distance range of 3.559(2)–4.651(3) Å. Cs1, Cs5, Cs7 and Cs8 are η¹-, η²- and η³-like surrounded by three Si₄ cages each, which are arranged in a triangular shape (comparable to the coordination sphere shown in Figure 3b). The remaining four cesium cations per asymmetric unit also show ionic contacts to two silicon clusters each by spanning edges, faces and vertices of the latter. The coordination spheres of all alkali metal cations are completed by four to nine ammonia molecules of crystallization (Figure 6b). Altogether, a two-dimensional [Si₄]⁴⁻·Cs⁺-network is formed. The anionic cluster and the cations built corrugated waves, comparable to Cs₄Pb₄·5NH₃ (Figure 4). The ammonia molecules of crystallization fill the space between the strands.
with stoichiometric amounts of sodium and ammonia yields in black shaped crystals of $[\text{Li(NH}_3\text{)}_4\text{Sn}_4\text{]}_4\cdot 4\text{NH}_3$. The asymmetric unit of the new compound consists of two tin atoms, two lithium atoms and ten ammonia molecules of crystallization.
All atoms are located on the general Wyckoff position 8f of the monoclinic space group I2/a (No. 15). As there is no indication for the presence of deprotonated ammonia molecules, the charge of the Sn₄ cluster sums up to −4. The tin cluster does not show direct contacts to lithium cations as all of these are coordinated by four ammonia molecules which results in tetrahedrally shaped [Li(NH₃)₄]⁺ complexes that can be considered as large and approximately spherical cationic units (Figure 6). For details, see Section 4.2. The ammonia lithium distances of 2.064(1)–2.116(1) Å in the tetrahedral cationic complex [Li(NH₃)₄]⁺ are in good agreement with literature-known lithiumtetraammine complexes [38]. The [Sn₄]⁴⁻ cage is coordinated by eight [Li(NH₃)₄]⁺ complexes, which span vertices and faces of the cluster (Figure 6a). The distances within the tetrahedron vary between 2.9277(8)–2.9417(8) Å and lie within the expected values for [Sn₄]⁴⁻ anions in ammoniate crystal structures. The Sn-Sn-Sn angles range between 59.882(20)° and 60.276(20)°.

3.6. K₄.₅Sn₄(OH)₀.₅·1.₇₅NH₃

Red, prismatic crystals of the composition K₄.₅Sn₄(OH)₀.₅·1.₇₅NH₃ could be synthesized by dissolving elemental tin with stoichiometric amounts of potassium in the presence of ¹BuOH in liquid ammonia. The hydroxide in the solvate structure is probably formed due to impurities on the potassium. The asymmetric unit of the solvate structure consists of four tetrasnannide tetraamnions, two hydroxide ions and seven ammonia molecules of crystallization. They all occupy general Wyckoff positions of the monoclinic space group P2₁/c (No. 14). The bond lengths of the tetrasnannides of 2.884(2)–2.963(2) Å are within the expected values for Sn-Sn distances in tin tetrahedranides [30]. Three of the four crystallographically independent tin anions are coordinated by 14 potassium cations, the fourth anion is coordinated by 16 cations at distances between 3.438(5) Å and 3.145(5) Å (Figure 7a,b). The cations coordinate vertex tin atoms or spans edges and faces of the tetrahedra.

![Figure 7](image_url)

Figure 7. Cationic coordination spheres of the two anionic components in K₄.₅Sn₄(OH)₀.₅·1.₇₅NH₃; (a) [Sn₄]⁴⁻ surrounded by 16 cations; (b) [Sn₄]⁴⁻ coordinated by 14 cations, as a representative for the other two crystallographically independent [Sn₄]⁴⁻ cages in the asymmetric unit; (c,d) cationic environment of the two hydroxide anions; probability factor: 50%.

Figure 7 additionally shows the coordination sphere of the second anionic component of the solvate structure, the hydroxide anions. They are characteristically surrounded by five potassium cations in a distorted square pyramidal manner. The coordination sphere of the cations is completed
by tin clusters, hydroxide ions or and ammonia molecules of crystallization (Figure 7c,d). Altogether, the structure of K$_4$Sn$_4$(OH)$_3$$cdot$1.75NH$_3$ consists of strands of ammonia molecules, hydroxide anions and potassium cations, which are connected via tetrastannide anions.

4. Discussion

In this section we discuss similarities and differences of the binary compounds towards the solvate structures with respect to the coordination spheres of the cations and the cluster anions.

4.1. NaPb Type Analogies

As already mentioned in the introduction, all alkali metal stannides and plumbides with the nominal composition AE, except the compounds containing lithium, crystallize in the tetragonal space group $I4_1/abd$ (No. 142) and belong to the NaPb structure type [10,18–21]. Considering the direct cationic environment of the tetrelide cluster in the binary phase (Figure 2c), the coordination number (CN) sums up to 16. With increasing content of ammonia molecules of crystallization, the coordination number of the cages decrease (Table 4). Figure 2 shows which cation-anion contacts are broken within the solvate structures. Generally, there are three different modes of the coordination of the cation towards the anion (Figure 8).

In the binary phases and Na$_4$Sn$_4$$cdot$13NH$_3$ [31,32] all triangular faces of the anions are capped $\eta^3$-like by cations. In contrast, in A$_4$E$_4$ 2NH$_3$ (A = K, Rb; E = Sn, Pb) [30] three faces and in Cs$_4$Pb$_4$$cdot$5NH$_3$ only one face of the [E$_4$]$^{4-}$ anions are coordinated $\eta^3$-like by the cations. In addition to the coordination of the faces, the edges of the [E$_4$]$^{4-}$ tetrahedra are coordinated $\eta^2$-like. For NaPb, Rb$_2$Sn$_4$ 2NH$_3$, Cs$_4$Sn$_4$ 2NH$_3$ and Rb$_2$Pb$_4$ 2NH$_3$, four $\eta^2$-like coordinated cations are present. In Cs$_4$Pb$_4$$cdot$5NH$_3$ five cations coordinate to the cage in a $\eta^2$-like fashion, in Na$_4$Sn$_4$$cdot$11.5NH$_3$ only two. Finally, the cationic environment of the [E$_4$]$^{4-}$ anions in the binary phase is completed by a total of eight cations which are bonded $\eta^1$-like to each vertex. In Rb$_2$Sn$_4$ 2NH$_3$, Cs$_4$Sn$_4$ 2NH$_3$, Rb$_2$Pb$_4$ 2NH$_3$ and Cs$_4$Pb$_4$$cdot$5NH$_3$ three and two vertices are coordinated by two cations, respectively. The other vertices each only show one tetrelide-alkali metal contact. Table 4 summarizes the anion coordinations and it becomes evident that the solvate structures with a small content of ammonia molecules of crystallization are more similar to the solid state structure, thus the three-dimensional cation-anion interactions are considerably less disturbed. Additionally, more anion-cation contacts appear in the solvate structures with the heavier alkali metals. Rubidium and cesium, as well as tin and lead are considered as soft acids and bases according to the HSAB theory [50]. The solvate structures containing sodium show much less anion-cation contacts due to the favored interaction of the hard base ammonia to the hard acid sodium cation (Table 5). Table 5 additionally shows the total coordination numbers of the cations, which is classified into cation-anion (A$^+$-E$^-$) and cation-nitrogen (A$^+$-NH$_3$) contacts. In Na$_4$Sn$_4$$cdot$13NH$_3$, Na$_4$Sn$_4$$cdot$11.5NH$_3$ and Cs$_4$Pb$_4$$cdot$5NH$_3$ the numbers of anion-cation contacts and the cation-nitrogen contacts are similar. In contrast, Rb$_2$Sn$_4$ 2NH$_3$, Cs$_4$Sn$_4$ 2NH$_3$ and Rb$_2$Pb$_4$ 2NH$_3$ show more A$^+$-E$^-$ contacts than ion-dipole interactions between the cation and the ammonia molecules of crystallization.

**Table 4.** Coordination number of the [E$_4$]$^{4-}$ cages in NaPb and related compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coordination Number (CN) E$^-$-A$^+$</th>
<th>$\eta^1$-like Coordination</th>
<th>$\eta^2$-like Coordination</th>
<th>$\eta^3$-like Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaPb Type</td>
<td>16</td>
<td>8</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Na$_4$Sn$_4$$cdot$13NH$_3$</td>
<td>4</td>
<td>/</td>
<td>/</td>
<td>4</td>
</tr>
<tr>
<td>Na$_4$Sn$_4$$cdot$11.5NH$_3$</td>
<td>5</td>
<td>/</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Cs$_4$Pb$_4$$cdot$5NH$_3$</td>
<td>12</td>
<td>6</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Rb$_2$Sn$_4$ 2NH$_3$/Cs$_4$Sn$_4$ 2NH$_3$/Rb$_2$Pb$_4$ 2NH$_3$</td>
<td>14</td>
<td>7</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>
4.2. KGe Type Analogies

Binary alkali metal compounds of silicon and germanium with the nominal composition AB (A = K-Cs) crystallize in the KGe structure type (Figure 5, for the corresponding literature see Table 1) [11–17]. Table 6 shows the number of cations coordinated to the [E₄]⁻⁻ cages. Here again, the decrease of the CN is directly related to the content of ammonia in the solvate structure. Like in the NaPb structure type, four cations coordinate η³-like to all triangular faces of the cages. However, unlike the NaPb type, no η²-like bonded cations are present in this solid state structure. Here, only single cation-anion contacts between the vertex atoms and the cations are built. The CN sums up to 16. The cationic environment of the [E₄]⁻⁻ clusters of the compounds Cs₄Ge₄.9NH₃ and [Li(NH₃)₄]₄Sn₄.4NH₃ is very similar to those of the KGe structure. It consists of four η³-like bonded cations/cationic complexes that are situated on the faces of the cages. However, in these ammoniates, every vertex is only coordinated by one cation/cationic complex instead of three. Thus, the CN of the cation-anion contacts and the η²-like bonded cations/cationic complexes that are situated on the faces of the cages. The coordination spheres of the cages are completed by two and three cations, respectively, which coordinate to edges (η²-like) of the cages. This kind of coordination is more prevalent in the NaPb structure type (Figure 2). The CN of the [Si₄]⁻⁻ cages sums up to 9/11 (Table 6).

Cs ammoniates of all group 14 elements are now known (Cs₄Si₄.7NH₃, Cs₄Ge₄.9NH₃, Cs₄Sn₄.2NH₃ and Cs₄Pb₄.5NH₃), which allows for comparison of the coordination number of the Cs cation. As mentioned in the introduction, the [E₄]⁻⁻ cages can be considered as roughly spherical with a radius calculated from the distance of the center of the tetrahedron to the edges (averaged distances) plus the van der Waals radius of the particular element [25]. Naturally, the sizes of the silicide (r: 3.58 Å) and the germanide (r: 3.67 Å) clusters are smaller than those of the stannide (r: 3.96 Å) and plumbide (r: 3.90 Å) clusters. This affects the CN of the cation. As listed in Tables 5 and 7, which show

![Figure 8. Different coordination modes of cations shown on the example of NaPb.](image)

**Table 5. Coordination number of the cations in NaPb and related ammoniates.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>CN total of Cations</th>
<th>A⁺⁻E⁻ Contacts</th>
<th>A⁺⁻NH₃ Contacts</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaPb Type</td>
<td>6–8</td>
<td>6–8</td>
<td>0</td>
</tr>
<tr>
<td>Na₄Sn₄·13NH₃</td>
<td>7</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Na₄Sn₄·11.5NH₃</td>
<td>5–6</td>
<td>2–3</td>
<td>0–3</td>
</tr>
<tr>
<td>Cs₄Pb₄·5NH₃</td>
<td>9–10</td>
<td>4–5</td>
<td>4–6</td>
</tr>
<tr>
<td>Rb₂Sn₄·2NH₃/Cs₄Sn₄·2NH₃/ Rb₄Pb₄·2NH₃</td>
<td>8–11</td>
<td>5–7</td>
<td>2–4</td>
</tr>
</tbody>
</table>

**4.2. KGe Type Analogies**

Binary alkali metal compounds of silicon and germanium with the nominal composition AB (A = K-Cs) crystallize in the KGe structure type (Figure 5, for the corresponding literature see Table 1) [11–17]. Table 6 shows the number of cations coordinated to the [E₄]⁻⁻ cages. Here again, the decrease of the CN is directly related to the content of ammonia in the solvate structure. Like in the NaPb structure type, four cations coordinate η³-like to all triangular faces of the cages. However, unlike the NaPb type, no η²-like bonded cations are present in this solid state structure. Here, only single cation-anion contacts between the vertex atoms and the cations are built. The CN sums up to 16. The cationic environment of the [E₄]⁻⁻ clusters of the compounds Cs₄Ge₄·9NH₃ and [Li(NH₃)₄]₄Sn₄·4NH₃ is very similar to those of the KGe structure. It consists of four η³-like bonded cations/cationic complexes that are situated on the faces of the cages. However, in these ammoniates, every vertex is only coordinated by one cation/cationic complex instead of three. Thus, the CN of the cation-anion contacts and the η²-like bonded cations/cationic complexes that are situated on the faces of the cages. The coordination spheres of the cages are completed by two and three cations, respectively, which coordinate to edges (η²-like) of the cages. This kind of coordination is more prevalent in the NaPb structure type (Figure 2). The CN of the [Si₄]⁻⁻ cages sums up to 9/11 (Table 6).

Cs ammoniates of all group 14 elements are now known (Cs₄Si₄·7NH₃, Cs₄Ge₄·9NH₃, Cs₄Sn₄·2NH₃ and Cs₄Pb₄·5NH₃), which allows for comparison of the coordination number of the Cs cation. As mentioned in the introduction, the [E₄]⁻⁻ cages can be considered as roughly spherical with a radius calculated from the distance of the center of the tetrahedron to the edges (averaged distances) plus the van der Waals radius of the particular element [25]. Naturally, the sizes of the silicide (r: 3.58 Å) and the germanide (r: 3.67 Å) clusters are smaller than those of the stannide (r: 3.96 Å) and plumbide (r: 3.90 Å) clusters. This affects the CN of the cation. As listed in Tables 5 and 7, which show
the coordination number of the cations in NaPb/KGe and the related ammoniates, the CN of Cs⁺ amounts to 9–11 in Cs₄Pb₄·5NH₃ and Cs₄Sn₄·2NH₃. In Cs₄Si₄·7NH₃ and Cs₄Ge₄·9NH₃ the CN sums up to 10–13 and thus is significantly higher. In addition, the total coordination number consists of the cation-anion (A⁺-E⁻) and the cation-nitrogen contacts (A⁺-NH₃). Considering the A⁺-E⁻ contacts in Cs₄Si₄·7NH₃ and Cs₄Ge₄·9NH₃, remarkably fewer (2–7) can be found in comparison to the ion-dipole interactions (4–9) between the cesium cations and the ammonia molecules of crystallization. In contrast, in Cs₄Pb₄·5NH₃ and Cs₄Sn₄·2NH₃ more A⁺-E⁻ contacts (4–7) than A⁺-NH₃ (2–6) interactions occur. The reduced cation-NH₃ contacts in the solvate structures of the heavier homologues tin and lead indicates that the size of the clusters has a significant impact on the quantity of ammonia molecules of crystallization that coordinate to the cesium cation and thus complete the coordination sphere.

Altogether, it is shown that the content of ammonia molecules of crystallization directly correlates with the CN of the cages to cations (see Section 4.1). This means that the presence of ammonia molecules results in broken anion-cation contacts within the ionic framework.

Table 6. Coordination number of the [E₄]⁴⁻ cages in KGe and related ammoniates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coordination Number (CN) E⁺-A⁺</th>
<th>η¹-like Coordination</th>
<th>η²-like Coordination</th>
<th>η³-like Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGe Type</td>
<td>16</td>
<td>12</td>
<td>/</td>
<td>4</td>
</tr>
<tr>
<td>Cs₄Si₄·7NH₃</td>
<td>9/11</td>
<td>3/4</td>
<td>2/3</td>
<td>4/4</td>
</tr>
<tr>
<td>Cs₄Ge₄·9NH₃</td>
<td>8</td>
<td>4</td>
<td>/</td>
<td>4</td>
</tr>
<tr>
<td>[Li(NH₃)₄]₂Sn₄·4NH₃</td>
<td>8</td>
<td>4</td>
<td>/</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 7. Coordination number of the cations in KGe and related ammoniates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CN of Cations</th>
<th>A⁺-E⁻ Contacts</th>
<th>A⁺-NH₃ Contacts</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGe Type</td>
<td>6</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Cs₄Si₄·7NH₃</td>
<td>10–13</td>
<td>2–7</td>
<td>4–9</td>
</tr>
<tr>
<td>Cs₄Ge₄·9NH₃</td>
<td>13</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>[Li(NH₃)₄]₂Sn₄·4NH₃</td>
<td>7</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

4.3. Effect of Additional Anions within Solvate Structures

In K₄.₅Sn₄(OH)₉.₅·1.₇5NH₃, the cationic environment slightly differs from the binary system NaPb and from the other solvate structures due to the presence of another anionic component, the hydroxide anion. As already mentioned in Section 3.6, the asymmetric unit consists of four crystallographically independent [Sn₄]⁴⁻ clusters. The coordination number of three of them has a value of 14, the CN of the fourth cluster is 16. Although ammonia molecules of crystallization are present in the structure, the CN of the clusters are very similar to the CN of the binary solid state system or are rather insignificantly smaller. Mainly, the differences lie in the manner of the coordination of the cations to the cages. In K₄.₅Sn₄(OH)₉.₅·1.₇5NH₃, only one to two (for Sn₄ (2)) cations span triangular faces of the cage, compared to the binary phase and the other solvate structures described in Section 4.1, where four and three cations coordinate in a η³-like fashion. The number of the η²-like bonded cations is somewhat higher. They can be found five or rather six times. The remaining cationic environment of the stannide clusters is built up by six to nine cations, which are η¹-like attached to vertex tin atoms. In the binary system, every vertex atom of the cluster shows two single cation-anion contacts, so eight η¹-like bonded cations appear here. Altogether, the presence of another anionic component and ammonia molecules of crystallization lead to different cationic coordinations of the anionic cages compared to the other solvate structures. But taking the slight content of ammonia molecules and hydroxide anion per stannide cluster into account, it is not surprising that the number of coordinating cations is almost equal to that in the binary phase NaPb.
5. Conclusions

We investigated the relations of ammoniate crystal structures of tetrelide tetrahedranides and the corresponding binary intermetallic phases. The involvement of ammonia strongly influences the structures of the compounds due to its character of rather acting as ligand towards the alkali metal cations than as an innocent solvent molecule. This is reflected in the CN of the cations as well as the anions. For the small alkali metal cations of lithium and sodium (hard acids) this even results in a formal enlargement of the cation radius which finally ends up in the structural similarities especially for Li-ammonia containing compounds to the binaries of the heavier homologues. Additional charged anions within the solvate crystal structures influence the overall crystal structure and this leads to a different cationic coordination of the anionic cages compared to the other solvate structures.

Author Contributions: C.L. and S.G. carried out experimental work (synthesis, crystallization, X-ray structure determination), C.L. and S.G. prepared the manuscript, N.K. designed and conceived the study.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Appendix A.1 Experimental Details

All operations were carried out under argon atmosphere using standard Schlenk and Glovebox techniques. Liquid ammonia was dried and stored on sodium in a dry ice cooled Dewar vessel for at least 48 h. Silicon (powder, 99%, 2N+, ABCR) and Lithium (99%, Chemmetal, Langelsheim) was used without further purification. Sodium (>98%, Merck, Deutschland) and potassium (>98%, Merck, Deutschland) were purified by liqutating. Rubidium and cesium were synthesized according to Hackspill [51] and distilled for purification. [18]crown-6 was sublimated under dynamic vacuum at 353 K. [2.2.2]cryptand (ABCR) was used without further purification. In the reaction mixtures containing the two chelating agents, crystals of the composition C_{12}H_{24}O_{6}·2NH_3 [52] and C_{18}H_{36}O_{6}N_{2}·2NH_3 [52] could additionally be observed. For the reaction mixtures with t-BuOH, surprisingly no crystal structures containing t-BuOH or t-BuO^- could be found.

Appendix A.1.1 Direct Reduction

[Li(NH_3)_4]_4Sn_4·4NH_3, Na_4Sn_4·11.5NH_3, K_4.5Sn_4(OH)_{0.5}·1.75NH_3 and Cs_4Pb_4·5NH_3: Tin and lead, respectively, as well as the stoichiometric amount of alkali metals, were placed in a three times baked out Schlenk vessel in a glovebox under argon atmosphere. For the synthesis of [Li(NH_3)_4]_4Sn_4·4NH_3, Na_4Sn_4·11.5NH_3 and K_4.5Sn_4(OH)_{0.5}·1.75NH_3 t-BuOH was additionally placed in the Schlenk vessel (the difference in applied amount of alkali metal and crystallized stoichiometry is explainable due to traces of water in t-BuOH despite intensive drying). About 10 mL of dry liquid ammonia was condensed on the mixture at 195 K. The appropriate amount of t-BuOH was added by a syringe at 195 K under immediate freezing. The blue ammonia alkali metal solution was allowed to react with t-BuOH and tin at 236 K. Gassing was observed first and the color of the solution changed from blue to dark red within few days. After storage at 236 K for a few weeks crystals of the above discussed compounds could be obtained.

[Li(NH_3)_4]_4Sn_4·4NH_3: 0.3 g Sn (2.6 mmol), 0.0905 g Li (13.1 mmol) and 1 mL t-BuOH (0.77 g, 10.4 mmol).

Na_4Sn_4·11.5NH_3: 0.95 g Sn (8.0 mmol), 0.4 g Na (17.4 mmol) and 1 mL t-BuOH (0.77 g, 10.4 mmol).

For N6, a split position was introduced as well as a SIMU restraint.

K_4.5Sn_4(OH)_{0.5}·1.75NH_3: 0.475 g Sn (4.0 mmol), 0.340 g K (8.7 mmol) and 0.5 mL t-BuOH (0.385 g, 5.2 mmol).

Cs_4Pb_4·5NH_3: 0.1729 g Pb (0.835 mmol), 0.1109 g Cs (0.835 mmol).
Appendix A.1.2 Solvolysis

Synthesis of the precursor Cs$_{12}$Si$_{17}$ and Cs$_{12}$Ge$_{17}$: For Cs$_{12}$Si$_{17}$, Cs (1.539 g, 11.581 mmol) and Si (0.461 g, 16.407 mmol), for Cs$_{12}$Ge$_{17}$, Cs (1.127 g, 8.481 mmol) and Ge (0.873 g, 12.015 mmol) were enclosed in tantalum containers and jacketed in an evacuated ampoule of fused silica. The containers were heated to 1223 K at a rate of 25 K·h$^{-1}$. The temperature was kept for 2 h. The ampoule was cooled down with a rate of 20 K·h$^{-1}$. The precursors were stored in a glove box under argon.

Cs$_4$Si$_4$·7NH$_3$ and Cs$_4$Ge$_4$·9NH$_3$: 50 mg of each precursor were dissolved in about 15 ml of liquid ammonia together with two chelating agents, [18]crown-6/dicyclohexano[18]crown-6 and [2.2.2]cryptand. The rufous solutions were stored at 197 K. After several months, very few crystals of the above discussed compounds could be obtained.

Cs$_4$Si$_4$·7NH$_3$: 50 mg (0.0245 mmol) of Cs$_{12}$Si$_{17}$, 9.4 mg (0.0252 mmol) dicyclohexano[18]crown-6 and 18.5 mg (0.0491 mmol) [2.2.2]cryptand. For Cs$_5$ a split position was introduced and a SIMU restraint was applied.

Cs$_4$Ge$_4$·9NH$_3$: 50 mg (0.0255 mmol) of Cs$_{12}$Ge$_{17}$, 0.0513 mg (0.194 mmol) [18]crown-6 and 0.044 mg (0.116 mmol) [2.2.2]cryptand. To prevent N2 and N3 to go non-positive definite (N.P.D.), the two atoms were refined isotropically and the atom radii were fixed at 0.05.

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