Electronic Supplementary Material (ESI) for ChemComm.

$[(\mu_2\text{-H})(\eta^2\text{-Ge}_4)\text{ZnPh}_2]^{3-}$, an Edge-On Protonated E_4 Cluster Crystallized from Liquid Ammonia Establishing the First Three-Center Two-Electron Ge-H-Ge Bond

Thomas Henneberger, Wilhelm Klein, Jasmin V. Dums, and Thomas F. Fässler*

Technische Universität München, Department of Chemistry, Lichtenbergstraße 4, 85747 Garching, Germany

Supporting Information

Content

Experimental

Syntheses. All operations and reactions were performed in a purified argon atmosphere, using standard Schlenk line and glove box techniques. 1,4,7,10,13,16-hexaoxacyclooctadecane ([18]crown-6; Merck) was purified by vacuum sublimation at 80°C. Liquid ammonia (Westfalen) was dried and stored over sodium metal.

The synthesis of $ZnPh_2$ was performed on the basis of different instructions:[1] 23.1 ml (0.22 mol) PhBr in 60 ml diethyl ether were added to 5.29 g (0.22 mol) Zn chips in 25 ml diethyl ether and boiled for 30 min under vigorous stirring. The red brown solution was cooled down to RT, then 10.14 g (74.4 mmol) $ZnCl_2$ in 80 ml diethyl ether were added and boiled for 2 h under vigorous stirring. The solution was filtered and the solvent removed in vacuum. The grey residue was sublimated over several hours at 180°C in dynamic vacuum.

The *Zintl* precursor phase $K_6Rb_6Ge_{17}$ was prepared analogously to the Si homologue[2] from stoichiometric mixtures of the elements in sealed tantalum containers which were encapsulated in an evacuated and fused silica tube. This mixture was heated to 900°C for 15 h and slowly cooled to room temperature with a rate of 0.5°C/min.

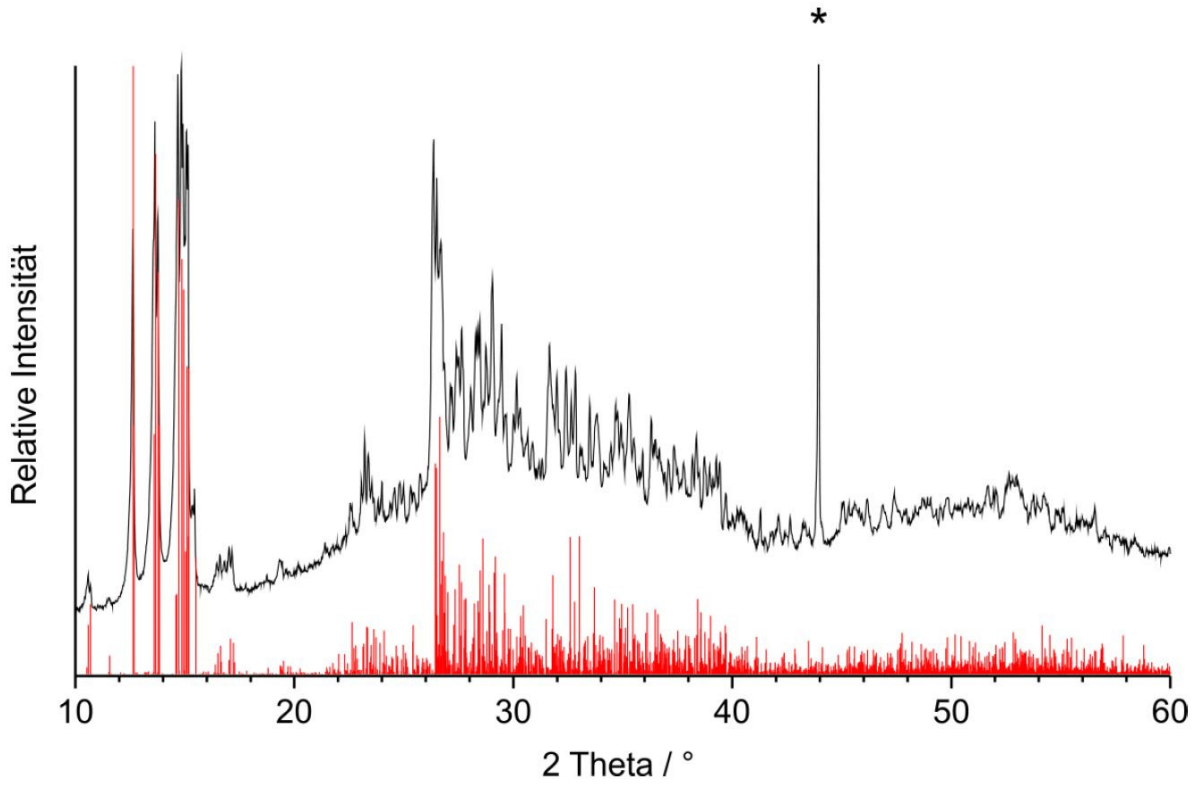

Figure S1. Powder diffractogram of $K_6Rb_6Ge_{17}$ (measurement time 12 h, Cu $K\alpha_1$ radiation) with underlying calculated reflections. For calculation the structure model of $K_{12}Si_{17}$[3] was used after substitution of Si and 50 % K by Ge and Rb, respectively. The powder was diluted with diamond powder, the diamond reflection is marked with an asterisk.

[K([18]crown-6)][Rb([18]crown-6)]$_2$[HGe$_4$ZnPh$_2$]·8 NH$_3$ (**1**) and *[K$_{0.3}$Rb$_{0.7}$([18]crown-6)]K$_{0.2}$Rb$_{2.8}$[Ge$_9$]·4.5 NH$_3$* (**2**). For the synthesis of the title compounds, 149 mg (0.075 mmol) $K_6Rb_6Ge_{17}$, 17 mg (0.075 mmol) $ZnPh_2$, and 36 mg (0.135 mmol) [18]crown-6 were dissolved in approximately 2 ml of ammonia. The dark red solution was stored at -70°C, orange crystals of **1** and yellow ones of **2** have been found after 30 and 36 months, respectively, in the same reaction vessel. The composition concerning the metals has been confirmed by EDX measurements on several crystals of both compounds.

X-ray crystal structure determination. Crystals were transferred from the mother liquor cooled with dry-ice/2-propanol into perfluoropolyalkyl ether oil cooled with a stream of liquid nitrogen. Suitable Single crystals were fixed on the tip of a glass capillary and positioned in a 120 K cold nitrogen stream using the crystal cap system. The single crystal intensity data were recorded on a Oxford Xcalibur3 diffractometer (Mo *Kα* radiation), data reduction and absorption correction was performed by using the *CrysAlis* software package.[4] The structure was solved by Direct Methods (*SHELXS-97*)[5] and refined by full matrix least-squares calculations (*SHELXL2014*).[6] All non-hydrogen atoms were treated with anisotropic displacement parameters, the hydrogen atom positions were geometrically calculated and refined with a riding model except for the cluster-bound H atom in compound **1** which has been identified from the largest peak in the difference electron density and was refined isotropically. Except for the K atom in **1**, both structures contain mixed alkali metal occupations at the K and Rb atom positions, and the relative amount of K and Rb has been refined independently for all cations. Further information concerning the structure determinations are given in Table S1. Details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk, on quoting the depository numbers CCDC 1859587 (**1**) and CCDC 1859588 (**2**).

Computational analyses. The Gaussian09 program package[7] with exchange correlation hybrid functional after Perdew, Burke and Ernzerhof (PBE0)[8] and def2-TZVP basis set for all considered elements Ge, Zn, C and H[9] was used for the computational analysis. The structures of $[HGe_4ZnPh_2]^{3-}$ and $[Ge_4ZnPh_2]^{4-}$ were investigated. For compensation of the negative charge a solvation model (polarizable continuum model, PCM)[10] for water was estimated. The structural parameter of the starting geometry were taken from the crystal structure and optimized afterwards. The nature of a stationary point on the potential energy surface could be confirmed by a frequency calculation. Additionally an optimization was carried out for an apex-protonation of $[HGe_4ZnPh_2]^{3-}$. Input coordinates are listed below. For data processing and visualization the program Vesta[11] was used.

EDX analyses. Several single crystals of each compound including the measured crystal were mounted on carbon tape and measured on a JEOL SEM 5900LV scanning electron microscope to determine the elemental composition. The composition of all presented compounds with respect to the elements heavier than sodium have been proven this way.

Table S1. Crystallographic data and details of the structure determinations of [K([18]crown-6)][Rb([18]crown-6)]$_2$[HGe_4ZnPh_2]·8 NH_3 (**1**) and [$K_{0.3}Rb_{0.7}$([18]crown-6)]$K_{0.2}Rb_{2.8}[Ge_9]$·4.5 NH_3 (**2**).

compound	**1**	**2**
composition	$C_{48}H_{107}Ge_4K_{1.09}N_8O_{18}Rb_{1.91}Zn$	$C_{12}H_{37.5}Ge_9K_{0.45}N_{4.5}O_6Rb_{3.55}$
crystal system	orthorhombic	monoclinic
space group	*Pbcn* (no. 60)	*C*2/*c* (no. 15)
temperature / °C	-150	-150
lattice parameters *a* / Å	12.8668(5)	38.5713(8)
b / Å	28.2571(9)	9.9970(2)
c / Å	20.0883(8)	19.0042(4)
α / Å	90	90
β / Å	90	94.337(2)
γ / Å	90	90
cell volume / Å^3	7303.7(4)	7307.0(3)
formula units	4	8
F(000)	3308	4935
molar mass / g mol^{-1}	1646.01	1315.11
calc. density / g cm^{-3}	1.497	2.391
wavelength / Å	0.71073	0.71073
absorption coef. / mm^{-1}	3.341	21.071
measured reflections	84521	62423
unique reflections	7173	7181
R_{int}	0.0790	0.0563
2θ region / °	5.34 – 51.99	5.50 – 52.0
reflections > 2σ	4177	5219
number of parameters	378	342
$R_1(F)$ [$I > 2\sigma$]	0.0345	0.0271
$wR_2(F^2)$ [$I > 2\sigma$]	0.0707	0.0480
$R_1(F)$ [all]	0.0694	0.0440
$wR_2(F^2)$ [all]	0.0757	0.0500
Goodness of Fit (F^2)	0.866	0.924
max./min. difference density / e$^-$Å^{-3}	0.688 / -0.540	0.953 / -1.253
depository no.	CCDC 1859587	CCDC 1859588

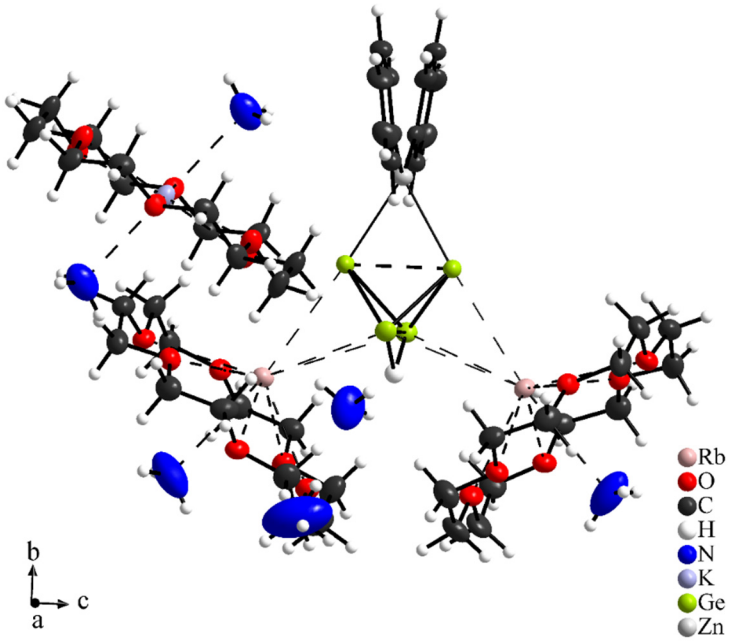

Figure S2. Section of the crystal structure of [K([18]crown-6)][Rb([18]crown-6)]$_2$[HGe$_4$ZnPh$_2$]·8 NH$_3$ (**1**) with main building groups, thermal displacement ellipsoids are drawn with 50 % probability.

Table S2. Selected interatomic distances [Å] for [K([18]crown-6)][Rb([18]crown-6)]$_2$[HGe$_4$ZnPh$_2$]·8 NH$_3$ (**1**).

atoms	distance	atoms	distance	atoms	distance
Ge1-Ge2	2.5098(5)	C21-C22	1.389(5)	Rb-N1	3.338(4)
Ge1-Ge2^{i}	2.5209(5)	C22-C23	1.370(5)	K-O7	2.794(2)
Ge1^{i}-Ge2	2.5209(5)	C23-C24	1.380(5)	K-O7^{ii}	2.794(2)
Ge1^{i}-Ge2^{i}	2.5098(5)	C24-C19	1.401(5)	K-O8	2.810(2)
Ge1-Ge1^{i}	2.8247(8)	Rb-Ge2	3.4570(5)	K-O8^{ii}	2.810(2)
Ge2-Ge2^{i}	2.6726(7)	Rb-Ge1^{i}	3.7500(6)	K-O9	2.822(2)
Ge1-H1	1.74(3)	Rb-Ge1	3.8520(6)	K-O9^{ii}	2.822(2)
Ge1^{i}-H1	1.74(3)	Rb-O1	3.011(3)	K-N2	2.921(4)
Ge2-Zn	2.5717(6)	Rb-O2	3.068(2)	K-N2^{ii}	2.921(4)
Ge2^{i}-Zn	2.5717(6)	Rb-O3	2.963(2)	N1-N4^{iii}	3.067(9)
Zn-C19	2.055(4)	Rb-O4	3.137(3)	N3-N4	3.121(8)
C19-C20	1.397(5)	Rb-O5	2.966(2)	N3-N3^{iv}	3.153(7)
C20-C21	1.387(5)	Rb-O6	3.183(2)	N4-N4^{iv}	2.973(16)

Symmetry codes: (i) –*x*+1, *y*, -*z*+1/2; (ii) -*x*, -*y*+1, -*z*; (iii) *x*+1/2, -*y*+1/2, -*z*; (iv) -*x*, *y*, -*z*+1/2.

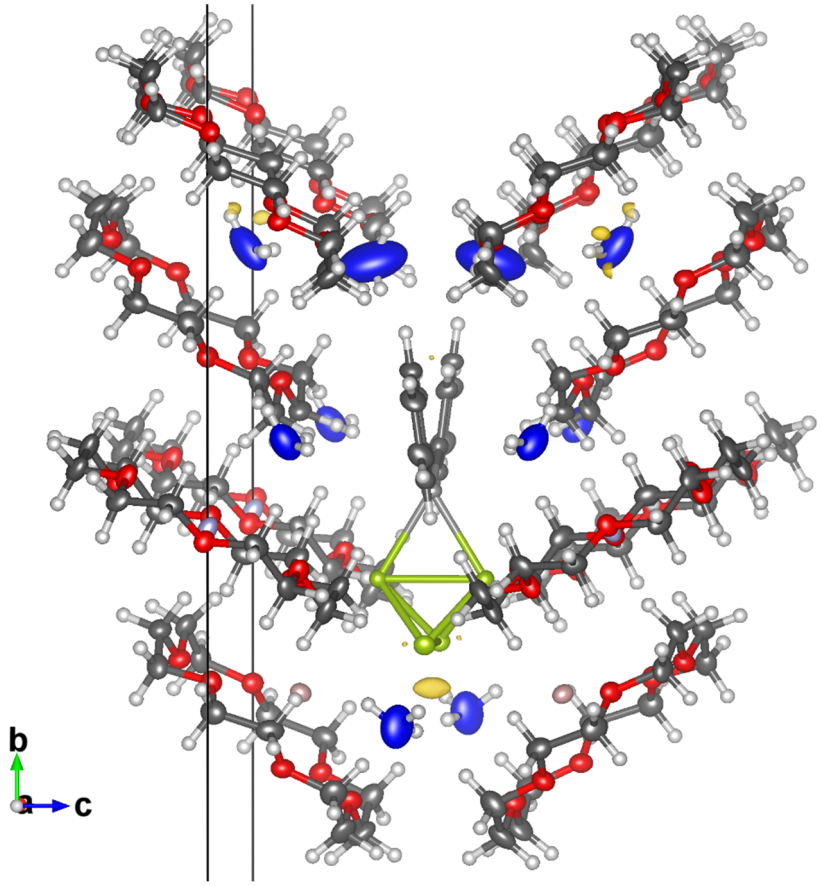

Figure S3. Illustration[11] of the residual electron density in [K([18]crown-6)][Rb([18]crown-6)]$_2$[HGe$_4$ZnPh$_2$]·8 NH$_3$ (**1**) after structure refinement without the cluster-bound H atom. Shown is a section of the crystal structure with the residual electron density higher than 0.7 e$^-$/Å^3 drawn in yellow colour. Atom colour code: Ge green, C black, H white, O red, Rb pink, K light blue, N dark blue, thermal displacement ellipsoids are drawn with 50 % probability.

Table S3. Interatomic distances [Å] if the experimental (**1**) and of the optimized structures of [HGe$_4$ZnPh$_2$]$^{3-}$ and [Ge$_4$ZnPh$_2$]$^{4-}$ and their deviation [%] compared to the experimental structure.

	1	[HGe$_4$ZnPh$_2$]$^{3-}$		[Ge$_4$ZnPh$_2$]$^{4-}$	
atoms	distance	distance	deviation	distance	deviation
Ge1-Ge2	2.5098(5)	2.51	0.0	2.54	0.8
Ge1-Ge2^i	2.5209(5)	2.52	0.0	2.54	1.2
Ge1^i-Ge2	2.5209(5)	2.52	0.0	2.54	1.2
Ge1^i-Ge2^i	2.5098(5)	2.51	0.0	2.54	0.8
Ge1-Ge1^i	2.8247(8)	2.80	0.7	2.64	6.4
Ge2-Ge2^i	2.6726(7)	2.71	1.5	2.67	0.0
Ge1-H1	1.74(3)	1.81	5.2	-	-
Ge1^i-H1	1.74(3)	1.81	5.2	-	-
Ge2-Zn	2.5717(6)	2.63	2.3	2.64	2.7
Ge2^i-Zn	2.5717(6)	2.63	2.3	2.64	2.7

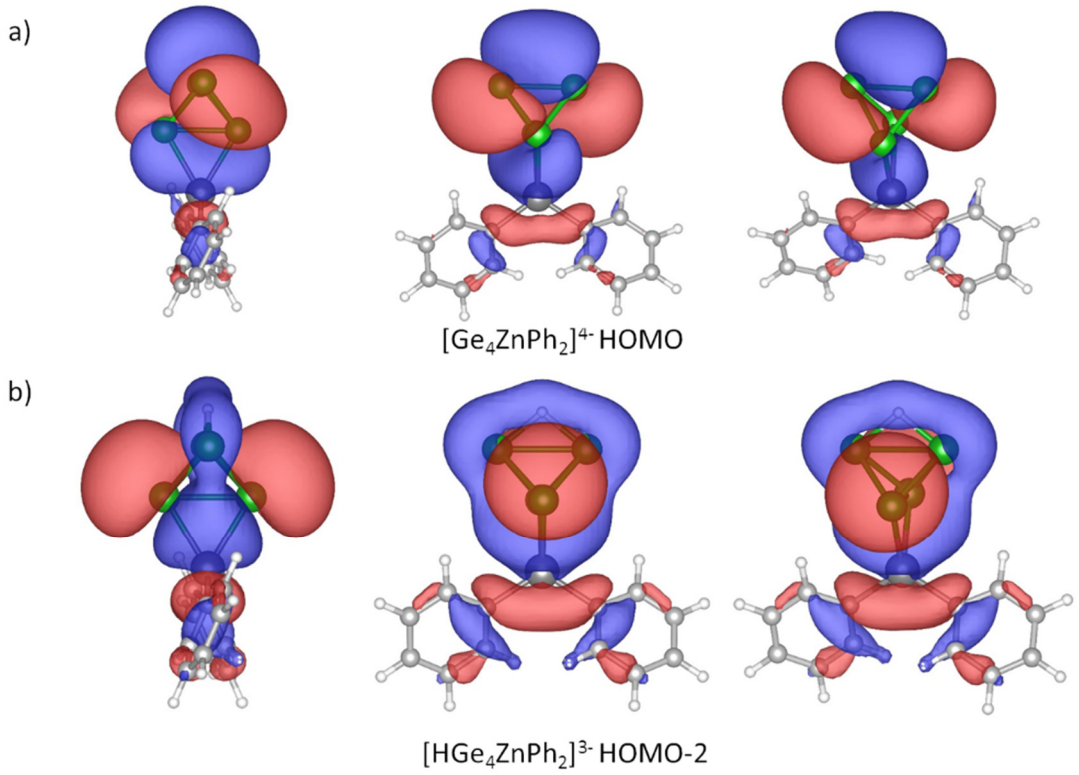

Figure S4. a) HOMO of $[Ge_4ZnPh_2]^{4-}$, which interacts with the s orbital of the proton along the Ge1-Ge1^{i} bond. b) HOMO-2 of $[HGe_4ZnPh_2]^{3-}$ including the 3c-2e bond of Ge1, Ge1^{i} and the Proton.

Table S4. (left) Starting values of the atomic coordinates for the structure optimization including an H atom bound to an apex of the tetrahedron; (right) final values after structure optimization.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ge	2.86715	1.40116	0.04662	Ge	-2.83685	-1.38520	0.03812
Ge	1.27571	-0.04048	1.35508	Ge	-1.28859	0.11092	1.33817
Zn	-0.98136	0.00007	0.00031	Zn	0.98940	0.01699	0.02852
C	-3.39103	1.76758	-0.55830	C	3.24911	-1.90224	-0.68324
H	-3.82399	0.84650	-0.94543	H	3.66076	-1.04101	-1.20720
C	-2.09725	1.74093	-0.01276	C	2.04260	-1.76587	0.02304
C	-1.63279	2.97652	0.46458	C	1.59764	-2.93515	0.65996
H	-0.63503	3.03666	0.89843	H	0.66319	-2.91153	1.21992
C	-2.38701	4.14547	0.40943	C	2.29223	-4.14073	0.60913
H	-1.98032	5.07634	0.79578	H	1.90466	-5.01592	1.12392
C	-3.66136	4.12558	-0.14438	C	3.48139	-4.22933	-0.10423
H	-4.25520	5.03258	-0.19511	H	4.02768	-5.16584	-0.15259
C	-4.16212	2.92530	-0.63205	C	3.95768	-3.09929	-0.75630
H	-5.15667	2.89219	-1.06909	H	4.88423	-3.15152	-1.32196
Ge	2.86603	-1.40185	-0.04688	Ge	-2.89335	1.41645	-0.09538
Ge	1.27542	0.04109	-1.35491	Ge	-1.25902	-0.01226	-1.36714
C	-3.39078	-1.76783	0.55895	C	3.53412	1.66269	0.31184
H	-3.82366	-0.84699	0.94670	H	3.99490	0.69305	0.49275
C	-2.09713	-1.74086	0.01313	C	2.15624	1.72802	0.04805
C	-1.63279	-2.97619	-0.46501	C	1.65858	3.02270	-0.16929
H	-0.63514	-3.03611	-0.89914	H	0.59678	3.15804	-0.37393
C	-2.38699	-4.14516	-0.41035	C	2.45830	4.16151	-0.13327
H	-1.98040	-5.07582	-0.79732	H	2.02140	5.14084	-0.30969
C	-3.66122	-4.12560	0.14377	C	3.81812	4.04837	0.12985
H	-4.25503	-5.03263	0.19413	H	4.44936	4.93067	0.16007
C	-4.16187	-2.92559	0.63222	C	4.35484	2.78755	0.35544
H	-5.15631	-2.89270	1.06952	H	5.41592	2.68131	0.56509
H	3.43914	-2.78726	-0.09359	H	-4.01598	-0.01468	-0.03870

*Crystal structure of [$K_{0.3}Rb_{0.7}$([18]crown-6)]$K_{0.2}Rb_{2.8}[Ge_9]$·4.5 NH_3 (**2**).*

Compound **2** crystallizes in the monoclinic space group *C*2/*c* with one Ge_9 cluster, one Rb/K([18]crown-6)$^+$ complex and three Rb/K^+ cations surrounded by NH_3 molecules. The Ge_9 cluster adopts nearly perfect C_{4v} symmetry and appears as a capped square antiprism with one planar square face and equal face diagonals. The Ge-Ge bond lengths are 2.7915(7)-2.8742(6) Å for the capped square and significantly shorter in a narrow range of 2.5640(6)-2.6129(6) Å for all other bonds. Seven triangular faces of the clusters are capped by cations with Rb/K-Ge distances above 3.4859(7) Å. The Ge_9 clusters are connected by free Rb/K cations and NH_3 molecules to form double layers parallel to the *bc* plane. These double layers are separated by layers of Rb/K-coordinating crown ether molecules, and the structure is clearly divided into regions of ionic and van-der-Waals interactions, respectively. Interestingly, there is no clear preference of the K and Rb cations for different chemical environments as it is found in **1**, however, at the position coordinated by the crown ether the Rb content is only 72 %, while all other sites contain Rb amounts of 88 % and higher. The structure is almost isotypic to the ones of [Rb([18]crown-6)]Rb_3Si_9·4 NH_3[12] and [Rb([18]crown-6)]$Rb_3[Si_{7.5}Ge_{1.5}]$·4 NH_3[13] with the additional finding of one NH_3 molecule in a split position, i.e. 0.5 NH_3 per formula unit.

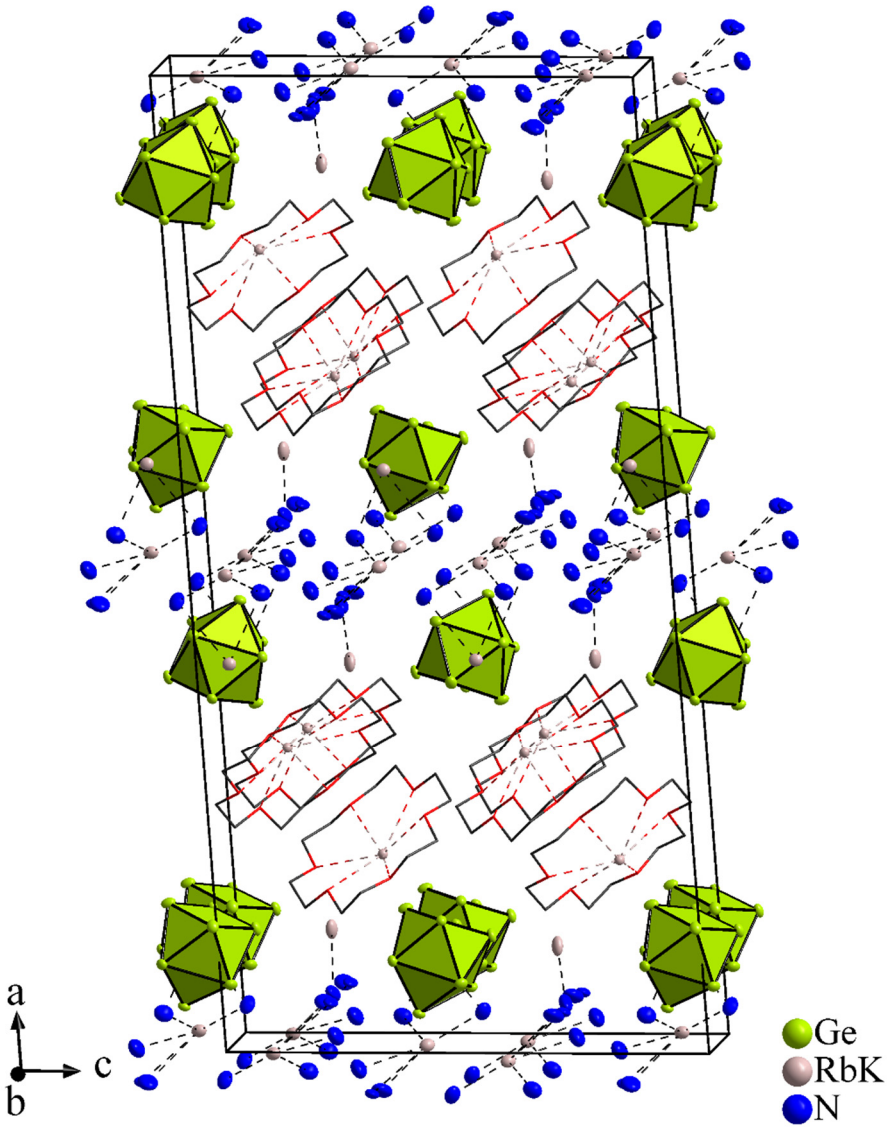

Figure S5. Extended unit cell of the crystal structure of $K_{0.3}Rb_{0.7}$([18]crown-6)]$K_{0.2}Rb_{2.8}[Ge_9]$·4.5 NH_3 (**2**). The displacement ellipsoids are shown with 50 % probability, crown ether molecules are drawn schematically, Ge_9 clusters as green polyhedra, H atoms are omitted for clarity.

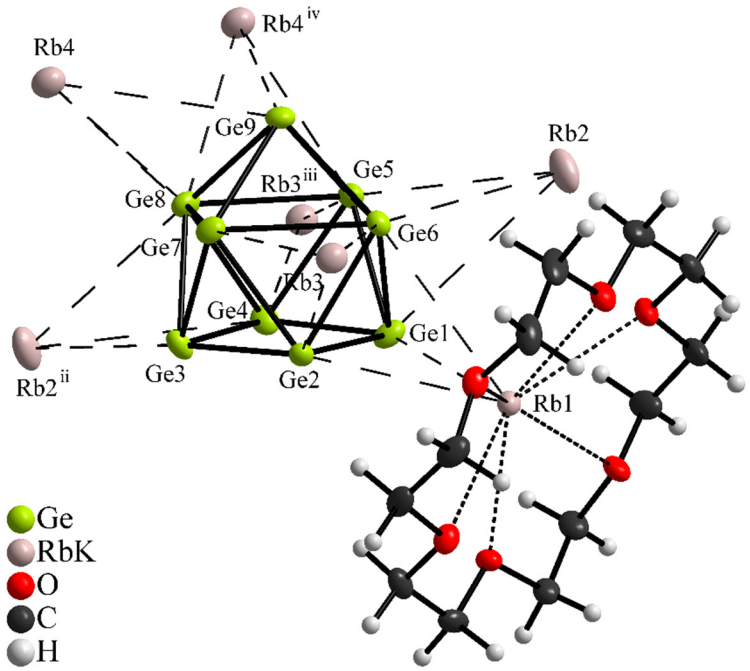

Figure S6. Ge_9 cluster environment by alkali metal cations in $K_{0.3}Rb_{0.7}$([18]crown-6)]$K_{0.2}Rb_{2.8}[Ge_9]\cdot 4.5\ NH_3$ (**2**). Displacement ellipsoids are drawn with 50 % probability, dashed bonds indicate Ge-Rb/K distances between 3.48 Å and 4.07 Å. Symmetry codes: (i) *-x*, *-y*+1, *-z*+1; (ii) *x*, *-y*, *z*+1/2; (iii) *x*, *y*-1, *z*; (iv) *-x*, *-y*, *-z*+1.

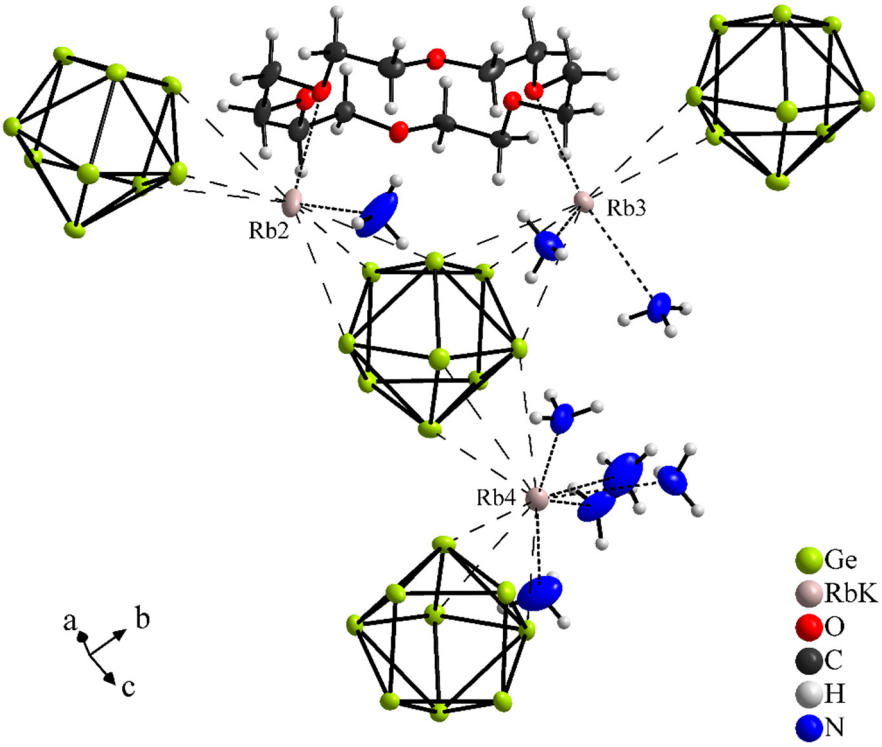

Figure S7. Environment of the non-sequestered alkali metal cations in $K_{0.3}Rb_{0.7}$([18]crown-6)]$K_{0.2}Rb_{2.8}[Ge_9]\cdot 4.5\ NH_3$ (**2**). Displacement ellipsoids are drawn with 50 % probability, dashed bonds indicate Ge-Rb/K distances between 3.48 Å and 4.07 Å.

Table S5. Selected interatomic distances [Å] for $[K_{0.3}Rb_{0.7}([18]crown\text{-}6)]K_{0.2}Rb_{2.8}[Ge_9]\cdot 4.5\ NH_3$ (**2**).

atoms	distance	atoms	distance	atoms	distance	atoms	distance
Ge1-Ge2	2.6129(6)	Ge6-Ge7	2.8742(6)	Ge5-Rb/K2	3.7365(7)	Rb/K1-O4	3.034(3)
Ge2-Ge3	2.5640(6)	Ge7-Ge8	2.7926(6)	Ge5-Rb/K3^{iii}	3.7802(6)	Rb/K1-O5	2.907(3)
Ge3-Ge4	2.5676(6)	Ge8-Ge5	2.8263(7)	Ge6-Rb/K3	3.7163(6)	Rb/K1-O6	2.912(3)
Ge4-Ge1	2.5825(7)	Ge5-Ge9	2.5872(6)	Ge6-Rb/K2	3.7274(6)	Rb/K2-N1	2.977(4)
Ge1-Ge3	3.5962(7)	Ge6-Ge9	2.5705(6)	Ge6-Rb/K1	3.8262(6)	Rb/K2-O1	3.160(3)
Ge2-Ge4	3.7043(6)	Ge7-Ge9	2.5728(6)	Ge7-Rb/K3	3.7678(6)	Rb/K3-N3	3.095(4)
Ge1-Ge5	2.5869(6)	Ge8-Ge9	2.5966(6)	Ge7-Rb/K4	3.8644(6)	Rb/K3-O5	3.200(3)
Ge1-Ge6	2.5888(6)	Ge1-Rb/K1	3.4915(6)	Ge8-Rb/K4	3.4859(7)	Rb/K3-N2	3.208(4)
Ge2-Ge6	2.5833(6)	Ge1-Rb/K2	4.0334(7)	Ge8-Rb/K4^{iv}	3.6317(7)	Rb/K4-N4a	3.033(10)
Ge2-Ge7	2.5968(6)	Ge2-Rb/K1	3.6302(6)	Ge8-Rb/K2^{ii}	3.8553(7)	Rb/K4-N2^{i}	3.043(4)
Ge3-Ge7	2.5891(6)	Ge2-Rb/K3	3.6713(6)	Ge9-Rb/K4^{iv}	3.6754(6)	Rb/K4-N4b	3.119(12)
Ge3-Ge8	2.5993(6)	Ge3-Rb/K2^{ii}	3.5308(6)	Ge9-Rb/K4	3.9606(7)	Rb/K4-N5	3.123(10)
Ge4-Ge8	2.5665(6)	Ge4-Rb/K3^{iii}	3.5876(6)	Rb/K1-O1	2.980(3)	Rb/K4-N3^{i}	3.222(4)
Ge4-Ge5	2.6066(6)	Ge4-Rb/K2^{ii}	4.0641(7)	Rb/K1-O2	2.952(3)	Rb/K3-Rb/K4	4.1990(6)
Ge5-Ge6	2.7915(6)	Ge5-Rb/K4^{iv}	3.7171(6)	Rb/K1-O3	2.849(3)	Rb/K4-Rb/K4	4.7490(6)

Symmetry codes: (i) -*x*, -*y*+1, -*z*+1; (ii) *x*, -*y*, *z*+1/2; (iii) *x*, *y*-1, *z*; (iv) -*x*, -*y*, -*z*+1.

Table S6. Fractional site occupations of the cations in **2**.

atoms	occupation	atoms	occupation
Rb1	0.722(3)	K1	0.278(3)
Rb2	0.990(3)	K2	0.010(3)
Rb3	0.951(3)	K3	0.049(3)
Rb4	0.883(3)	K4	0.117(3)

Table S7. Geometric parameters of E_9 clusters in **2** and isotypic and other related compounds.

compound	*SE* [a]	h_2/h_1 [b]	h_3/h_1 [b]	d_2/d_1 [c]	α [d]/°	γ [e]/°	point group	reference
2	22	1.00	1.29	1.03	2.5	24.4	C_{4v}	this work
$[Rb([18]crown\text{-}6)]\ Rb_3[Si_9]\cdot 4\ NH_3$	22	1.02	1.31	1.01	1.1	22.0	C_{4v}	[12]
$[Rb([18]crown\text{-}6)]\ Rb_3[Si_{7.5}Ge_{1.5}]\cdot 4\ NH_3$	22	1.03	1.32	1.02	1.2	22.5	C_{4v}	[13]
$K_4Ge_9\cdot 9\ NH_3$	22	1.04	1.30	1.00	0.0	21.5	C_{4v}	[14]
$K_5Ge_9(OH)\cdot 11\ NH_3$	22	1.00	1.27	1.03	2.5	12.3	C_{4v}	[15]
$[K_{0.8}Rb_{3.2}]Si_9\cdot 5\ NH_3$	22	1.01	1.28	1.04	2.6	20.5	C_{4v}	[16]
$Rb_4Si_9\cdot 5\ NH_3$	22	1.01	1.27	1.05	3.2	26.6	C_{4v}	[2]

a) *SE*: skeleton electrons; b) h_1, h_2, h_3: heights of the best trigonal prism in the [E_9] cluster; c) d_1, d_2: diagonals of the most planar square face; d) α: dihedral angle of the two halves of the most planar square face; e) γ: deviation from coplanarity of opposed triangular faces of the best trigonal prism.

References

[1] (*a*) P. R. Markies, G. Schat, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets, A. L Spek, *Organometallics* 1990, **9**, 2243-2247; (*b*) K. Schwetlick, *Organikum*, 23. Auflage, Wiley-VCH Verlag, Weinheim, 2009; (*c*) N. I. Sheverdina, I. E. Paleeva, N. A. Zaitseva, K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR* 1964, **155**, 623.

[2] M. Waibel, F. Kraus, S. Scharfe, B. Wahl, T. F. Fässler, *Angew. Chem.* 2010, **122**, 6761; *Angew. Chem. Int. Ed.* 2010, **49**, 6611.

[3] C. Hoch, M. Wendorff, C. Röhr, *J. Alloys Compd.* 2003, **361**, 206.

[4] CrysAlis CCD and CrysAlis RED, version 1.171.33.34d. Oxford Diffraction, Yarnton, Oxfordshire, England, 2009.

[5] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.

[6] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, **71**, 3.

[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009).

[8] (*a*) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865; (*b*) C. Adamo, V. Barone, *J. Chem. Phys.* 1999, **110**, 6158.

[9] (*a*) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* 1998, **294**, 143; (*b*) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.

[10] V. Barone, M. J. Cossi, *J. Phys. Chem. A* 1998, **102**, 1995.

[11] K. Momma, F. Izumi, *J. Appl. Crystallogr.* 2011, **44**, 1272.

[12] S. Joseph, C. Suchentrunk, F. Kraus, N. Korber, *Eur. J. Inorg. Chem.* 2009, **2009**, 4641.

[13] M. Waibel, C. B. Benda, B. Wahl, T. F. Fässler, *Chem. Eur. J.* 2011, **17**, 12928.

[14] C. Suchentrunk, J. Daniels, M. Somer, W. Carrillo-Cabrera, N. Korber, *Z. Naturforsch.* 2005, **60b**, 277.

[15] C. B. Benda, H. He, W. Klein, M. Somer, T. F. Fässler, *Z. Anorg. Allg. Chem.* 2015, **641**, 1080.

[16] T. Henneberger, W. Klein, T. F. Fässler, *Z. Anorg. Allg. Chem.* 2018, **644**, 1018.