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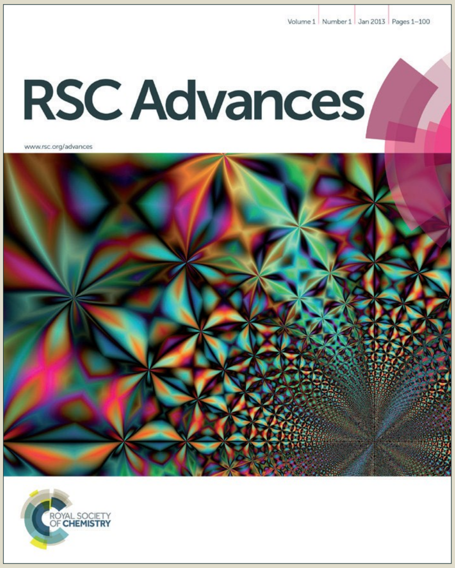

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Mixed guanidinato-amido Ge(IV) and Sn(IV) complexes with Ge=E (E = S, Se) double bond and SnS_4, Sn_2Se_2 rings†

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The first bulky guanidinate supported germathioamide [{ArNC(N^iPr_2)NAr}GeN($SiMe_3$)$_2$(S)]; (Ar = 2,6– Me_2–C_6H_3) (**3**) and germaselanoamide [{ArNC(N^iPr_2)NAr}GeN($SiMe_3$)$_2$(Se)] **(4)** complexes with Ge=S (**3**) and Ge=Se (**4**) moieties, have been synthesized and structurally characterized. Both compounds **3** and **4** were prepared by the oxidative addition of elemental sulfur and selenium, respectively, to the heteroleptic germylene complex [{ArNC(N^iPr_2)NAr}GeN($SiMe_3$)$_2$](**1**) in THF/ether at room temperature. Similarly, reaction of compound [{ArNC(N^iPr_2)NAr}SnN($SiMe_3$)$_2$] (**2**) with equimolar amount of elemental chalcogens (S and Se) led to the formation of cyclic tetrasulfido tin [{ArNC(N^iPr_2)NAr}SnN($SiMe_3$)$_2$(S_4)] (**5**) with SnS_4 ring and dimeric bridged seleno tin [{ArNC(N^iPr_2)NArN($SiMe_3$)$_2$Sn(μ–Se)}$_2$] (**6**) with Sn_2Se_2 ring, respectively. All compounds **3-6** were confirmed by multinuclear NMR spectroscopy, elemental analysis and single crystal X-ray structural analysis.

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†Electronic supplementary information (ESI) available: NMR spectra (^{1}H, ^{13}C and ^{29}Si) for compounds **3 – 6.** CCDC 1436337-1436340

Introduction

In recent years there has been rapid progress in the synthesis of molecular compounds with formal double bonds between the heavier group 14 and 16 elements M=E (M = Si, Ge, Sn; E = S, Se, Te).[1] The synthesis of such species is quite challenging due to the high polarity and/or weak π-orbital overlap in the M=E bonds.[1,2] Therefore, to isolate such highly reactive molecules, synthetic chemists have been utilized a wide variety of bulky ligand systems such as diketiminate,[3] amidinate,[4] aminotroponiminate (ATI),[5] diamido,[6] iminophosphonamide,[7] N-heterocyclic carbene(NHC)[8] and related ligands.[9] The oxidative addition reaction of chalcogens to either homoleptic or heteroleptic tetrelenes (MR_2) is the general synthetic approach for the multiple bonded (M=E) compounds. The reactivity studies of heteroleptic six or five membered Ge(II) and Sn(II) heterocycles is well documented.[1] In contrast, there have been limited reports of the reactivity of heteroleptic four membered Ge(II) and Sn(II) heterocycles.[10] Although, since the first guanidinate metal complex by Lappert in 1970,[11] various guanidinate supported Ge(II) and Sn(II) complexes with their reactivity studies have been reported.[12] Surprisingly, there have been no reports on oxidative addition of chalcogens to guanidinate supported Ge(II) and Sn(II) amide complexes. However, Richeson and co-workers reported oxidative addition of chalcogens to the mixed (amidinato) (amido) germanium(II) and tin(II) complexes.[13] (see I-III, Chart 1). Especially of great interest are compounds with amido substituent, where the amido -$\{N(SiMe_3)_2\}$ can easily be replaced to synthesize a variety of new compounds. More importantly, Hill and co-workers have shown that the catalytic activity of main group complexes bearing M-$\{N(SiMe_3)_2\}$ group, in which M-amide acts as a precatalyst.[14] Very recently, Coles[15] thoroughly reviewed on main group metal complexes of which bearing a bis-trimethylsilylamido ligand, $[N\{SiMe_3\}_2]^-$. This ligand was widely utilized due to its bulkiness, lipophilicity, the simplicity of its ^{1}H NMR spectra and lack of β-hydrogen atoms. Moreover, the anion $[N\{SiMe_3\}_2]^-$ is readily formed upon deprotonation of the commercially available hexamethyldisilazane (HMDS), facilitating its use in coordination chemistry. In this regard, we have previously reported that NHC supported magnesium and zinc bis(amide) complexes as precatalysts for guanylation reactions.[16] And also, we have reported that structurally characterized heteroleptic bulky guanidinate ligand[17a] $[\{ArNC(N^iPr_2)NAr\}^-$; (Ar = 2,6– Me_2–C_6H_3)] stabilized germanium(II) and tin(II) amide complexes *i.e.,* $[\{ArNC(N^iPr_2)NAr\}GeN(SiMe_3)_2]$(**1**), $[\{ArNC(N^iPr_2)NAr\}SnN(SiMe_3)_2]$(**2**).[17b] Herein, we report the oxidative addition of chalcogens (S and Se) to the guanidinate supported Ge(II) (**1**) and Sn(II) (**2**) amide complexes.

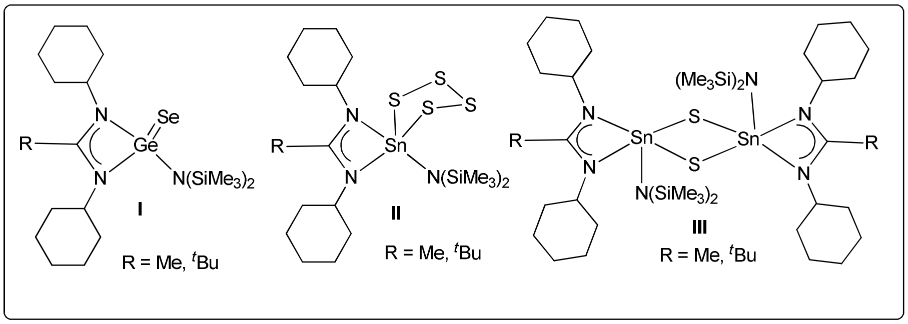
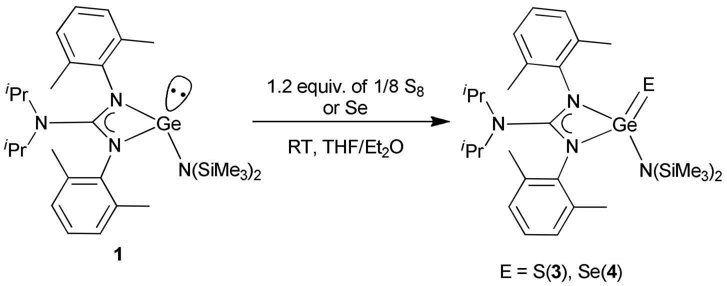


Chart 1. Four membered germanium and tin chalcogenido heterocycles bearing amido group

Results and discussion

Synthesis and spectroscopic characterization of complexes 3-6

The reaction of compound [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$] (**1**) with equimolar amount of elemental sulfur powder in THF at room temperature led to the formation of thermally stable mixed guanidinato/amido supported germanium(IV) complex with Ge=S moiety (*vide supra*) [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(S)] (**3**) (Scheme 1).

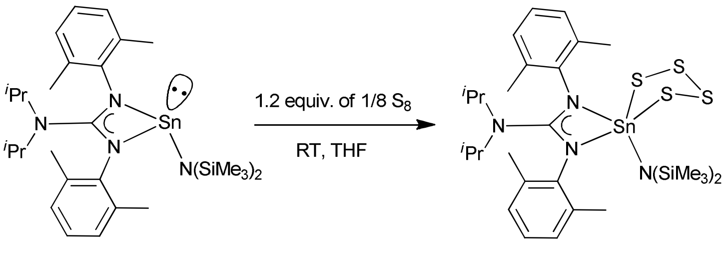


Scheme 1 Synthesis of (guanidinato) (amido) germanium sulphide (**3**) and selenide (**4**) complexes.

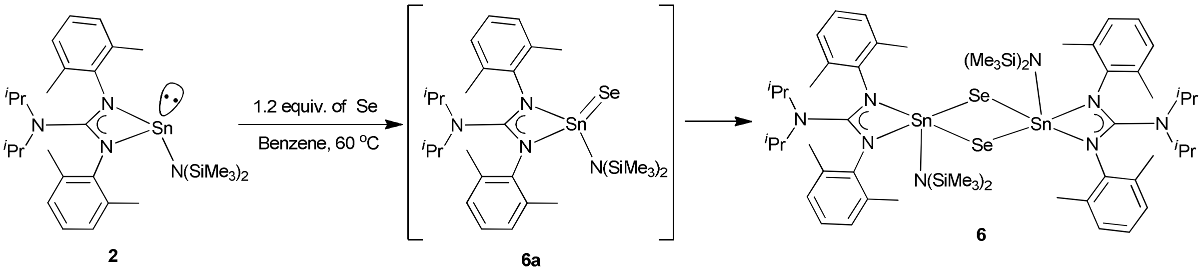
Similarly, the reaction of compound **1** with one equivalent of selenium powder in diethyl ether afforded the germanium complex with Ge=Se moiety [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(Se)] **(4).** Both compounds **3** and **4** are colourless crystalline, thermally stable, air and moisture sensitive solids. These are well soluble in organic solvents such as diethyl ether, THF, toluene, benzene and sparingly soluble in *n*-hexane.

In a manner similar to the syntheses of complexes **3** and **4,** the reaction of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**2**) with an excess or exact amount of elemental sulfur in THF at room temperature, gave the exclusively tetrasulphido tin(IV) complex [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S$_4$)] (**5**) as a stable light orange crystal in good yield (Scheme

2). Further, we treated one equivalent of elemental selenium with compound **2** at room temperature in THF. The ^{1}H NMR and ^{29}Si NMR spectra of aliquot indicate the presence of mixture of compounds, exhibiting two peaks at 0.41 and 0.49 ppm for N(Si*Me*$_3$)$_2$ moiety in ^{1}H NMR spectrum and showing two peaks at 5.22 and 5.32 ppm, for N(*Si*Me$_3$)$_2$ in ^{29}Si NMR spectrum. From these spectroscopic observations, we presume that mixture of products are [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–Se)}$_2$] (**6**) (*vide supra*) and [{ArNC(N^{i}Pr$_2$)NAr}N(SiMe$_3$)$_2$Sn=Se] (**6a**) (Scheme 3).



Scheme 2 Synthesis of tetrasulphido tin(IV) complex (**5**).



Scheme 3 Synthesis of dimeric bridged μ-selenotin(IV) complex (**6**).

Further, the same reaction was performed in benzene solvent at 60 °C, instead of THF, which undergo rapid reaction to yield exclusively the tin complex [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–

Se)}$_2$] (**6**) as a light yellow crystalline solid with high yield. Like complexes **3** and **4**, both compounds **5** and **6** are soluble in organic solvents, thermally stable, air and moisture sensitive. All compounds **3-6** were characterized by multinuclear (^{1}H, ^{13}C and ^{29}Si) NMR spectroscopy, elemental analysis and single crystal X-ray spectroscopy methods.

^{1}H NMR spectra of **3** and **4** showed that the aryl methyl protons *i.e.,* Ar-CH_3 of guanidinate ligand are magnetically non-equivalent and resonating as two singlets at 2.45 and 2.97 ppm (**3**) and 2.46 and 2.99 ppm (**4**)**.** In contrast, only one signal observed in corresponding precursor complex in **1** at 2.58 ppm. Interestingly, the ^{1}H NMR spectrum of **5** exhibited that the aryl methyl protons *i.e.,* Ar-CH_3 of guanidinate ligand as one singlet at 2.45 ppm, in contrast to the corresponding precursor complex (**2**) in which it is showing two resonances at 2.50 and 2.60 ppm. However, ^{1}H NMR spectrum of complex **6** shows two singlets at 2.47 and 3.00 ppm. And also, ^{1}H NMR spectra exhibit singlet at 0.32 (**3**), 0.34(**4**), 0.3(**5**) and 0.48(**6**), respectively for the N(SiMe_3)$_2$ moiety, these resonances are shifted downfield as compared to the compounds **1** (0.26 ppm) and **2** (0.2 ppm)[17b] and other signals such as Ar-*H*, C*H*(CH$_3$)$_2$ and CH(CH_3)$_2$ for all compounds (**3-6**) were as expected for the guanidinate ligand.

^{13}C NMR spectra of compounds **3, 4, 5** and **6** show a characteristic peak for the N$_3$*C* carbon atom of the guanidinate ligand 167.7, 167.9, 168.0 and 169.9 ppm respectively, these values are significantly shifted downfield as compared to the corresponding ligand[17a] of these metal complexes and other reported free tetra substituted guanidines (148-160 ppm).[18]

^{29}Si{^{1}H} spectra of compounds **3** and **4** showed signals at 3.31(**3**) and 3.02 (**4**) ppm respectively, and these values are shifted downfield as compared to the compound **1** (–3.68 ppm). Similarly, ^{29}Si{^{1}H} spectrum of compounds **5** and **6** exhibited signals at 5.52(**5**) and 5.25(**6**) ppm respectively, these values are also shifted downfield as compared to the compound **2** (–3.69 ppm).[17b]

Further efforts were made to isolate tin complexes such as [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S)] with Sn=S and [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–S)}$_2$] with Sn$_2$S$_2$ ring. Accordingly, sulfur was added to a solution of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**2**) in C$_6$D$_6$ and followed by heating at 60 °C for 12, in which ^{1}H NMR spectrum reveals mixture of products. And also, we investigated the reaction of compound **5** with three equivalents of triphenylphosphine to possibly afford the monomer [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S)] with a formal Sn=S bond, instead a mixture of products, including compound **1** was observed in the ^{1}H NMR spectrum.

Single crystal X-ray structural characterization of complexes 3-6

Crystals of the complex [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(S)] (**3**) suitable for X-ray diffraction were grown from its diethyl ether with few drops of toluene solution at –30 °C. Compound **3** crystallizes in the monoclinic system with *C*2/*c* space group. The molecular structure, selected bond distances and bond angles have depicted in the figure 1.

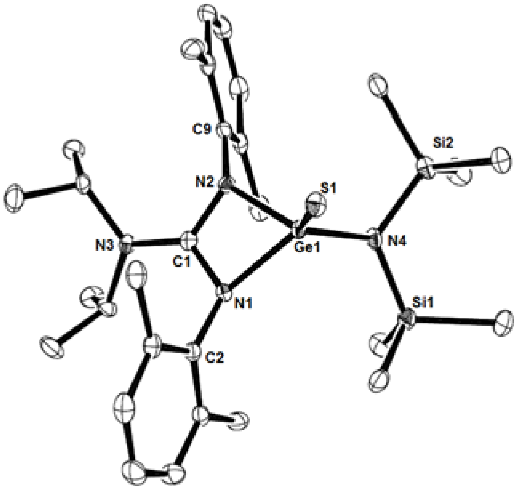


Fig. 1 ORTEP diagram of C$_{29}$H$_{50}$GeN$_4$SSi$_2$ with the probability ellipsoids drawn at the 30% level.

Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **3**: Ge1–S1 2.0735(15), Ge1–N1 1.984(4), Ge1–N2 1.949(4), Ge1–N4 1.843(4), C1–N1 1.359(6), C1–N2 1.351(6), N3–C1 1.355(6), N1–C2 1.443(6), Si1–N4 1.753(5), Si2–N4 1.759(4); N2–Ge1–N1 67.56(17), N4–Ge1–N1 113.06(17), N4–Ge1–N2 110.24(18), N1–Ge1–S1 119.36(12), N4–Ge1–S1 117.44(14), N2–C1–N1 107.6(4), N3–C1–N1 126.9(5), Si1–N4–Si2 119.8(2), Si1–N4–Ge1 118.9(2), Si2–N4–Ge1 117.6(2).

The solid state structure of **3** reveals that the Ge centre is bonded to the guanidinate ligand in [*N,N'*] chelate fashion and the other sites are occupied by N atom of the amido ligand and sulfur atom, resulting in a distorted tetrahedral geometry. The most characteristic feature of the complex **3** is the presence of Ge=S bond and it is the first example of a monomeric germathioamide with germanium in a four membered heterocycle ring. The Ge1–S1 bond distance 2.0735(15) Å in compound **3** is well in agreement with other reported germanium complexes bearing Ge=S moiety; [PhNC(Me)CHC(Me)NPh](Cl)Ge=S] (2.074(1) Å)[19] [2,6-^{i}Pr$_2$(C$_6$H$_3$N)P(Ph$_2$)(N^{t}Bu)]GeS(Cl)] (2.048(2) Å,[7] [CH{MeCN(2,6- ^{i}Pr$_2$C$_6$H$_3$)}$_2$]Ge(S)Cl 2.053(6) Å,[20] [CH{MeCN(2,6- ^{i}Pr$_2$ C$_6$H$_3$)}$_2$]Ge(S)SH 2.064(4) Å.[21] The Ge1–S1 bond distance 2.0735(15) Å for compound **3** is more consistent with a double bond than a single bond. Because, theoretical calculations for $H_2Ge=S$ molecule predicted that the 2.04 Å[19, 22] for Ge=S bond. However, Ge–S single covalent bond distance is 2.26 Å. The Ge=S bond length is slightly longer than the other kinetically stabilized germanechalcogenones.[23] And also, the Ge1–S1 bond distance 2.0735(15) Å in compound **3** is well in agreement with Okazaki and coworker's heavy ketone Tb(Tip)Ge=S (2.049(3) Å.[1k]

Due to the change of germanium centre environment from tricoordinate to tetra coordinate the Ge–N(amido) bond distance in **3** Ge1–N4 1.843(4) Å, is shorter by 0.0965 Å than that of the corresponding distance in **1** (Ge1–N3 1.9395(4) Å). For the same reason the Ge1–N1 bond distance also shorter by 0.114 Å than corresponding bond length of Ge1–N1 in compound **1**. The N2–Ge1–N1 bond angle 67.56(17)^{o} is slightly wider than the corresponding bond angle observed in **1** (N2–Ge1–N1 (64.12(4)^{o}).

The compound **4** crystallizes in the monoclinic system with $P2_1/c$ space group. Both compounds **3** and **4** are isostructural. Compound **4** is the first example of bulky guanidinate supported germanium selenoamide. However, closely related amidinate supported germanium selenoamide complexes are reported by Richeson and co-workers.[13a] The molecular structure, selected bond distances and bond angles have shown in figure 2.

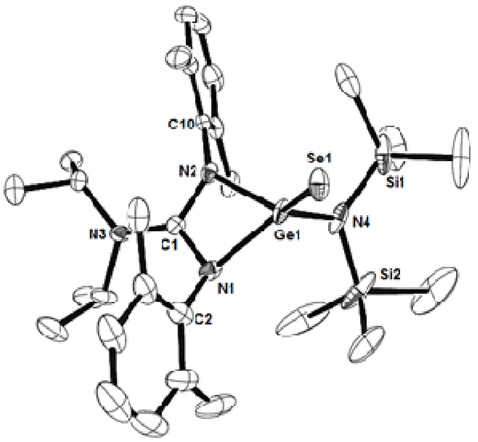


Fig. 2 ORTEP diagram of $C_{29}H_{50}GeN_4SeSi_2$ with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **4**: Ge1–Se1 2.2061(4), Ge1–N1 1.973(2), Ge1–N2 1.959(2), Ge1–N4 1.850(2), Si1–N4

1.760(3), Si2–N4 1.735(3), N2–C1 1.342(3), N1–C1 1.342(3), N3–C1 1.345(3); N2–C1–N1 107.5(2), N2–Ge1–N1 67.87(9), N4–Ge1–N1 113.12(12), N4–Ge1–N2 104.26(10), N4–Ge1–Se1 116.96(8), N2–Ge1–Se1 124.73(6), N1–Ge1–Se1 120.22(7), Si1–N4–Ge1 116.55(15), Si2–N4–Ge1 117.32(17), Si2–N4–Si1 122.72(15), N3–C1–N1 124.5(2).

The Ge1–Se1 bond length 2.2061(4) Å in **4** was found to be identical with other germanium complexes containing Ge=Se moiety; [{2,6-^{i}Pr$_2$(C$_6$H$_3$N)P(Ph$_2$)(N^{t}Bu)}GeSe(O^{t}Bu)] (2.2003(2) Å),[7] [{C$_6$H$_{11}$NC(Me)NC$_6$H$_{11}$}Ge{N(SiMe$_3$)$_2$}Se] (2.2113(3) Å),[13a] [PhNC(Me)CHC(Me)NPh](Cl)Ge=Se (2.210(1) Å),[19] germaselenoesters [(*t*-Bu)$_2$ATI]Ge(Se)O^t-Bu (2.2193(7) Å),[5e] (η^4-Me$_8$taa)GeSe (2.247(1) Å).[24] However, Ge1–Se1 bond length 2.2061(4) Å in **4** is slightly longer than that of Okazaki and coworker's heavy ketone, *i.e.,* Tbt(Tip) Ge=Se (Ge=Se 2.180(2) Å).[1k] The short Ge–Se bond length is revealing of a double bond or a Ge–Se bond with an added percentage of ionic character. The Ge–N(amido) bond distance in **4** Ge1–N4 1.850(2) Å, is shorter by 0.0895 Å than that of the corresponding distance in **1** (Ge1–N3 1.9395(4)). The N2–Ge1–N1 bond angle 67.87(9)^o is slightly wider than the corresponding bond angle observed in **1** (N2–Ge1–N1 (64.12(4)^o).

Further, we have performed theoretical calculations to confirm the presence of double bond between germanium and sulphur or selenium atoms (see ESI† for Fig S13and Fig S14). The Wiberg Bond Index (WBI) was computed at B3LYP/6-31+G(d) level of theory. The atomic coordinates were taken from the .cif files of compounds **3** & **4** and no further geometry optimization was carried out. The Wiberg Bond Index (WBI) of Ge–S in compound **3** and Ge–Se in compound **4** are 1.49 and 1.52, respectively, indicating the existence of double bond between germanium and sulfur or selenium atoms.

Single crystals of **5** were obtained from diethyl ether and few drops of toluene solution at –30 °C. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ (see Figure 3).

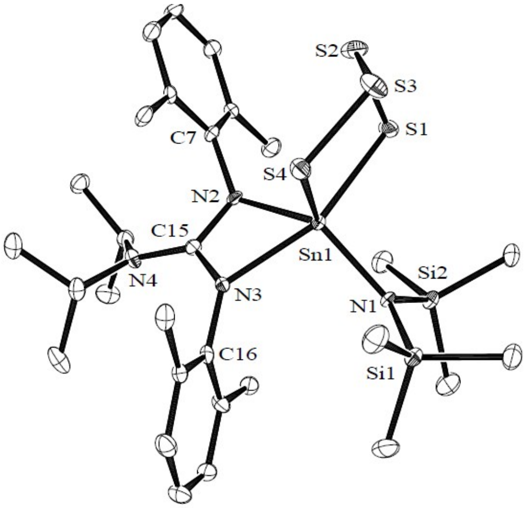


Fig. 3 ORTEP diagram of $C_{29}H_{50}SnN_4S_4Si_2$ with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **5**: Sn1–S1 2.4997(16), Sn1–S4 2.456 (15), Sn1–N1 2.062(4), Sn1–N2 2.167(4), Sn1–N3 2.240(4), Si1–N1 1.745(4), Si2–N1 1.748(5), N2–C(15) 1.354(6), N3–C(16) 1.421(6), N4–C(15) 1.358(6), S1–S2 2.043(2), S2–S3 2.036(2); N1–Sn1–N2 128.31(16), N1–Sn1–N3 99.28(16), N2–Sn1–N3 60.5(16), N1–Sn1–S1 97.95(12), N1–Sn1–S4 119.18(12), N3–C(15)–N2 110.2(4), N3–C(15)–N4 125.8(5), Si1–N1–Si2 119.0(2), Si1–N1–Sn1 121.9(2), Si2–N1–Sn1 118.4(2), S3–S4–Sn1 101.10(7), S2–S1–Sn1 97.82(7), S3–S2–S1 101.28(9), S(4)–Sn(1)–S(1) 95.43(5).

This complex shows the Sn centre in a distorted five co–ordinated geometry consisting of (*N,N’*) chelate guanidinate, amido and (S1 and S4) chelate tetrasulphido ligands. The noteworthy feature of this molecule is five membered SnS_4 ring. In this structure, five membered SnS_4 is in distorted half chair conformation. The bond angle S1–Sn1–S4 of compound **5** is 95.43(5)° is comparable to the structurally characterized SnS_4 rings.[13b, 25] The average S–S bond distance (2.045 Å) in SnS_4 (S1–S2 2.043(2), S2–S3 2.036(2), S(3)–S(4) 2.057(2) Å) is good in agreement with the average S–S bond distance (2.050 Å) for orthorhombic sulfur.

Sn–N(amido) bond distance in **5** Sn1–N1 2.062(4) Å, is shorter by 0.087 Å than that of the corresponding distance in **2** (Sn1–N1 2.149(5)). Sn–N(amido) bond distance in **5** Sn1–N1 2.062(4) Å is comparable with related amidinate stabilized tetrasulfido tin(IV) complexes $[\{C_6H_{11}NC(^tBu)NC_6H_{11}\}Sn(N(SiMe_3)_2)(S_4)]$ (2.065(2) Å). The Sn1–N3 2.275(5) bond distance in compound **5** slightly longer by 0.0054 Å than corresponding bond length of Sn1–N4 2.234(4) in compound **2** and Sn1–N2 2.167(4) bond distance is shorter by 0.108 Å compare to the Sn1–N3 2.275(5) in compound **2**.

Compound **6** (see Figure 4) also crystallizes in the triclinic space group $P\bar{1}$ which is dimeric species with bridging seleno ligand. The alternative tin and selenium atom in four membered $[Sn(\mu\text{–}Se)]_2$ ring core is planar. The central Sn atom coordination is covered by amido and bidentate guanidinate ligand and two bridged seleno $[Sn(\mu\text{–}Se)]_2$ unit.

Sn–N(amido) bond distance in **6** Sn1–N7 2.062(10) and Sn2–N8 2.083(10)Å, is shorter by 0.087 and 0.066 Å than that of the corresponding distance in starting material **2** (Sn1–N1 2.149(5)). The bridged Sn1–Se1 2.5676(17), Sn1–Se2 2.5658(18) bond distance in compound **6** is slightly longer than bridged seleno amide compound $[\{Sn(N(SiMe_3)_2)_2(\mu\text{-}Se)\}_2]$ Sn–Se 2.538(1) and 2.544(1) Å[26] and Sn–Se 2.528 Å in $[\{Sn(L_1)(\mu\text{-}Se)\}_2]$.[6] These Bond lengths of N1–Sn1 and N2–Sn1 in compound **6** are comparatively shorter than the compound **2.** The bond angle of N1–Sn1–N2 59.7(4)° is very similar with the free guanidinate tin amide (**2**) N3–Sn1–N4 59.13(17) °. Bond angles of Sn1–Se1–Sn2 89.51° and Sn1–Se2–Sn2 89.37° are wider than compound $[\{Sn[N(SiMe_3)_2]_2(\mu\text{-}Se)\}_2]$ Sn–Se–Sn' (85.09°). Se2–Sn2–Se1 90.62(6)° bond angle is shorter than $[\{Sn(N(SiMe_3)_2)_2(\mu\text{-}Se)\}_2]$ Se–Sn–Se’ (94.91^{o}) and compound $[\{Sn(L_1)(\mu\text{ -}Se)\}_2]$ 97.5^{o}. These difference of bond length and bond angles of compound **6** with $[\{Sn(N(SiMe_3)_2)_2(\mu\text{-}Se)\}_2]$ and $[\{Sn(L_1)(\mu\text{ -}Se)\}_2]$ due to environment change of metal center from tetra coordinate to pentacoordinate.

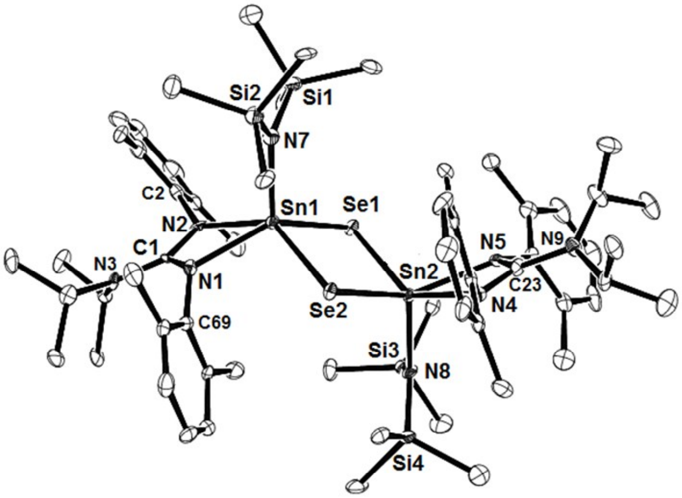


Fig. 4 ORTEP diagram of $C_{58}H_{100}N_8Se_2Si_4Sn_2$ with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **6**: Sn1–Se1 2.5676(17), Sn1–Se2 2.5658(18), Sn2–Se1 2.5662(18), Sn2–Se2 2.5616(17), Sn1–N1 2.231(10), Sn1–N2 2.270(11), Sn1–N7 2.062(10), Sn2–N4 2.222(10), Sn2–N5 2.268(10), Sn2–N8 2.083(10), N1–C1 1.332(16), N3–C1 1.411(14), N4–C23 1.338(16), N9–C23 1.403(15), Si1–N7 1.764(12), Si2–N7 1.733(11), Si3–N8 1.761(11), Si4–N8 1.719(11); N1–Sn1–N2 59.7(4), N7–Sn1–N1 110.6(4), N7–Sn1–N2 103.2(4), C1–N1–Sn1 94.3(8), N1–Sn1–Se2 88.7(3), N2–Sn1–Se2 138.5(3), N1–Sn1–Se1 140.5(3), N8–Sn2–N4 110.9(4), N8–Sn2–N5 102.0(4), N4–Sn2–N5 59.7(4), N8–Sn2–Se2 113.3(3), N4–Sn2–Se2 88.5(3), Se2–Sn2–Se1 90.62(6), Sn2–Se1–Sn1 89.37(6), Si4–N8–Si3 120.7(6), Si4–N8–Sn2 121.1(6).

Conclusion

In summary, we have synthesized and structurally characterized first mixed guanidinato/amido ligands supported germanium complexes with Ge=E (E= S or Se) double bond by oxidative addition of elemental sulfur or selenium to the [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$](**1**). Further, [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**2**) upon treatment with sulfur and selenium led to the formation of cyclic tetrasulphido and μ–seleno tin complexes bearing five membered SnS$_4$ and four membered Sn$_2$Se$_2$ rings, respectively.

Experimental

General

All manipulations were carried out under atmosphere of high purity dinitrogen or argon gas using standard Schlenk–line and cannula techniques or nitrogen filled MBraun glove box. Solvents were collected from MBraun Solvent Purification System and degassed prior to use. Benzene– d$_6$ was dried over potassium mirror and freez-thawed twice prior to use. [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$] (**1**) and [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**2**) were prepared according to reported literature procedures.[17b] Sulfur and selenium powders were purchased from Sigma–Aldrich and used without further purification. Melting points were taken in sealed glass capillaries under nitrogen on an electro thermal apparatus and are uncorrected. ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on Bruker AV–400 (^{1}H: 400 MHz, ^{13}C{^{1}H}: 100 MHz and ^{29}Si{^{1}H} NMR 80 MHz) and were referenced to the resonances of the solvent used. Elemental analyses were performed in a Vario Micro Cube Elementar CHNS /O analyzer.

X-ray

Crystallographic data for compounds **3-6** are given in Table 1. For all the compounds crystals were removed from the reaction Schlenk flask under inert atmosphere and immediately coated with silicon oil on a glass slide. Suitable crystals were mounted on a glass fiber at 100K; temperature was controlled using an Oxford Cryostream 700 instrument. Data were collected with a Bruker AXS SMART Apex CCD detector and with an INCOATEC micro source (Mo-Kα radiation, $\lambda = 0.71073$ Å, multilayer optics). The software SADABS was used for absorption correction SHELXTL[27] and Olex2[28] for space group, structure determination and refinements. The least-squares refinement techniques on F^2 were performed until the model converged. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model.

Disordered toluene molecule is present in the X-ray structure of **3.** Single X-ray crystal structure of compound **5** reveals that the presence of two identical molecules of **5** in the asymmetric unit along with one molecule of diethyl ether. CCDC 1436337-1436340 (for compounds **3-6**) contains the supplementary crystallographic data for this paper.

Computational studies

The Wiberg Bond Index (WBI) was computed at B3LYP/6-31+G(d) level of theory.

Table 1: Crystal data for compounds **3-6**

Compounds	**3**	**4**	**5**	**6**
CCDC	1436337	1436338	1436339	1436340
Formula	$C_{71}H_{104}Ge_2N_8S_2Si_4$	$C_{29}H_{50}GeN_4SeSi_2$	$C_{58}H_{100}N_8S_8Si_4Sn_2.C_4H_{10}O$	$C_{58}H_{100}N_8Se_2Si_4Sn_2$
Mol.mass	1391.32	662.46	1589.79	1417.12
Size (mm)	0.28 × 0.16 × 0.11	0.2 × 0.15 × 0.12	0.22 × 0.17 × 0.15	0.13x 0.087 x 0.058
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$C\,2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	37.184(6)	18.6303(10)	12.328(3)	13.142(13)
b (Å)	10.4649(15)	10.2343(5)	18.377(4)	14.843(17)
c (Å)	26.604(8)	18.6276(9)	18.647(4)	18.533(2)
α (°)	90	90	106.217(5)	96.409(7)
β (°)	131.927(3)	90.622(3)	107.376(4)	91.916(6)
γ (°)	90	90	94.718(4)	110.364(6)
V (Å3)	7702(4)	3551.5(3)	3807.8(15)	3357.9(19)
Z	4	4	2	2
ρ (gcm^{-3})	1.200	1.239	1.387	1.402
μ (Mo-$K\alpha$) (mm^{-1})	0.940	1.977	0.982	1.940
T (K)	100	100	100	100
θ (max.)	25.329	26	25.552	25.80
Unique reflections	7025	6983	41667	12769
F(000)	2952.0	1384.0	1660.0	1456
R(int)	0.0637	0.0430	0.0724	0.1469
Parameters	411	348	796	696
*R*1	0.0622	0.0377	0.0466	0.0908
w*R*2	0.1663	0.0859	0.1032	0.2035
GOF	1.075	1.050	1.013	0.973

Synthesis of [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(S)] (3).

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$] (**1**) (0.150 g, 0.257 mmol, 1.0 equiv) in THF (10 mL) was added 1.2 equiv of sulfur (0.010 g, 0.312 mmol, 1.2 equiv) at room temperature and stirred for another 12 h and noticed the formation of a clear yellow solution. All the volatiles were removed and extracted with diethyl ether (20 mL). Filtered through Celite using frit, solvent volume was reduced (10 mL) and few drops of toluene was added and stored at –30 °C. Colourless crystals of compound suitable for X–ray diffraction analysis are obtained after one day. Yield 0.14 g (88%); m. p. 182 – 187 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.32 (s, 18H, NSi(C*H*$_3$)$_3$), 0.57 (d, *J* = 8.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.45 (s, 6H, C*H*$_3$), 2.97 (s, 6H, C*H*$_3$), 3.85 (sept, *J* = 8.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.89–6.91 (m, 6H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 5.2 (Si–*C*), 20.3 (Ar–*C*H$_3$), 21.5(Ar–*C*H$_3$), 23.7 (*i*Pr–*C*H$_3$), 52.3 (N–*i*Pr–*C*H), 127.2 (Ar–*C*), 128.9 (Ar–*C*), 130.0 (Ar–*C*), 135.9 (Ar–*C*), 139.1 (Ar–*C*), 140.1 (Ar–*C*), 167.7 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C,): δ = 3.31 (N*Si*(CH$_3$)$_3$) ppm. Anal Calcd for $C_{29}H_{50}GeN_4SSi_2$ (615.61): C, 56.58; H, 8.19; N, 9.10. Found C, 56.28; H, 8.02; N, 8.91.

Synthesis of [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(Se)] (4).

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$](**1**) (0.250 g, 0.428 mmol, 1.0 equiv) in diethyl ether (15 mL) was added one equiv of selenium powder (0.04 g, 0.507 mmol, 1.2 equiv) at room temperature and stirring was continued for another 12 h. The reaction mixture was filtered through Celite and a clear yellow solution was reduced (7 mL) and kept it for crystallization at –30 °C. Colourless crystals for X–ray diffraction analysis were obtained after one day.

Yield 0.245 g (86%); m. p. 190 – 195 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.34 (s, 18H, NSi(C*H*$_3$)$_3$), 0.57 (d, *J* = 8.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.46 (s, 6H, C*H*$_3$), 2.99 (s, 6H, C*H*$_3$), 3.84 (sept, *J* = 8.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.88–6.91 (m, 6H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 5.3 (Si–*C*), 20.4 (Ar–*C*H$_3$), 22.1(Ar–*C*H$_3$), 23.7 (*i*Pr–*C*H$_3$), 52.2 (N–*i*Pr–*C*H), 127.2 (Ar–*C*), 128.3 (Ar–*C*), 130.1 (Ar–*C*), 135.9 (Ar–*C*), 139.0 (Ar–*C*), 140.1 (Ar–*C*), 167.9 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C,): δ = 3.02 (N*Si*(CH$_3$)$_3$) ppm. Anal Calcd for $C_{29}H_{50}GeN_4SeSi_2$ (662.51): C, 52.57; H, 7.61; N, 8.46. Found C, 52.07; H, 7.21; N, 8.36

Synthesis of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S$_4$)] (5).

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**2**) (0.270 g, 0.428 mmol, 1.0 equiv) in THF (10 mL) was added 1.2 equiv of sulfur (0.017 g, 0.531 mmol, 1.2 equiv) in THF (2 mL) at room temperature and stirred for another 12 h and noticed the formation of a clear yellow solution. All the volatiles were removed and extracted with diethyl ether (20 mL). Filtered through Celite using frit, solvent volume was reduced (8 mL) and few drops of toluene was added and stored at –30 °C. Colourless crystals of compound suitable for X–ray diffraction analysis are obtained after one day. Yield 0.29 g (89%); m.p. 195 – 200 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.30 (s, 18H, NSi(C*H*$_3$)$_3$), 0.55 (d, *J* = 8.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.54 (s, 12H, C*H*$_3$), 3.78 (sept, *J* = 8.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.87 (m, 6H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 6.4 (Si–*C*), 20.7 (Ar–*C*H$_3$), 24.0 (Ar–*C*H$_3$), 52.9 (N–*i*Pr–*C*H), 126.4 (Ar–*C*), 129.2 (Ar–*C*), 136.4 (Ar–*C*), 141.9 (Ar–*C*), 167.9 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C,): δ = 5.54 (N*Si*(CH$_3$)$_3$) ppm. Anal Calcd for $C_{29}H_{50}N_4S_4Si_2Sn$ (757.88): C, 45.96; H, 6.65; N, 7.39. Found C, 45.43; H, 6.39; N, 6.82

Synthesis of [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–Se)}$_2$](6)

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (0.2 g, 0.317 mmol, 1.0 equiv) in benzene (20 mL) was added one equiv of selenium powder (0.03 g, 0.38 mmol, 1.2 equiv) at room temperature and the reaction mixture was heated to 60 °C and continued the stirring for 12 h and a yellowish solution with some black colour precipitate was observed. All the volatiles were removed and extracted with diethyl ether (20 mL). Filtered through Celite using frit, solvent volume was reduced (8 mL) and few drops of toluene was added and stored at –30 °C. The reaction mixture was filtered through Celite and a clear yellow solution was reduced (8 mL) and kept it for crystallization at –20 °C. Colourless crystals for X–ray diffraction analysis were obtained after one day. Yield 0.19 g (85%); m.p. 215 – 220 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.49 (s, 18H, NSi(C*H*$_3$)$_3$), 0.58 (d, *J* = 4.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.47 (s, 6H, C*H*$_3$), 3.03 (s, 6H, C*H*$_3$), 3.87 (sept, *J* = 7.3 Hz, 2H, C*H*(CH$_3$)$_2$), 6.84–6.91 (m, 4H, Ar–*H*), 7.05 (d, *J* = 8.0 Hz, 2H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 7.1 (Si–*C*), 20.6 (Ar–*C*H$_3$), 22.7(Ar–*C*H$_3$), 24.4 (*i*Pr–*C*H$_3$), 52.6 (N–*i*Pr–*C*H), 125.8 (Ar–*C*), 129.1 (Ar–*C*), 129.4 (Ar–*C*), 136.1 (Ar–*C*), 138.0 (Ar–*C*), 143.1 (Ar–*C*), 169.9 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C,): δ = 5.24 (N*Si*(CH$_3$)$_3$) ppm. Anal Calcd for $C_{58}H_{100}N_8Se_2Si_4Sn_2$ (1417.15): C, 49.16; H, 7.11; N, 7.91. Found C, 48.63; H, 7.01; N, 7.54.

Acknowledgments

The authors thank the National Institute of Science Education and Research (NISER), Bhubaneswar, Department of Atomic Energy (DAE) Govt. of India for X-ray single crystal diffractometer and computational facilities and IIT Bhubaneswar for access to the CHNS facility. Authors also thank Dr. Himansu S. Biswal for the theoretical calculations. We also thank the anonymous reviewers for their helpful suggestions.

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Table of Contents

The oxidative addition of chalcogens (S and Se) to the guanidinate supported Ge(II) and Sn(II) amide complexes