Intermediates and Products of the Reaction of Zn(II) Organyls with Tetrel Element *Zintl* Ions: Cluster Extension *versus* Complexation

C. Wallach, K. Mayer, T. Henneberger, W. Klein, T.F. Fässler

Technische Universität München, Department Chemie,
Lichtenbergstraße 4, 85747 Garching, Germany

Supporting Information

Table S1: Crystallographic details for compounds **1** – **8.**

Compound	**1**	**2**	**3**	**4**
formula unit	$C_{40}H_{88}N_6O_{12}K_2Ge_4Zn_2$	$H_{18}N_6K_6Sn_8Zn$	$C_{56}H_{135.2}N_{13.4}O_{18}K_3Ge_9Zn$	$C_{32}H_{99}N_{13}O_{12}K_2Zn_5$
fw [g·mol^{-1}]	1344.46	1522.03	2120.64	1263.29
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.8577(4)	9.6916(6)	14.6139(7)	11.554(2)
b [Å]	14.5738(5)	12.2418(7)	14.9181(6)	14.140(3)
c [Å]	18.8964(7)	18.6684(8)	23.6002(8)	18.988(4)
α [°]	80.349(3)	99.120(4)	97.552(3)	89.02(3)
β [°]	74.590(3)	90.067(4)	91.645(3)	77.37(3)
γ [°]	69.598(3)	94.894(5)	117.312(3)	87.11(3)
V [Å^3]	2940.45(2)	2178.7(2)	4508.7(3)	3023.2(1)
Z	2	2	2	2
T [K]	150(2)	120(2)	150(2)	150(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g·cm^{-3}]	1.518	2.320	1.562	1.388
μ [mm^{-1}]	3.017	5.635	3.416	2.148
collected reflections	80187	50041	93046	69261
independent reflections	11534	8378	17700	11852
R_{int} / R_δ	0.0515/0.247	0.0912/0.0626	0.0891/0.0574	0.0192/0.114
parameters / restraints	597/12	289/0	913/0	611/12
R_1 [$I > 2\,\sigma(I)$ / all data]	0.0304/0.0396	0.0322/0.0494	0.0509/0.0793	0.0267/0.0340
wR_2 [$I > 2\,\sigma(I)$ / all data]	0.0704/0.0761	0.0667/0.0694	0.1210/0.1374	0.0613/0.0668
goodness of fit	1.062	0.919	1.022	1.104
max./min. diff. el. density [e·Å^{-3}]	2.262/-1.382	1.311/-0.935	1.012/-0.880	0.768/-0.572
depository no.	CCDC 1982121	CSD 1982122	CCDC 1982123	CCDC 1982124

Compound	**5**	**6**	**7**	**8**
formula unit	$C_{48}H_{96}N_{10}O_{12}K_2Zn_2$	$C_{30}H_{39}O_6K_{0.84}Rb_{0.16}Zn$	$C_{47}H_{76}NO_8KZn$	$C_{22}H_{45}N_2O_6K$
fw [g·mol^{-1}]	1214.28	607.38	887.55	472.70
space group	$P\bar{1}$	$Pca2_1$	$P2_1/c$	$Pbca$
a [Å]	11.963(5)	21.842(2)	15.7570(5)	10.1910(2)
b [Å]	12.328(5)	7.2588(15)	13.1722(5)	16.1458(3)
c [Å]	12.683(6)	18.322(3)	23.6712(8)	32.8773(9)
α [°]	107.43(4)	90	90	90
β [°]	106.66(4)	90	94.486(3)	90
γ [°]	104.16(3)	90	90	90
V [Å^3]	1594.0(1)	2904.9(8)	4898.0(3)	5409.7(2)
Z	1	4	4	8
T [K]	120(2)	120(2)	120(2)	150(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g·cm^{-3}]	1.265	1.389	1.204	1.161
μ [mm^{-1}]	0.942	1.269	0.635	0.231
collected reflections	16857	30260	55312	148069
independent reflections	6272	5705	9472	5311
R_{int} / R_δ	0.0828/0.1765	0.1990/0.3101	0.0706/0.1068	0.0382/0.0115
parameters / restraints	344/0	343/72	552/0	295/0
R_1 [$I > 2\,\sigma(I)$ / all data]	0.0510/0.1097	0.0540/ 0.1647	0.0455/0.0950	0.0353/0.0422
wR_2 [$I > 2\,\sigma(I)$ / all data]	0.1003/0.1106	0.0902/ 0.1059	0.1018/0.1107	0.0939/0.0987
goodness of fit	0.768	0.655	0.840	1.021
max./min. diff. el. density [e·Å^{-3}]	0.913/-0.608	0.826/-0.486	0.659/-0.489	0.354/-0.313
CCDC	CCDC 1982125	CCDC 1982126	CCDC 1982127	CCDC 1982128

Crystal structures of 1 – 8 and selected bond lengths of 1a – 8a

$[K([2.2.2]crypt)]_2[(ZnEt)_2(\eta^3,\eta^3\text{-}Ge_4)]\cdot 2\ NH_3$ (**1**)

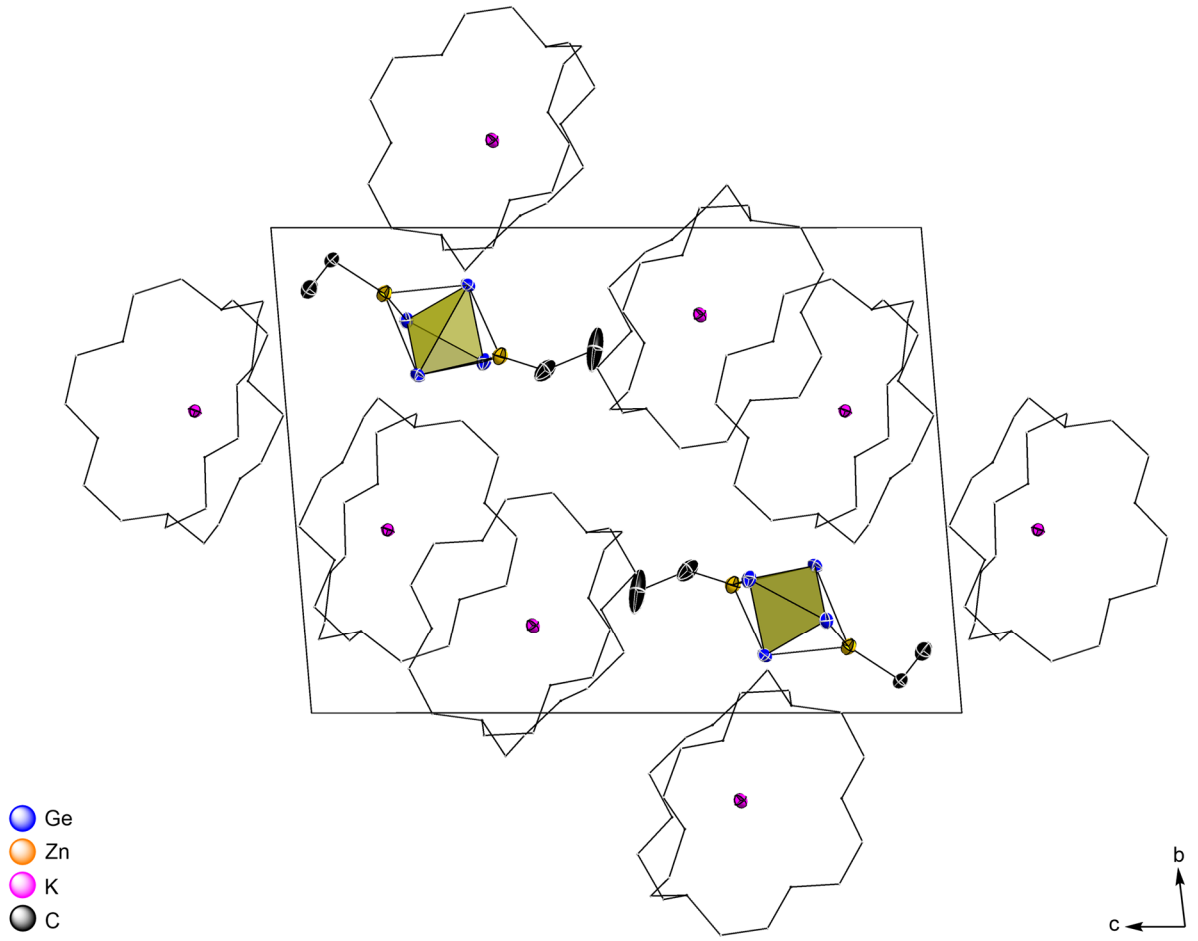

Figure S1: Crystal structure of compound **1**, view along [$\bar{1}$00]. All ellipsoids are shown at a 50 % probability level as octants. Color code: Ge: blue; Zn: orange; K: purple; C: black. The clusters are shown as polyhedra. Ammonia molecules as well as protons are omitted. Cryptand molecules are presented as wire/stick for clarity.

Table S2: Selected bond lengths in **1**.

Atoms	Bond lengths [Å]	Atoms	Bond lengths [Å]
Ge1 – Ge2	2.9279(4)	Ge3 – Ge4	2.4714(4)
Ge1 – Ge3	2.5859(4)	Ge1 – Ge4	2.5970(4)
Ge2 – Ge3	2.5976(4)	Ge2 – Ge4	2.6046(4)
Ge1 – Zn1	2.5159(4)	Ge1 – Zn2	2.5267(4)
Ge2 – Zn1	2.5177(4)	Ge2 – Zn2	2.5134(4)
Ge3 – Zn1	2.7096(5)	Ge4 – Zn2	2.6822(5)
Zn1 – C37	2.009(3)	Zn2 – C39	2.004(3)
C37 – C38	1.534(4)	C39 – C40	1.523(6)

$[K]_6[(\eta^2\text{-}Sn_4)Zn(\eta^2\text{-}Sn_4)]\cdot 16\ NH_3$ (**2**)

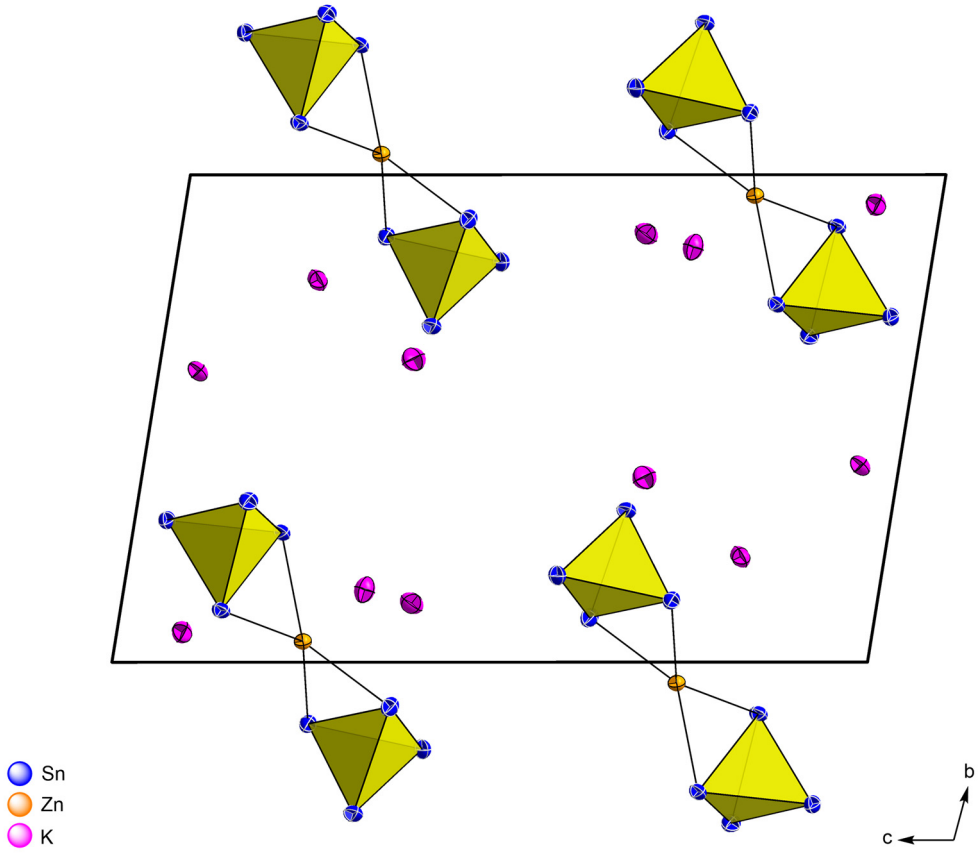

Figure S2: Crystal structure of compound **2**, view along [$\bar{1}$00]. All ellipsoids are shown at a 50 % probability level. Color code: Sn: blue; Zn: orange; K: purple. The clusters are shown as polyhedra. Ammonia molecules are omitted for clarity.

Table S3**:** Selected bond lengths in **2**.

Atoms	Bond lengths [Å]	Atoms	Bond lengths [Å]
Zn1 – Sn1	2.7450(8)	Zn1 – Sn5	2.7512(8)
Zn1 – Sn2	2.7611(8)	Zn1 – Sn6	2.7258(8)
Sn1 – Sn2	3.0785(6)	Sn5 – Sn6	3.0723(6)
Sn1 – Sn3	2.9038(6)	Sn5 – Sn7	2.8964(6)
Sn1 – Sn4	2.9071(6)	Sn5 – Sn8	2.9033(6)
Sn2 – Sn3	2.9100(6)	Sn6 – Sn7	2.8998(6)
Sn2 – Sn4	2.8904(6)	Sn6 – Sn8	2.8827(6)
Sn3 – Sn4	2.9492(6)	Sn7 – Sn8	2.9402(6)

[K([2.2.2]crypt)]$_3$[(η^4-Ge$_9$)(ZnEt)]·8 NH$_3$ (**3**)

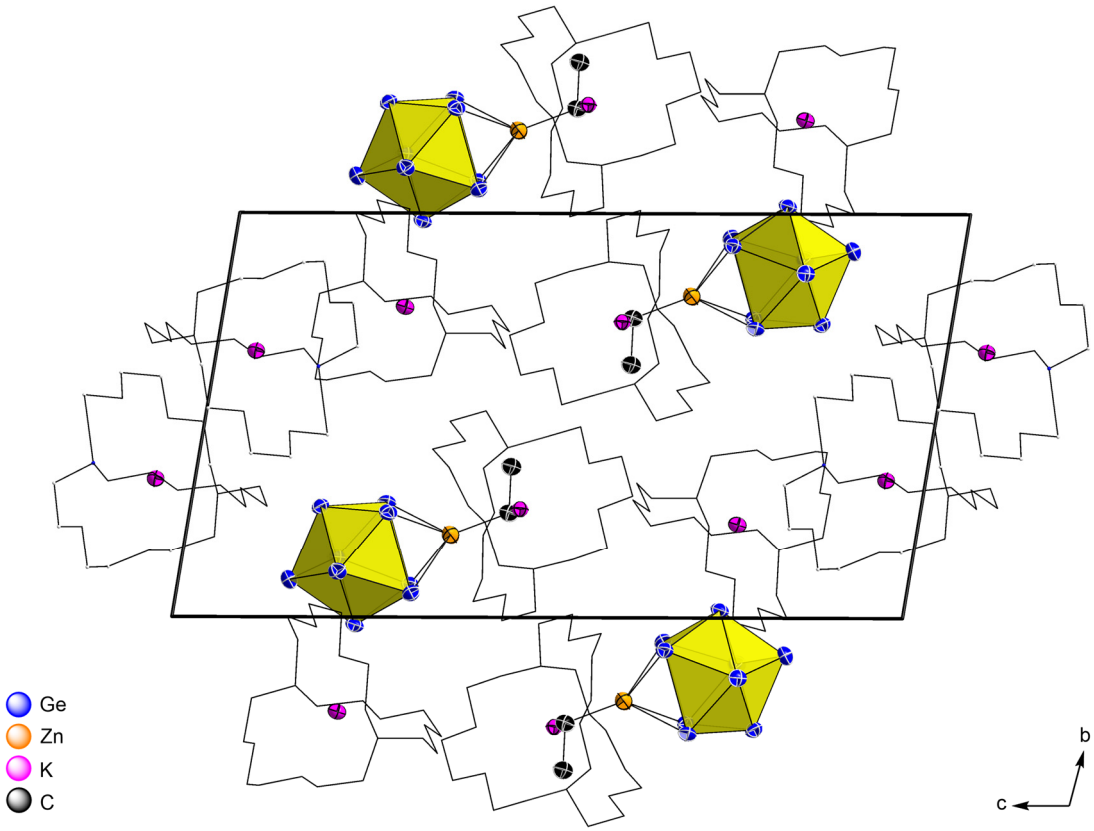

Figure S3: Crystal structure of compound **3**, view along [$\bar{1}$00]. All ellipsoids are shown at a 50 % probability level. Color code: Ge: blue; Zn: orange; K: purple; C: black. The clusters are shown as polyhedra. Ammonia molecules as well as protons are omitted, cryptand molecules are presented as wire/stick for clarity.

Table S4: Selected bond lengths in **3**.

Atoms	Bond lengths [Å]	Atoms	Bond lengths [Å]
Ge1–Zn	2.6437(9)	Ge5–Ge9	2.5813(8)
Ge2–Zn	2.6001(8)	Ge6–Ge9	2.6001(8)
Ge3–Zn	2.5921(9)	Ge7–Ge9	2.5645(8)
Ge4–Zn	2.6105(8)	Ge8–Ge9	2.5733(8)
Ge1–Ge2	2.7643(8)	Ge5–Ge6	2.8036(8)
Ge2–Ge3	2.7962(8)	Ge6–Ge7	2.8131(8)
Ge3–Ge4	2.7868(8)	Ge7–Ge8	2.8612(8)
Ge4–Ge1	2.7493(8)	Ge8–Ge5	2.8465(8)
Ge1–Ge5	2.5590(7)	Ge3–Ge7	2.5591(7)
Ge1–Ge6	2.5717(7)	Ge3–Ge8	2.5494(7)
Ge2–Ge6	2.5692(7)	Ge4–Ge5	2.5742(7)
Ge2–Ge7	2.5478(7)	Ge4–Ge8	2.5590(8)
Zn–C1	2.015(5)	C1–C2	1.515(7)

$[K(18\text{-crown-}6)]_2[(ZnPh_2)_2(\mu_2\text{-}NH_2)_2]\cdot 8\ NH_3$ (**4**)

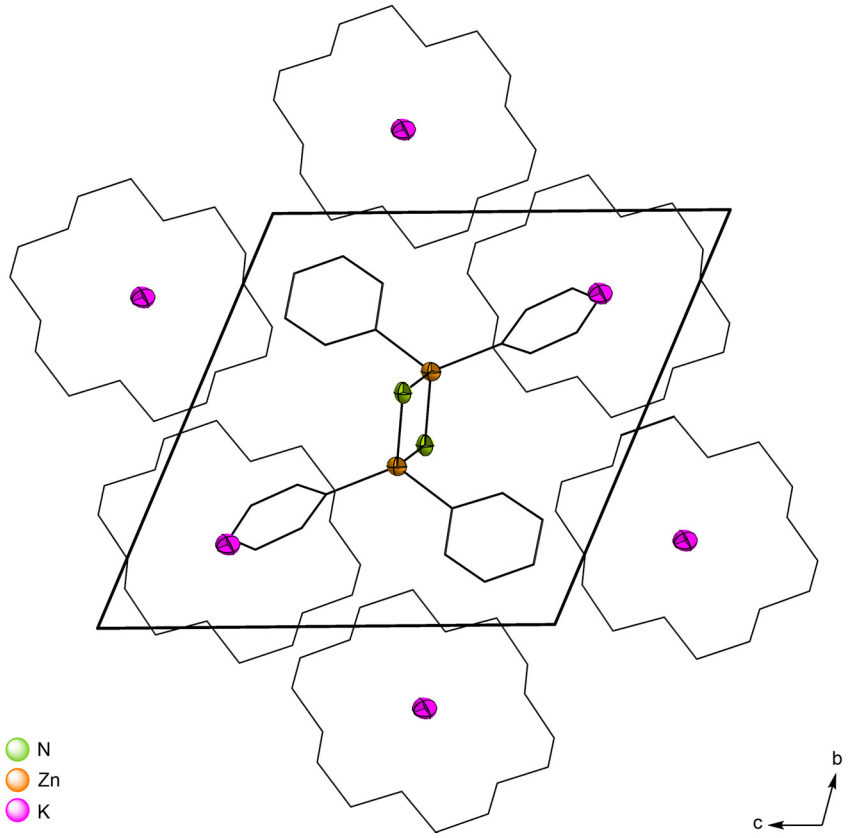

Figure S4: Crystal structure of compound **4**, view along [$\bar{1}$00]. All ellipsoids are shown at a 50 % probability level. Color code: N: green; Zn: orange; K: purple. Ammonia molecules as well as protons are omitted, crown ether molecules as well as phenyl groups are presented as wire/stick for clarity.

Table S5: Selected bond lengths in **4** (Symmetry operation: i: - (1-x), (1-y), (1-z)).

Atoms	Bond lengths [Å]
Zn–N	2.104(4)
Zn–N^i	2.045(4)
Zn–C13	2.046(4)
Zn–C19	2.034(4)

$[K(18\text{-crown-}6)]_2\{[Zn(\mu_2\text{-}NH_2)_4][(ZnEt)_2(\mu_2\text{-}NH_2)_2]_2\}\cdot 5\ NH_3$ (**5**)

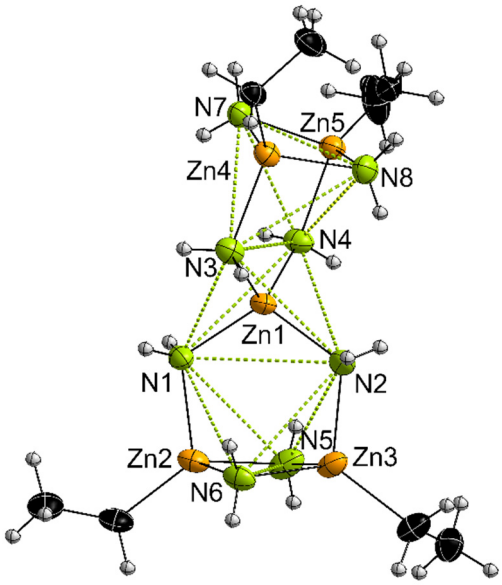

Figure S5: Molecular structure of the pentanuclear Zn complex **5a**. All ellipsoids are shown at a 50 % probability level. Color code: Zn: orange; N: light blue; C: black; H: grey.

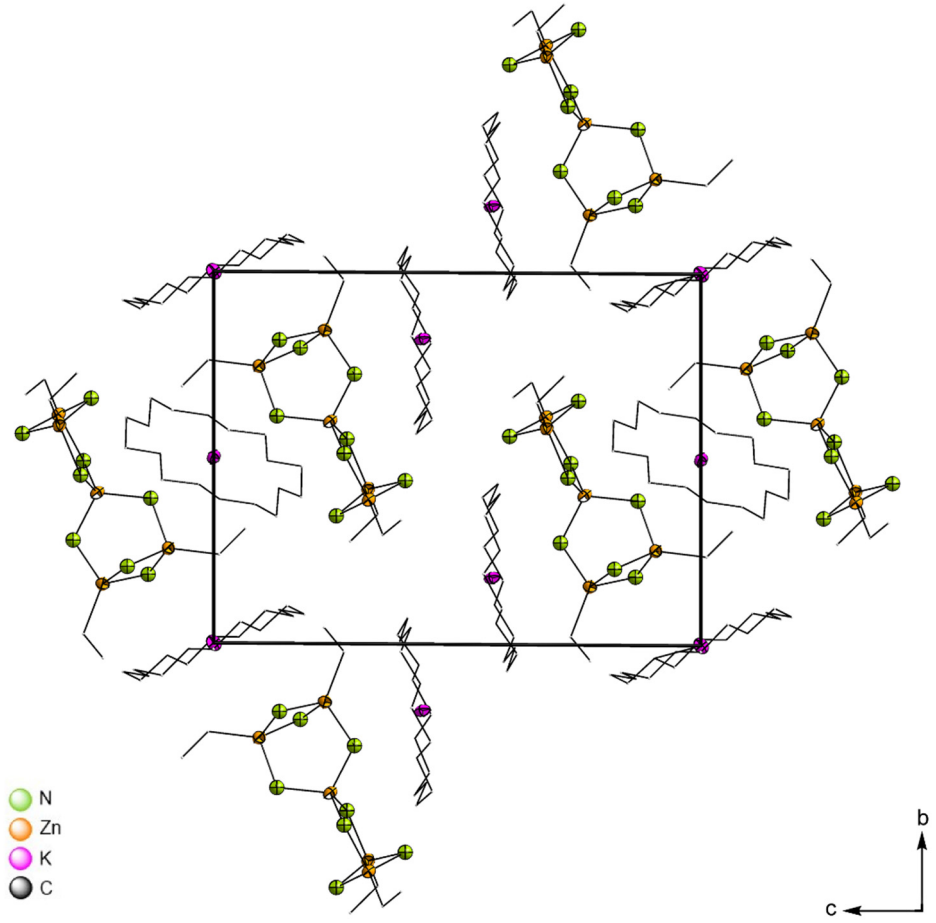

Figure S6: Crystal structure of compound **5**, view along [$\bar{1}$00]. All ellipsoids are shown at a 50 % probability level. Color code: N: green; Zn: orange; K: purple. Ammonia molecules as well as protons are omitted, crown ether molecules as well as ethyl groups are presented as wire/stick for clarity.

Table S6: Selected bond lengths in **5**.

Atoms	Bond lengths [Å]	Atoms	Bond lengths [Å]
Zn1 – N1	2.0550(2)	Zn1 – N3	2.042(2)
Zn1 – N2	2.038(2)	Zn1 – N4	2.052(2)
Zn2 – N1	2.0649(2)	Zn4 – N3	2.081(2)
Zn2 – N5	2.060(2)	Zn4 – N7	2.080(2)
Zn2 – N6	2.089(2)	Zn4 – N8	2.075(2)
Zn3 – N2	2.077(2)	Zn5 – N4	2.063(2)
Zn3 – N5	2.075(2)	Zn5 – N7	2.0778(2)
Zn3 – N6	2.080(2)	Zn5 – N8	2.084(2)
Zn2 – C25	2.052(3)	C25 – C26	1.534(4)
Zn3 – C27	2.047(2)	C27 – C28	1.580(3)
Zn4 – C29	2.031(2)	C29 – C30	1.515(4)
Zn5 – C31	2.039(2)	C31 – C32	1.534(3)

$[K_{0.8}Rb_{0.2}(18\text{-crown-6})][ZnPh_3]$ (**6**)

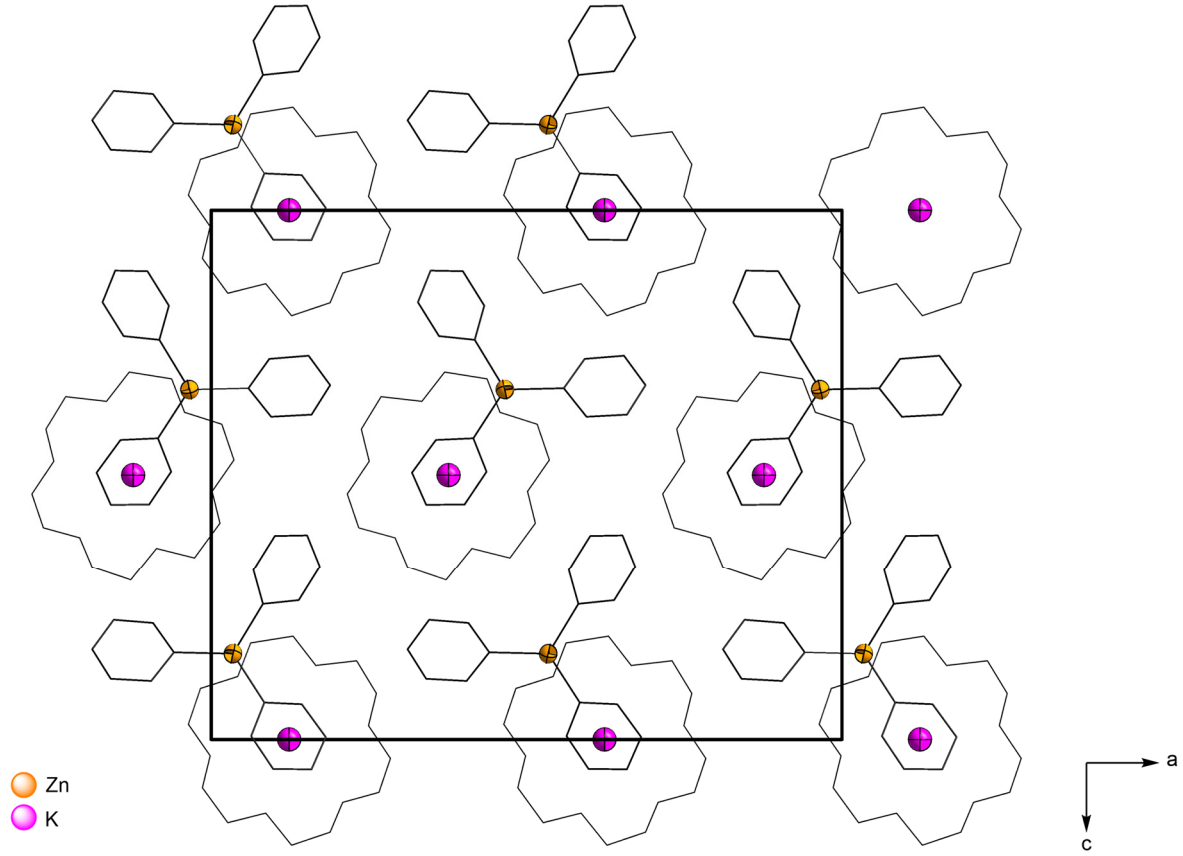

Figure S7: Crystal structure of compound **6**, view along [0$\bar{1}$0]. All ellipsoids are shown at a 50 % probability level. Color code: Zn: orange; K/Rb: purple; C: black. Protons are omitted, crown ether molecules as well as phenyl groups are presented as wire/stick for clarity.

Table S7: Selected bond lengths in **6**.

Atoms	Bond lengths [Å]
Zn–C13	2.013(1)
Zn–C19	2.018(2)
Zn–C25	2.030(8)
C16–C17	1.343(2) (shortest C–C)
C13–C14	1.420(2) (longest C–C)

[K(18-crown-6)][$ZnMes_3$]·NH_3·2 thf (**7**)

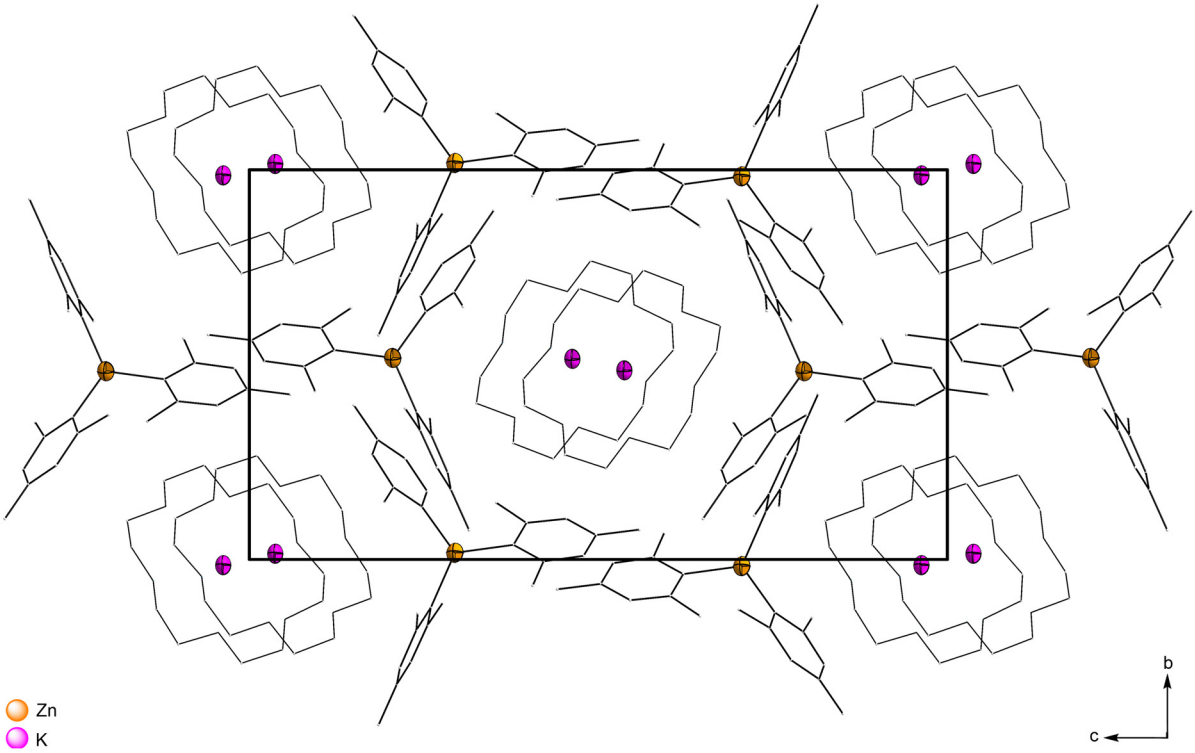

Figure S8: Crystal structure of compound **7**, view along [$\bar{1}$00]. All ellipsoids are shown at a 50 % probability level. Color code: Zn: orange; K: purple; C: black. Protons, NH_3 as well as thf molecules are omitted, crown ether molecules as well as mesityl groups are presented as wire/stick for clarity.

Table S8: Selected bond lengths in **7**.

Atoms	Bond lengths [Å]
Zn–C13	2.041(3)
Zn–C22	2.042(3)
Zn–C31	2.047(3)
C33–C34	1.382(4) (shortest C–C)
C25 C29	1.521(4) (longest C–C)

[K(18-crown-6)][Cp*]·2 NH_3 (**8**)

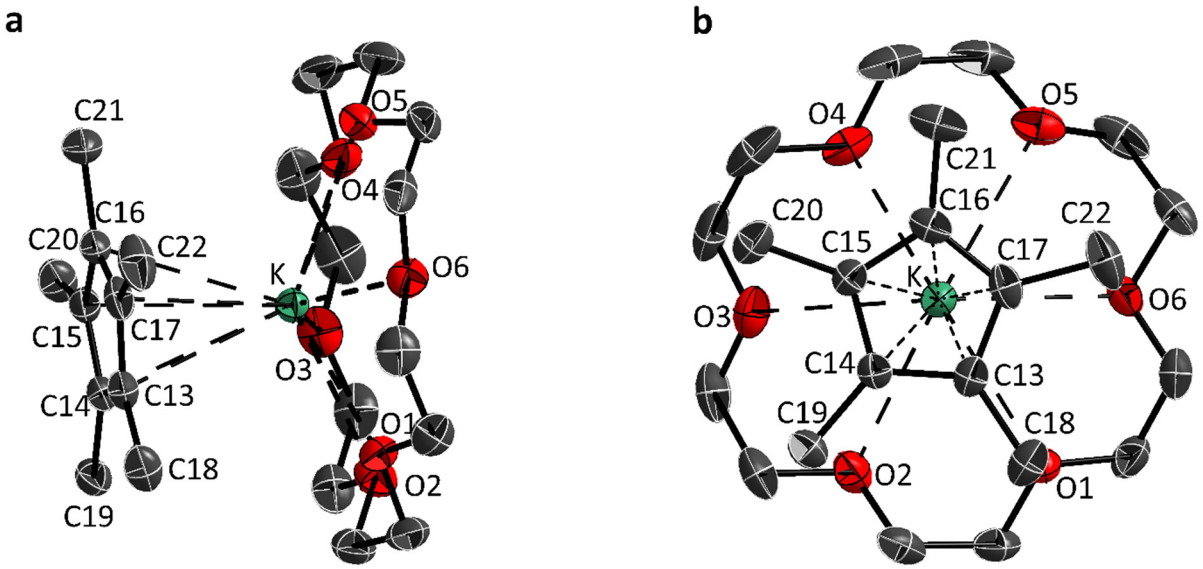

Figure S9: Molecular structure of **8a** in a) side view and b) top view. All ellipsoids are shown at a 50 % probability level. C: black; K: purple; O: red. Ammonia molecules as well as protons are omitted.

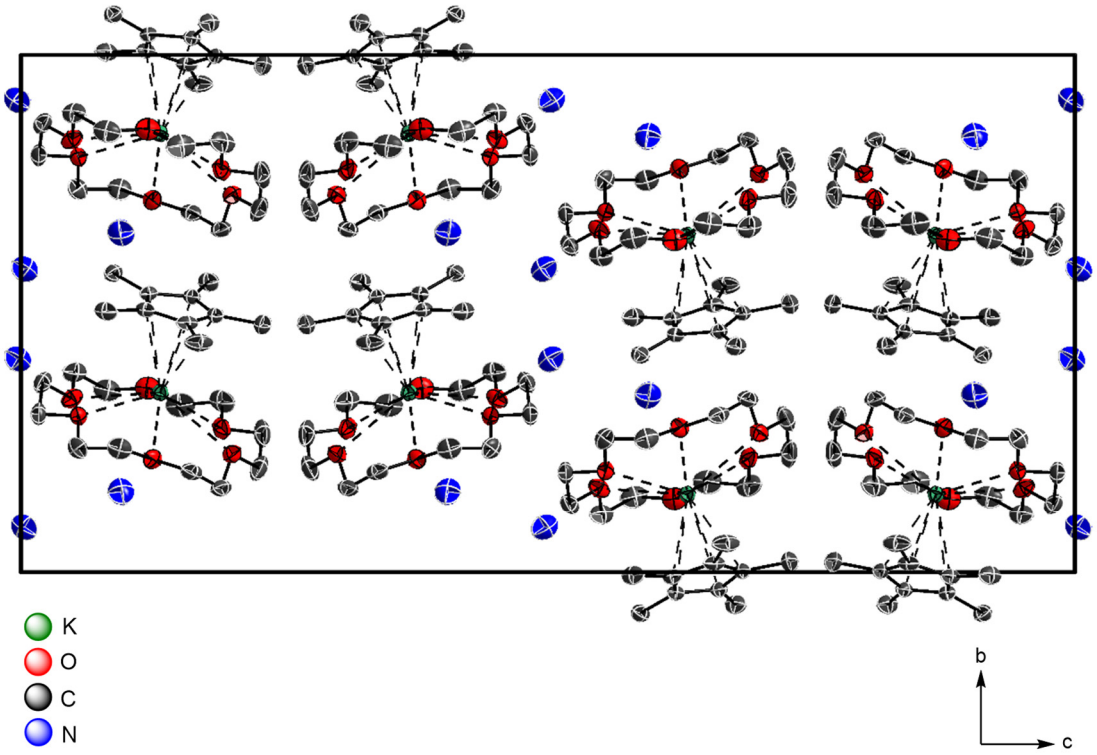

Figure S10: Crystal structure of compound **8**, view along [100]. All ellipsoids are shown at a 50 % probability level. Color code: K: green; C: black; O: red; N blue. Protons are omitted for clarity.

Table S9: Selected bond lengths in **8**.

Atoms	Bond lengths [Å]	Atoms	Bond lengths [Å]
K–O1	2.9647(10)	C13–C14	1.415(2)
K–O2	3.1146(11)	C14–C15	1.415(2)
K–O3	2.9132(12)	C15–C16	1.407(2)
K–O4	2.8872(11)	C16–C17	1.413(2)
K–O5	3.0673(11)	C17–C13	1.412(2)
K–O6	2.9768(11)	C13–C18	1.505(2)
K–C13	3.0278(13)	C14–C19	1.506(2)
K–C14	3.1194(13)	C15–C20	1.507(2)
K–C15	3.1531(13)	C16–C21	1.506(2)
K–C16	3.0744(14)	C17–C22	1.504(2)
K–C17	2.9941(14)		

ESI-MS spectra

ESI-MS analyses were performed on a Bruker Daltronic HCT mass spectrometer (dry gas temperature: 300 °C; injection speed: 240 µL/h), and the data evaluation was carried out using the Bruker Compass Data Analysis 4.0 SP 5 program (Bruker). Data evaluation was performed using OriginPro2016G (Origin Lab) and Excel 2016 (Microsoft). The sample preparation was as follows:

Reaction for anion **1a**: Onto a mixture of K_4Ge_4 (35 mg, 80 µmol, 1 eq.), $ZnEt_2$ (160 µL, 160 µmol, 2 eq.) and [2.2.2]crypt (53.1 mg, 140 µmol, 1.8 eq.) 2 mL of liquid ammonia are condensed.

Reaction for anion **3a**: Onto a mixture of K_4Ge_9 (40 mg, 50 µmol, 1 eq.), $ZnEt_2$ (100 µL, 100 µmol, 2 eq.) and [2.2.2]crypt (33.5 mg, 90 µmol, 1.8 eq.) 2 mL of liquid ammonia are condensed.

After the addition of ammonia, the obtained dark red solutions were stirred at -78 °C for 4 h using a glass stirring bar and subsequently stored in a freezer at -40 °C for 2 weeks. Afterwards, the solvent was evaporated, the residue extracted with acetonitrile (1 mL), and the obtained solution was injected into the measuring device after filtration. Due to slow molecular dynamics at -40 °C product formation is a long lasting process and signal-to-noise ratios of such ESI-MS measurements are usually low. However, signals at *m/z* 802.0 $\{[K([2.2.2]crypt)][Ge_4(ZnEt)]\}^-$ (ionization product of **1a**, negative-ion mode, 2500 V, 300 °C) and *m/z* 746.2 for $[Ge_9(ZnEt)]^-$ (**3a**, negative-ion mode, 2500 V, 300 °C) could be detected and are in good accordance to the theoretical isotope distribution (black bars in Figures 1 and S11). Sn-containing samples could not be measured due to their high instability which led to an immediate metal mirror formation in the injection needle.

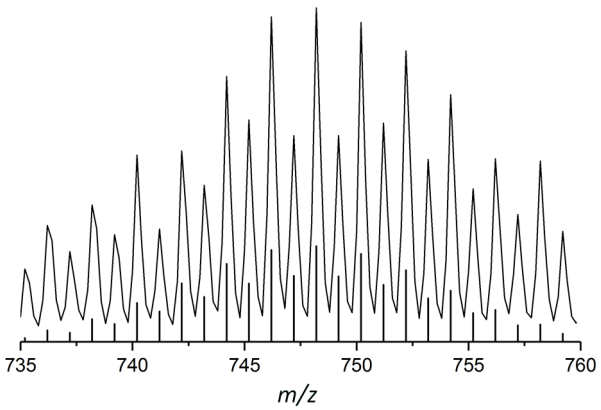

Figure S11: ESI-MS spectrum of $[Ge_9(ZnEt)]^-$ (**3a**) in MeCN (negative-ion mode, 2500 V, 300 °C) monitoring the molecule peak at *m/z* 746.2. The calculated pattern is presented as red bars. Due to the low concentration of **3a** in the injected solution, the signal to noise ratio was low.