1: A solution of 'N$_2$Me$_2$S$_2$-H$_2$' (696 mg, 2.29 mmol) in MeOH (35 mL) and 1N LiOMe in MeOH (9.16 mL, 9.16 mmol) was added dropwise to a boiling MeOH suspension of [RuCl$_2$(MeCN)$_4$] (768 mg, 2.29 mmol) and P*i*Pr$_3$ (0.89 mL, 4.57 mmol). The resulting yellow solution was heated for another 45 min under reflux, filtered while hot, and stored at −20 °C for 12 h. The precipitated yellow crystals were separated at −20 °C, washed with MeOH (50 mL), and dried in vacuo for 12 h (980 mg, 69 %). Correct elemental analyses. IR (KBr): $\tilde{\nu} = 2245$ (ν_{CN}) cm^{-1}; ^{1}H NMR (269.7 MHz, CD$_2$Cl$_2$): $\delta = 7.53-6.70$ (m, 8H; C$_6$H$_4$), 3.33 (s, 3H; CH$_3$), 3.28 (s, 3H; CH$_3$), 3.30–2.20 (m, 4H; C$_2$H$_4$), 2.20 (s, 3H; CH$_3$CN), 2.19–2.09 (m, 3H; P(CH)), 1.36–1.24 (m, 18H; (CH$_3$)); ^{13}C{^{1}H} NMR (67.7 MHz, CD$_2$Cl$_2$): $\delta = 157.7$ (CH$_3$CN), 154.3, 153.9, 153.1, 151.7, 131.5, 131.2, 126.0, 125.7, 123.4, 122.0, 120.3, 119.9 (C$_6$H$_4$), 68.4, 62.0 (C$_2$H$_4$), 50.3, 47.8 (CH$_3$), 27.6 (d, J(P,C) = 18 Hz), 20.8, 19.5 (P(C$_3$H$_7$)); ^{31}P{^{1}H} NMR (161.7 MHz, CD$_2$Cl$_2$): $\delta = 50$ (s); FD-MS (CH$_2$Cl$_2$, ^{102}Ru, rel. intensity): m/z (%): 564 (100) [Ru(P*i*Pr$_3$)('N$_2$Me$_2$S$_2$')]$^+$, 605 (12) [Ru(MeCN)(P*i*Pr$_3$)('N$_2$Me$_2$S$_2$')]$^+$.

2: A stream of N$_2$ was passed through a solution of **1** (1.58 g, 2.6 mmol) in toluene (50 mL), until the ν_{N_2} IR band of **2** showed maximum intensity (ca. 30 min). At the end of the reaction, the solution was gently heated to 40–50 °C to remove liberated MeCN. After filtration, *n*-hexane (200 mL) was added precipitating unreacted **1**, which was removed after 30 min. The remaining *n*-hexane/toluene solution was reduced in volume to about 100 mL by passing a stream of N$_2$ through the solution. Yellow-green **2** precipitated, was separated, washed with Et$_2$O (3 mL), and dried in vacuo for 3 h (720 mg, 46 %). Correct elemental analyses. IR (KBr): $\tilde{\nu} = 2113$ (ν_{N_2}) cm^{-1}; ^{1}H NMR (269.7 MHz, THF): $\delta = 7.47-6.77$ (m, 8H; C$_6$H$_4$), 3.42 (s, 3H; CH$_3$), 3.38 (s, 3H; CH$_3$), 3.37–2.30 (m, 4H; C$_2$H$_4$), 2.30–2.23 (m, 3H; P(CH)), 1.38–1.30 (m, 18H; (CH$_3$)); ^{13}C{^{1}H} NMR (67.7 MHz, THF): $\delta = 155.8$, 155.0, 153.6, 153.4, 134.0, 133.9, 128.9, 128.8, 124.4, 123.6, 123.5, 123.0 (C$_6$H$_4$), 70.7, 64.5 (C$_2$H$_4$), 54.2, 50.1 (CH$_3$), 30.1 (d, J(P,C) = 18 Hz), 23.0, 21.8 (P(C$_3$H$_7$)); ^{31}P{^{1}H} NMR (161.7 MHz, THF): $\delta = 48$ (s); FD-MS (THF, ^{102}Ru, rel. intensity): m/z (%): 564 (100) [Ru(P*i*Pr$_3$)(N$_2$Me$_2$S$_2$)]$^+$, 592 (8) [Ru(N$_2$)(P*i*Pr$_3$)(N$_2$Me$_2$S$_2$)]$^+$.

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Synthesis and Characterization of RbLi$_7$Ge$_8$ with Isolated *closo*-[Li$_4$Ge$_{12}$]$^{8-}$ Ions, Lithium-Capped Truncated Tetrahedra of Ge$_{12}$$^{12-}$**

Svilen Bobev and Slavi C. Sevov*

Zintl phases with isolated clusters of more than four atoms were very rare fifteen years ago, when only a few examples were known.[1] Since then, however, this number has skyrocketed with many examples of Groups 13 (Tr = Triels) and 14 (Tt = Tetrels) as well as some heteroatomic species.[2] Furthermore, many compounds in the A–Tt systems (A = alkali metal) were found to contain isolated deltahedral clusters, often referred to as Zintl ions, that were previously either unknown[3] or could be crystallized from solutions only.[4] Understanding the electronic structure and bonding in Zintl phases with deltahedral clusters combines both the assumption for complete electron transfer from the alkali metal atoms to the clusters (the Zintl–Klemm concept)[1, 5] with the Wade's rules for electron counting in deltahedral boranes.[6] Our interest has focused especially on clusters of

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Group 14, which initially started with the discovery of the first *nido*-Ge_9^{4-} deltahedra in the solid-state compound Cs_4Ge_9.[4a] This developed into systematic and thorough studies of the binary and pseudo-binary systems A–Tt and (A′/A″)–Tt, respectively, where A′ and A″ are two different alkali metals. The latter systems produced a number of interesting results, especially when A′ and A″ were of very different size. Thus, the first stoichiometric silicon and germanium clathrates of type II, $A_8Na_{16}Tt_{136}$ (A = Rb, Cs; Tt = Si, Ge), were synthesized in a rational way only when the smaller sodium was combined with the much larger rubidium or cesium.[7] Similarly, the same alkali metals combined with tin provided the novel phases $A_3Na_{10}Sn_{23}$ (A = K, Rb, Cs) made of clathrate layers of tin and intercalated with cations and tin tetrahedra.[8] Lastly, an *arachno* cluster of eight atoms, a square antiprism of Sn_8^{6-} isoelectronic with Bi_8^{2+} of the same geometry,[9] was synthesized only when lithium was combined with rubidium or potassium in the compounds $A_4Li_2Sn_8$ (A = K, Rb).[10] The much smaller and more covalent lithium in the latter not only provides electrons but also stabilizes the clusters by capping the open square faces of the tin square antiprisms to form the *closo* species $[Li_2Sn_8]^{4-}$.[10] Here we report the synthesis and structure of another lithium-based pseudo-binary compound, $RbLi_7Ge_8$, which contains the largest isolated clusters of Group 14, truncated tetrahedra of Ge_{12}^{12-} stabilized similarly by lithium that caps all four hexagonal faces to form a 16-atom *closo*-$[Li_4Ge_{12}]^{8-}$ cluster.

The new compound $RbLi_7Ge_8$ was synthesized by direct fusion of the elements.[11] Lithium was purposely used in a combination with a heavy alkali metal. Its substantial covalency, much smaller size, strong polarizing power, and higher electronegativity, provide for quite different interactions with the early p-block elements. These properties of lithium have been exploited quite extensively in the past and a number of novel compounds that form with lithium only have been reported.[12–15] The heavy alkali metal, on the other hand, provides for different packing requirements and more complete electron transfer. For example, the defect diamond-type structure of Li_8Ge_8 (= LiGe)[12] differs significantly from the structure of the new compound $RbLi_7Ge_8$ although only one of eight lithium atoms is formally "replaced" by rubidium.

The structure of $RbLi_7Ge_8$ was determined from single-crystal X-ray diffraction studies.[16] It contains two different isolated germanium clusters of Ge_4^{4-} and Ge_{12}^{12-} in equimolar ratio (Figure 1). The former are the same well known tetrahedra found in the classical A_4Ge_4 (A = K, Rb, Cs),[17] as well as some compounds with mixed alkali metal cations $(A'_xA''_{1-x})_4Ge_4$ for $x = 0.125$, 0.25, and 0.5.[13] The novel clusters of Ge_{12}^{12-} are only the third type of germanium clusters in addition to the Ge_4^{4-} tetrahedra and the monocapped square antiprisms of *nido*-Ge_9^{4-}. The geometry of Ge_{12}^{12-} is truncated tetrahedron with four triangular and four hexagonal faces (Figure 2), and all germanium atoms are three-bonded. The range of Ge–Ge distances in Ge_{12}^{12-} (2.505(2)–2.603(2) Å) is somewhat broader than that in Ge_4^{4-} (2.567(2)–2.569(2) Å), although both have exactly the same average, 2.568 Å. These distances compare also very well with distances of Ge_4^{4-} in other compounds[13, 17] and those of Ge_9^{4-}.[4]

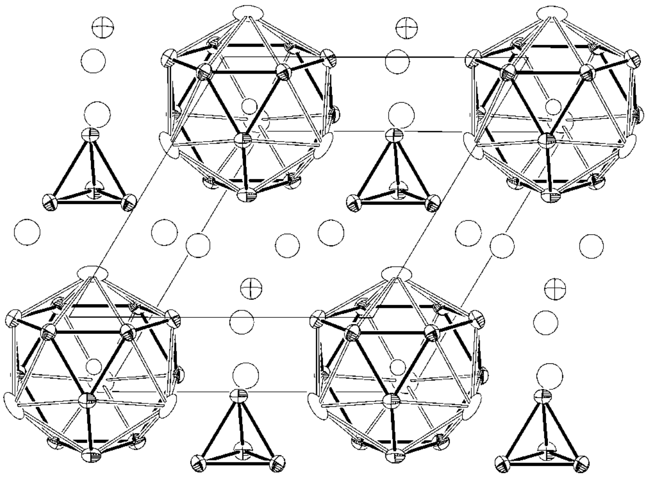

Figure 1. General view of the structure of $RbLi_7Ge_8$ (Ge: full ellipsoids, Li: empty ellipsoids, Rb: crossed ellipsoids, 80% probability level) with the hexagonal cell outlined. The vertices of the clusters of Ge_{12}^{12-} and Ge_4^{4-} are connected with thick full bonds, while the lithium atoms capping the faces of Ge_{12}^{12-} are connected with open lines.

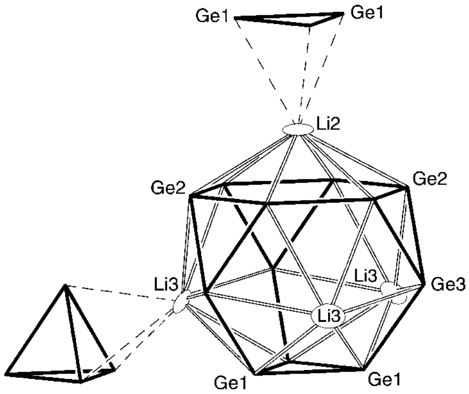

Figure 2. Structure of one *closo*-$[Li_4Ge_{12}]^{8-}$ ion, a lithium-capped truncated tetrahedron Ge_{12}^{12-} (50% thermal ellipsoids). All Ge–Ge contacts are shown with thick full bonds, while the capping Li atoms are connected with open lines. The intercluster interactions of Li2 with a triangular face of another $[Li_4Ge_{12}]$ cluster and the interactions of one of the three Li3 atoms with a neighboring Ge_4 tetrahedra are shown with broken thin lines. Intracluster distances [Å]: Ge1–Ge1 2.587(2), Ge1–Ge3 2.505(2), Ge2–Ge2 2.603(2) in Ge2-Ge2-Ge3 triangles and 2.533(2) between them, Ge2–Ge3 2.593(1), Li2–Ge2 2.95(2), Li3–Ge1 2.93(1), Li3–Ge2 2.97(2), Li3–Ge3 2.98(1).

The clusters in $RbLi_7Ge_8$ are well separated (the shortest intercluster distance is 4.2323(9) Å). They are arranged in nearly flat layers perpendicular to the *c* axis, and the cations are found between the layers as well as between the clusters within the layers. As expected, the cations cap faces, edges, and vertices of the clusters, and one lithium atom centers the truncated tetrahedron of Ge_{12}^{12-}. The Rb–Ge and Li–Ge distances are in the ranges 3.743(1)–4.430(2) and 2.69(5)–3.044(9) Å, respectively.

The stoichiometry and the bonding of $RbLi_7Ge_8$ can be readily rationalized by the Zintl–Klemm concept.[1, 5] All germanium atoms carry a charge of 1 – each for being three-bonded. These charges are counterbalanced by exactly the same number of alkali metal cations available in the formula. In other words, $RbLi_7Ge_8$ is an electronically balanced compound, a saltlike Zintl phase. Indeed, this is supported by our extended-Hückel molecular orbital calculations, the dark-to-black colored and very brittle crystals, and, most importantly, by the diamagnetism observed for the compound.[18]

Another, perhaps more interesting way to view the bonding in this mixed-cation compound is to consider the lithium atoms capping the hexagonal faces of the truncated tetrahedra as part of the clusters. This, as already discussed, is well justified by the substantially more covalent Li–Ge interactions.[12] Thus, Ge_{12}^{12-} is completed to a *closo*-$[Li_4Ge_{12}]^{8-}$ deltahedral cluster of 16 atoms (Figure 1 and 2). In a similar manner the square faces of the square-antiprismatic *arachno*-Sn_8^{6-} found in $A_4Li_2Sn_8$ (A = K, Rb) are capped by lithium to form the deltahedral *closo*-$[Li_2Sn_8]^{4-}$.[10] $[Li_4Ge_{12}]$ is centered by another lithium atom with very similar distances to the sixteen vertices (twelve germanium and four lithium). They are in the narrow range of 2.98(4) to 3.08(3) Å, and indicate that the overall shape of the cluster is very close to spherical.

Sixteen-atom species of this geometry of tetracapped truncated tetrahedra are known but usually as interconnected in networks.[19, 20] Despite the *closo* shape, however, it is known that such clusters "violate" Wade's rules[6] (intrinsically) because of their nearly ideal T_d symmetry.[19] They require $2n+4$ cluster-bonding electrons instead of the usual $2n+2$ for *closo* clusters,[21] which means $2 \times 16+4 = 36$ electrons for $[Li_4Ge_{12}]$. In addition to the bonding electrons, the vertices of such "naked" clusters should carry a lone pair of electrons each. This, however, shall not be expected for the lithium vertices since this would lead to the impossible and unrealistic charge of more than 2 – per lithium. Instead, each capping lithium atom of $[Li_4Ge_{12}]$ is in turn "capped" by a triangle of germanium atoms from a nearby tetrahedron or another truncated tetrahedron (Figure 2) and interacts with the three lone pairs provided by these germanium atoms. The interaction can be modeled as four-center, six-electron bonding in a trigonal pyramid with an "open" base. The bases are the "capping" triangular faces of germanium which, of course, are not really open but since the lone pairs are not involved in the bonding of the triangular face they can be considered as isolated from each other. The MO diagram of such a model contains one low-lying totally bonding combination of all four orbitals, that is the Li s orbital and the three germanium lone pairs, and this is followed by a doubly degenerate nonbonding combination of the three lone pairs and an antibonding combination of the four orbitals. The net result for six electrons is bonding where two of the six electrons provide for the three Li–Ge bonding interactions and the remaining four electrons are the two pairs of nonbonding electrons delocalized on the three germanium atoms. The same situation is observed in $A_4Li_2Sn_8$ (A = K, Rb), where the lithium atoms that cap the open square faces of the square-antiprismatic Sn_8 interact also with the lone pairs of two tin atoms forming an edge of a neighboring Sn_8 cluster.[10] The Li–Ge interactions can be viewed also as localized in resonance structures where the lithium is *exo*-bonded to one germanium atom at a time by sharing its pair of electrons, while the other two germanium atoms retain their nonbonding lone pairs of electrons. Thus, through the interactions between the capping lithium atoms and the neighboring clusters each *closo*-$[Li_4Ge_{12}]^{8-}$ cluster is "connected" to two other such clusters along the *c* axis and to three tetrahedra in the *xy* plane.

The negated need of lone pairs on the four lithium vertices of the 16-atom clusters means that only 24 electrons are needed for lone pairs for the remaining twelve vertices, the germanium atoms. The cluster, therefore, requires total of 60 electrons which includes the 36 bonding electrons discussed above. The sixteen atoms provide total of 52 electrons, that is 4×1 from lithium and 12×4 from germanium. Thus, the $[Li_4Ge_{12}]$ cluster will have a negative charge of 8 – . The Ge_4 tetrahedra are known to carry a charge of 4 – , and therefore, the formula can be rewritten as $Rb_2Li_{14}Ge_{16} = Rb_2Li_{10}\{[Ge_4]^{4-}\}\{[Li_4Ge_{12}]^{8-}\}$ or as $Rb_2Li_9\{[Ge_4]^{4-}\}$-$\{(Li@[Li_4Ge_{12}])^{7-}\}$ since one lithium cation centers the big cluster.

The new compound and the other mixed-cation compounds mentioned above illustrate nicely the delicate balance between packing efficiency, electronic requirements, and covalent interactions. By using carefully selected combinations of alkali metals one can possibly change the packing modes, while the overall cation to anion ratio and, therefore, charge are kept constant. This will be, most likely, the best way towards stabilization of other yet-to-be-found compounds that are otherwise inaccessible in pure binary systems. As seen here, similarly to the *arachno*-Sn_8^{6-} that exists only in the lithium-containing $A_4Li_2Sn_8$ (A = K, Rb) Zintl phase as a *closo*-$[Li_2Sn_8]^{4-}$ ion,[10] the Ge_{12}^{12-} is stabilized only in $RbLi_7Ge_8$ as a *closo*-$[Li_4Ge_{12}]^{8-}$ ion.

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intended to produce $Rb_3Li_{10}Ge_{23}$, the Li/Ge analogue of the known $A_3Na_{10}Sn_{23}$ ($A = K$, Rb, Cs).[8] After the structure and the exact stoichiometry of the compound were determined from single-crystal X-ray diffraction data, $RbLi_7Ge_8$ was synthesized from the corresponding stoichiometric mixture of elements by heating at 1000 °C for 4 h and then cooling down to room temperature at a rate of $20\,^\circ C\,h^{-1}$. All reactions were carried out in tubular niobium containers that were sealed at the two ends by arc-welding. These containers are then placed in fused-silica ampoules, and the latter are evacuated (below discharge) and sealed. Attempts to synthesize the corresponding K and Cs analogues have been unsuccessful so far. Nevertheless, these reactions yielded K_3LiGe_4 (*Pnma*, $a = 7.758(9)$, $b = 9.931(8)$, $c = 12.400(9)$ Å) and Cs_3LiGe_4 (*Cmcm* $a = 6.944(4)$, $b = 15.510(8)$, $c = 9.88(1)$ Å) isostructural with the known K_3LiSi_4 and Cs_3LiSi_4,[14] respectively. However, both reactions yielded traces of other, yet unidentified phases, and currently under way is a search for optimal compositions and reaction conditions.

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[16] Structure determination: Crystals selected from the initial reaction were sealed in capillaries and checked for singularity. For the best one (barlike shape, $0.12 \times 0.10 \times 0.08$ mm) a hemisphere of data was collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, ω-2θ scans, $2\theta_{max} = 60^\circ$, RT). The data were corrected for absorption with the aid of the average of 3 Ψ scans at different θ angles. The structure was solved by direct methods and refined on F^2 with the SHELXTL-V5.1 software package. Crystal data: hexagonal, $P6_3mc$ (no. 186), $a = 9.8946(7)$, $c = 16.269(3)$ Å; $V = 1379.4(3)$ Å^3; $Z = 4$; $\mu = 206.34\ cm^{-1}$; $\rho_{calcd} = 3.442\ g\,cm^{-3}$. The refinement of all but two lithium atoms with anisotropic thermal parameters converged to $R1/wR2$ ($I > 2\sigma(I)$) = 0.0362/0.0755 and $R1/wR2$ (all data) = 0.0491/0.0804 for 1270 independent reflections (4475 total number of reflections) and 62 variables. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411606.

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[18] Magnetic measurements: The magnetization of 14 mg of selected crystals of $RbLi_7Ge_8$ was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10–280 K. The data were corrected for the holder and for ion-core diamagnetism. The susceptibility is negative and temperature independent in the range $-(1.63-1.82) \times 10^{-4}\ emu\,mol^{-1}$. This is consistent with a diamagnetic compound.

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[20] Similar truncated tetrahedra made of aluminum and capped by magnesium may exist in the metallic alloy "$Mg_{17}Al_{12}$" (powder diffraction work: P. Schobinger-Papamantellos, P. Fischer, *Naturwissenschaften* **1970**, *57*, 128). Nevertheless, this can not be established unequivocally by powder diffraction for two elements that differ by one electron only.

[21] This "violation" for the tetracapped truncated tetrahedron is very similar to that observed for the simple tetrahedron which also due to the T_d symmetry requires $2n+4$ electrons.

Controlled Synthesis of Cross-Linked Ultrathin Polymer Films by Using Surface-Initiated Atom Transfer Radical Polymerization**

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Covalent attachment of polymer chains to solid substrates by surface-initiated polymerization is an effective method for tailoring surface properties such as wetting, adhesion, and biocompatibility. Following Rühe and Prucker's successful work on free radical polymerization from surfaces,[1a] several research groups recently reported the use of controlled/living polymerization techniques[1b–h] to grow polymer chains from a surface in a well-defined manner. Several research groups also used surface-initiated polymerizations to generate patterned polymers on surfaces for lithographic applications.[1c,e, 2, 3] The grafted polymer layers have higher resistance to wet chemical etchants than the patterned monolayers from which they are grown.

Cross-linked polymer films, compared to linear polymer brush analogues, should yield even better mechanical and chemical stability and provide new pathways to functionalized surfaces for molecular recognition. However, the preparation of cross-linked thin films is an experimental challenge. Direct polymerization of cross-linkable monomers in solution usually results in an insoluble three-dimensional polymeric gel that cannot be deposited as a uniform thin coating. Cross-linked films can be prepared by deposition of a cross-linkable polymer precursor followed by a cross-linking reaction; however, the method is not straightforward and it usually is difficult to control film thickness and the curing reaction. Herein we report direct polymerization of ethylene glycol dimethacrylate (EGDMA) from a surface to form cross-linked polymer films (Figure 1).

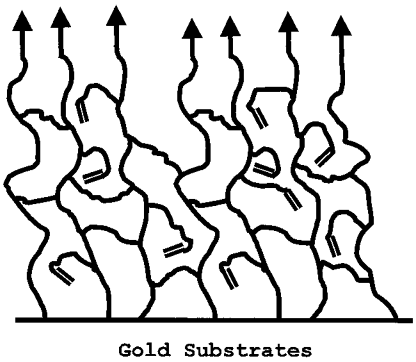

Figure 1. Schematic illustration of a cross-linked film growing from a gold substrate.

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