Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Synthesis and characterization of pristine *closo* - $[Ge_{10}]^{2-}$

Manuel M. Bentlohner, Christina Fischer and Thomas F. Fässler*

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Figures and Tables

1 Experimental Details

General Methods: All manipulations took place under a purified argon atmosphere using a glove box and standard Schlenk technique. The Zintl compound of the nominal composition Rb_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements Rb and Ge (99.999% Chempur) at 650°C for 48 h in a tantalum ampoule.[1] *En* (Merck) was refluxed with calcium hydride (Merck) and immediately used after collection. The water-content of *en* was qualitatively checked according to a method described elsewhere.[2] 1,4-Bis(trimethylsilyl)butadiyne (Alfa Aesar 98%) was used as received. Toluene was dried over molecular sieve (4 Å) in a solvent purificator (MBraun MB-SPS). Cryptand[2.2.2] (Merck) was dried in a vacuum for 8 h.

Synthesis of $[Rb(222\text{-crypt})]_2[Ge_{10}](en)_{1.5}$: A solution of 7-amino-1-(trimethylsilyl)-5-aza-hepta-3-en-1-yne in *en* (60 µmol/mL) was prepared by dissolving bis(trimethylsilyl)butadiyne (15.2 mg, 78 µmol) in 1.3 ml *en*. [3] In a Schlenk tube 1.3 mL of the solution of 7-amino-1-(trimethylsilyl)-5-aza-hepta-3-en-1-yne (78 µmol, 1 eq.) in *en* was carefully dropped onto Rb_4Ge_9 (77.6 mg, 78 µmol, 1 eq.), and a dark red mixture was obtained. The reaction mixture was stirred for 20 h, whereby the color of the mixture became greenish, but no precipitate was formed. The reaction mixture was filtered over glass fibers and carefully layered with a solution of cryptand[2.2.2] (90.4 mg, 312 µmol, 4 eq.) in 4 mL toluene. After two weeks, dark purple, pillar-shaped crystals had formed (yield ca. 10-20%). Crystal size: 0.3 x 0.25 x 0.05 mm³; unit cell parameters: a = 10.8759(2), b = 13.4395(3), c = 21.2958(4) Å, α = 85.907(2)° , β = 88.885(2)°, γ = 88.995(2)°, V = 3104.2(11) Å^3, triclinic space group $P\bar{1}$; Z = 2, ρ_{calc} = 1.862 g cm^{-3}, μ = 6.38 mm^{-1}, θ_{max} = 26.00°, 65291 measured reflections, 11569 independent reflections, R_{int} = 0.081, R_1 = 0.041, wR_2 = 0.078 for reflections with $I > 2\sigma(I)$, R_1 = 0.095, wR_2 = 0.091 for all data. Min/max residual electron density: -0.87/1.12 e Å^{-3}. CCDC 1479637 contains 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/data_request/cif. ESI-MS (negative ion mode): m/z (%): 1188 (85) $\{Ge_{10}Rb(222\text{-crypt})\}^-$, 812 (5) $\{Ge_{10}Rb\}^-$, 725

(3) Ge_{10}^{-}; Raman ν [cm^{-1}] = 95 (w), 102 (w), 131 (w), 138 (w), 145 (w), 155 (w), 166 (w), 209 (s);

X-Ray data collection and structure determination: A single crystal was fixed on the top of a glas fiber with perfluorinated ether and positioned in a cold N_2 stream at 123 K. The single crystal X-ray diffraction data were recorded on an Oxford-Diffraction Xcalibur3 diffractometer (Mo-K_α radiation). The crystal structure was solved by Direct Methods using the SHELX software.[4] The positions of the hydrogen atoms were calculated and refined using a riding model. All non-hydrogen atoms were treated with anisotropic displacement parameters.

Electrospray ionization mass spectrometry (ESI-MS) investigations: ESI-MS was done on a HCT mass spectrometer (Bruker Daltronic) in the negative ion mode (-); Preparation of **1**/*acn*: Several crystals of **1** were washed with toluene and dissolved in *acn*, giving an intensively brown, transparent solution. Prior to injection into the ESI-MS the solution was filtered; preparation of Rb_4Ge_9/*en* and Rb4Ge_9/**3**/*en*: The Rb_4Ge_9/**3**/*en* mixture was prepared according to the synthesis described for [Rb(222-crypt)]$_2$[Ge_{10}](en)$_{1.5}$. The Rb_4Ge_9/*en* mixture was prepared by dissolving Rb_4Ge_9 (40 mg, 0.04 mmol, 1 eq.) in 0.67 mL *en*. Upon addition of Rb_4Ge_9 to *en* a dark orange-green solution and a large amount of a yellow precipitate were obtained. The mixture was stirred for 20 h, where upon the color became deep-green, and the yellow precipitate dissolved; prior to the measurement both reaction mixtures were filtered and diluted with *en* (1:100). Measurement conditions: capillary voltage: 4.5 kV(*acn*)/2.5kV(*en*), capillary exit: -166(*acn*)/-180(*en*) V, drying gas temperature: 125 °C (*acn*/*en*), injection rate: 240 µL/h(*acn*/*en*).

Raman spectroscopy: Raman measurements were performed on single crystals sealed in glass capillaries with a Raman microscopy spectrometer (Senterra Raman spectrometer: Bruker Corporation; diode laser: 785 nm, 1 mW).

2 Crystallographic details

Figure S1. The *closo*-$[Ge_9]^{2-}$ Zintl cluster.[5] For a detailed discussion on the disorder see original publications.[5,6]

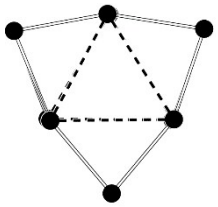


Table S1. Selected crystallographic data of **1**

Compound	**1**
Formula	$Ge_{10}Rb_2C_{39}H_{84}N_7O_{12}$
fw (g mol^{-1})	1739.97
space group (no.)	$P\bar{1}$ (2)
a (Å)	10.8759(2)
b (Å)	13.4395(3)
c (Å)	21.2985(4)
α (deg)	85.907(2)
β (deg)	88.885(2)
γ (deg)	88.995(2)
V (Å^3)	3104.2(1)
Z	2
T (K)	123(2)
λ (Å)	0.71073
ρ_{calcd} (g cm^{-3})	1.862
μ (mm^{-1})	6.38
collected reflections	65291
independent reflections	11569
R_{int}	0.081
parameters / restraints	631 / 6
R_1 [all data / $I > 2\,\sigma(I)$]	0.095 / 0.041
wR_2 [all data / $I > 2\,\sigma(I)$]	0.091 / 0.078
goodness of fit	0.855
max./min. diff. el. density (e Å^{-3})	1.12 / -0.87

Figure S2. Drawing of the unit cell of **1**. $[Ge_{10}]^{2-}$ clusters are shown as dark-grey polyhedra. Cryptand[2.2.2] is shown schematically, displacement ellipsoids of rubidium are shown at a probability level of 50% at 123 K. Solvent and hydrogen atoms are omitted for clarity.

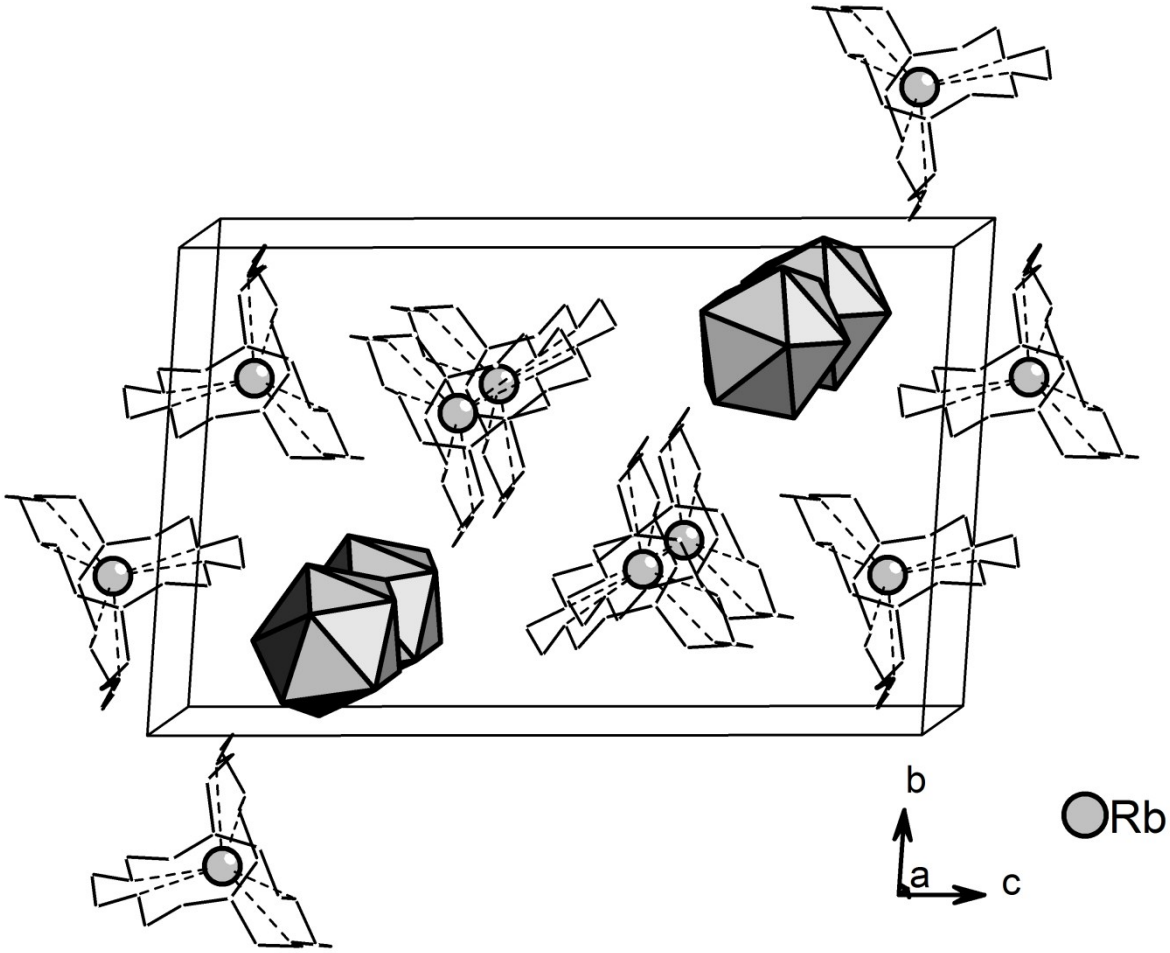


Table S2. Bond lengths [Å] in **1a**

Ge1—Ge5	2.573(1)	Ge4—Ge9	2.566(1)
Ge1—Ge4	2.584(1)	Ge4—Ge5	2.799(1)
Ge1—Ge3	2.587(1)	Ge5—Ge9	2.543(1)
Ge1—Ge2	2.588(1)	Ge5—Ge6	2.552(1)
Ge2—Ge6	2.546(1)	Ge6—Ge10	2.567(1)
Ge2—Ge7	2.559(1)	Ge6—Ge7	2.809(1)
Ge2—Ge3	2.760(1)	Ge6—Ge9	2.822(1)
Ge2—Ge5	2.792(1)	Ge7—Ge10	2.587(1)
Ge3—Ge7	2.535(1)	Ge7—Ge8	2.780(1)
Ge3—Ge8	2.564(1)	Ge8—Ge10	2.611(1)
Ge3—Ge4	2.797(1)	Ge8—Ge9	2.798(1)
Ge4—Ge8	2.551(1)	Ge9—Ge10	2.590(1)

Table S3. Bond angles [deg] in **1a**

Ge3—Ge1—Ge2	64.47 (3)	Ge1—Ge5—Ge4	57.33 (3)
Ge6—Ge2—Ge7	66.76 (3)	Ge2—Ge5—Ge4	90.00 (3)
Ge6—Ge2—Ge1	110.40 (4)	Ge2—Ge6—Ge5	66.42 (3)
Ge7—Ge2—Ge1	110.49 (4)	Ge2—Ge6—Ge10	110.36 (4)
Ge6—Ge2—Ge3	103.83 (4)	Ge5—Ge6—Ge10	109.72 (4)
Ge7—Ge2—Ge3	56.77 (3)	Ge2—Ge6—Ge7	56.84 (3)
Ge1—Ge2—Ge3	57.74 (3)	Ge5—Ge6—Ge7	102.68 (3)
Ge6—Ge2—Ge5	56.89 (3)	Ge10—Ge6—Ge7	57.32 (3)
Ge7—Ge2—Ge5	102.95 (3)	Ge2—Ge6—Ge9	102.70 (3)
Ge1—Ge2—Ge5	57.00 (3)	Ge5—Ge6—Ge9	56.20 (3)
Ge3—Ge2—Ge5	90.10 (3)	Ge10—Ge6—Ge9	57.21 (3)
Ge7—Ge3—Ge8	66.09 (3)	Ge7—Ge6—Ge9	89.51 (3)
Ge7—Ge3—Ge1	111.32 (4)	Ge3—Ge7—Ge2	65.62 (3)
Ge8—Ge3—Ge1	109.98 (4)	Ge3—Ge7—Ge10	111.17 (4)
Ge7—Ge3—Ge2	57.61 (3)	Ge2—Ge7—Ge10	109.30 (4)
Ge8—Ge3—Ge2	103.36 (3)	Ge3—Ge7—Ge8	57.46 (3)
Ge1—Ge3—Ge2	57.79 (3)	Ge2—Ge7—Ge8	102.94 (3)
Ge7—Ge3—Ge4	103.55 (3)	Ge10—Ge7—Ge8	58.09 (3)
Ge8—Ge3—Ge4	56.61 (3)	Ge3—Ge7—Ge6	102.76 (3)
Ge1—Ge3—Ge4	57.21 (3)	Ge2—Ge7—Ge6	56.39 (3)
Ge2—Ge3—Ge4	90.69 (3)	Ge10—Ge7—Ge6	56.63 (3)
Ge8—Ge4—Ge9	66.31 (3)	Ge8—Ge7—Ge6	90.27 (3)
Ge8—Ge4—Ge1	110.49 (4)	Ge4—Ge8—Ge3	66.31 (3)
Ge9—Ge4—Ge1	109.81 (4)	Ge4—Ge8—Ge10	110.17 (4)
Ge8—Ge4—Ge3	57.08 (3)	Ge3—Ge8—Ge10	109.45 (4)
Ge9—Ge4—Ge3	102.91 (3)	Ge4—Ge8—Ge7	103.60 (4)
Ge1—Ge4—Ge3	57.30 (3)	Ge3—Ge8—Ge7	56.45 (3)
Ge8—Ge4—Ge5	102.46 (4)	Ge10—Ge8—Ge7	57.24 (3)
Ge9—Ge4—Ge5	56.38 (3)	Ge4—Ge8—Ge9	57.10 (3)
Ge1—Ge4—Ge5	56.95 (3)	Ge3—Ge8—Ge9	102.92 (4)
Ge3—Ge4—Ge5	89.21 (3)	Ge10—Ge8—Ge9	57.08 (3)
Ge9—Ge5—Ge6	67.29 (3)	Ge7—Ge8—Ge9	90.59 (3)
Ge9—Ge5—Ge1	110.90 (4)	Ge5—Ge9—Ge4	66.44 (3)
Ge6—Ge5—Ge1	110.70 (4)	Ge5—Ge9—Ge10	109.27 (4)
Ge9—Ge5—Ge2	103.63 (3)	Ge4—Ge9—Ge10	110.39 (4)
Ge6—Ge5—Ge2	56.69 (3)	Ge5—Ge9—Ge8	102.68 (3)
Ge1—Ge5—Ge2	57.51 (3)	Ge4—Ge9—Ge8	56.59 (3)
Ge9—Ge5—Ge4	57.17 (3)	Ge10—Ge9—Ge8	57.83 (3)
Ge6—Ge5—Ge4	103.89 (4)	Ge5—Ge9—Ge6	56.51 (3)

Ge4—Ge9—Ge6	102.87 (3)	Ge7—Ge10—Ge9	99.97 (3)
Ge10—Ge9—Ge6	56.42 (3)	Ge6—Ge10—Ge8	99.82 (3)
Ge8—Ge9—Ge6	89.63 (3)	Ge7—Ge10—Ge8	64.67 (3)
Ge6—Ge10—Ge7	66.05 (3)	Ge9—Ge10—Ge8	65.09 (3)
Ge6—Ge10—Ge9	66.37 (3)		

3 Electrospray-ionization mass spectra (ESI-MS)

Figure S3. ESI-MS (-) of crystals of **1** dissolved in *acn*. a) Full spectrum and b) magnified sections, showing the most prominent fragments in detail. The measured spectrum and simulated pattern are depicted in black and as red columns, respectively. Unknown signals are marked with *.

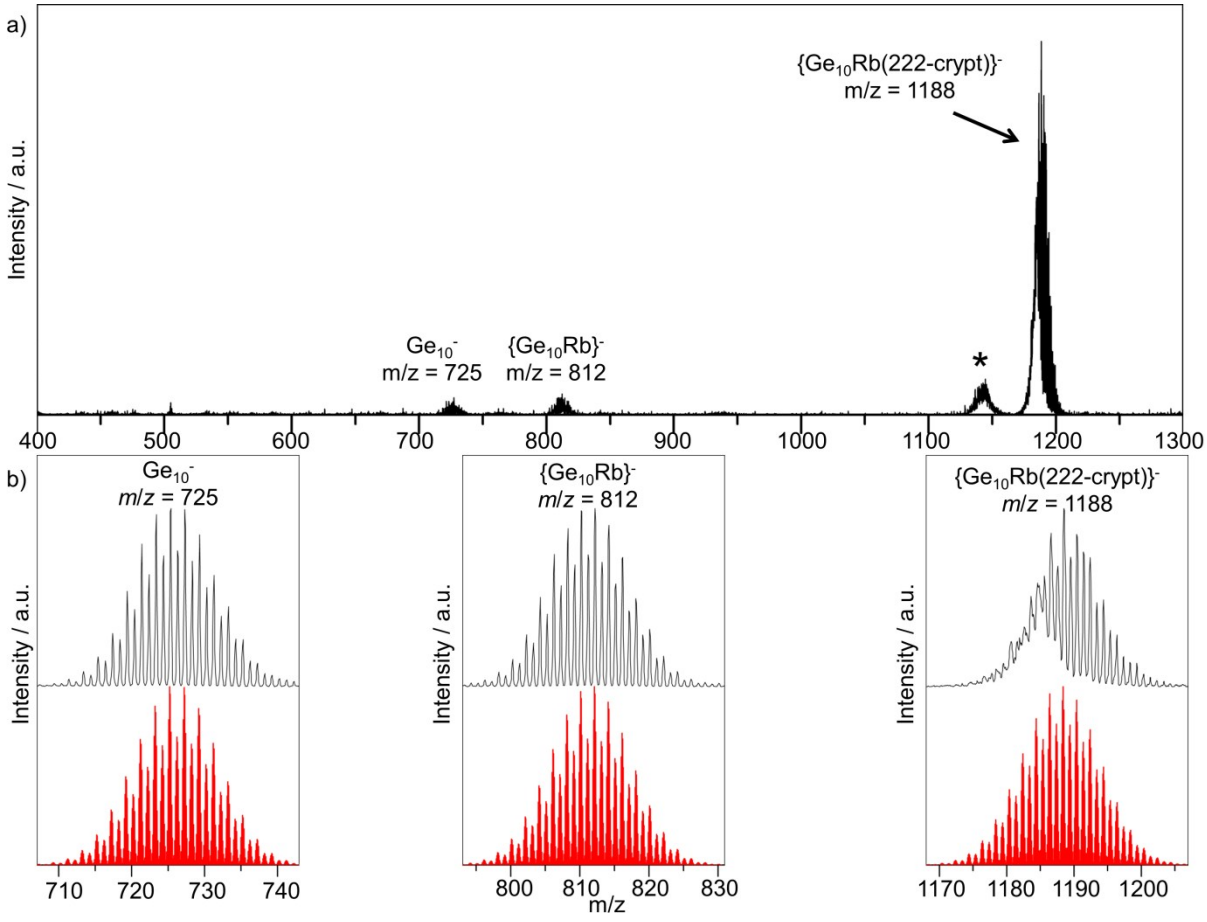


Figure S4. ESI-MS (-) of the reaction solutions a) Rb_4Ge_9/*en* and b) Rb_4Ge_9/**3**/*en*. The measured spectra (black) and simulated patterns (coloured), R = 7-amino-5-aza-hepta-2,4-dien-2-yl = $C_6H_{11}N_2$.

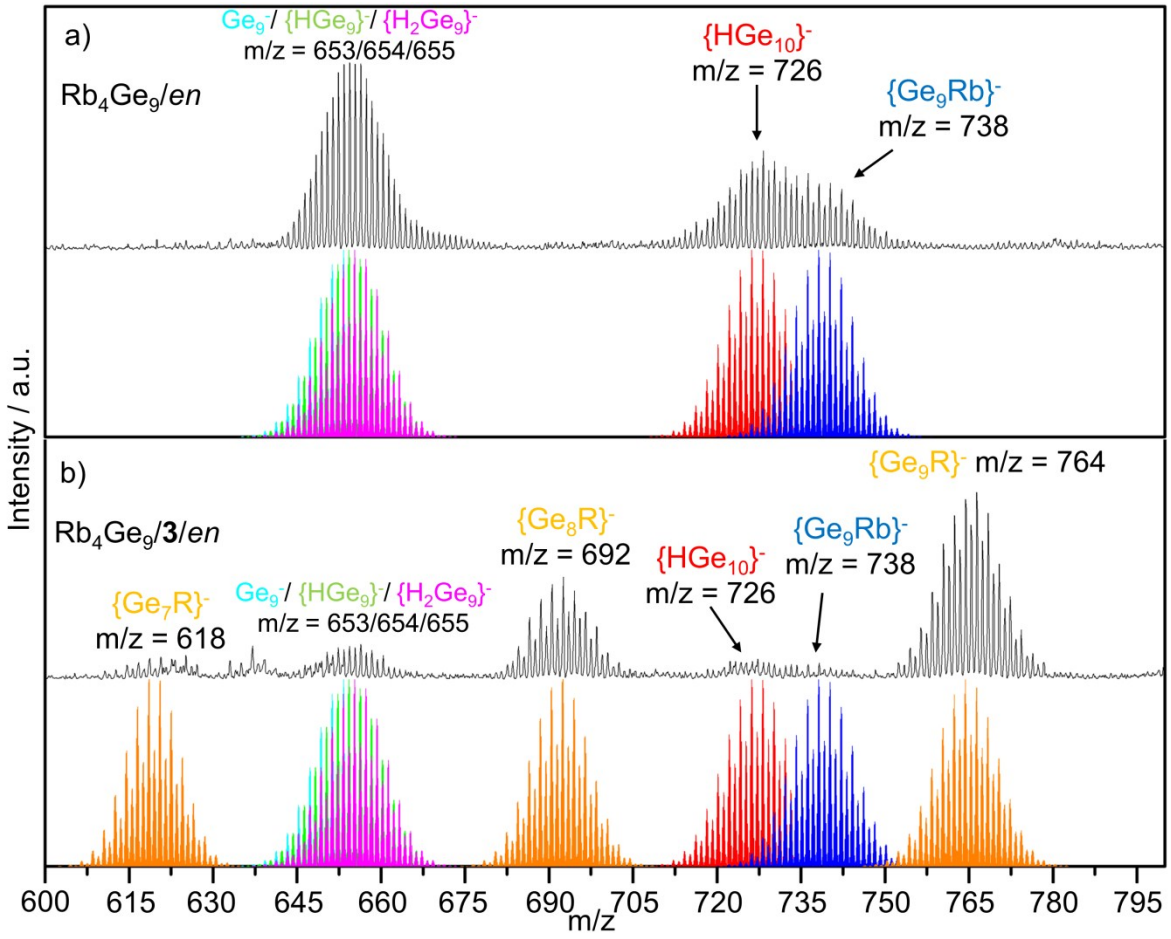
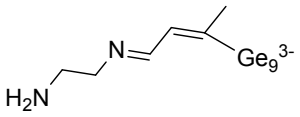


Figure S5. The $[R–Ge_9]^{3–}$ (R = 7-amino-5-aza-hepta-2,4-dien-2-yl) originating from the reaction of $[Ge_9]^{4–}$ with 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne.



Scheme S1. Half reaction (oxidation) of the formation of $[Ge_{10}]^{2–}$ from $[Ge_9]^{4–}$ occurring upon dissolution of Rb_4Ge_9 in *en*.

$$Rb_4Ge_9 \xrightarrow{\text{Dissolve in } en} Ge_9^{4-} + 4\ Rb^+ \longrightarrow 9/10\ Ge_{10}^{2-} + 22/10\ e^- + 4\ Rb^+$$

4 References

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