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Synthesis and Characterization of $Ge_2\{Sn(X)Ar^{\#}\}_3$ and $Ga_2\{Ge(X)Ar^{\#}\}_3$ ($Ar^{\#} = C_6H_3$-2,6-Mes_2), X = (Cl/I): Rare Examples of Mixed Heavier Group 14/14, 13/14 Element Clusters

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*Summary: Treatment of $Ar^{\#}ECl$ ($Ar^{\#} = C_6H_3$-2,6-Mes_2; E = Ge or Sn) with 1 equiv of the reducing agent KC_8 or 'GaI' led to the isolation and characterization of the two new main group clusters $Ge_2\{Sn(X)Ar^{\#}\}_3$, **1**, and $Ga_2\{Ge(X)Ar^{\#}\}_3$, **2** (X = Cl or Cl/I), which have trigonal bypyramidal Ge_2Sn_3 or Ga_2Ge_3 frameworks. Cluster **1** is a singlet biradicaloid, whereas **2** is a very rare heavier group 13/14 element cluster, and the first with a Ga/Ge framework.*

The synthesis of homonuclear clusters of the heavier main group 13 and 14 elements, i.e., $[M_nR_m]^{x-}$, $n > m$, $x = 0, 1, 2$, etc., which contain atoms unsubstituted by organic or other groups, is a topic of considerable current interest. An impressive number of heavier group 13 metal complexes with up to 84 metal atoms is known.[1] In contrast, the corresponding group 14 element clusters are not as well studied.[2] In pioneering work, Sita and co-workers synthesized the compounds Sn_5Ar_6[3] and Sn_7Ar_8[4] (Ar = C_6H_3-2,6-Et_2) in the early 1990s, and although the number of organic substituents exceeds the number of tin atoms, the compounds contain at least two unsubstituted tins. In addition a similar compound, $Sn_5\{C_6H_3\text{-}2,6\text{-}(O^iPr)_2\}_6$, has been reported recently by Drost and co-workers.[5] The tin compounds are of further interest in that they are non-Kekulé species with biradical character.[6,7] Other neutral heavier group 14 element clusters with unsubstituted atoms include the tin clusters $Sn_8\{(SiMe_3)_3\}_6$[8] and $Sn_8(C_6H_3\text{-}2,6\text{-}Mes_2)_4$[9] and the germanium species $Ge_8\{N(SiMe_3)_2\}_6$[10] as well as the octahedral $Ge_4(GeAr')_2$ and $Sn_4(GeAr')_2$ (Ar′ = C_6H_3-2,6-$Dipp_2$, Dipp = C_6H_3-2,6-$^iPr_2$).[11] The latter is the first well-characterized cluster with two different heavier group 14 elements in its framework. Mixed element clusters with two different heavier main group elements are of interest since it is probable that they will have interesting electronic properties.[12] Such clusters are relatively common for group 13 /15 element species,[13] but are quite scarce for groups 14/14 and group 13/14 combinations.[14,15] Here we report two new structurally related clusters having heterobicyclopentane frameworks that are composed of the element pairs Ge/Sn and Ga/Ge.

The clusters $Ge_2\{Sn(Cl)Ar^{\#}\}_3$, **1**, and $Ga_2\{Ge(Cl/I)(Ar^{\#})\}_3$, **2**, were synthesized[16] by the reduction of an $Ar^{\#}SnCl/GeCl_2$ mixture with KC_8 or by the reaction of $Ar^{\#}GeCl$ ($Ar^{\#} = C_6H_3$-2,6-Mes_2) with a suspension of 'GaI' in toluene.[17] Unsuccessful attempts were also made to prepare the corresponding Ge/Ge and Ga/Sn clusters. Our investigation of the synthesis of **1** arose from studies of the above-mentioned mixed octahedral cluster $Sn_4(GeAr')_2$,[11] which featured four unsubstituted tins. We wished to prepare the analogous species, $Ge_4(SnAr')_2$, for comparison. Investigation of a variety of synthetic conditions and aryl groups led only to the

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(16) A mixture of $Ar^{\#}SnCl$ (0.467 g, 1.0 mmol)[a] and $GeCl_2$(dioxane) (0.232 g, 1.0 mmol) was dissolved in THF and added to a well-stirred THF suspension of KC_8 in a dry ice bath. A deep red solution was obtained, which became brown on reaching room temperature. The volatile materials were removed under reduced pressure, and the residue was extracted into toluene. Filtration, followed by slow cooling, afforded almost black crystals of **1**. Yield: 0.213 g 42%, mp 95−110 °C (dec); ^1H NMR (C_6D_6, 25 °C, 399.8 MHz) δ ppm, 2.019 (s 12H, *o*-CH_3), 2.157(s, 6H, *p*-CH_3), 6.814 (s, 4H, *m*-Mes), 6.947 (d, 2H, *m*-C_6H_3, $^3J_{H-H} = 8.0$ Hz), 7.188 (t, 1H $^3J_{H-H} = 8$ Hz); ^{13}C NMR (C_6D_6, 25 °C, 100.59 MHz) 20.98, 23.03, 130.45, 135.57, 136.24, 137.71, 146.24; ^{119}Sn NMR (C_6D_6, 25 °C, 147.07 MHz) δ ppm 456.0 ppm. **2**: A toluene suspension of 'GaI' (0.196 g, 1 mmol) was added to a toluene solution of $Ar^{\#}GeCl$[a] (1 mmol, 0.421 g) dropwise at 0 °C. The solution was allowed to reach ambient temperature and stirred for 16 h. The orange solution was then concentrated and filtered. Storage at ca. −30 °C for 1 week yielded orange/red crystals of **2**. Yield = 56%, mp 210 °C (dec); ^1H NMR (C_6D_6, 25 °C, 399.8 MHz) δ 2.057 (s 12H, *o*-CH_3), 2.102 (s, 6H, *p*-CH_3), 6.799 (s, 4H, *m*-Mes), 6.954 (d, 2H, *m*-C_6H_3, $^3J_{H-H} = 8.0$ Hz), 7.365 (t, 1H, $^3J_{H-H} = 8$ Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 100.59 MHz) 21.094 (*p*-CH_3) 21.895 (*o*-CH_3), 129.512 (*m*-Mes), 130.513 (*m*-C_6H_3), 132.216 (*p*-C_6H_3), 136.424 (*p*-Mes), 137.981 (*o*-Mes), 147.552 (*i*-Mes), 148.210 (*o*-C_6H_3). (a) Simons, R. S.; Pu, L.; Olmstead, M. M, Power, P. P. *Organometallics* **1997**, *16*, 1920.

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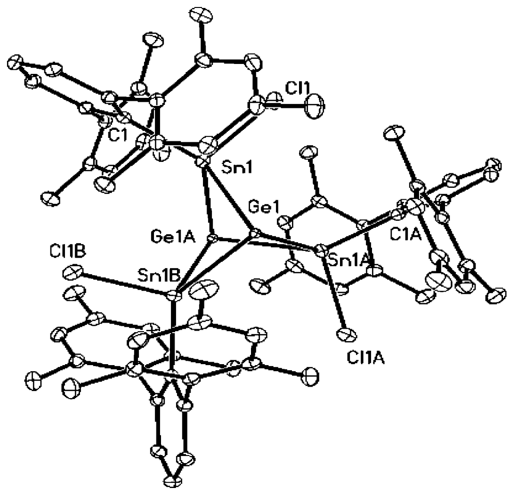

Figure 1. Thermal ellipsoid plot (30%) of **1**. H atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): Sn(1)−Ge(1) = 2.7400(6), Sn(1)−C(1) = 2.141(5), Sn(1)−Cl(1) = 2.379(2), Ge(1)- - -Ge(1a) = 3.363(1), C(1)−Sn(1)−Cl(1) = 103.8(2), C(1)−Sn(1)−Ge(1) = 126.90(9), Cl(1)−Sn(1)−Ge(1) = 109.41(3), Sn(1)−Ge(1)−Sn(1A) = 84.29(2), Ge(1)−Sn(1)−Ge(1A) = 78.42(3).

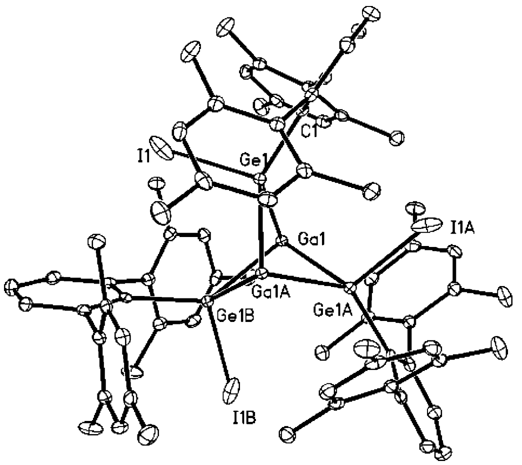

Figure 2. Thermal ellipsoid plot (30%) of **2**. H atoms and Cl occupancy are not shown for clarity. Selected bond distances (Å) and angles (deg): Ge(1)−Ga(1) = 2.4934(6), Ge(1)−C(1) = 1.974(4), Ge(1)−Cl(1) = 2.200(3), Ge(1)−I(1) 2.597(3), Ga(1)- -Ga(1A) = 3.078(1), C(1)−Ge(1)−Cl(1) = 106.5(2), C(1)−Ge(1)−Ga(1) = 127.82(8), Cl(1)−Ge(1)−Ga(1) = 107.41(9), Ga(1)−Ge(1)−Ga(1a) = 76.23(3), Ge(1)−Ga(1)−Ge(1A) = 85.90(2).

isolation of the almost black, crystalline **1** in good yield. It was characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy ($\delta = 456$ ppm) and by X-ray crystallography.[15] Compound **1** crystallizes in a trigonal space group as well-separated molecules that have a trigonal bipyramidal, bicyclo[1.1.1]pentane Ge_2Sn_3 structure in which the bridgehead (or axial) germaniums carry no substituent and the equatorial tins are each bonded to Cl and Ar$^\#$ groups. The molecule is characterized by a 3-fold axis of symmetry along the Ge−Ge vector (Ge- -Ge separation = 3.363(7) Å). The Ge−Sn, Sn−C, and Sn−Cl bond lengths are 2.7400(6), 2.141(5), and 2.379(2) Å, respectively, and the Sn−Ge−Sn and Ge−Sn−Ge angles are 82.29(2)° and 78.42(3)°. The Sn- -Sn separation is 3.677(1) Å.

The reaction of ‘GaI’ and Ar$^\#$GeCl in toluene afforded orange crystals of **2** in moderate yield. The crystals were found to be isomorphous to those of **1** with almost equal unit cell parameters. The structures are very similar and there is a 3-fold axis of symmetry along the Ga- -Ga vector (Ga−Ga separation = 3.078(1) Å). The Ga−Ge and Ge−C bond lengths are 2.4934(6) and 1.974(4) Å, with a Ge- -Ge separation of 3.398(2) Å. The halide site at each germanium has a mixed occupancy composed of 81% chlorine and 19% iodine, which probably arises from exchange of the Ge−Cl moiety with the ‘GaI’. The Ge−Ga−Ge and Ga−Ge−Ga angles are 85.90(2)° and 76.23(3)°.

The $Ge_2\{Sn(Cl)Ar^\#\}_3$ species **1** is only the second example of a cluster with a framework of two different heavier group 14 elements (cf. $Sn_4(GeAr')_2$).[11] It bears a structural resemblance to the corresponding all tin Sn_5Ar_6[2] cluster of Sita. Remarkably, the distance between the bridgehead germaniums, 3.363(2) Å, is similar to that between the bridgehead tins in Sn_5Ar_6 (3.361(1) Å) and the related Sn_7Ar_8 (3.348(1) Å), even though the Ge−Sn bond in **1** is ca. 0.1 Å shorter than the corresponding Sn−Sn bonds in Sn_5Ar_6.[3] The longer bridgehead distance in **1** is accompanied by a narrower angle (by ca. 5°) at the bridgehead Ge atom and a wider (by ca. 6°) Ge−Sn−Ge angle. Such differences can be partly explained on the basis of the electronegative Cl substituent on tin. Thus, despite the large Ar$^\#$ substituent, the C−Sn−Cl angle in **1** (103.8(2)°) is less than the average C−Sn−C angle in Sn_5Ar_6. This finding is in accordance with the Walsh/Bent rule.[19] The narrowing of the angle between the tin substituents leads in turn to a wider GeSnGe angle and thus a greater Ge−Ge separation. The lengthened Sn−Sn bridgehead separation (3.423(1) Å, C−Sn−C = 104.62° (av)) reported in $Sn_6\{C_6H_3\text{-}2,6\text{-}(O^iPr)_2\}_6$,[4] which has more electron-withdrawing substituents than Sn_5Ar_6, is also in accord with these arguments. These structural data appear to confirm that the distance between bridgehead atoms, and therefore the amount of biradical character, can be systematically varied by changing the constituent atoms of the cluster and their substituents, as demonstrated recently by Bertrand and co-workers for boron−phosphorus diradicaloids. [20] Compound **1** has an intense color which arises from an orbitally allowed HOMO−LUMO transition. The chemical shift of the ^{119}Sn NMR signal is in the same region observed for Sn_5Ar_6 (350.0 ppm) and $Sn_5\{C_6H_3\text{-}2,6(OPr^i)_2\}_6$[5] (328.4 ppm) and is shifted approximately 100 ppm downfield due to the deshielding effect of the halide substituent.

The Ga/Ge compound **2** is a very rare example of a cluster with a framework of heavier group 13 and 14 elements. Although there are several heavier group 13

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(18) Crystal data for **1**: $M = 1457.92$, trigonal, $P63/m$, $a = 13.0931(13)$ Å, $c = 22.405(3)$ Å, $Z = 2$, $D_c = 1.545$ Mg m^{-3}, μ(Mo Kα) = 0.503 mm^{-1}, $T = 91$ K, 3471 independent reflections collected on a Bruker Smart 1000 instrument. Refinement of 3471 reflections (127 parameters) with $I > 2.0\sigma(I)$ converged at final R1 = 0.0435, wR2 = 0.1585. Crystal data for **2**: $M = 1459.49$, trigonal, $P63/m$, $a = 12.943(3)$ Å, $c = 22.537(6)$ Å, $Z = 2$, $D_c = 1.482$ Mg m^{-3}, μ(Mo Kα) = 0.503 mm^{-1}, $T = 91$ K, 36 951 (2584 independent) reflections collected on an Bruker Smart 1000 instrument. Refinement of 2584 reflections (143 parameters) with $I > 2.0\sigma(I)$ converged at final R1 = 0.0334, wR2 = 0.0693.

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clusters with peripheral silyl or germyl substituents,[1] only two heavier group 13/14 clusters have been structurally characterized: the anion $[\{GaSi(SiMe_3)_3\}_3(GaSiMe_2)(SiSiMe_3)]^-$ [14] and the neutral $SiAl_{14}(\eta^5\text{-}C_5Me_5)_6$.[15] Compound **2** is the first structurally characterized group 13/14 cluster with a Ga−Ge framework. The overall structural motif of **2** is very similar to that of **1**. The Ga−Ge distance (2.4934(6) Å) is marginally longer than the sum of the covalent radii[21] and is consistent with single bonding. This is in agreement with the fact that the number of available framework electrons remains sufficient to form six two center-electron bonds between the Ga and Ge atoms. The trigonal pyramidal geometry at formally trivalent gallium is unusual (Ga- - -Ga = 3.078(1) Å). However pyramidal gallium geometry, in which gallium is bound to three, four, or five neighboring atoms, has been observed in the numerous clusters of Schnöckel, Linti, and co-workers.[1] The appearance of **2** differs considerably from that of **1** in that it has an orange color. This difference is more likely due to the fact that the framework of **2** has two electrons less than **1** and that the HOMO−LUMO energy difference as reflected in the $Ge_2Sn_3H_6$ and $Ga_2Ge_3H_6$ models shows the chromophore is quite different in each molecule. Calculations[22] on **1** and **2** reproduce the Ge−Sn (2.743 Å) and Ge−Ga (2.476 Å) distances quite accurately. The calculated distances between the bridgehead atoms Ge−Ge = 3.282 Å in **1** and Ga−Ga = 2.675 Å are significantly (0.2−0.4 Å) shorter than the experimentally observed values. However, such differences are probably due to the electronic properties of the ligands in **1** and **2**, which, as already discussed, have longer bridgehead distances than in previously reported species for electronic reasons.

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Supporting Information Available: CIF data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Using covalent radii of 1.22 Å for Ge and 1.25 Å for Ga.

[22] The geometry optimizations were performed in gaseous phase using DFT theory with the hybrid B3LYP functional. In the molecular structures used for the theoretical investigations the bulky groups connected to the Ge (or Sn) atoms were replaced with the hydrogens. The structure containing the Sn and Ge atoms (**M1**) was optimized with Los Alamos LanL2DZ basis set using an effective core potential (ECP) approximation due to the size of the Sn atoms, while for the Ga−Ge model cluster (**M2**) the 6-31g* basis set was used. The symmetry for both structures was constrained to D_{3h} for all the optimization steps. All the calculations were performed with the Gaussian03 package,[a] and the representations of the molecular structures were generated with the MOLEKEL program.[b] The optimized geometrical parameters (bond distances [Å] and angles [deg]) are close to those found in the crystal structures of **1** and **2**. **M1**: Ge−Ge 3.282, Ge−Sn 2.743, Sn−Ge−Sn 87.9, Ge−Sn−Ge 73.5. **M2**: Ga−Ga 2.675, Ga−Ge 2.476, Ga−Ge−Ga 65.4, Ge−Ga−Ge 95.7. The calculated Ge−Ge (Ga−Ga) distances in **M1** and **M2** are shorter than those found in the X-ray crystal structures of the corresponding clusters. The longest distances found in the crystalline matrix are most probably related to the more important sterical constraints imposed by the bulky ligands. (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomeli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck,K. Raghavachari, J. B. Foresman, J. Ciolowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Reploge, and J. A. Pople. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) *MOLEKEL 4.3*, P. Flukiger, H. P. Luthi, S. Portmann, J. Weber; Swiss Center for Scientific Computing: Manno (Switzerland), 2000−2002.