Mixed-Metal Main-Group Clusters

Synthesis and Characterization of Neutral, Homo and Heteronuclear Clusters with Unsubstituted Germanium or Tin Atoms**

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Stable polyhedral clusters of the formula M_nR_m ($n > m$; M = Si–Pb (tetrel; a tetrel is a group 14 element); R = organo or related group) that contain several tetrels unsubstituted by organic or related groups are rare.[1–4] The synthesis of such species is of interest as it could allow the crystallization of well-defined larger tetrel clusters of nanometer dimensionality that may have unusual electronic properties. Generally speaking, most currently known tetrel clusters can be categorized as either Zintl anions,[5] for example M_5^{2-} or M_9^{n-} (M = Ge, Sn or Pb; $n = 2, 3$ or 4), or as neutral clusters of the formula M_nR_n (M = Si–Pb, $n = 4, 6, 8$ or 10)[6] where each tetrel carries one substituent. In contrast, the substituent poor polyhedral tetrel clusters are represented only by the compounds $Sn_8\{Si(SiMe_3)_3\}_6$,[2] $Sn_8\{C_6H_3\text{-}2,6\text{-}Mes_2\}_4$[3] and the germanium species $Ge_8\{N(SiMe_3)_2\}_6$[4] that was recently reported by Schnepf and co-workers. The tin compounds

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were obtained either by thermolysis[2] or by reduction/ligand stripping of an aryl tin(II) halide precursor Sn(Cl)C_6H_3-2,6-Mes_2.[3] The more recent synthesis of $Ge_8\{N(SiMe_3)_2\}_6$ represented a new departure in that it employed germanium(I) bromide trapped at low temperature as the germanium source.[4] This approach is analogous to that employed by Schnöckel and co-workers[7] for the synthesis of numerous aluminum and gallium clusters with unsubstituted metals through the use of low oxidation state Al^I and Ga^I halides. It is believed that the disproportionation of these generally unstable species provides a pathway through which clusters involving unsubstituted metal atoms are formed and trapped by ligands attached to the cluster surface. The reduction of the low valent aryl tin(II) halide Sn(Cl)C_6H_3-2,6-Mes_2 near room temperature to give the cluster $Sn_8\{C_6H_3\text{-2,6-}Mes_2\}_4$[3] suggested to us that it might be possible to use the low valent tetrel(II) halides themselves to introduce unsubstituted tetrel atoms into a cluster. We now describe a new strategy for the synthesis of tetrel clusters of this type and show that it can be used to synthesize species in which the majority of tetrel atoms carry no organic substituent. Furthermore, we show that this approach allows the synthesis and the first detailed structural characterization of a stable species in which two different tetrels comprise the cluster framework.[8]

The clusters $Ge_6Ar'_2$ (**1**) or $Sn_4(GeAr')_2$ (**2**) ($Ar' = C_6H_3$-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-$i$$Pr_2$) were synthesized by the reduction of a 1:1 proportion of Ge(Cl)Ar′[9] and $GeCl_2$·dioxane or $SnCl_2$ with three equivalents of KC_8 in THF at room temperature. The Ge_6 derivative **1** (Figure 1) was isolated as orange crystals, and the Sn_4Ge_2 cluster **2** (Figure 2) was obtained as red crystals in about 40% and 20% yields, respectively. Both compounds were characterized by X-ray crystallography;[10] the structures are broadly similar with distorted octahedral hexatetrel cores in which two of the six vertices are substituted by Ar′ groups. The unsubstituted Ge_4 (**1**) and Sn_4 (**2**) atom sets comprise almost perfectly square arrays which have Ge–Ge and Sn–Sn separations that average 2.86(1) Å and 3.12(1) Å. The average Ar′Ge–Ge and Ar′Ge–Sn distances in **1** and **2** are 2.50(2) in 2.72(2) Å. The orientation of the central aryl rings of the terphenyl substituents is coplanar with respect to each other in **1** and almost perpendicular in **2** but this is probably a packing effect. ^1H, ^{13}C NMR and UV/Vis data for **1** and **2** are unremarkable. The solution ^{119}Sn NMR spectrum of **2** displayed a downfield signal at $\delta = 1583$.

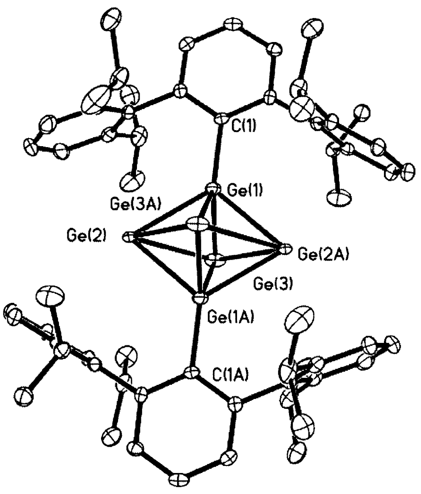

Figure 1. Structure of **1**; H atoms are not shown. Representative bond lengths [Å] and angles [°]: Ge1-Ge2 2.546(1), Ge1-Ge3 2.498(2), Ge1-Ge2A 2.532(1), Ge1-Ge3A 2.503(2), Ge2-Ge3 2.883(2), Ge2-Ge3A 2.886(2), Ge1-C1 1.974(6), C1-Ge1-Ge3 125.0(2), C1-Ge1-Ge2 126.0(2), Ge2-Ge1-Ge3 68.70(5), Ge3-Ge2-Ge3A 88.66(5), Ge2-Ge3-Ge2A 91.34(5)°.

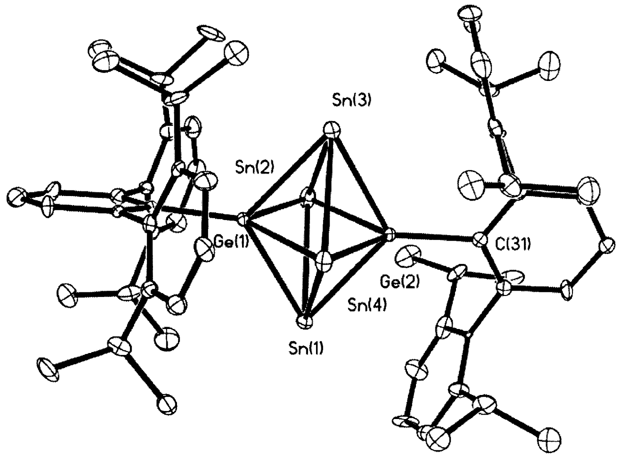

Figure 2. Structure of **2**; H atoms are not shown. Representative bond lengths [Å] and angles [°]: Ge1-Sn1 2.763(2), Ge1-Sn2 2.714(2), Ge1-Sn3 2.728(2), Ge1-Sn4 2.704(2), Sn1-Sn2 3.098(2), Sn1-Sn4 3.135(2), Sn2-Sn3 3.115(2), Sn3-Sn4 3.143(2), Ge2-C3(1) 1.98(1), Sn1-Ge1-C11 128.3(4), Sn3-Ge1-C11 128.3(4), Sn1-Ge1-Sn2 69.10(5), Sn2-Ge1-Sn3 69.85(5), Sn2-Sn1-Sn4 90.19(4), Sn1-Sn2-Sn3 90.60(4), Sn2-Sn3-Sn4 89.72(4), Sn1-Sn4-Sn3 89.41(4).

The observation of unsubstituted germanium or tin atoms in the structures clearly arises from the inclusion of $GeCl_2$ or $SnCl_2$ in the reaction mixtures as similar experiments involving the reduction of Ge(Cl)Ar′ or Sn(Cl)Ar′ or Sn(Cl)Ar′ without $GeCl_2$ or $SnCl_2$ give the alkyne analogues Ar′MMAr′ (M = Ge[11] or Sn[12]) exclusively. The distorted octahedral core of **1** or **2** is their most conspicuous structural feature. It is plausible to view this finding to be in agreement with Wade's Rules[13] which predict a closo structure for the hypothetical Ge_6^{2-} or $Ge_2Sn_4^{2-}$ clusters since they have $n+1$ electron pairs (n = no. of vertices) available for cluster bonding in **1** and **2**. Thus, each unsubstituted tetrel provides two electrons and each substituted moiety provides three electrons to afford a total of seven electron pairs. Recent calculations by King and co-workers for Ge_6^{2-} have predicted that a regular octahedral structure with a Ge–Ge bond lengths of 2.687 Å as the global minimum for Ge_6^{2-}.[14] This value can be compared to the average of 2.63 Å for the twelve Ge–Ge bond lengths in **1**. The substitution of organic groups at two of the six germanium atoms in **1** introduces large distortions to the octahedron. The separation of the four unsubstituted germanium atoms is over 0.3 Å greater than the Ar′Ge–Ge bond lengths, and although the angles within the plane formed by Ge(2), Ge(3), Ge(2A) and Ge(3A) are near 90°, the corresponding Ge(2)-Ge(1)-Ge(2A) and Ge(3)-Ge(1)-

Ge(3A) angles associated with the substituted germanium atoms have opened out to 107.75(3) and 106.33(3)°. The Ge–Ge distances may be compared with those observed in the substituted clusters Ge_6R_6 (R = Dipp[15] or $CH(SiMe_3)_2$[16]); Ge–Ge range 2.465(1)–2.584(2) Å), $[PPh_4]_2[Ge_6\{M(CO)_5\}_6]$ (M = Cr, Mo, or W, Ge–Ge = 2.541(1)–2.592(4) Å,[17] and in the species $Ge_8[N(SiMe_3)_2]_6$ where bond lengths of about 2.67 and 2.50 Å were observed for the R_2NGe–$Ge(NR_2)$ and Ge–$Ge(NR_2)$ (R = $SiMe_3$) germanium bonds. A similar pattern of distortion is seen in the structure of **2** where the distances between the unsubstituted tin atoms average 3.12(2) Å and the Ge–Sn distances are in the range 2.701(2)–2.746(2) Å. The latter distances are longer than the two center-two-electron Ge–Sn bonds in compounds of the type $R_3MM'R_3$ (M = Ge; M = Sn; R = organic group; range 2.573(2)–2.652(2) Å.[18] The unsubstituted Ge–Ge and Sn–Sn bond lengths in **1** and **2** lie at the longer end of the ranges generally found in Zintl anions and approach the distances seen in the square M_4 moieties of the $[M_9]^{4-}$ Zintl species[19,20] or the "long" Sn–Sn contacts (3.107(2) Å) in $Sn_8(C_6H_3\text{-}2,6\text{-}Mes_3)_4$.[3] The weak M–M contacts within the M_4 squares receive support from the ^{119}Sn NMR chemical shift which lies well downfield toward a region most commonly associated with two coordinate tin(II) species.[21] The NMR data suggest that writing the structures of **1** or **2** with the bonds between the unsubstituted germanium or tin atoms omitted also is a plausible representation of their bonding environment. Work to isolate a wider range of stable group 14 clusters with larger numbers of unsubstituted atoms (nanosized clusters) and the extension of the range of stable heteronuclear neutral clusters to other heavier main group elements is in hand.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions.

1: Ar′GeCl (0.505 g, 1 mmol)[4] and $GeCl_2$(dioxane), (0.232 g, 1 mmol) was added dropwise to a suspension of KC_8 (0.111 g, K) in THF (20 mL). After the reaction had been stirred for 16 h, the THF was removed under reduced pressure and the resultant red solid was extracted into hexanes (40 mL). The volume was reduced to incipient crystallization and storage of the solution at about −5 °C for 48 h afforded **1** as orange crystals. m.p. 69–71 °C; ^1H NMR (C_6D_6, 399.7 MHz, 25 °C): $\delta = 0.94$ (d, $^3J_{HH} = 6.8$ Hz, 24H; *o*-C(CH_3)$_2$), 1.24 (d, $^3J_{HH} = 6.8$ Hz, 24H; *o*-CH(CH_3)$_2$), 2.709 (sept, $^3J_{H,H} = 6.8$ Hz, 18H; *o*-CH(CH_3)$_2$)), 6.98 (d, $^3J_{H,H} = 7.2$, Hz, 4H; *m*-C_6H_3), 7.08 (d, $^3J_{H,H} = 8.0$ Hz, 8H; *m*-Dipp), 7.20 (t, $^3J_{H,H} = 7.2$ Hz, 4H; *p*-C_6H_3), 7.22 ppm (t, $^3J_{H,H} = 8.0$ Hz, 4H; *p*-Dipp); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz, 25 °C): $\delta = 24.31$ (*o*-CH(CH_3)$_2$), 25.76 (*o*-CH(CH_3)$_2$), 31.06 (*o*-CH(CH_3)$_2$), 122.69 (*m*-Dipp), 123.01 (*p*-C_6H_3), 136.75 (*m*-C_6H_3), 140.49 (*p*-Dipp), 146.57 (*i*-Dipp), 146.68 (*i*-C_6H_3), 147.22 (*o*-Dipp), 150.76 ppm (*o*-C_6H_3); UV/Vis (hexane): λ_{max}, (ε) 500 nm (69,800).

2: A mixture of Ar′GeCl (0.505 g, 1 mmol)[9] and $SnCl_2$ (0.19 g, 1 mmol) in THF solution (20 mL) was added dropwise to a suspension of KC_8 (0.117 g, K) in THF (20 mL). After the reaction had been stirred for 16 h the THF was removed under reduced pressure and the resultant red solid was extracted into hexanes (40 mL). The solution was concentrated and stored at room temperature for 2 weeks, which afforded deep red cyrstals of **2** in 17 % yield. m.p. 100–110 °C, ^1H NMR (C_6D_6, 399.7 MHz, 25 °C): $\delta = 1.016$ (d, $^3J_{H,H} = 6.8$ Hz, 24H; *o*-CH(CH_3)$_2$), 1.137 (d, $^3J_{H,H} = 6.8$ Hz, 24H; *o*-CH(CH_3)$_2$), 2.84 (sept, $^3J_{H,H} = 6.8$ Hz, 18H; *o*-CH(CH_3)$_2$)), 6.979 (d, $^3J_{H,H} = 7.2$ Hz, 4H; *m*-C_6H_3), 7.1535 (d, $^3J_{H,H} = 8.0$ Hz, 8H; *m*-Dipp), 7.174 (t, $^3J_{H,H} = 7.2$ Hz, 4H; *p*-C_6H_3), 7.234 ppm (t, $^3J_{H,H} = 8.0$ Hz, 4H; *p*-Dipp); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz, 25 °C): $\delta = 24.18$ (*o*-CH(CH_3)$_2$), 24.42 (*o*-CH(CH_3)$_2$), 34.71 (*o*-CH(CH_3)$_2$), 120.56 (*m*-Dipp), 122.67 (*p*-C_6H_3), 137.41 (*m*-C_6H_3), 141.08 (*p*-Dipp), 146.66 (*i*-Dipp), 148.21 (*o*-Dipp), 149.92 ppm (*o*-C_6H_3), (*i*-C_6H_3 carbon was not observed); ^{119}Sn NMR (C_6D_6), $\delta = 1583.5$ ppm.

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[1] Two neutral tin clusters, Sn_5Ar_6 and Sn_7Ar_8 (Ar = C_6H_3-2,6-Et_2)$_2$, that contain two unsubstituted tin atoms are known, but the number of organic substituents exceeds that of the metal atoms as some metal atoms carry two organic substituents. They were obtained from the thermolysis of $(SnAr_2)_3$. See; L. R. Sita, *Adv. Organomet. Chem.* **1995**, *38*, 187 for an account of this and related work. In addition, a cationic germanium cluster containing unsubstituted germanium atoms $[(tBu_3Si)_6Ge_{10}I]^+$ has been structurally characterized: A. Sekiguchi, Y. Ishida, Y. Kabe, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 8776.

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[8] The extraction of Zintl phases such as $Sn_{9-x}E_x^{4-}$ (E = Ge or Pb; $x = 0$–9) with ethylene diamine, and their study by ^{119}Sn NMR spectroscopy, have proven the existence of mixtures of anionic heteronuclear tetrel clusters. No crystal structures have been determined, however. See: R. W. Rudolph, W. L. Wilson, R. C. Taylor, *J. Am. Chem. Soc.* **1981**, *103*, 2480.

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[10] Crystal data for **1** and **2**·hexane with $Mo_{K\alpha}$ ($\lambda = 0.7107$ Å) radiation at 90 K: **1**, monoclinic, *P*2(1)/*n*, orange block, $a = 10.9496(11)$, $b = 19.2684(19)$, $c = 13.7857(14)$ Å, $\beta = 98.547(2)°$, $V = 2876.2(5)$ Å^3, $Z = 2$, *R1* (obs data) = 0.0589, *wR2* (all data) = 0.1523, GOF = 0.966; **2**·hexane: monoclinic, $P2_1/c$, red block, $a = 16.928(4)$, $b = 15.442(4)$, $c = 25.196(7)$ Å, $\beta = 103.857(5)°$, $V = 6395(3)$ Å^3, $Z = 4$, *R*1 (obs data) = 0.1001, *wR*2 (all data) = 0.2465, GOF = 1.146. CCDC-210326 (**1**) and CCDC-210327 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). The structure of **1** displayed disorder problems involving the unsubstituted Ge_4 array such that three plausible Ge_4 arrangements are possible. The major (70 %) array features an almost square Ge_4 unit similar in structure to the Sn_4 moiety in the tin counterpart. The remaining 30 % is divided between two rectangular Ge_4 arrays that have "short" bond lengths in the range 2.71–2.73 Å and longer (probably non-bonded) Ge–Ge separations in the range 3.41–3.64 Å. The positions of the minority Ge atoms were clearly shown on a difference electron-density map. Distances between the main Ge atoms and minority atoms are too large to allow a description based on large amplitudes of motion. The

final *R* index for **2** is higher than normal for a correct structure. The reason for this is an overlap of parts of the main reciprocal lattice and an extraneous lattice, either from a twin component or a misoriented crystal fragment. By removing reflections with large I_o/I_c discrepancies, it was possible to lower *R* and reduce the magnitude of the largest difference peak. These operations are purely cosmetic, however, as they resulted in no discernible structural changes. Final refinement was therefore performed with the offending reflections included.

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