Supplementary Information

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

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

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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$_4$Ge$_9$ 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-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$_4$Ge$_9$ (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 mm$^3$; unit cell parameters: $a = 10.8759(2)$ Å, $b = 13.4395(3)$ Å, $c = 21.2958(4)$ Å, $\alpha = 85.907(2)^\circ$, $\beta = 88.885(2)^\circ$, $\gamma = 88.995(2)^\circ$, $V = 3104.2(11)$ Å$^3$, triclinic space group $P\bar{1}$; $Z = 2$, $\rho_{\text{calc}} = 1.862$ g cm$^{-3}$, $\mu = 6.38$ mm$^{-1}$, $\theta_{\text{max}} = 26.00^\circ$, 65291 measured reflections, 11569 independent reflections, $R_{\text{int}} = 0.081$, $R_1 = 0.041$, $wR_2 = 0.078$ 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) $\{\text{Ge}_{10}\text{Rb}(222\text{-crypt})\}^-$, 812 (5) $\{\text{Ge}_{10}\text{Rb}\}^-$, 725
Ge$_{10}^{-}$; Raman $\nu$ [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 glass 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$_\alpha$ radiation). The crystal structure was solved by Direct Methods using the SHELX software. 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/acf: 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$_4$Ge$_9$/en and Rb$_4$Ge$_9$/3/en: The Rb$_4$Ge$_9$/3/en mixture was prepared according to the synthesis described for [Rb(222-crypt)]$_2$(Ge$_{10}$)(en)$_{1.5}$. The Rb$_4$Ge$_9$/en mixture was prepared by dissolving Rb$_4$Ge$_9$ (40 mg, 0.04 mmol, 1 eq.) in 0.67 mL en. Upon addition of Rb$_4$Ge$_9$ 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

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<td>$b$ (Å)</td>
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<td>$c$ (Å)</td>
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Figure S2. Drawing of the unit cell of 1. \([\text{Ge}_{10}]^{2-}\) 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

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

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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) Rb₄Ge₉/en and b) Rb₄Ge₉/3/en. The measured spectra (black) and simulated patterns (coloured), R = 7-amino-5-aza-hepta-2,4-dien-2-yl = C₆H₁₁N₂.

**Figure S5.** The [R–Ge₉]³⁻ (R = 7-amino-5-aza-hepta-2,4-dien-2-yl) originating from the reaction of [Ge₉]⁴⁻ with 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne.

**Scheme S1.** Half reaction (oxidation) of the formation of [Ge₁₀]²⁻ from [Ge₉]³⁻ occurring upon dissolution of Rb₄Ge₉ in en.
4 References