Synthesis and Crystal Structures of the Polygermanide Ammoniates $K_4Ge_9 \cdot 9\ NH_3$, $Rb_4Ge_9 \cdot 5\ NH_3$ and $Cs_6Ge_{18} \cdot 4\ NH_3$

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Z. Naturforsch. **60b,** 277 – 283 (2005); received October 26, 2004

The new compounds $K_4Ge_9 \cdot 9\ NH_3$ and $Rb_4Ge_9 \cdot 5\ NH_3$ were prepared by the extraction of K_4Ge_9 and Rb_4Ge_9 with liquid ammonia and characterized by low temperature X-ray structure analysis. They both contain monocapped square antiprismatic Ge_9^{4-} anions. $Cs_6Ge_{18} \cdot 4\ NH_3$ was prepared by the extraction of $K_2Cs_2Ge_9$ with liquid ammonia in the presence of $[(Bu)_3MeN](Br_2I)$ as an oxidizing agent, and contains a $[Ge_9\text{-}Ge_9]^{6-}$ dimer in which two Ge_9^{4-} anions are linked by a single Ge-Ge bond.

Key words: Zintl Anion, Germanide, Low-Temperature Crystal Structure Analysis, Liquid Ammonia, Solvate Crystal

Introduction

The nonatetrelide Zintl anions E_9^{4-} (E = Ge, Sn, Pb) are by now well established chemical entities both in the solid state and in solution; the available data have been recently reviewed by Fässler [1]. One of the most exciting recent developments in this field is the emergence of a synthetic chemistry *with* these Zintl anions. A first step in this direction was the report on Ge_{18}^{6-} [2] built from two nonatetrel cages linked *via* a single covalent bond, which was followed by an infinitesimal chain of Ge_9-anions in $[K\text{-}18\text{-}crown\text{-}6]_2\,{}^1_\infty[Ge_9]$ [3]. A different kind of covalent linkage was found in the anion $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$ [4]. Additionally, nonagermanide anions have been linked by mercury atoms, yielding ${}^1_\infty[HgGe_9]^{2-}$-chains in the compound $[K\text{-}crypt]_2[HgGe_9](en)_2$ [5], or were modified by the addition of substituents in $[Ph_2E\text{-}Ge_9\text{-}EPh_2]^{2-}$ (E = Sb, Bi) [6]. The common preparative approach to this chemistry is the extraction of binary alkali metal germanides with chelating solvents in the presence of macrocyclic alkali metal ligands. An alternative approach, the direct reduction of the group 14 elements with solutions of alkali metals in liquid ammonia, has been shown to work for Sn_9^{4-} and Pb_9^{4-} [7], but has failed to produce significant amounts of Ge_9^{4-} up to now. Given the interesting new developments in polygermanide chemistry, we adopted the extraction route for liquid ammonia. In this article we report the structural characterization of the solvate compounds $K_4Ge_9 \cdot 9\ NH_3$ (**1**) and $Rb_4Ge_9 \cdot 5\ NH_3$ (**2**) as well as the compound $Cs_6Ge_{18} \cdot 4\ NH_3$ (**3**), in which two nonagermanide cages were oxidatively coupled by using $[(Bu)_3MeN](Br_2I)$ as an oxidizing agent.

Results and Discussion

$K_4Ge_9 \cdot 9\ NH_3$ (**1**) was prepared by reacting a potassium germanide of the nominal composition K_4Ge_9 with liquid ammonia, and the resulting crystals were characterized by low-temperature X-ray crystallography (Table 1). The structure of **1** consists of a three-dimensional network formed by numerous contacts between nine-atom germanide cages Ge_9^{4-} and potassium cations K^+ (Fig. 1). The coordination spheres of the cations are completed by several molecules of ammonia, there are no unattached ammonia molecules of solvation present in the structure. The anion Ge_9^{4-}

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Table 1. Crystallographic data of the compounds **1**, **2** and **3**.

Parameters	**1**	**2**	**3**
Chem. formula	$Ge_9K_4N_9H_{27}$	$Ge_9Rb_4N_5H_{15}$	$Ge_{36}Cs_{12}N_8H_{12}$
M_r [g/mol]	3852.63	4322.05	8665.94
Temp [K]	123	123	123
Cryst. system	orthorhombic	monoclinic	monoclinic
Space group	*Pnma* (no. 62)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	18.213(1)	9.000(2)	8.9640(8)
b (Å)	15.778(1)	14.901(4)	14.175(1)
c (Å)	9.525(1)	16.977(5)	14.991(1)
β (deg)	—	91.49(3)	93.69(1)
V (Å^3)	2737.2(5)	2276(1)	1900.93
Z	4	4	2
ρ_c[g/cm]	2.337	3.153	3.785
$F(000)$	1816	1944	1880
λ(Mo-K$_\alpha$)	0.71073	0.71073	0.71073
2θ Range [°]	3.3 – 51.89	1.82 – 50.0	3.3 – 52.1
All reflections	39247	8534	26172
Independent refl.	2771	3996	3630
No. of param.	164	210	139
No. of restraints	0	208	0
R_{int}	0.0669	0.056	0.0674
R_1 ($I > 2\sigma$(I))	0.0413	0.047	0.0291
wR_2 ($I > 2\sigma$(I))	0.0896	0.105	0.0580
R_1 (all data)	0.0953	0.0811	0.0505
wR_2 (all data)	0.0572	0.1053	0.0719
GOOF	1.037	1.136	1.016
Largest peak and hole [e/Å^3]	$3.17/-1.66$	$1.74/-1.41$	$1.15/-1.33$

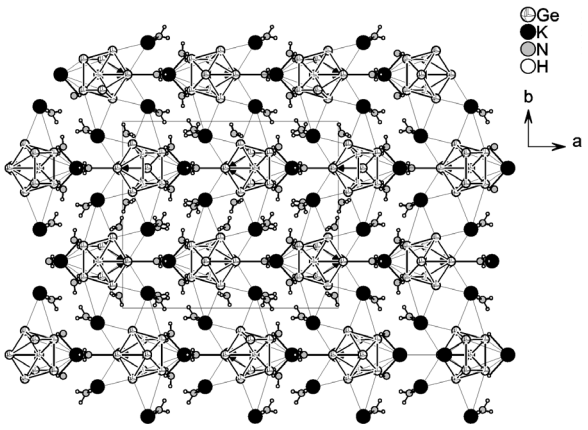


Fig. 1. Cutout of the structure of $K_4Ge_9 \cdot 9\,NH_3$ (**1**), projected onto the *ab*-plane.

displays the well-documented [1] monocapped square antiprismatic structure with approximate C_{4v} symmetry (Fig. 2). Due to its 22 skeletal electrons, this cluster can be described as a nido-cluster in accordance with the Wade rules [8]. The atoms Ge(1), Ge(2) and Ge(4) are situated on a mirror plane. As a result of this site symmetry, the basal four-angular face Ge(5)-Ge(6)-Ge(6)#1-Ge(5)#1 of the cage, which is usually closely checked for deviations towards D_{3h} symmetry, is truly planar. However, with bond distances ranging from 2.568(1) to 2.643(1) Å (Table 2), this face is far from being an ideal square. The intracage Ge-Ge bond lengths (Table 2) range from 2.5471(9) Å to 2.910(1) Å; these values are in good agreement with already known structures like that of Rb_4Ge_9(en) [9]. The nonagermanide cage has 21 contacts to surrounding potassium cations (Fig. 3) with appreciable differences in their distances, as can be seen in Table 3.

The cations K(1), K(2), K(3) and K(3)#1 bridge edges of the cage, and each of the cations K(1)#2, K(3) and K(3)#4 bridge a triangular face. The cation

Table 2. Intracage bond lengths [Å] of Ge_9^{4-} in $K_4Ge_9 \cdot 9\,NH_3$ (**1**).

Ge(1)-Ge(3)	2.5471(9)	Ge(1)-Ge(4)	2.547(1)
Ge(1)-Ge(2)	2.578(1)	Ge(2)-Ge(5)	2.592(1)
Ge(2)-Ge(3)	2.809(1)	Ge(4)-Ge(6)	2.583(1)
Ge(4)-Ge(3)	2.910(1)	Ge(5)-Ge(6)	2.570(1)
Ge(5)-Ge(3)	2.571(1)	Ge(5)-Ge(5)$^{\#1}$	2.643(1)
Ge(6)-Ge(6)$^{\#1}$	2.568(1)	Ge(6)-Ge(3)	2.591(1)

Symmetry operation used to generate equivalent atoms: $^{\#1}$ $x, -y+1/2, z$.

Table 3. Selected K-Ge distances [Å] in $K_4Ge_9 \cdot 9\,NH_3$ (**1**).

Ge(1)-K(3)	3.475(1)	Ge(1)-K(1)	3.531(2)
Ge(1)-K(2)	3.566(2)	Ge(2)-K(1)	3.593(2)
Ge(4)-K(1)$^{\#2}$	3.480(2)	Ge(4)-K(2)	3.854(2)
Ge(5)-K(2)$^{\#3}$	3.620(2)	Ge(5)-K(3)$^{\#4}$	4.055(1)
Ge(6)-K(1)$^{\#2}$	3.557(2)	Ge(6)-K(2)$^{\#3}$	3.816(2)
Ge(6)-K(3)$^{\#4}$	4.304(1)	Ge(3)-K(3)$^{\#4}$	3.468(1)
Ge(3)-K(3)	3.806(1)		

Symmetry operations used to generate equivalent atoms: $^{\#2}$ $x, y, z+1$; $^{\#3}$ $x-1/2, -y+1/2, -z+1/2$; $^{\#4}$ $-x, -y, -z$.

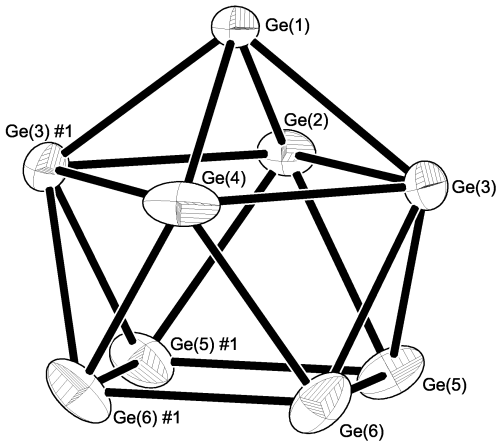


Fig. 2. Nonagermanide anion Ge_9^{4-} in the compound $K_4Ge_9 \cdot 9\,NH_3$ (**1**). Symmetry operation used to generate equivalent atoms: $^{\#1}$ $x, -y+1/2, z$.

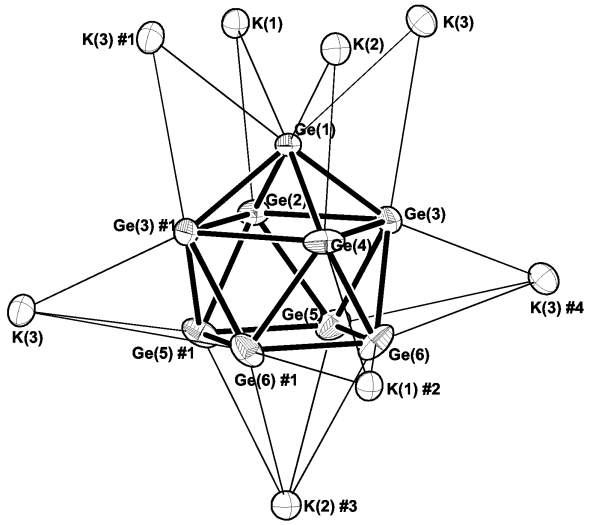


Fig. 3. Coordination of Ge_9^{4-} by K^+ in the compound $K_4Ge_9 \cdot 9\ NH_3$ (**1**). Symmetry operations used to generate equivalent atoms: #1 $x, -y+1/2, z$; #2 $x, y, z+1$; #3 $x-1/2, -y+1/2, -z+1/2$; #4 $-x, -y, -z$.

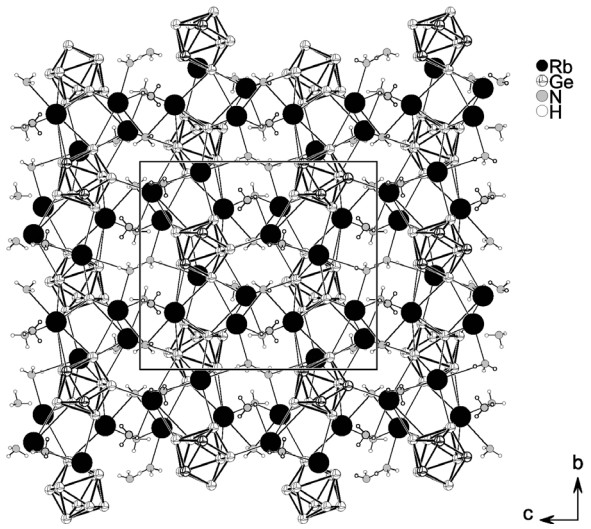


Fig. 4a. Cutout of the structure of $Rb_4Ge_9 \cdot 5\ NH_3$ (**2**), projected onto the *bc*-plane.

K(2)#3 caps the basal face in an unusual η^4-like coordination, which was already described by Guloy [10]. The distance of K(2)#3 to the center of the basal plane is 3.238 Å. This is more than double of the distance of the capping atom Ge(1) to the adjacent rectangular face Ge(2), Ge(3), Ge(3)#1, Ge(4), which has a value of 1.562 Å.

$Rb_4Ge_9 \cdot 5\ NH_3$ (**2**) was prepared by extracting Rb_4Ge_9 with liquid ammonia in a special glas apparatus at room temperature over the period of one month. The structure of **2** is also characterized by a three-dimensional network of nonagermanide anions Ge_9^{4-} and the counter cations, with the ammonia molecules of solvation coordinating to the Rb^+ cations (Fig. 4a). The compound crystallizes in the monoclinic space group $P2_1/c$ (no. 14). As expected, the nonagermanide cage is very similar to that in compound **1**. However, due to the lack of site symmetry in this case, the torsion angle Ge(1)-Ge(3)-Ge(9)-Ge(5) of the basal plane

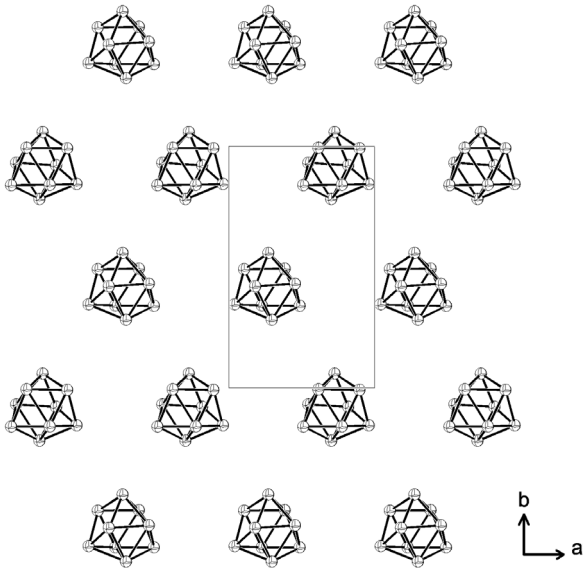


Fig. 4b. Pseudo-hexagonal layer of Ge_9 clusters in $Rb_4Ge_9 \cdot 5\ NH_3$ (**2**).

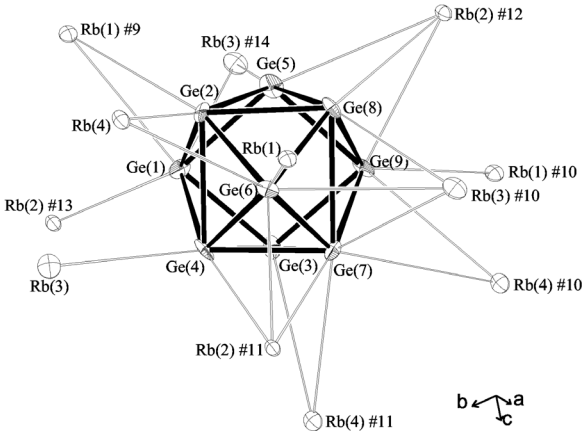


Fig. 5. Coordination of Ge_9^{4-} by Rb^+ in the compound $Rb_4Ge_9 \cdot 5\ NH_3$ (**2**). Symmetry operations used to generate equivalent atoms: #9 $x-1, y, z$; #10 $-x+1, y-1/2, -z+3/2$; #11 $x, 1/2-y, 1/2+z$; #12 $-x+1, -y, -z+1$; #13 $x-1, -y+1/2, z+1/2$; #14 $-x, y-1/2, -z+3/2$.

Table 4. Intracage bond lengths [Å] of Ge_9^{4-} in $Rb_4Ge_9 \cdot 5\ NH_3$ (**2**).

Ge(1)-Ge(2)	2.569(1)	Ge(1)-Ge(3)	2.558(1)
Ge(1)-Ge(4)	2.584(1)	Ge(1)-Ge(5)	2.593(2)
Ge(2)-Ge(6)	2.564(1)	Ge(2)-Ge(5)	2.594(1)
Ge(2)-Ge(8)	2.716(1)	Ge(2)-Ge(4)	2.894(1)
Ge(3)-Ge(7)	2.572(1)	Ge(3)-Ge(9)	2.586(1)
Ge(3)-Ge(4)	2.612(1)	Ge(4)-Ge(6)	2.573(1)
Ge(4)-Ge(7)	2.694(1)	Ge(5)-Ge(8)	2.538(1)
Ge(5)-Ge(9)	2.574(2)	Ge(6)-Ge(8)	2.565(1)
Ge(6)-Ge(7)	2.576(1)	Ge(7)-Ge(9)	2.564(1)
Ge(8)-Ge(9)	2.586(1)		

Table 5. Rb-Ge distances [Å] in $Rb_4Ge_9 \cdot 5\ NH_3$ (**2**).

Rb(1)$^{\#9}$-Ge(1)	3.658(1)	Rb(1)-Ge(6)	3.697(1)
Rb(1)$^{\#10}$-Ge(9)	3.881(1)	Rb(1)$^{\#9}$-Ge(2)	3.932(1)
Rb(2)$^{\#11}$-Ge(6)	3.574(1)	Rb(2)$^{\#12}$-Ge(9)	3.643(1)
Rb(2)$^{\#12}$-Ge(8)	3.650(1)	Rb(2)$^{\#13}$-Ge(1)	3.672(1)
Rb(2)$^{\#11}$-Ge(7)	3.907(1)	Rb(2)$^{\#12}$-Ge(5)	3.915(1)
Rb(2)$^{\#11}$-Ge(4)	4.006(1)	Rb(3)$^{\#14}$-Ge(5)	3.485(1)
Rb(3)$^{\#10}$-Ge(8)	3.546(1)	Rb(3)-Ge(4)	3.584(1)
Rb(3)$^{\#10}$-Ge(7)	3.586(1)	Rb(3)$^{\#10}$-Ge(6)	3.935(1)
Rb(3)$^{\#14}$-Ge(1)	4.064(2)	Rb(4)$^{\#10}$-Ge(9)	3.760(2)
Rb(4)$^{\#11}$-Ge(7)	3.789(1)	Rb(4)$^{\#10}$-Ge(7)	3.812(1)
Rb(4)$^{\#11}$-Ge(3)	3.857(2)	Rb(4)-Ge(2)	3.896(1)
Rb(4)-Ge(6)	3.968(1)		

Symmetry operations used to generate equivalent atoms: $^{\#9}$ $x-1, y, z$; $^{\#10}$ $-x+1, y-1/2, -z+3/2$; $^{\#11}$ $x, 0.5-y, 0.5+z$; $^{\#12}$ $-x+1, -y, -z+1$; $^{\#13}$ $x-1, -y+1/2, z+1/2$; $^{\#14}$ $-x, y-1/2, -z+3/2$.

of the cage is not zero, but has a negative value of −6.90 degrees. This deviation from planarity shows that the overall distortion of the cage occurs not towards D_{3h} symmetry but rather in the opposite direction, causing the face diagonal Ge(1)-Ge(9) to be an inward facing edge. In an ideal C_{4v}-symmetric cluster the bond lengths Ge(3)-Ge(5) and Ge(1)-Ge(9) with values of 3.411(2) Å and 3.854(2) Å would adopt the same length.

The nonagermanide cage possesses 23 contacts with twelve rubidium cations (Fig. 5), ranging from a single coordination of only one germanium atom to the capping of two of the triangular faces. The bond lengths shown in Fig. 5 are listed in Tables 4 and 5.

Inspection of the distribution of Ge_9 clusters (centered at $x,y,z \cong 0.25, 0.41, 0.25$) in the structure of **2** reveals that they are arranged in layers assembled in a hexagonal-close-packed (*hcp*) fashion (ABAB layer sequence) with the Rb atoms and NH_3 molecules occupying "interstitial" positions (Fig. 4b). The pseudo-hexagonal layers are stacked along the *c* axis ($c_h = c$, $a_h = a \approx b/\sqrt{3}$). A similar *hcp* arrangement of X_9 clusters (X = Ge, Pb), but much more distorted, is observed in the Cs_4Pb_9 structure [11].

Table 6. Bond length [Å] in $Cs_6Ge_{18} \cdot 4\ NH_3$ (**3**).

Ge(1)-Ge(2)	2.595(1)	Ge(1)-Ge(3)	2.599(1)
Ge(1)-Ge(4)	2.613(1)	Ge(1)-Ge(5)	2.597(1)
Ge(2)-Ge(3)	2.779(1)	Ge(2)-Ge(5)	2.872(1)
Ge(2)-Ge(7)	2.610(1)	Ge(2)-Ge(6)	2.686(1)
Ge(3)-Ge(7)	2.611(1)	Ge(3)-Ge(4)	2.820(1)
Ge(4)-Ge(5)	2.811(1)	Ge(4)-Ge(8)	2.573(1)
Ge(4)-Ge(9)	2.612(1)	Ge(5)-Ge(6)	2.541(1)
Ge(5)-Ge(9)	2.575(1)	Ge(6)-Ge(7)	2.513(1)
Ge(6)-Ge(9)	2.667(1)	Ge(7)-Ge(8)	2.516(1)
Ge(8)-Ge(9)	2.666(1)	Ge(7)-Ge(7)	2.468(1)

Table 7. Cs-Ge distances [Å] in $Cs_6Ge_{18} \cdot 4\ NH_3$ (**3**).

Cs(1)-Ge(6)	3.667(1)	Cs(1)-Ge(8)	3.870(1)
Cs(1)-Ge(3)	3.987(1)	Cs(1)$^{\#20}$-Ge(5)$^{\#20}$	3.706(1)
Cs(1)$^{\#20}$-Ge(4)$^{\#20}$	3.717(1)	Cs(1)$^{\#21}$-Ge(2)$^{\#21}$	4.004(1)
Cs(2)$^{\#20}$-Ge(5)$^{\#20}$	3.652(1)	Cs(2)$^{\#21}$-Ge(6)	3.705(1)
Cs(2)$^{\#21}$-Ge(7)$^{\#16}$	3.743(1)	Cs(2)$^{\#21}$-Ge(9)$^{\#21}$	3.869(1)
Cs(2)$^{\#21}$-Ge(3)	3.976(1)	Cs(2)$^{\#24}$-Ge(4)$^{\#20}$	3.766(1)
Cs(3)-Ge(6)	3.863(1)	Cs(3)$^{\#12}$-Ge(9)$^{\#21}$	3.863(1)
Cs(3)$^{\#20}$-Ge(1)$^{\#20}$	3.902(1)		

Symmetry operations used to generate equivalent atoms: $^{\#12}$ $1-x, -y, -z+1$; $^{\#16}$ $1+x, y, z$; $^{\#20}$ $1/2+x, 1/2-y, 1/2+z$; $^{\#21}$ $1+x, y, z$; $^{\#22}$ $-x, 1-y, 1-z$; $^{\#23}$ $1-x, 1-y, 1-z$; $^{\#24}$ $3/2+x, 1/2-y, 1/2+z$.

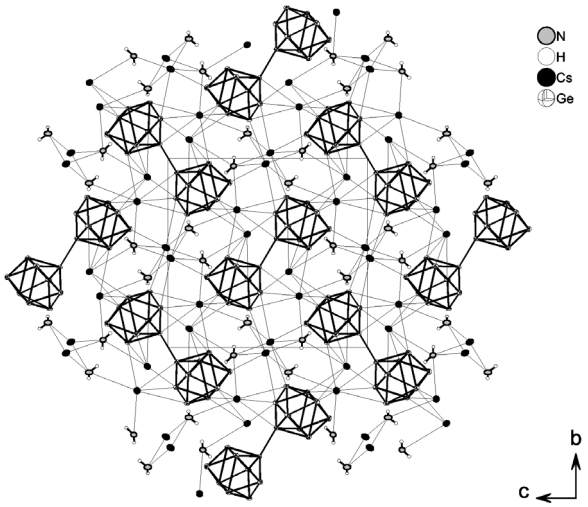


Fig. 6. View of the crystal structure of $Cs_6Ge_{18} \cdot 4\ NH_3$ (**3**) projected onto the *bc*-plane.

While the compounds **1** and **2** were synthesized by the extraction of alkali metal germanides containing the same metal-germanium ratio as the resulting solvate crystals, $Cs_6Ge_{18} \cdot 4\ NH_3$ (**3**) resulted from an alkali metal nonagermanide solution in liquid ammonia, to which a nearly equimolar amount of $[(Bu)_3MeN](Br_2I)$ was added as an oxidising agent. The structure of **3** is built of Ge_{18}^{6-} anions, ce-

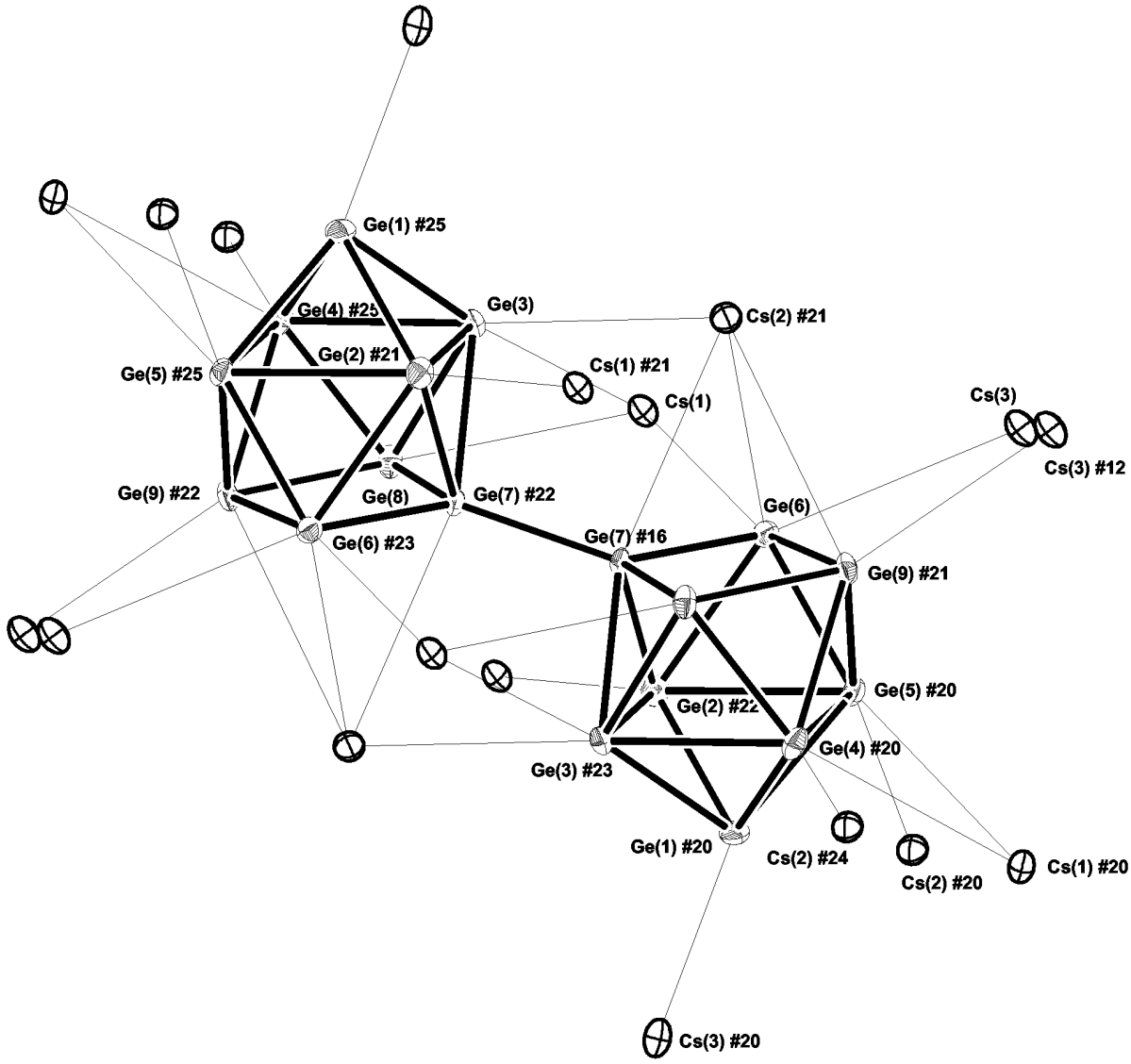


Fig. 7. Coordination of Ge_{18}^{6-} by Cs^+ in the compound $Cs_6Ge_{18} \cdot 4\ NH_3$ (**3**). Symmetry operations used to generate equivalent atoms: #12 $1-x, -y, 1-z$; #16 $1+x, y, z$; #20 $1/2+x, 1/2-y, 1/2+z$; #21 $1+x, y, z$; #22 $-x, 1-y, 1-z$; #23 $1-x, 1-y, 1-z$; #24 $3/2+x, 1/2-y, 1/2+z$; #25 $1/2-x, 1/2+y, 1/2-z$.

sium cations Cs^+ and ammonia molecules of solvation (Fig. 6). The anion Ge_{18}^{6-} (Fig. 7) is formed by two Ge_9-subunits linked by a single bond between two atoms at the square base of the again approximately monocapped square antiprismatic cages. To our knowledge this is the first [Ge_9] dimer which could be isolated without the use of sequestering agents like cryptands or crown ethers. The bond length between the deltahedral clusters is 2.468(1) Å (Table 6), while the comparable bond length in the compound [K-crypt]$_2$Cs$_4$([Ge$_9$-Ge$_9$])(en)$_6$ [2] has a value of 2.488 Å. The dimer resides on a centre of symmetry. Its bond lengths and angles are in good agreement with those of the previously described Ge_{18}^{6-} anions in [K-crypt]$_2$Cs$_4$([Ge$_9$-Ge$_9$])(en)$_6$ [2] and [K(18-crown-6)]$_3$Cs$_3$[Ge$_9$-Ge$_9$](en)$_2$ [12]. As was expected, the Ge_9-cages are significantly distorted in the dimer. The exo-bond is collinear to the shorter diagonal

Ge(7)-Ge(9) of the basal four-angled face, which measures 3.287(1) Å, while the longer diagonal Ge(6)-Ge(8) has a value of 3.999(1) Å. These different bond lengths indicate that the clusters show idealized C_{2v} and not C_{4v} symmetry, which can also be observed in the structures reported by Xu and Sevov [2] and Hauptmann and Fässler [12]. The dihedral angle at the basal face Ge(6)-Ge(7)-Ge(8)-Ge(9) has a value of 2.34 degrees, which shows only a small deviation from planarity. The dimer is coordinated by altogether eighteen cesium cations (Fig. 7), the corresponding atomic distances are given in Table 7.

The formation of the $[Ge_9\text{-}Ge_9]^{6-}$ dimer by the addition of an Br_2I^- salt to the ammonia solution of the monomer cages is very similar to the oxidative coupling of two $P_{11}{}^{3-}$ cages to the novel $P_{22}{}^{4-}$ ion by $Br_3{}^-$ in the same solvent reported previously [13]. This fact, as well as the similarity of the ammoniate structures investigated here with the ammoniate structures of alkali metal polyphosphides like $Cs_3P_{11}\cdot 3\ NH_3$ [14], indicate that the considerably better explored principles of polyphosphide chemistry in liquid ammonia may well be transferable to polygermanide chemistry.

Experimental Section

All preparations were carried out under dry argon in glass vessels or in a glove box.

(1) $K_4Ge_9\cdot 9\ NH_3$: A binary phase of the nominal composition K_4Ge_9 was prepared from a stoichiometric mixture of the elements in a sealed silica ampoule. 0.28 g (7.16 mmol) K and 1.16 g (15.9 mmol) Ge were heated to 650 °C (10 °C/h), then annealed at 650 °C for 96 hours and finally cooled down to room temperature (10 °C/h). 0.25 g of K_4Ge_9 were then filled in a vacuum dried glass vessel and 30 ml of dried liquid ammonia was added. The reaction vessel was stored at −43 °C for two months. During this time, yellow prism-shaped crystals of **1** had formed. The thermally unstable crystals were transferred directly from the mother liquor to the diffractometer using an end-capped perfluorether oil.

The diffraction data were collected with graphite monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation on a STOE IPDS at −150 °C. The structure was solved by direct methods (SHELXS-97) [15] and refined on F^2 (SHELXL-97) [16]. An DIFABS-type absorbtion correction was applied with the help of the PLATON program package [17].

(2) $Rb_4Ge_9\cdot 5\ NH_3$: Rubidium and germanium were filled in a niobium ampoule at a ratio of 4 to 9. The mixture was heated to 800 °C and the temperature was held for one week. Finally, the reaction vessel was cooled down with an increment of 5 °C/h. The solid product was extracted with 40 ml of ammonia for one month at room temperature. Deeply red cuboid-like crystals were obtained.

The diffraction data were collected with graphite monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation on an Enraf-Nonius-CAD4 at −150 °C with $\omega 2/\theta$-scanning. The structure solution was solved by direct methods (SHELXS-86) [18] and refined on F^2 (SHELXL-93) [19]. An empirical absorption correction based on 10 ψ-scans was applied. All hydrogen atoms were located in the difference Fourier synthesis and refined with a "riding"-model. The ammonia molecules were restrained to uniform H-H and N-H-distances.

(3) $Cs_6Ge_{18}\cdot 4\ NH_3$: A ternary phase of the nominal composition $K_2Cs_2Ge_9$ was prepared from a stoichiometric mixture of the elements in a sealed silica ampoule. 0.2 g (5.11 mmol) K, 0.7 g (5.29 mmol) Cs and 1.7 g (23.4 mmol) Ge were heated to 650 °C (10 °C/h), then annealed at 650 °C for 120 hours and finally cooled down to room temperature (10 °C/h). The product was of deep violet colour. 0.19 g (0.2 mmol) of $K_2Cs_2Ge_9$ and 0.08 g (0.16 mmol) $Me(Bu)_3NBr_2I$ were then filled in a vacuum dried glass vessel and 30 ml of dried liquid ammonia was added. The reaction vessel was stored at −43 °C for one month. After this period, deeply red prism-shaped crystals had formed, which were again transferred to the diffractometer directly from the mother liquor.

The diffraction data were collected with graphite monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation on a STOE IPDS at −150 °C. The structure was solved by direct methods (SHELXS-97) [15] and refined on F^2 (SHELXL-97) [16]. The atoms excepting hydrogen were refined anisotropic. Not all of the hydrogen atoms could be located in the difference Fourier synthesis or attached *via* an HFIX command. An DIFABS-type absorption correction was applied with the help of the PLATON program package [17]. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, on quoting the deposition number CSD-411319 ($K_4Ge_9\cdot 9\ NH_3$), CSD-411320 ($Rb_4Ge_9\cdot 5\ NH_3$) and CSD-411321 ($Cs_6Ge_{18}\cdot 4\ NH_3$).

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