Cubane Complexes with Two (or More) Group 14−Group 16 Double Bonds: Synthesis and X-ray Structures of $Sn_4Se_2(NtBu)_4$ and $Ge_4Se_3(NtBu)_4$

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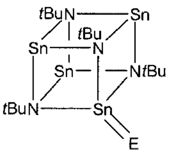
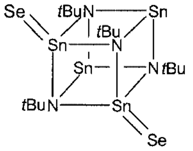
Monomeric complexes with two or three terminal M=Se bonds, $Sn_4Se_2(NtBu)_4$ or $Ge_4Se_3(NtBu)_4$, respectively, are produced by oxidation of $(MNtBu)_4$ (M = Sn, Ge) with selenium in hot toluene.

The varied uses of binary Group 14−16 compounds as semiconductors, in thermoelectric devices and for optoelectronic materials,[1] have provided a stimulus for investigations of potential single-source precursors.[2,3] In addition to these practical applications, there is a fundamental interest in compounds containing a formal double bond between heavier Group 14 and 16 elements.[4] These highly reactive functionalities may be stabilized either by attaching two extremely bulky groups to the Group 14 element to give a three-coordinate ketone analogue[5] or by intramolecular heteroatom coordination leading to four- or five-coordinate metal centers.[6] Although there have been impressive advances in the range and diversity of these so-called "heavy ketones",[4] no examples of compounds containing more than one Group 14-Group 16 double bond have been reported.

Recently we described the unexpected formation and X-ray structure of the stannatellone $[tBuNSn(\mu\text{-}NtBu)_2\text{-}TeNtBu](\mu_3\text{-}SnTe)$ in which the Sn=Te functionality is stabilized by three tBuN ligands.[7] This finding prompted us to investigate the oxidation of divalent tin or germanium in the cubic molecules $(MNtBu)_4$ (M = Sn, Ge)[8] by chalcogens as a source of complexes containing several terminal M=E bonds (E = S, Se, Te). In this communication we report the synthesis and X-ray structures of **2** and **3**, which contain two or three M=Se bonds, respectively, as well as the monochalcogenides **1a** and **1c**.



1a, E = S
1b, E = Se
1c, E = Te



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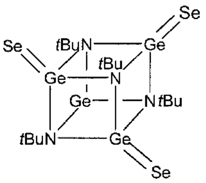

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The reaction of $(SnNtBu)_4$ with one equivalent of sulfur in toluene at 85 °C produces **1a** in 87% yield. The use of an excess of sulfur in this reaction yields insoluble products, suggesting the formation of polymers involving bridging, rather than terminal, sulfide ligands, upon further oxidation of **1a** with sulfur. Richeson et al. have shown that there is a delicate balance between the formation of terminal and bridging SnS bonds in the case of the amidinate complexes $[SSn\{CyNC(R)NCy\}_2]_n$.[6c] A monomeric structure ($n = 1$) is observed for R = tBu, whereas a dimer ($n = 2$) with bridging sulfide ligands is found for R = Me.

The reaction of $(SnNtBu)_4$ with four equivalents of selenium in boiling toluene yields the distannaselone **2b** in 64% yield whereas the monostannatelone **1c** is obtained in 68% yield from the reaction of $(SnNtBu)_4$ with an excess of tellurium under similar conditions. The lack of formation of the distannatellone presumably reflects the weaker oxidizing power of tellurium compared to that of selenium. The compounds **1a**, **1c** and **2** were characterized by ^1H NMR spectra, X-ray crystallography[9−11] and, in the case of **1c** and **2**, by CHN analyses. The stannathione **1a** exhibits a molecular ion in the FAB mass spectrum.

The molecular structures of **1c** and **2**, accompanied by pertinent metrical parameters, are depicted in Figure 1 and 2, respectively. The structure of **1a** resembles that of **1c** and

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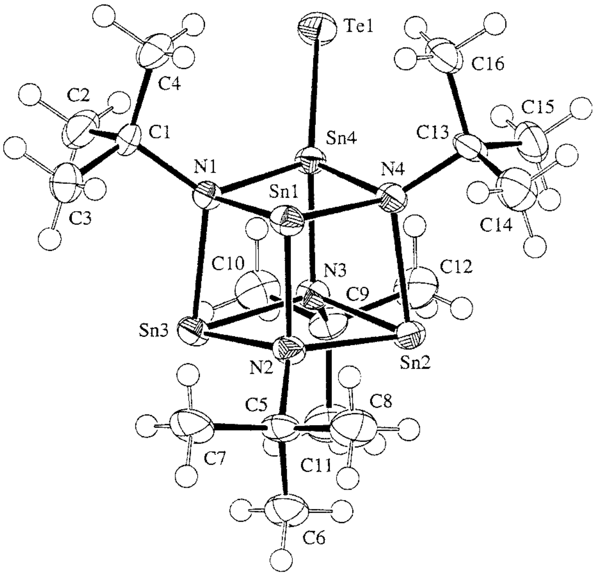

Figure 1. X-ray structure of **1c**; selected bond lengths (Å) and bond angles (deg): Sn(4)−Te(1) 2.589(1), $|\mathrm{Sn^{IV}{-}N}|$ 2.124(4) range 2.116(4)−2.130(4), $|\mathrm{Sn^{II}{-}N}|$ 2.217(5), range 2.191(5)−2.229(5), $|\mathrm{N{-}Sn^{IV}{-}N}|$ 85.0(2), $|\mathrm{N{-}Sn^{II}{-}N}|$ 80.6(2); selected bond lengths (Å) and bond angles (deg) for **1a**: Sn(1)−S(1) 2.262(3), Sn(4)−S(2) 2.255(3), $|\mathrm{Sn^{IV}{-}N}|$ 2.114(8), range 2.112(6)−2.142(8), $|\mathrm{Sn^{II}{-}N}|$ 2.217(9), range 2.186(5)−2.229(6), $|\mathrm{N{-}Sn^{IV}{-}N}|$ 85.2(3), |N−Sn(2)−N| 80.5(3)

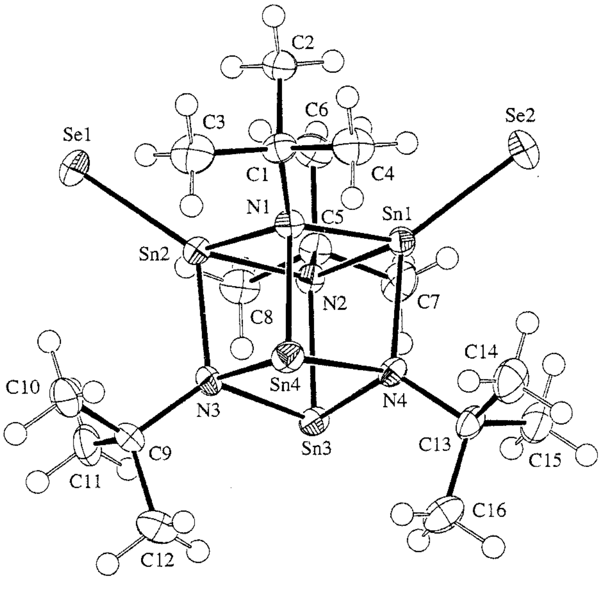

Figure 2. X-ray structure of **2**; selected bond lengths (Å) and bond angles (deg): Sn(1)−Se(2) 2.372(1), Sn(2)−Se(1) 2.363(1), $|\mathrm{Sn^{IV}{-}N}|$ 2.141(5), range 2.122(5) − 2.157(5), $|\mathrm{Sn^{II}{-}N}|$ 2.233(5) range 2.206(5)−2.253(5), b$|\mathrm{N{-}Sn^{IV}{-}N}|$ 84.3(2), $|\mathrm{N{-}Sn^{II}{-}N}|$ 80.0(2)

selected bond lengths and bond angles are given in the caption to Figure 1. All three structures contain terminal Sn=E bonds (E = S, Se or Te) and the framework of the $(\mathrm{SnN}t\mathrm{Bu})_4$ cube is maintained. There are no significant intermolecular contacts. The Sn=S bond length of 2.262(3) Å in **1a** is similar to the value of 2.280(5) Å found in the five-coordinate amidinate complex [S=Sn{CyNC(*t*Bu)-NCy}$_2$].[6c] The Sn=Te bond length of 2.589(1) Å in **1c** is indistinguishable from the value of 2.592(1) Å found for [*t*BuNSn(μ-N*t*Bu)$_2$TeN*t*Bu](μ$_3$-SnTe) in which the tin atom is in an identical four-coordinate environment.[7] The mean Sn=Se bond length of 2.367(7) Å in **2** can be compared with values of 2.398(1) Å[6d] or 2.394(1) Å[6f] for related five-coordinate complexes. Two general trends are evident from the structural data for these three complexes. First, the mean $\mathrm{Sn^{IV}{-}N}$ bond length is 0.09 Å shorter than the mean $\mathrm{Sn^{II}{-}N}$ distance, reflecting the higher ionic character in the $\mathrm{Sn^{IV}{-}N}$ bonds. Secondly, the mean bond angle $\mathrm{N{-}Sn^{IV}{-}N}$ is about 4.5° larger than the value of $\mathrm{N{-}Sn^{II}{-}N}$, suggesting that the stereochemical influence of the Sn=E bonding electrons is less pronounced than that of the lone pair of electrons on the $\mathrm{Sn^{II}}$ centres.

The ^{1}H NMR spectrum of **1a** in C_6D_6 at 23 °C shows two resonances at $\delta = 1.47$ and 1.25 ppm, attributable to N*t*Bu groups, with the expected 3:1 relative intensities. By contrast, the ^{1}H NMR spectra of **1c** and **2** in C_6D_6 at 23 °C both exhibit singlets at $\delta = 1.42$ ppm. These observations imply fluxional behaviour involving rapid exchange of chalcogen substituents between $\mathrm{Sn^{II}}$ and $\mathrm{Sn^{IV}}$ sites in **1c** and **2**. Similar observations have been reported for the *bis* adduct $(\mathrm{SnN}t\mathrm{Bu})_4{\cdot}2\mathrm{AlCl_3}$, which exhibits a singlet at $\delta =$ 1.32 ppm in the ^{1}H NMR spectrum (in C_7D_8) at 28 °C.[12] The low solubility of these imidotin chalcogenides precluded further investigation of this phenomenon by low temperature NMR spectroscopy. We note, however, that selenium exchange is approximately two orders of magnitude faster than sulfur exchange for (porphyrinato)tin(II) complexes.[13] The solid-state ^{119}Sn NMR spectrum for **2** shows the expected two resonances for $\mathrm{Sn^{II}}$ and $\mathrm{Sn^{IV}}$ sites at $\delta =$ +1347 and −111 ppm, respectively [cf. $\delta = +1142$ for $(\mathrm{SnN}t\mathrm{Bu})_4$].

These findings indicate that the oxidation of the remaining $\mathrm{Sn^{II}}$ centers becomes more difficult after the initial oxidation of one or two $\mathrm{Sn^{II}}$ sites in $(\mathrm{SnN}t\mathrm{Bu})_4$, presumably as a result of the electron-withdrawing effect of the chalcogen substituents. Consequently, we also investigated the chalcogen oxidation of the germanium(II) cube $(\mathrm{GeN}t\mathrm{Bu})_4$,[8] which should be more easily oxidized than the $\mathrm{Sn^{II}}$ analogue.

The reaction of $(\mathrm{GeN}t\mathrm{Bu})_4$ with four equivalents of tellurium in boiling toluene for one day produces $\mathrm{Ge_4Te(N}t\mathrm{Bu})_4$, the germanium analogue of **1c**, in 42% yield.[14,15] By contrast, oxidation with selenium under similar conditions yields the trigermaselone $\mathrm{Ge_4Se_3(N}t\mathrm{Bu})_4$ (**3**) as yellow air-sensitive crystals in about 60% yield. An X-ray structural determination of **3** (Figure 3)[16] revealed three Ge=Se double bonds with a mean bond length of 2.187(1) Å [cf. 2.196(4) Å and 2.2212(3) Å in the amidinate complexes [CyNC(R)NCy]$_2$Ge=Se (R = Me, *t*Bu), in which the germanium centers are also four-coordinate].[6b] The mean $\mathrm{Ge^{IV}{-}N}$ bond length is 0.11 Å shorter than the mean $\mathrm{Ge^{II}{-}N}$ distance and the bond angle $\mathrm{N{-}Ge^{IV}{-}N}$ is 4.8° larger than the value of $\mathrm{N{-}Ge^{II}{-}N}$. The ^{1}H NMR spectrum of **3** in C_6D_6 at 23 °C shows two resonances with the expected 1:3 relative intensities, implying that any selenium exchange is slow on the NMR time scale. However, limited

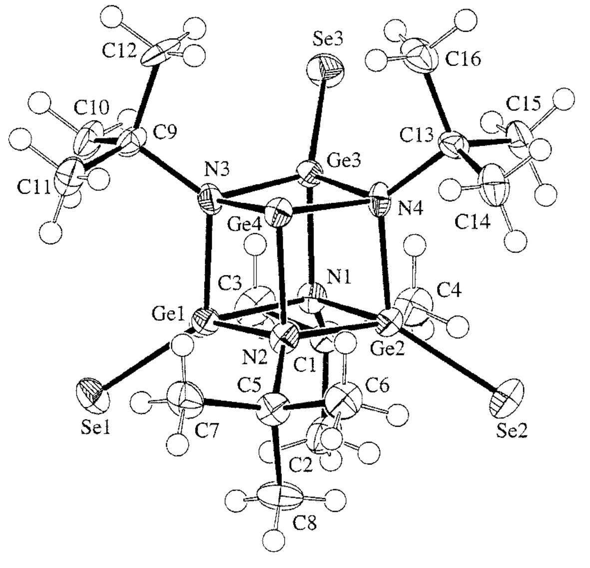

Figure 3. X-ray structure of **3**; selected bond lengths (Å) and bond angles (deg): Ge(1)−Se(1) 2.1852(13), Ge(2)−Se(2) 2.1872(13), Ge(3)−Se(3) 2.1871(13), |Ge^{IV}−N| 1.958(7), range 1.944(7)−1.985(7), |Ge^{II}−N| 2.068(7), range 2.064(7)−2.071(7), |N−Ge^{IV}−N| 85.8(3), |N-Ge^{II}−N| 81.0(3)

solubility precluded the measurement of the ^{77}Se NMR spectrum.

In summary, the oxidation of the cubic systems ($MN\textit{t}Bu$)$_4$ with selenium provides a facile route to the first complexes containing more than one Group 14-Group 16 double bond. Tetraselones [$M_4Se_4(NR)_4$] (M = Sn, Ge) would be of particular interest as potential single-source precursors to binary semi-conductors such as SnSe, via the thermodynamically favoured elimination of RN=NR. Achievement of this goal will require either a more easily oxidized imidotin(II) cubane, for example (SnNPh)$_4$,[17] or a more reactive source of selenium.

Experimental Section

1a: The reagents (SnN*t*Bu)$_4$ [18] and Ge(N*t*Bu)$_4$ [8] were prepared from M(NMe$_2$)$_2$ and *tert*-BuNH$_2$ by modifications of the literature procedures. A mixture of (SnN*t*Bu)$_4$ (0.400 g, 0.527 mmol) and cyclooctasulfur (0.017 g, 0.530 mmol) in toluene was heated at 85 °C for one day. The yellow solution was filtered and solvent was removed under vacuum to give yellow crystals of **1a** (0.361 g, 0.456 mmol, 87%). ^{1}H NMR (C$_6$D$_6$, 23 °C): δ = 1.47 (s, 27 H, *t*Bu), 1.25 (s, 9 H, *t*Bu) ppm. MS (FAB): *m*/*z* = 792 [M + H]$^+$.

1c: A mixture of (SnN*t*Bu)$_4$ (0.362 g, 0.477 mmol) and tellurium powder (0.243 g, 1.90 mmol) in toluene (30 mL) was heated at 125 °C for two days. The orange solution was removed by cannula from unchanged tellurium. Orange crystals of **1c** (0.287 g, 0.324 mmol, 68%) were obtained after one day at −23 °C. $C_{16}H_{36}N_4Sn_4Te$ (886.92): calcd. C 21.67, H 4.09, N 6.32; found C 20.60, H 4.10, N 5.65. ^{1}H NMR (C$_6$D$_6$, 23 °C): δ = 1.42 (s) ppm.

2: A mixture of (SnN*t*Bu)$_4$ (0.406 g, 0.535 mmol) and grey selenium powder (0.169 g, 2.14 mmol) in toluene (40 mL) was heated at 125 °C for one day. The yellow solution was decanted by cannula from unchanged selenium. Yellow crystals of **2** (0.314 g, 0.342 mmol, 64%) were obtained after one day at −23 °C. **2**·C$_7$H$_8$, $C_{23}H_{43}N_4Se_2Sn_4$ (1009.3): calcd. C 27.37, H. 4.39, N 5.55; found C 26.64, H 4.58, N 5.46. ^{1}H NMR (C$_6$D$_6$, 23 °C): δ = 1.42 (s) ppm.

3: A mixture of (GeN*t*Bu)$_4$ (0.030 g, 0.052 mmol) and grey selenium powder (0.016 g, 0.203 mmol) was heated at 130 °C in toluene (20 mL) for one day. The yellow-orange solution was decanted from unchanged selenium and stored at −16 °C for one day to give yellow crystals of **3** (0.025 g, 0.031 mmol, 59%). ^{1}H NMR (C$_6$D$_6$, 23 °C): δ = 1.67 (s, 9 H, *t*Bu), 1.33 (s, 27 H, *t*Bu) ppm. **3**·C$_7$H$_8$.

X-ray quality crystals of **1a**·0.5C$_7$H$_8$, **1c**·0.5C$_7$H$_8$, **2**·C$_7$H$_8$ and **3**·C$_7$H$_8$ were obtained by recrystallization from toluene at −23 °C.

X-ray data were collected on a Nonius Kappa CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at 170 K. All of the structures contained disordered toluene molecules in the lattice.

Acknowledgments

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[9] Crystal data for **1a**·0.5C$_7$H$_8$: crystal size 0.27 × 0.15 × 0.18 mm, orthorhombic, *Pnma*, *a* = 22.0498(1) Å, *b* = 10.9784(3) Å, *c* = 23.7983(4) Å, *V* = 5760.9(2) Å^3, *Z* = 8. The asymmetric unit is composed of two half molecules of the complex lying on a mirror plane and a half molecule of toluene of solvation. Least-squares refinement on F^2 based on 6836 unique reflections [5754 reflections with $I > 2\sigma(I)$] gave a final R_1 of 0.051.

[10] Crystal data for **1c**·0.5C$_7$H$_8$: crystal size 0.12 × 0.12 × 0.06 mm, monoclinic, $P2_1/n$, *a* = 12.9436(3) Å, *b* = 13.3315(3) Å, *c* = 18.0675(5) Å, β = 104.7156(8)°, *V* = 3015.4(1) Å^3, *Z* = 4. Least squares refinement on F^2 based on 7454 unique reflections [4771 reflections with $I > 2\sigma(I)$] gave a final R_1 of 0.043.

[11] Crystal data for **2**·C_7H_8: crystal size 0.20 × 0.08 × 0.07 mm, orthorhombic, $P2_12_12_1$, a = 10.6423(2) Å, b = 13.3534(2) Å, c = 23.3413(3) Å, V = 3317.05(9) Å^3, Z = 4. The Se atoms are disordered with occupancy factors of 0.958(2); the remaining fraction Se(12) with occupancy factor 0.085(3) is bonded to Sn(4). Least-squares refinement on F^2 based on 7383 unique reflections [6823 reflections with $I > 2\sigma(I)$] gave a final R_1 of 0.032.

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[16] Crystal data for **3**·C_7H_8: $C_{23}H_{44}Ge_4N_4Se_3$, M = 903.86, colourless prisms (0.05 × 0.05 × 0.02 mm), orthorhombic, space group $P2_12_12_1$, a = 10.4013(3), b = 13.4568(3), c = 22.9765(8) Å, V = 3216.0(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.867 g cm^{-3}, μ(Mo-K_α) = 7.12 mm^{-1}. Least squares refinement on F^2 based on 3186 unique reflections [2605 reflections with $I > 2.00\ \sigma(I)$] gave a final R_1 = 0.036. The carbon atoms of the disordered toluene molecule were allowed isotropic displacement parameters. CCDC-198992 (**1a**), -198993 (**1c**), -198994 (**2**), -198995 (**3**) contain 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 CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; or E-mail: deposit@ccdc.cam.ac.uk).

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