SUPPORTING INFORMATION

Stepwise coordination of {Cu(C_5Me_5)} with tri-silylated Ge_9 cluster

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Contents:

1 Synthesis Details

1.1 General

All manipulations and reactions were performed under dry Ar atmosphere using standard Schlenk or glovebox techniques. All solvents were dried and freshly distilled prior to use. Crypt-222[1] was dried in vacuo for at least 18 hours. HypCl[2], CuI were purchased and used as received. $K(C_5Me_5)$ is prepared by reacting KHMDS[3] with $H(C_5Me_5)$ (1:1) in toluene. $K[Ge_9Hyp_3]$ and $[K(crypt\text{-}222)][Ge_9Hyp_3]$ were prepared according to literatures.[4] Single crystal photos related to this work are shown in Figure S1-S3.

NMR spectra were measured on a Bruker Avance Ultrashield 400 MHz. The ^1H NMR and ^{13}C NMR spectra were calibrated using the residual signals of the used deuterated solvents. Chemical shifts are reported in parts per million (ppm) relative to TMS, with the solvent peaks serving as internal reference.[5] Abbreviations for signal multiplicities are: singlet (s), doublet (d).

1.2 Synthesis of $[K(crypt\text{-}222)]\{Cu(C_5Me_5)(Ge_9Hyp_3)\}$ ($[K(crypt\text{-}222)]$1)

181 mg (0.1 mmol) of $[K(crypt\text{-}222)][Ge_9Hyp_3]$, 19 mg (0.1 mmol) of CuI and 18 mg (0.1 mmol) of $K(C_5Me_5)$ were dissolved in THF (3 mL). The reaction mixture was stirred for 6 hours at room temperature. The resulting dark red solution was filtered, then carefully layered by n-hexane (3 mL), and stored for crystallization at -35 °C. After 3 days, orange block crystals of compound [K(crypt-222)]**1** were observed in the test tube in approximately 75% yield overall.

^{1}H NMR (400 MHz, THF-d_8): δ [ppm] = 3.61 (d, J = 12.8 Hz, 24H), 2.60 (s, 12H), 1.99 (s, 15H), 0.30 (s, 81H). **^{13}C NMR** (101 MHz, THF-d_8) δ [ppm] = 105.21, 71.55, 68.70, 55.00, 12.01, 3.59. **^{29}Si NMR** (79 MHz, THF-d_8) δ [ppm] = -11.01, -109.02.

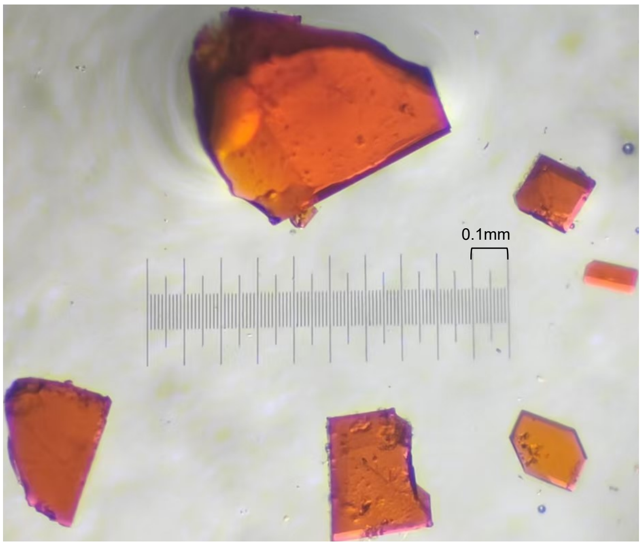

Figure S1. Crystal photographs of [K(crypt-222)]**1** taken under a light microscope.

1.3 Synthesis of $[K(crypt\text{-}222)][\{Cu(C_5Me_5)\}_2(Ge_9Hyp_3)]\cdot 0.3THF$ ($[K(crypt\text{-}222)]$2·0.3THF)

202 mg (0.1 mmol) of [K(crypt-222)]**1**, 21 mg (0.11 mmol) of CuI and 20 mg (0.11 mmol) of $K(C_5Me_5)$ were dissolved in THF (3 mL). The reaction mixture was stirred for 6 hours at room temperature. The resulting dark brown solution was filtered, then carefully layered by n-hexane (3 mL), and stored for crystallization at -35 °C. After 3 days, black block crystals of compound [K(crypt-222)]**2**·0.3THF were observed in the test tube in approximately 80% yield overall.

One pot: 181 mg (0.1 mmol) of $[K(crypt\text{-}222)][Ge_9Hyp_3]$, 40 mg (0.21 mmol) of CuI and 36.8 mg (0.21 mmol) of $K(C_5Me_5)$ were dissolved in THF (3 mL). The reaction mixture was stirred for 6 hours at room temperature. The resulting dark brown solution was filtered, then carefully layered by n-hexane (3 mL), and stored for crystallization at -35 °C. After 3 days, orange block crystals of compound [K(crypt-222)]**1** (minor) and black block crystals of compound [K(crypt-222)]**2**·0.3THF (major) were observed in the test tube.

^{1}H NMR (400 MHz, THF-d_8) δ [ppm] = 3.61 (d, J = 12.9 Hz, 24H), 2.59 (s, 12H), 2.00 (s, 23H), 0.33 (s, 81H). **^{13}C NMR** (101 MHz, THF-d_8) δ [ppm] = 105.67, 71.53, 68.69, 54.99, 12.35, 3.69. **^{29}Si NMR** (79 MHz, THF-d_8) δ [ppm] = -9.11, -107.14.

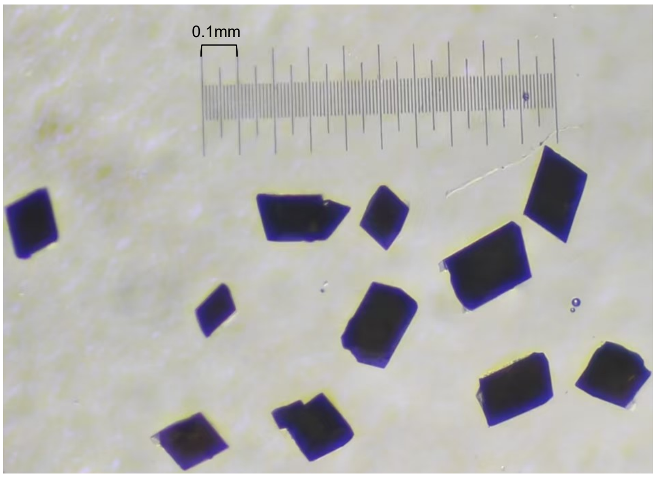

Figure S2. Crystal photographs of **[K(crypt-222)]2·0.3THF** taken under a light microscope.

1.4 Synthesis of [K(THF)$_6$][Cu(Ge$_9$Hyp$_3$)$_2$] ([K(THF)$_6$]E)

Compound [Li(THF)$_6$]**E**, which was reported in ref.[6] to be obtained from a reaction of [Li(THF)$_4$][Ge$_9$Hyp$_3$] in THF with [Cu[Al(OCH(CF$_3$)$_2$)$_4$]$_2$ in 1,2-F$_2$C$_6$H$_4$.

[K(THF)$_6$]**E** could be isolated selectively from a reaction of K[Ge$_9$Hyp$_3$] and CuI in THF: 144 mg (0.1 mmol) of K[Ge$_9$Hyp$_3$] and 10 mg (0.05 mmol) of CuI were dissolved in THF (3 mL). The reaction mixture was stirred for 6 hours at room temperature. The resulting dark red solution was filtered, then carefully layered by n-hexane (3 mL), and stored for crystallization at -35 °C. After 3 days, red block crystals of compound [K(THF)$_6$]**E** were observed in the test tube in approximately 80% yield overall.

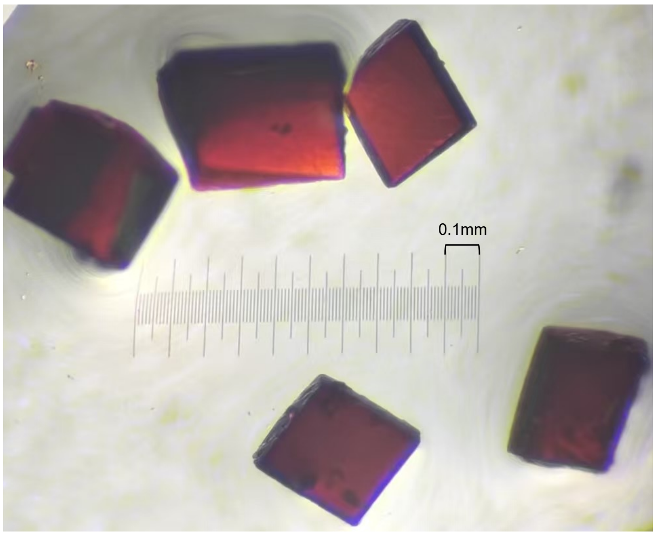

Figure S3. Crystal photographs of **[K(THF)$_6$]E** taken under a light microscope.

1.5 Synthesis of [(Ge$_9$Hyp$_3$)Cu(Ge$_9$Hyp$_3$)Cu(PPh$_3$)] (F)

F has been reported in ref.[7]. In this work, 332 mg (0.1 mmol) of [K(THF)$_6$]**E**, 21 mg (0.11 mmol) of CuI and 29 mg (0.11 mmol) of PPh$_3$ were dissolved in THF (3 mL). The reaction mixture was stirred for 6 hours at room temperature. Afterwards the THF is removed under reduced pressure. The dried reaction mixture is then extracted with n-hexane to give a dark red solution. The extract was concentrated under vacuum and then stored at −35 °C for crystallization. After 1 week, black block crystals of compound **F** were observed in the test tube in approximately 50% yield overall.

2 Single-Crystal X-Ray Crystallography (SCXRD)

2.1 Single-Crystal X-ray Diffraction

Data for [K(crypt-222)]**1**, [K(crypt-222)]**2**·0.3THF were collected from a Bruker SMART APEX-II CCD diffractometer, and [K(THF)$_6$]**E** was collected from a Rigaku (Mo) X-ray Source with graphite monochromated Mo-*K*α (λ = 0.71073 Å) radiation. Multi-scan absorption correction was applied with the

SADABS program. The structure was solved by using an intrinsic phasing approach with SHELXT 2018/2 and refined by full-matrix least-squares methods against F^2 using SHELXL 2018/3.[8] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined with isotropic displacement parameters. Some of their coordinates were refined freely and some on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. The relatively large tendency for disorder of the crypt-222 molecules required the application of restraints to this large number of atoms (the alternative application of the back-Fourier-transform method did not produce more reliable results). Due to the moderate quality of the crystal data of **[K(crypt-222)]1** with twinning and disorder problems, the heavily disordered solvent contribution to the overall structure factors were calculated and subtracted by back Fourier transform with the SQUEEZE algorithm in the PLATON program package,[9], and we modelled crypt-222 with plenty of restrain commands. In compound [K(crypt-222)]**2**, small residuals (not worth modelling) appear near the heavy atoms, which are common for heavy metal atoms. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[10] CCDC 2496952-2496954 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif. The crystal data and experimental parameters of the structure determinations are collected in Table S1. Supplementary views of the crystal structures are provided in Figures S4 – S9, created with Diamond 4.[11] Structural parameters are given in Tables S2 – S4.

Table S1. Crystal data and details of the structure determination of compound [K(crypt-222)]1, compound [K(crypt-222)]2, and compound [K(THF)$_6$]E.

Compound	**[K(crypt-222)]1**	**[K(crypt-222)]2·0.3THF**	**[K(THF)$_6$]E**
Empirical formula	$C_{55}H_{132}CuGe_9KN_2O_6Si_{12}$	$C_{66.25}H_{149.50}Cu_2Ge_9KN_2O_{6.31}Si_{12}$	$C_{78}H_{210}CuGe_{18}KO_6Si_{24}$
Formula weight, [g mol^{-1}]	2010.65	2231.90	3328.25
Temperature/K	150	150	150
Crystal system	monoclinic	monoclinic	hexagonal
Space group	$P2_1/n$	$P2_1/c$	$R\overline{3}$
a/Å	18.2014(16)	16.4552(14)	23.6847(4)
b/Å	25.5890(19)	24.525(2)	23.6847(4)
c/Å	20.2737(17)	28.508(2)	23.4153(6)
α/°	90	90	90
β/°	90.100(4)	98.022(3)	90
γ/°	90	90	120
Volume/Å^3	9442.6(13)	11392.2(17)	11375.4(5)
Z	4	4	3
ρ_{calc} g/cm^3	1.414	1.301	1.458
μ/mm^{-1}	3.275	2.902	3.896
F(000)	4112	4578	5058
Radiation	Mo-Kα (λ = 0.71073)	Mo-Kα (λ = 0.71073)	Mo-Kα (λ = 0.71073)
2*Θ* range for data collection/°	4.018 to 49.418	4.072 to 49.532	5.22 to 51.994
Index ranges	$-21 \leq h \leq 21$ $-30 \leq k \leq 30$ $-23 \leq l \leq 23$	$-19 \leq h \leq 19$ $-28 \leq k \leq 28$ $-33 \leq l \leq 33$	$-29 \leq h \leq 29$, $-29 \leq k \leq 29$, $-28 \leq l \leq 28$
Reflections collected	519655	229785	51987
Independent reflections	16067 [R_{int} = 0.1018, R_{sigma} = 0.0303]	19451 [R_{int} = 0.0627, R_{sigma} = 0.0286]	4974 [R_{int} = 0.0498, R_{sigma} = 0.0235]
Data/restraints/parameters	16067/586/984	19451/0/911	4974/0/233
Goodness-of-fit on F^2	1.039	1.098	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0242, wR_2 =	R_1 = 0.0423, wR_2 =	R_1 = 0.0399, wR_2 =

	0.0617	0.1158	0.0912
Final R indexes [all data]	R_1 = 0.0271, wR_2 = 0.0632	R_1 = 0.0514, wR_2 = 0.1198	R_1 = 0.0494, wR_2 = 0.0952
Largest diff. peak/hole / e Å^{-3}	0.50/-0.29	1.22/-0.51	0.51/-0.37
CCDC deposition number	2496952	2496953	2496954

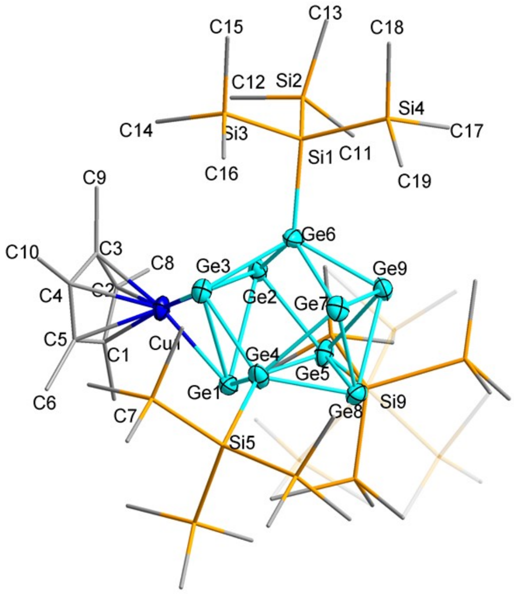

Figure S4. Molecular structure of the anion **1** with full labelling scheme (except for C, Si atoms). Thermal ellipsoids of Ge/Cu atoms are shown at 50% probability. H atoms are omitted for clarity.

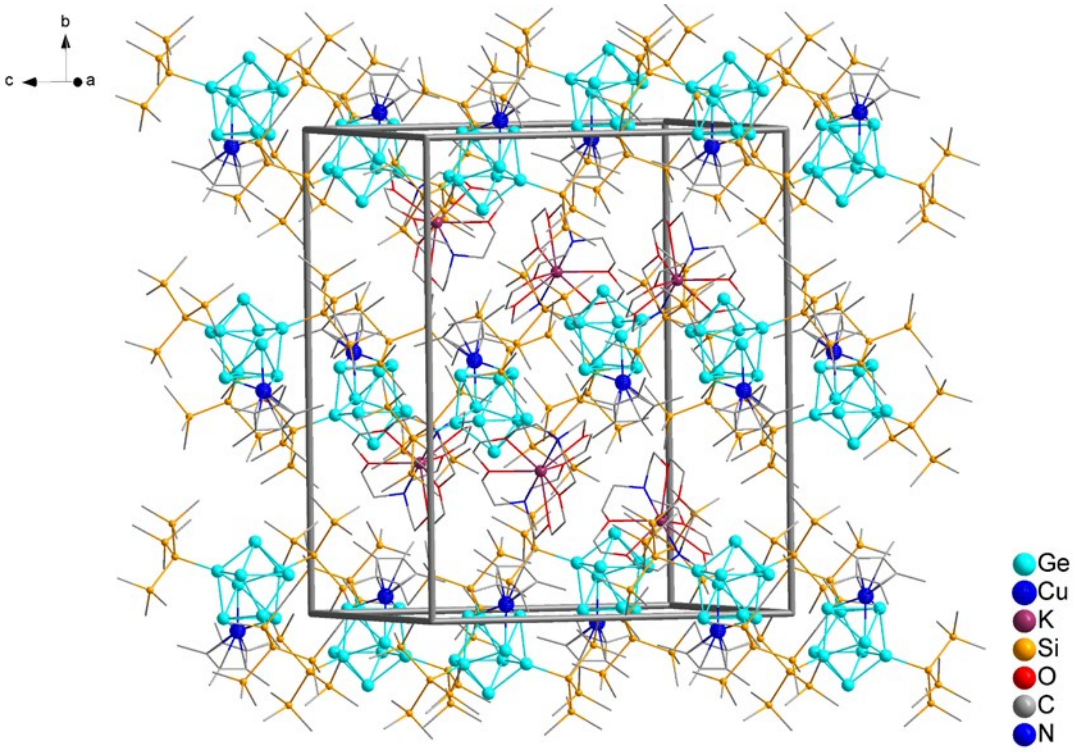

Figure S5. Unit cell view of compound [K(crypt-222)]**1**. H atoms are omitted for clarity.

Table S2. Selected interatomic distances (in Å) and bond angles (in degrees) of the experimental structures of the anion in [K(crypt-222)]1.

Atom-Atom	Distance (exp)	Atom-Atom	Distance (exp)

Ge1–Ge2	2.907(2)	Ge5–Ge8	2.556(2)
Ge1–Ge3	2.885(2)	Ge5–Ge9	2.556(2)
Ge1–Ge4	2.522(2)	Ge5–Si9	2.374(5)
Ge1–Ge5	2.513(2)	Ge6–Ge7	2.551(2)
Ge1–Cu1	2.467(2)	Ge6–Ge9	2.548(2)
Ge2–Ge3	2.883(2)	Ge6–Si1	2.377(4)
Ge2–Ge5	2.512(2)	Ge7–Ge8	2.651(2)
Ge2–Ge6	2.527(2)	Ge7–Ge9	2.649(2)
Ge2–Cu1	2.468(2)	Ge8–Ge9	2.665(2)
Ge3–Ge4	2.524(2)	Cu1–C1	2.224(19)
Ge3–Ge6	2.520(2)	Cu1–C2	2.239(17)
Ge3–Cu1	2.450(2)	Cu1–C3	2.242(19)
Ge4–Ge7	2.555(2)	Cu1–C4	2.242(16)
Ge4–Ge8	2.551(2)	Cu1–C5	2.215(17)
Ge4–Si5	2.377(4)		

Atom-Atom-Atom	**Angles (exp)**	**Atom-Atom-Atom**	**Angles (exp)**
Ge3–Ge1–Ge2	59.70(6)	Ge3–Ge6–Ge7	87.96(7)
Ge4–Ge1–Ge2	96.76(7)	Ge3–Ge6–Ge9	120.83(8)
Ge4–Ge1–Ge3	55.16(6)	Ge9–Ge6–Ge7	62.58(6)
Ge5–Ge1–Ge2	54.62(6)	Si1–Ge6–Ge2	116.27(14)
Ge5–Ge1–Ge3	99.11(7)	Si1–Ge6–Ge3	122.98(13)
Ge5–Ge1–Ge4	91.57(7)	Si1–Ge6–Ge7	121.95(13)
Cu1–Ge1–Ge2	53.94(6)	Si1–Ge6–Ge9	116.10(13)
Cu1–Ge1–Ge3	53.80(6)	Ge4–Ge7–Ge8	58.63(6)
Cu1–Ge1–Ge4	108.31(8)	Ge4–Ge7–Ge9	99.66(7)
Cu1–Ge1–Ge5	107.23(8)	Ge6–Ge7–Ge4	86.60(7)
Ge3–Ge2–Ge1	59.77(6)	Ge6–Ge7–Ge8	99.84(7)
Ge5–Ge2–Ge1	54.69(6)	Ge6–Ge7–Ge9	58.66(6)
Ge5–Ge2–Ge3	99.20(7)	Ge9–Ge7–Ge8	60.37(6)
Ge5–Ge2–Ge6	91.70(7)	Ge4–Ge8–Ge5	89.94(7)
Ge6–Ge2–Ge1	96.78(7)	Ge4–Ge8–Ge7	58.80(6)
Ge6–Ge2–Ge3	55.04(6)	Ge4–Ge8–Ge9	99.35(7)
Cu1–Ge2–Ge1	53.89(6)	Ge5–Ge8–Ge7	101.88(7)
Cu1–Ge2–Ge3	53.82(6)	Ge5–Ge8–Ge9	58.58(6)
Cu1–Ge2–Ge5	107.24(8)	Ge7–Ge8–Ge9	59.76(6)
Cu1–Ge2–Ge6	108.21(8)	Ge5–Ge9–Ge7	101.95(7)
Ge2–Ge3–Ge1	60.53(5)	Ge5–Ge9–Ge8	58.58(6)
Ge4–Ge3–Ge1	55.09(6)	Ge6–Ge9–Ge5	90.19(7)
Ge4–Ge3–Ge2	97.31(7)	Ge6–Ge9–Ge7	58.76(6)
Ge6–Ge3–Ge1	97.51(7)	Ge6–Ge9–Ge8	99.55(7)
Ge6–Ge3–Ge2	55.29(6)	Ge7–Ge9–Ge8	59.86(6)
Ge6–Ge3–Ge4	87.96(7)	Ge1–Cu1–Ge2	72.17(7)
Cu1–Ge3–Ge1	54.35(6)	Ge3–Cu1–Ge1	71.85(7)
Cu1–Ge3–Ge2	54.41(6)	Ge3–Cu1–Ge2	71.77(7)
Cu1–Ge3–Ge4	108.79(8)	C1–Cu1–Ge1	105.7(5)
Cu1–Ge3–Ge6	109.05(8)	C1–Cu1–Ge2	127.5(6)
Ge1–Ge4–Ge3	69.75(6)	C1–Cu1–Ge3	159.6(6)
Ge1–Ge4–Ge7	120.71(8)	C1–Cu1–C2	36.0(7)
Ge1–Ge4–Ge8	82.92(7)	C1–Cu1–C3	58.8(7)
Ge3–Ge4–Ge7	87.78(7)	C1–Cu1–C4	60.5(7)
Ge3–Ge4–Ge8	120.87(8)	C2–Cu1–Ge1	130.0(6)
Ge8–Ge4–Ge7	62.57(6)	C2–Cu1–Ge2	104.6(5)

Si5–Ge4–Ge1	116.97(14)	C2–Cu1–Ge3	156.7(6)
Si5–Ge4–Ge3	122.33(13)	C2–Cu1–C3	34.3(7)
Si5–Ge4–Ge7	121.30(14)	C2–Cu1–C4	59.3(7)
Si5–Ge4–Ge8	116.77(13)	C3–Cu1–Ge1	163.6(6)
Ge1–Ge5–Ge8	82.98(7)	C3–Cu1–Ge2	112.0(5)
Ge1–Ge5–Ge9	118.61(8)	C3–Cu1–Ge3	124.5(6)
Ge2–Ge5–Ge1	70.69(6)	C3–Cu1–C4	35.5(8)
Ge2–Ge5–Ge8	118.68(8)	C4–Cu1–Ge1	144.5(6)
Ge2–Ge5–Ge9	82.79(7)	C4–Cu1–Ge2	143.0(6)
Ge8–Ge5–Ge9	62.85(6)	C4–Cu1–Ge3	109.3(5)
Si9–Ge5–Ge1	123.21(16)	C5–Cu1–Ge1	112.4(5)
Si9–Ge5–Ge2	122.61(16)	C5–Cu1–Ge2	164.3(6)
Si9–Ge5–Ge8	118.25(15)	C5–Cu1–Ge3	123.8(6)
Si9–Ge5–Ge9	117.83(15)	C5–Cu1–C1	37.3(8)
Ge2–Ge6–Ge7	120.55(8)	C5–Cu1–C2	60.5(7)
Ge2–Ge6–Ge9	82.63(7)	C5–Cu1–C3	59.4(7)
Ge3–Ge6–Ge2	69.68(6)	C5–Cu1–C4	36.0(7)

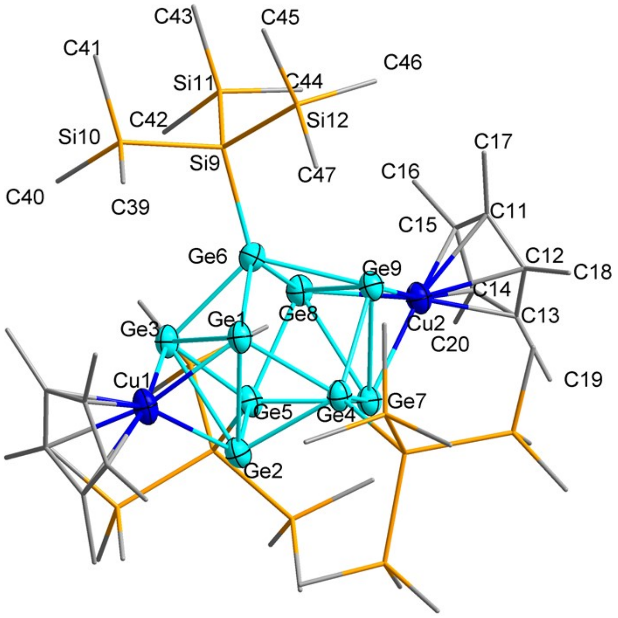

Figure S6. Molecular structure of the anion **2** with full labelling scheme (except for C, Si atoms). Thermal ellipsoids of Ge/Cu atoms are shown at 50% probability. H atoms are omitted for clarity.

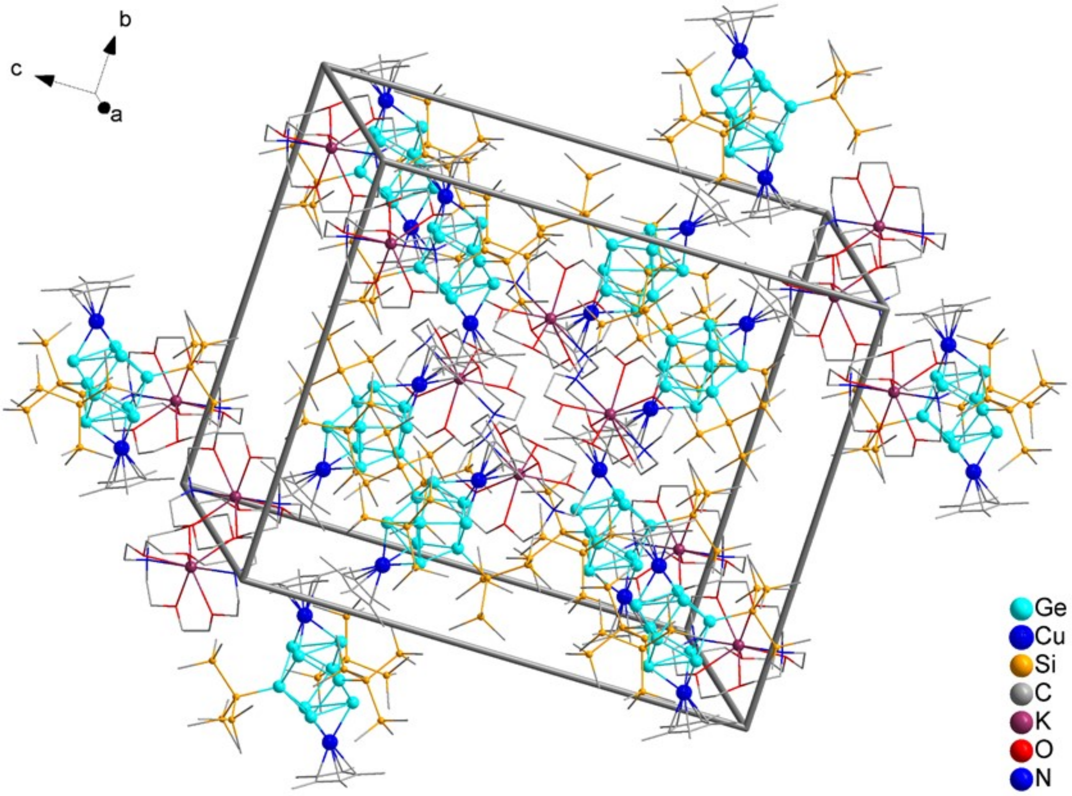

Figure S7. Unit cell view of compound [K(crypt-222)]**2**·0.3THF. H atoms are omitted for clarity.

Table S3. Selected interatomic distances (in Å) and bond angles (in degrees) of the experimental structures of the anion in [K(crypt-222)]2.

Atom-Atom	Distance (exp)	Atom-Atom	Distance (exp)
Ge1–Ge2	2.8794(8)	Ge6–Ge9	2.5572(7)
Ge1–Ge3	2.8769(7)	Ge6–Si9	2.3933(15)
Ge1–Ge4	2.5343(7)	Ge7–Ge8	2.8446(7)
Ge1–Ge6	2.5391(7)	Ge7–Ge9	2.8479(7)
Ge1–Cu1	2.4675(8)	Ge7–Cu2	2.4789(8)
Ge2–Ge3	2.8724(8)	Ge8–Ge9	2.8327(7)
Ge2–Ge4	2.5340(7)	Ge8–Cu2	2.4846(8)
Ge2–Ge5	2.5276(7)	Ge9–Cu2	2.4883(7)
Ge2–Cu1	2.4564(8)	Cu1–C1	2.328(5)
Ge3–Ge5	2.5414(7)	Cu1–C2	2.315(5)
Ge3–Ge6	2.5427(7)	Cu1–C3	2.241(5)
Ge3–Cu1	2.5006(8)	Cu1–C4	2.210(5)
Ge4–Ge7	2.5438(7)	Cu1–C5	2.275(5)
Ge4–Ge9	2.5441(7)	Cu2–C11	2.273(5)
Ge4–Si1	2.3858(14)	Cu2–C12	2.287(5)
Ge5–Ge7	2.5450(7)	Cu2–C13	2.277(5)
Ge5–Ge8	2.5424(8)	Cu2–C14	2.255(5)
Ge5–Si5	2.3865(14)	Cu2–C15	2.261(5)
Ge6–Ge8	2.5415(7)		

Atom-Atom-Atom	Angles (exp)	Atom-Atom-Atom	Angles (exp)
Ge3–Ge1–Ge2	59.867(18)	Ge6–Ge8–Ge7	98.81(2)
Ge4–Ge1–Ge2	55.375(19)	Ge6–Ge8–Ge9	56.514(18)
Ge4–Ge1–Ge3	97.76(2)	Ge9–Ge8–Ge7	60.215(18)
Ge4–Ge1–Ge6	89.49(2)	Cu2–Ge8–Ge5	109.90(3)

Ge6–Ge1–Ge2	97.85(2)	Cu2–Ge8–Ge6	110.92(3)
Ge6–Ge1–Ge3	55.578(19)	Cu2–Ge8–Ge7	54.94(2)
Cu1–Ge1–Ge2	54.03(2)	Cu2–Ge8–Ge9	55.34(2)
Cu1–Ge1–Ge3	55.15(2)	Ge4–Ge9–Ge6	88.87(2)
Cu1–Ge1–Ge4	108.38(3)	Ge4–Ge9–Ge7	55.958(18)
Cu1–Ge1–Ge6	109.97(3)	Ge4–Ge9–Ge8	97.93(2)
Ge3–Ge2–Ge1	60.023(19)	Ge6–Ge9–Ge7	98.35(2)
Ge4–Ge2–Ge1	55.385(19)	Ge6–Ge9–Ge8	55.986(19)
Ge4–Ge2–Ge3	97.89(2)	Ge8–Ge9–Ge7	60.100(18)
Ge5–Ge2–Ge1	98.18(2)	Cu2–Ge9–Ge4	109.93(3)
Ge5–Ge2–Ge3	55.710(19)	Cu2–Ge9–Ge6	110.28(3)
Ge5–Ge2–Ge4	89.70(2)	Cu2–Ge9–Ge7	54.86(2)
Cu1–Ge2–Ge1	54.39(2)	Cu2–Ge9–Ge8	55.21(2)
Cu1–Ge2–Ge3	55.31(2)	Ge1–Cu1–Ge3	70.77(2)
Cu1–Ge2–Ge4	108.75(3)	Ge2–Cu1–Ge1	71.58(2)
Cu1–Ge2–Ge5	110.17(3)	Ge2–Cu1–Ge3	70.82(2)
Ge2–Ge3–Ge1	60.110(18)	C1–Cu1–Ge1	116.64(14)
Ge5–Ge3–Ge1	97.92(2)	C1–Cu1–Ge2	116.10(15)
Ge5–Ge3–Ge2	55.256(19)	C1–Cu1–Ge3	170.72(13)
Ge5–Ge3–Ge6	89.71(2)	C2–Cu1–Ge1	148.83(14)
Ge6–Ge3–Ge1	55.460(19)	C2–Cu1–Ge2	105.32(14)
Ge6–Ge3–Ge2	97.94(2)	C2–Cu1–Ge3	138.88(14)
Cu1–Ge3–Ge1	54.08(2)	C2–Cu1–C1	35.4(2)
Cu1–Ge3–Ge2	53.87(2)	C3–Cu1–Ge1	163.64(15)
Cu1–Ge3–Ge5	108.31(3)	C3–Cu1–Ge2	124.73(15)
Cu1–Ge3–Ge6	108.79(3)	C3–Cu1–Ge3	111.19(14)
Ge1–Ge4–Ge7	122.13(3)	C3–Cu1–C1	60.05(19)
Ge1–Ge4–Ge9	84.26(2)	C3–Cu1–C2	36.17(19)
Ge2–Ge4–Ge1	69.24(2)	C3–Cu1–C5	61.19(18)
Ge2–Ge4–Ge7	83.60(2)	C4–Cu1–Ge1	126.45(14)
Ge2–Ge4–Ge9	121.91(3)	C4–Cu1–Ge2	161.89(14)
Ge7–Ge4–Ge9	68.08(2)	C4–Cu1–Ge3	111.11(14)
Si1–Ge4–Ge1	119.35(4)	C4–Cu1–C1	60.3(2)
Si1–Ge4–Ge2	116.07(4)	C4–Cu1–C2	60.8(2)
Si1–Ge4–Ge7	118.44(4)	C4–Cu1–C3	37.2(2)
Si1–Ge4–Ge9	121.99(4)	C4–Cu1–C5	36.84(19)
Ge2–Ge5–Ge3	69.03(2)	C5–Cu1–Ge1	106.15(13)
Ge2–Ge5–Ge7	83.70(2)	C5–Cu1–Ge2	148.72(16)
Ge2–Ge5–Ge8	121.31(3)	C5–Cu1–Ge3	139.24(16)
Ge3–Ge5–Ge7	121.74(2)	C5–Cu1–C1	35.6(2)
Ge3–Ge5–Ge8	83.58(2)	C5–Cu1–C2	59.9(2)
Ge8–Ge5–Ge7	67.99(2)	Ge7–Cu2–Ge8	69.94(2)
Si5–Ge5–Ge2	123.61(4)	Ge7–Cu2–Ge9	69.97(2)
Si5–Ge5–Ge3	117.74(4)	Ge8–Cu2–Ge9	69.45(2)
Si5–Ge5–Ge7	120.26(4)	C11–Cu2–Ge7	164.35(14)
Si5–Ge5–Ge8	115.06(4)	C11–Cu2–Ge8	124.35(14)
Ge1–Ge6–Ge3	68.96(2)	C11–Cu2–Ge9	107.31(13)
Ge1–Ge6–Ge8	121.25(3)	C11–Cu2–C12	36.09(18)
Ge1–Ge6–Ge9	83.90(2)	C11–Cu2–C13	60.94(18)
Ge3–Ge6–Ge9	121.40(3)	C12–Cu2–Ge7	129.21(13)
Ge8–Ge6–Ge3	83.57(2)	C12–Cu2–Ge8	160.34(13)
Ge8–Ge6–Ge9	67.50(2)	C12–Cu2–Ge9	110.17(13)

Si9–Ge6–Ge1	119.12(4)	C13–Cu2–Ge7	110.48(13)
Si9–Ge6–Ge3	121.11(4)	C13–Cu2–Ge8	150.74(13)
Si9–Ge6–Ge8	119.57(4)	C13–Cu2–Ge9	139.38(13)
Si9–Ge6–Ge9	117.48(4)	C13–Cu2–C12	36.37(18)
Ge4–Ge7–Ge5	89.09(2)	C14–Cu2–Ge7	121.37(14)
Ge4–Ge7–Ge8	97.63(2)	C14–Cu2–Ge8	116.62(14)
Ge4–Ge7–Ge9	55.967(19)	C14–Cu2–Ge9	168.02(13)
Ge5–Ge7–Ge8	55.959(19)	C14–Cu2–C11	60.71(18)
Ge5–Ge7–Ge9	98.28(2)	C14–Cu2–C12	60.39(18)
Ge8–Ge7–Ge9	59.685(18)	C14–Cu2–C13	36.62(19)
Cu2–Ge7–Ge4	110.24(3)	C14–Cu2–C15	36.28(19)
Cu2–Ge7–Ge5	110.00(3)	C15–Cu2–Ge7	153.68(14)
Cu2–Ge7–Ge8	55.13(2)	C15–Cu2–Ge8	105.03(14)
Cu2–Ge7–Ge9	55.171(19)	C15–Cu2–Ge9	133.90(14)
Ge5–Ge8–Ge7	56.046(19)	C15–Cu2–C11	36.43(19)
Ge5–Ge8–Ge9	98.73(2)	C15–Cu2–C12	60.25(18)
Ge6–Ge8–Ge5	89.72(2)	C15–Cu2–C13	60.89(18)

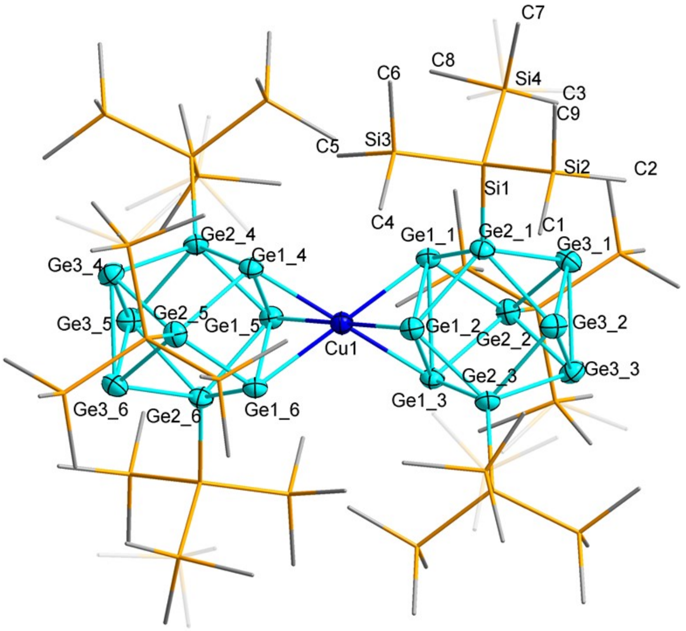

Figure S8. Molecular structure of the anion **E** with full labelling scheme (except for C, Si atoms). Thermal ellipsoids of Ge/Cu atoms are shown at 50% probability. H atoms are omitted for clarity.

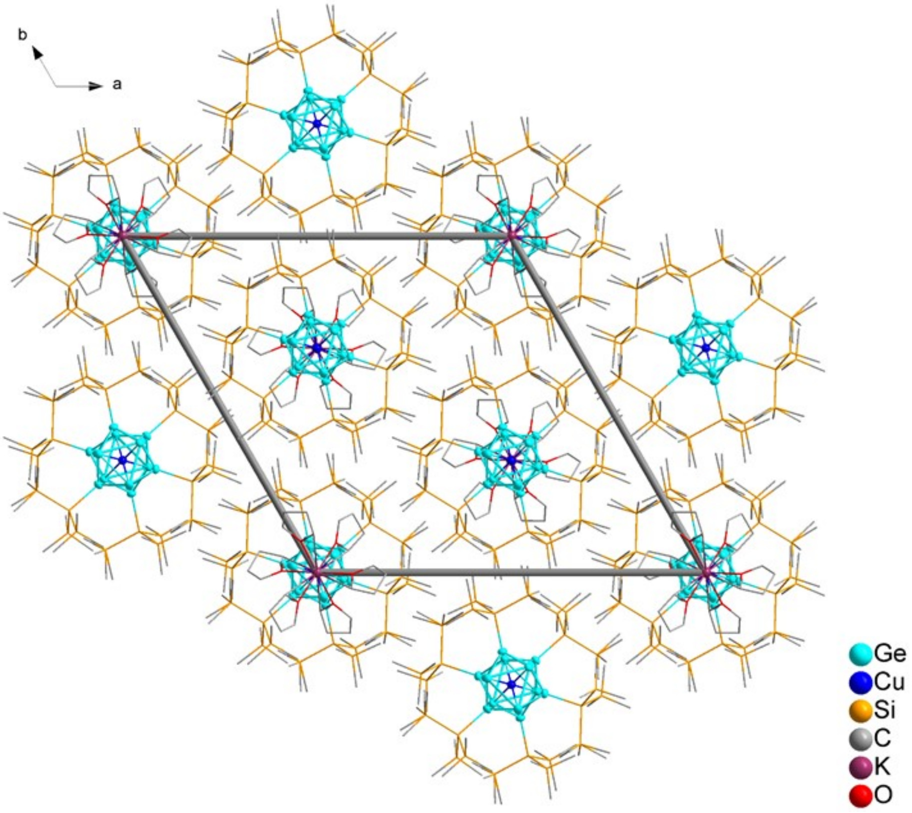

Figure S9. Unit cell view of compound [K(THF)$_6$]**E**. H atoms are omitted for clarity.

Table S4. Selected interatomic distances (in Å) and bond angles (in degrees) of the experimental structures of the anion in [K(THF)$_6$]E.

Atom-Atom	Distance (exp)	Atom-Atom	Distance (exp)
Ge1–Ge1_1	2.8517(6)	Ge3–Ge3_1	2.6349(7)
Ge1–Ge1_2	2.8517(6)	Ge2–Ge3	2.5520(5)
Ge1–Ge2	2.5192(5)	Ge2–Ge3_1	2.5497(5)
Ge1–Ge2_2	2.5217(5)	Ge2–Si1	2.3792(10)
Ge1–Cu1	2.5762(4)	Ge3–Ge3_2	2.6348(7)
Atom-Atom-Atom	**Angles (exp)**	**Atom-Atom-Atom**	**Angles (exp)**
Ge1_1–Ge1–Ge1_2	60.0	Ge2–Ge3–Ge3_1	58.862(16)
Ge2_2–Ge1–Ge1_1	98.838(12)	Ge2_2–Ge3–Ge3_1	101.269(14)
Ge2_2–Ge1–Ge1_2	55.506(14)	Ge2_2–Ge3–Ge3_2	58.950(16)
Ge2–Ge1–Ge1_1	55.588(14)	Ge2–Ge3–Ge3_2	101.205(14)
Ge2–Ge1–Ge1_2	98.896(12)	Ge3_2–Ge3–Ge3_1	60.0
Ge2–Ge1–Ge2_2	92.09(2)	Ge1–Cu1–Ge1_3	112.787(13)
Ge2_2–Ge1–Cu1	110.430(16)	Ge1_2–Cu1–Ge1_1	67.211(13)
Ge2–Ge1–Cu1	110.510(15)	Ge1–Cu1–Ge1_1	67.212(13)
Cu1–Ge1–Ge1_1	56.394(6)	Ge1_4–Cu1–Ge1_1	112.790(13)
Cu1–Ge1–Ge1_2	56.394(6)	Ge1_4–Cu1–Ge1_2	112.787(13)
Ge1–Ge2–Ge1_1	68.905(19)	Ge1–Cu1–Ge1_2	67.212(13)
Ge1_1–Ge2–Ge3	118.008(18)	Ge1_5–Cu1–Ge1_4	67.213(13)
Ge1_1–Ge2–Ge3_1	83.448(17)	Ge1_4–Cu1–Ge1_3	67.211(13)
Ge1–Ge2–Ge3_1	118.099(18)	Ge1_5–Cu1–Ge1_3	67.212(13)
Ge1–Ge2–Ge3	83.452(16)	Ge1_2–Cu1–Ge1_3	112.787(13)
Ge3_1–Ge2–Ge3	62.19(2)	Ge1–Cu1–Ge1_4	180.0
Si1–Ge2–Ge1_1	122.78(3)	Ge1_1–Cu1–Ge1_3	180.0

Si1–Ge2–Ge1	127.63(3)	Ge1_5–Cu1–Ge1	112.788(13)
Si1–Ge2–Ge3	118.17(3)	Ge1_5–Cu1–Ge1_2	179.999(14)
Si1–Ge2–Ge3_1	114.05(3)	Ge1_5–Cu1–Ge1_1	112.791(13)
Ge2_2–Ge3–Ge2	90.68(2)		

3 Energy-Dispersive X-Ray Spectroscopy (EDS)

EDS analysis of single crystal of compound [K(crypt-222)]**1**, [K(crypt-222)]**2**·0.3THF and [K(THF)$_6$]**E** were carried out using an Oxford X-Max 80 instrument (UK). The spectra are shown in Figures S10-S12. Several measurements produced unreasonably large values for the % K and Si. After excluding K and Si from the calculations, the results obtained closely matched the expected atomic ratios. We believe that accumulation of K and Si at the crystal surface upon exposure to air is responsible for the anomalous results. This is observed commonly for very these very air-sensitive compounds.

Table S5. EDS analysis of [K(crypt-222)]**1**, [K(crypt-222)]**2** and [K(THF)$_6$]**E**.

		[K(crypt-222)]**1**			
Element	Mass Norm. %	Atom %	Abs. error % (1 sigma)	Element ratio observed	Element ratio calc
Si	52.90	72.33	1.06	33.83	12.00
K	5.14	5.05	0.34	2.36	1.00
Cu	5.59	3.38	0.56	1.58	1.00
Ge	36.37	19.24	1.18	9.00	9.00
Total	100.00	100.00			
		[K(crypt-222)]**2**·0.3THF			
Element	Mass Norm. %	Atom %	Abs. error % (1 sigma)	Element ratio observed	Element ratio calc
Si	26.15	46.26	0.6	10.52	12.00
K	3.33	4.24	0.24	0.96	1.00
Cu	12.70	9.93	0.60	2.26	2.00
Ge	57.82	39.57	0.91	9.00	9.00
Total	100.00	100.00			
		[K(THF)$_6$]**E**			
Element	Mass Norm. %	Atom %	Abs. error % (1 sigma)	Element ratio observed	Element ratio calc
Si	38.09	0.38	61.15	30.68	24.00
K	0.09	0.08	0.11	0.06	1.00
Cu	4.04	0.22	2.86	1.43	1.00
Ge	57.78	0.42	35.88	18.00	18.00
Total	100.00	100.00			

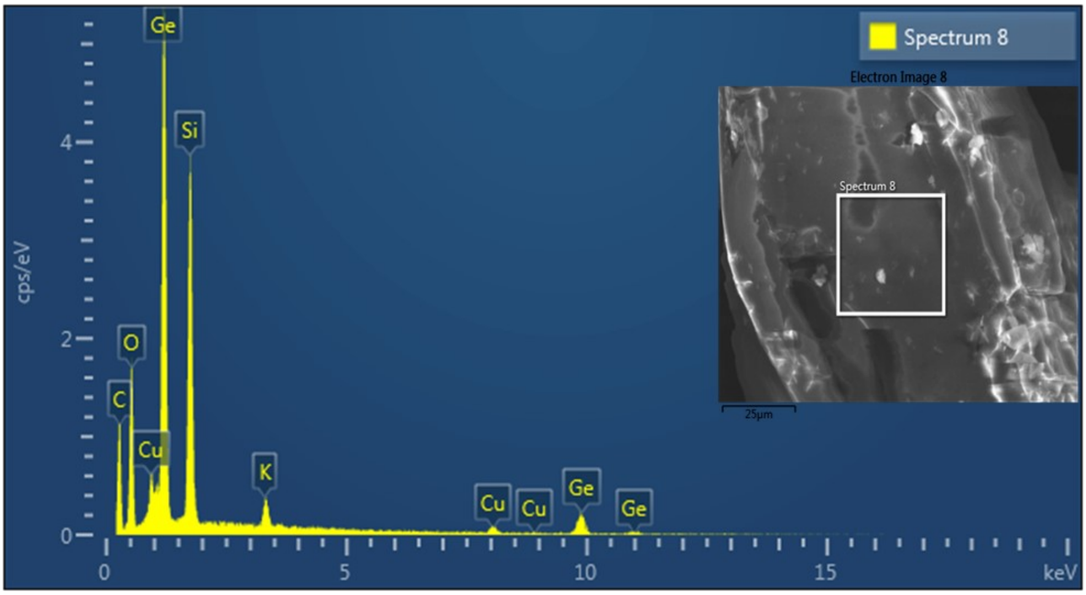

Figure S10. EDS analysis of [K(crypt-222)]**1**.

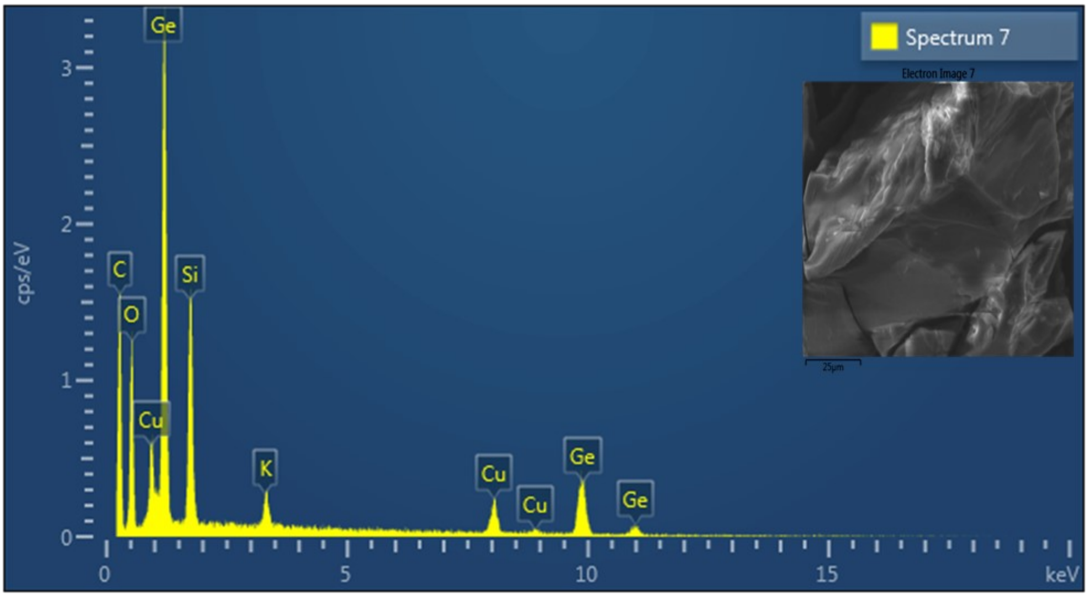

Figure S11. EDS analysis of [K(crypt-222)]**2**·0.3THF.

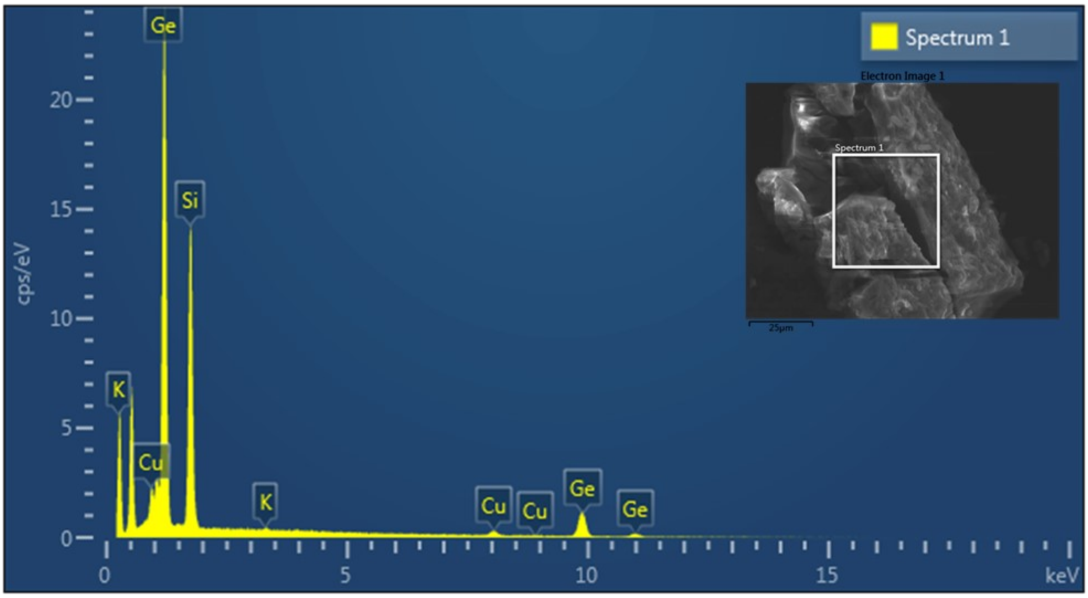

Figure S12. EDS analysis of [K(THF)$_6$]**E**.

4 NMR Spectra

^{1}H NMR, 13C NMR and ^{29}Si NMR spectra recorded from solutions of single-crystals of compounds [K(crypt-222)]**1** and [K(crypt-222)]**2**·0.3THF are provided in Figures S13 –S18.

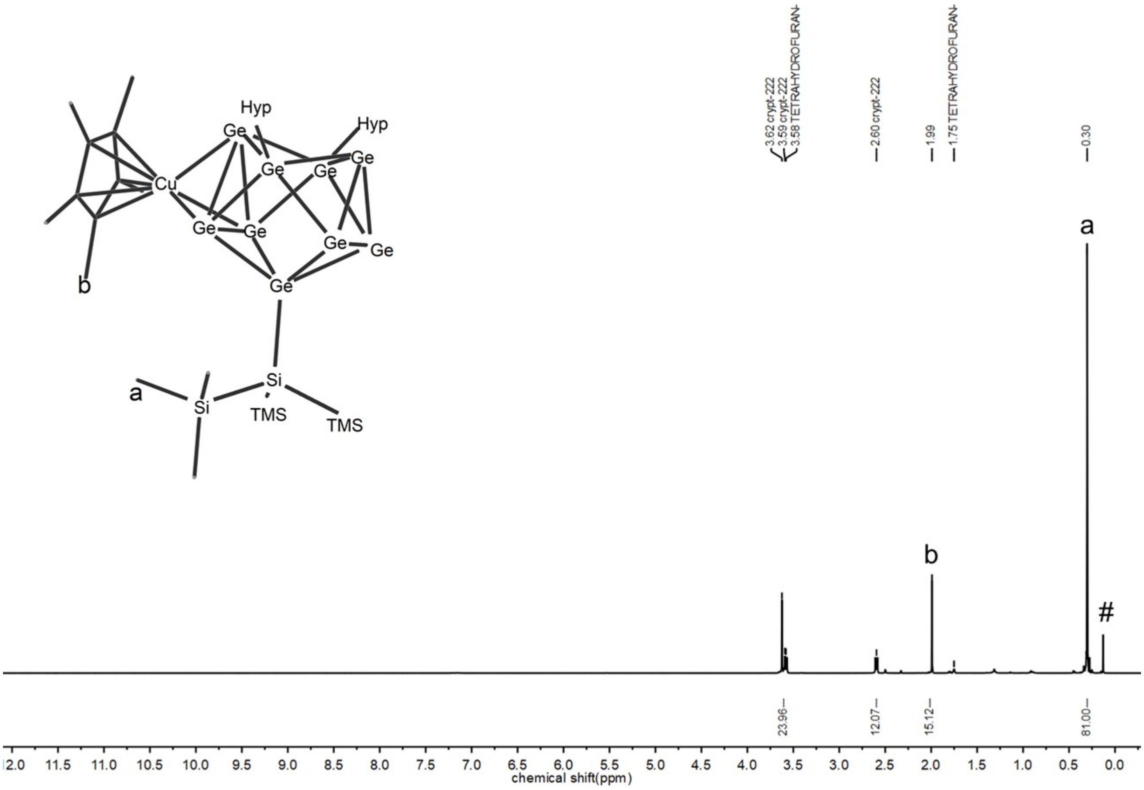

Figure S13. ^{1}H NMR spectrum (THF-d8) of [K(crypt-222)]**1**. Signal marked with # is caused by silicon grease.

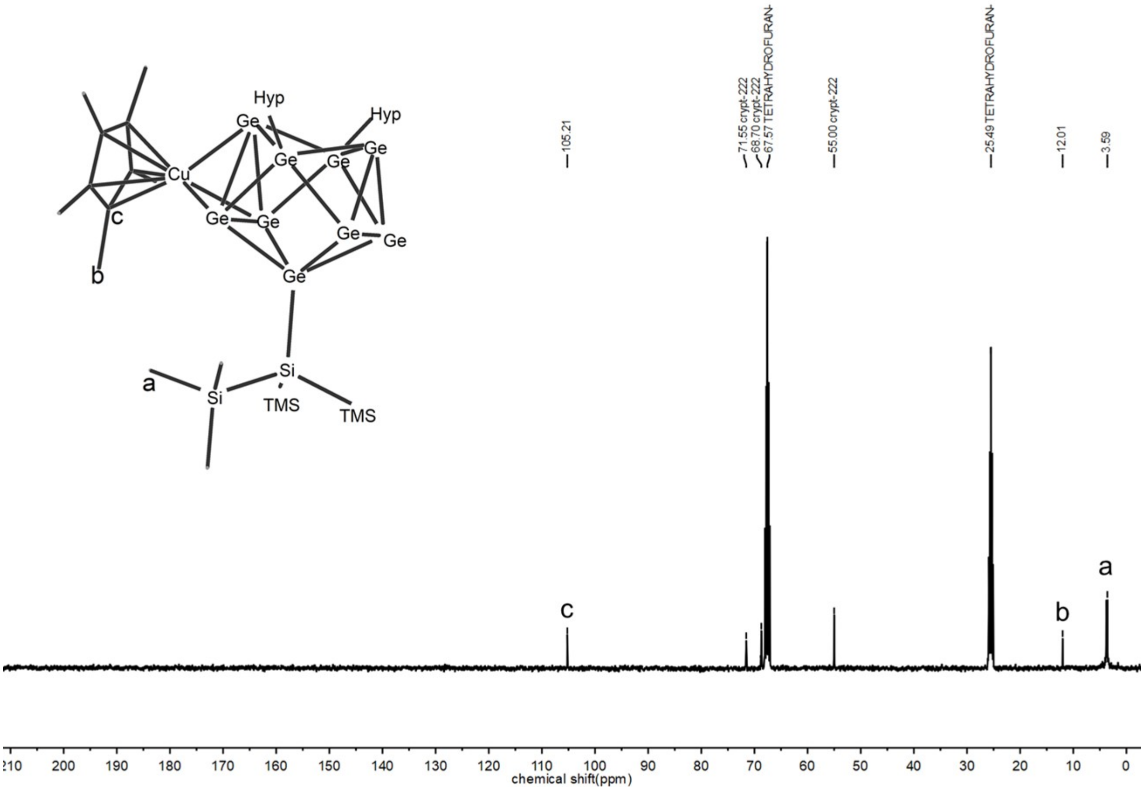

Figure S14. ^{13}C NMR spectrum (THF-d8) of [K(crypt-222)]**1**.

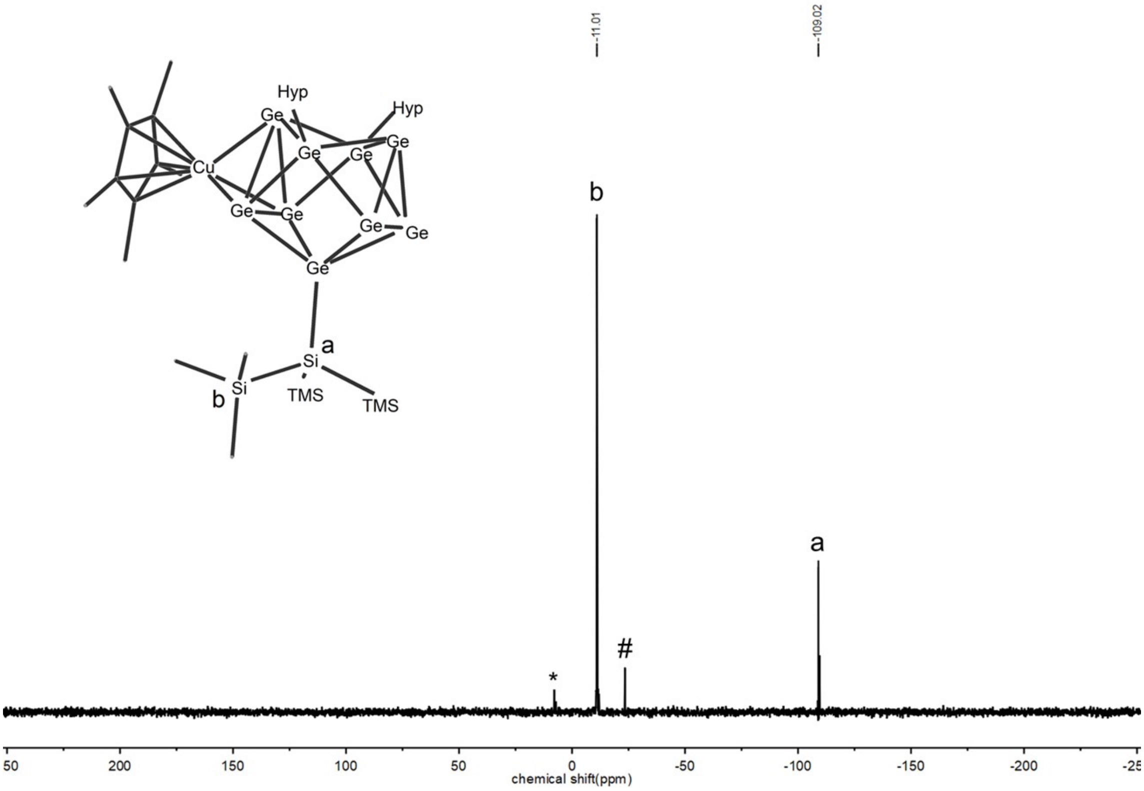

Figure S15. ^{29}Si NMR spectrum (THF-d8) of [K(crypt-222)]**1**. Asterisked signals are caused by unidentified impurities; signal marked with # is caused by silicon grease.

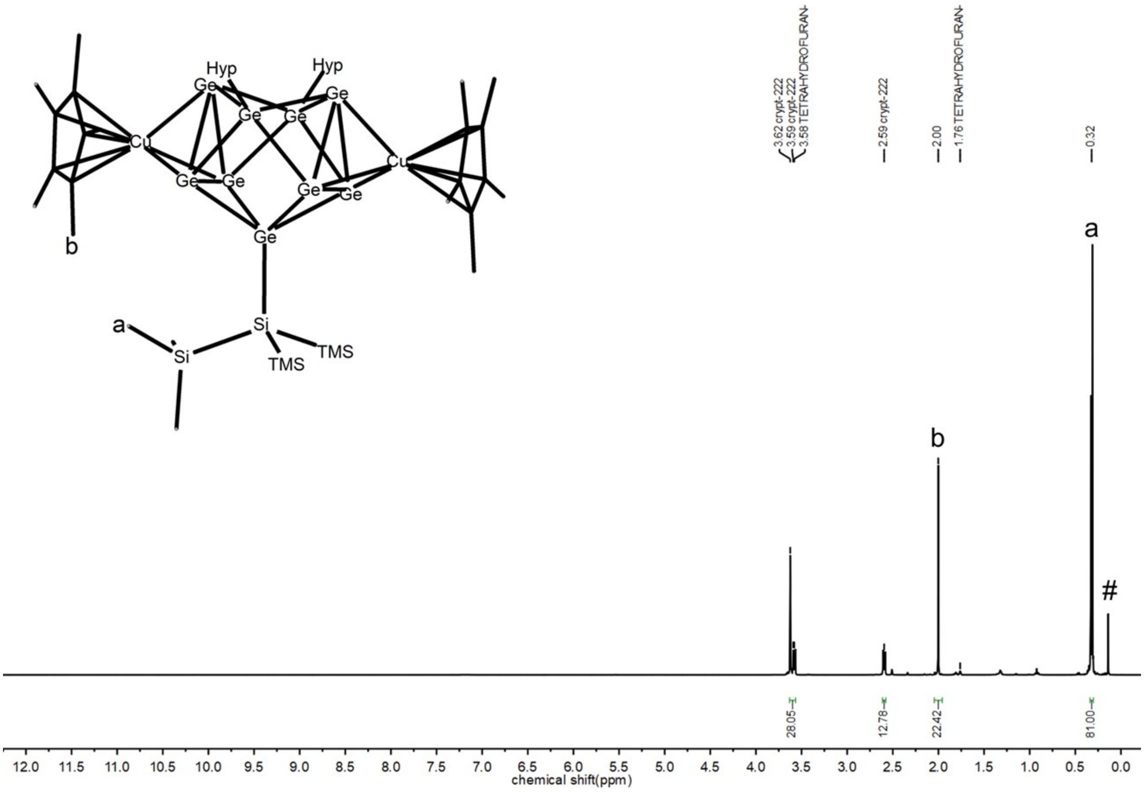

Figure S16. ^{1}H NMR spectrum (THF-d8) of [K(crypt-222)]**2**·0.3THF. Signal marked with # is caused by silicon grease.

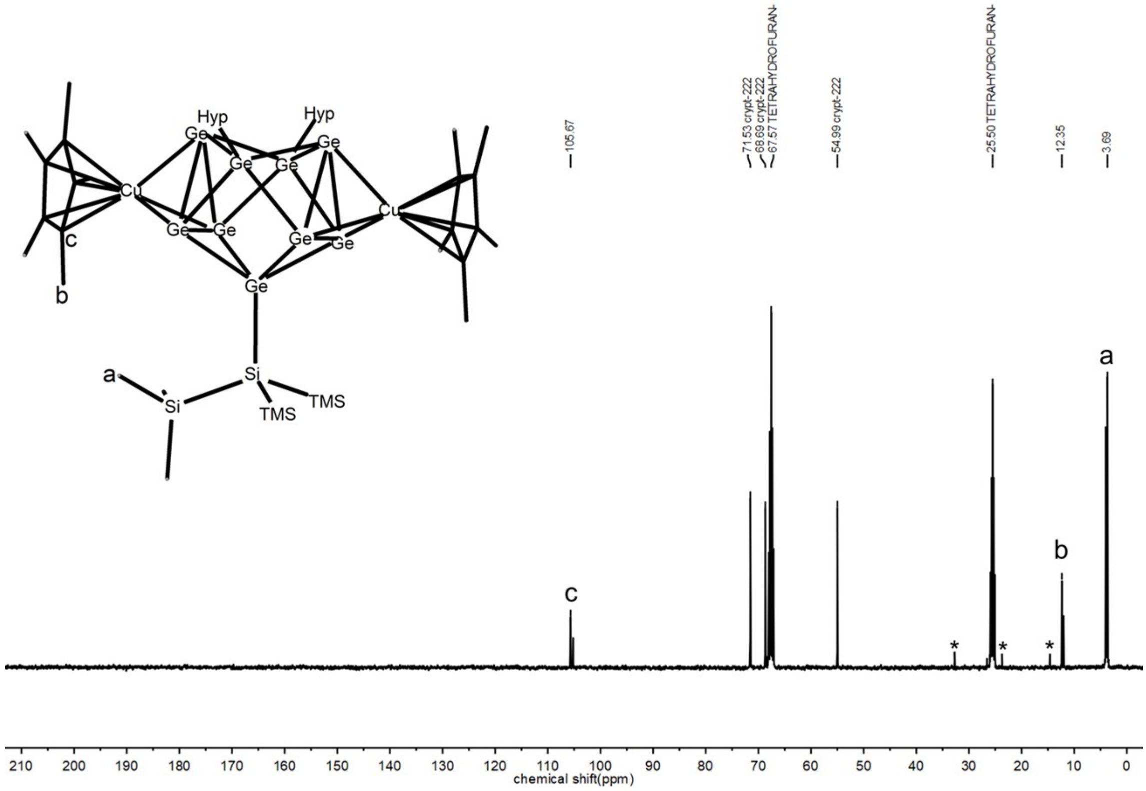

Figure S17. ^{13}C NMR spectrum (THF-d8) of [K(crypt-222)]**2**·0.3THF. Asterisked signals are caused by unidentified impurities.

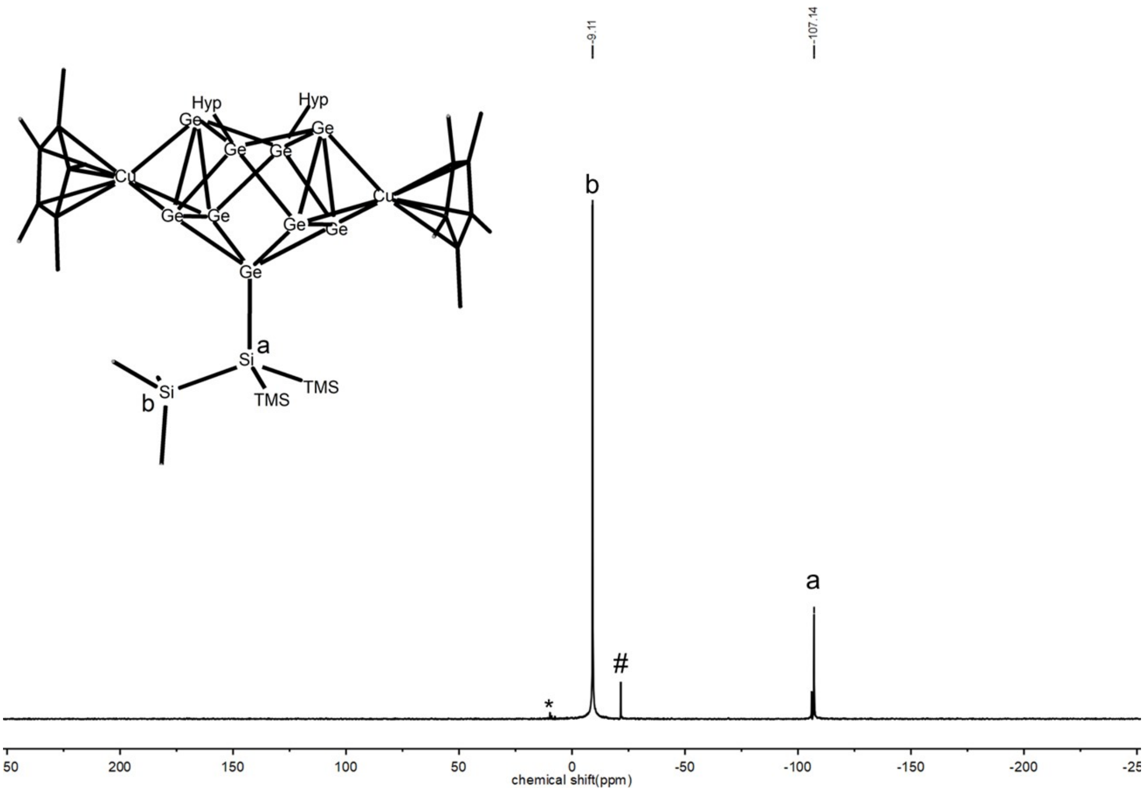

Figure S18. ^{29}Si NMR spectrum (THF-d8) of [K(crypt-222)]**2**·0.3THF. Asterisked signals are caused by unidentified impurities; signal marked with # is caused by silicon grease.

5 References for the Supporting Information

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