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Homoleptic Low-Valent Polyazides of Group 14 Elements

Benjamin Peerless, Theo Keane, Anthony J. H. M. Meijer and Peter Portius*[c]

First examples of coordinatively unsaturated, homoleptic azido complexes of low-valent group 14 elements are reported. A simple strategy uses low-valent precursors, ionic azide transfer reagents and bulky cations to obtain salt-like compounds containing $E(N_3)_3^-$ of Ge(II)/Sn(II) which are fully characterised, including XRD. Remarkably, these compounds are kinetically stable at r.t. and isolable in sub-gram quantities.

Binary azides are known for all elements in Group 14 and exist as covalent $E(N_3)_4$ compounds (E = C, Si),[2] as hyper-coordinate $E(N_3)_6^{2-}$ complexes (Si-Pb)[1] and as $E(N_3)_2$ compounds (Sn, Pb).[5c] However, no low-valent, homoleptic Group 14 complex has yet been reported. All known binary p-block azides are highly endothermic primary explosives most of which possess exceedingly high electrostatic and friction sensitivities and a propensity to release N_2. As covalent, N-rich compounds, their isolation is generally challenging and experimental characterisation is limited.[5] In contrast, stability-inducing effects of hyper-coordination and of bulky, weakly coordinating counter ions (WCC)[6] allow many salt-like homoleptic polyazides to be synthesised in bulk and characterised fully, including via X-ray crystallography and IR spectroscopy.[5a] owing to azide groups (N_3) giving rise to intense bands in the mid-IR region. It has been shown that azide anions (N_3^-) are able to coordinate to low-valent centres in compounds such as $E(L)(N_3)$ and $E(L')(N_3)_2$, E = Ge, Sn.[3,4] On the other hand, the stability of low valent molecules, e.g. carbenes, silylenes, germylenes, stannylenes,[7] increases by saturating the electron deficient centre with sterically demanding, electron donating groups, such as N-based $C(N^iPr)_2(N^iPr_2)$ and $HC\{(CMe)(2,6-^iPr_2C_6H_3N)\}_2$ ligands.[7a,d] This insight has led to tri- and tetracoordinate complexes bearing uni-, bi- and terdentate ligands, e.g. $E(NHC)X_2$, $Ge(NHC)_2Cl^+$ and $Ge\{HB(Me_2pz)_3\}Cl$, E = Si, Ge; X = Cl-I, N_3; NHC = N-heterocyclic carbene.[8,4a] Exploitation of these concepts permitted the synthesis and characterisation of the first low-valent and homoleptic Ge and Sn azides described in this paper.

Compounds already containing WCC ions and low-valent germanium, $AsPh_4 GeCl_3$, PPh_4GeCl_3,[9] $PPNGeCl_3$[10] (**1a-c**), were prepared in high yield from the $GeCl_2(diox)$ adduct[19] and WCC chlorides[20] (Scheme 1, route A).[F1,11] These colourless, moderately air sensitive crystalline trichlorogermanates react readily with THF suspensions of NaN_3. In situ IR spectra of the reaction (**2b**) show bands due to asymmetric NNN stretches, $\nu_{as}(N_3)$, typical for coordinated N_3 groups at $\bar{\nu}_{max} / (cm^{-1}) = 2092$ and 2058, which have grown fully after a reaction time of 1 h. Exposure of the reaction solution to fresh NaN_3 results in no further spectral change. From the solution, a highly air sensitive, colourless solid (**3b**) was precipitated, the IR spectrum of which exhibits the finger print of
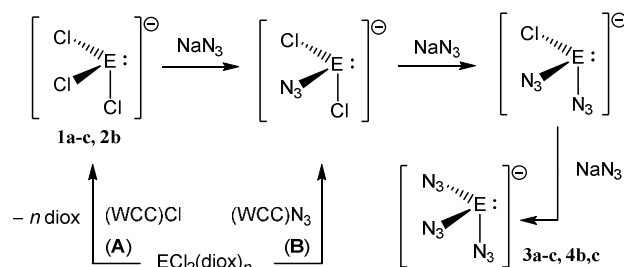
Scheme 1 Synthesis of azido(chloro) germanates(1−) and stannates(1−), E = Ge, n = 1 (**1**, **3**); E = Sn, n = 0 (**2**, **4**); WCC = AsPh₄ (**a**), PPh₄ (**b**), N(PPh₃)₂ (PPN, **c**).

PPh_4^+ and the $\nu_{as}(N_3)$ bands. The $\nu_{as}(N_3)$ frequencies lie within the range of those reported previously for semi-covalent germanium(II) azides (2027-2077 cm^{-1}, Fig. 1), below those of Ge(IV) azides $(Ge(N_3)_4, PPN_2Ge(N_3)_6, \textbf{5c})$[1b] and above that of the N_3^- ion. While solution ^1H, ^{13}C and ^{31}P NMR spectra of **3b** show signals of the WCC cations only, two peaks are observed in the ^{14}N NMR spectra at −263 and −207 ppm next to the solvent (−136 ppm) with FWHM line widths of 552, 147 and 24 Hz, respectively. These characteristics are typical for the N_α and N_γ nuclei of coordinated N_3 groups while the signal for N_β is obscured by solvent.[5a]

Alternative routes to **3** and **4** uses WCC azides as azide transfer reagents. GeCl$_2$(diox) reacts directly also with (PPN)N$_3$ in MeCN solution (Scheme 1, route B). Intriguingly, equimolar reactant mixtures produce only one ν_{as}(N$_3$) band (2078 cm^{-1}); increasing the stoichiometric ratio (1 : 2) results in two additional bands (2088, 2066 cm^{-1}), while at ratios of 1 : 9 and above only bands at 2095, 2064 cm^{-1} and that of N$_3^-$ were detected. These observations are interpreted tentatively in terms of the formation of mono, di- and triazido complexes.
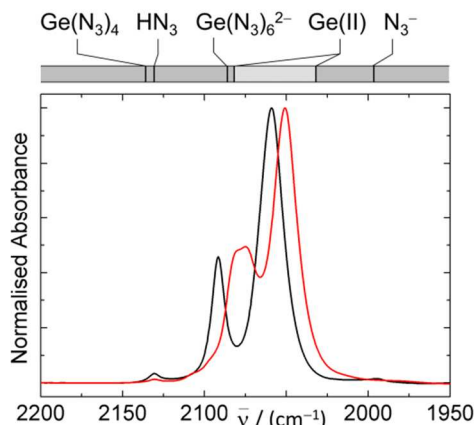
Figure 1 IR spectra of Ge(N$_3$)$_3^-$ (black), Sn(N$_3$)$_3^-$ (red) in THF; ν_{as}(N$_3$) frequency ranges of related azides, Ge(N$_3$)$_4$,[12] HN$_3$, Ge-(N$_3$)$_6^{2-}$,[1b] L$_n$Ge(II) azides L$_1$ = {Me$_2$(^{t}BuO)Si}$_2$N;[4c] L$_2$ = ^{n}Pr$_2$-ATI, Mes$_2$DAP,[4f,g] (NHC)$^{2+}$;[3] L$_3$ = HB(R$_2$pz)$_3$, (C$_5$R$_5$)Co{P(O)-(OEt)$_2$}$_3$,[4a,e,10] (2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_2$H$_2$N$_2$CGe(N$_3$)$_2$[8d] and N$_3^-$,[4e] are indicated in the top bar; see Table S1 for exact values.

Tin dichloride was subjected to a similar treatment as GeCl$_2$(diox) using WCC(N$_3$) and NaN$_3$; however, complete Cl / N$_3$ exchange requires a larger excess of azide transfer reagent. Similar observations as with **3b** were made, including the intermediate rise and decay of a ν_{as}(N$_3$) band (2064 cm^{-1}), the ultimate rise of bands of the final product **4b** (2081, 2050 cm^{-1}) in the expected region between Sn(N$_3$)$_6^{2-}$ and charge-neutral Sn(II) monoazides (Tab. S1), and ^{14}N resonances at −218.5 ppm (FWHM ≈32 Hz) and −260.0 ppm (166 Hz). The ^{14}N NMR signals of **3b** and **4b**, in particular those assigned to N$_\alpha$, are deshielded in comparison to those of E(N$_3$)$_6^{2-}$ dianions.[1b,5a,17] **3b** and **4b** are soluble in MeCN, THF and CH$_2$Cl$_2$.

The synthetic strategy was extended to AsPh$_4^+$ and PPN$^+$ counter ions affording compounds **3a,c** and **4c** (Scheme 1, A) which all have spectroscopic properties analogous to those of **3b** and **4b** described already. The combined analytical evidence, including the absence of chlorine in **3b** and the ^{119}Sn NMR signal of **4b** (δ = −220 ppm, see SI) point to the formation of anionic complexes in compounds of the type (WCC)E(N$_3$)$_3$ as the final products of Cl / N$_3$ exchange.

Further insight into the nature of intermediates and products of the exchange reactions was obtained from quantum chemical calculations[20] on the ECl$_{(3-n)}$(N$_3$)$_n^-$ species, which were performed at the B3LYP/cc-pVTZ level[21] with effective core potentials[22] for Ge and Sn. Solvent (THF) was described using PCM.[23] The calculations found conformational isomerism resulting in several minima for n = 1, 2, 3, that were close in energy. These conformers are related by rotation of ligands. Since rotational barriers of sterically unhindered N$_3$ groups are small (cf. GeH$_3$N$_3$, ~1 kJ mol^{-1}),[13] fast interconversion involves all significantly thermally populated rotamers above the minimum energy conformation (E_{rel} < 5.8 kJ mol^{-1}). This process is likely to result in averaged absorption bands weighted by the rotamer population (rotamers may have more than one degenerate, absolute spatial configuration, and inter-rotamer vibrational energy transfer

are unaccounted for). Taking account of the theoretical equilibrium mole fractions, absorption intensities and scaled vibrational frequencies,[24] approximate average frequencies of the in-phase and out-of-phase ν_{as}(N$_3$) stretches and the qualitative intensity ratios could be determined (Tab. S1), which match those observed (e.g. Ge(N$_3$)$_3^-$, 2059, 2091 vs. 2060, 2093; Sn(N$_3$)$_3^-$, 2051, 2080 vs. 2050, 2078 cm^{-1}). This approach leads to the assignment of the observed bands of intermediates to GeCl$_2$(N$_3$)$^-$, GeCl(N$_3$)$_2^-$, SnCl$_2$(N$_3$)$^-$ and SnCl(N$_3$)$_2^-$. Calculations using the Gauge-Independent Atomic Orbital method[25] verify the assignment of ^{14}N NMR data (see SI).

Crystals of azido germanates were grown from THF-Et$_2$O (1 : 10) solutions at −18 °C (**3b**, needles) or by diffusion of Et$_2$O into concentrated THF solutions (**3c**).[F2,†] According to single crystal X-ray diffraction studies, **3b** consists of PPh$_4^+$ and Ge(N$_3$)$_3^-$ ions (Fig. 2). The shortest *interionic* Ge⋯N and N⋯N distances were found to
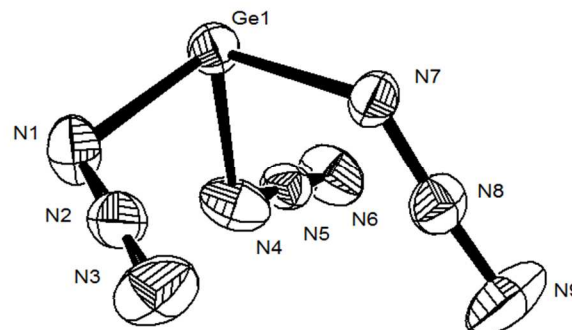
Figure 2 Thermal ellipsoid plot (50%) of Ge(N$_3$)$_3^-$ in the crystal of PPh$_4$Ge(N$_3$)$_3$ (**3b**). Bond lengths [Å] Ge1-N7 1.984(2), Ge1-N1 1.988(3), Ge1-N4 2.011(3), N1-N2 1.213(3), N2-N3 1.148(3), N4-N5 1.209(3), N5-N6 1.142(3), N7 N8 1.206(3), N8-N9 1.140(3), angles [°] N7-Ge1-N1 93.59(10), N7-Ge1-N4 94.29(10), N1-Ge1-N4 91.05(11), N2-N1-Ge1 116.4(2), N5-N4-Ge1 118.7(2), N8-N7-Ge1 121.3(2).

be 4.13 and 5.07 Å, respectively (Fig. 4, left), hence, covalent {[Ge(N$_3$)$_3$]$^-$}⋯{[Ge(N$_3$)$_3$]$^-$} interactions are absent (Fig. 3). Germanium is coordinated by three, essentially linear N$_3$ ligands and occupies the apical position in a trigonal-pyramidal Ge[N]$_3$ framework. The ligands are bound in the fashion typical of covalent azides and adopt Ge–N$_\alpha$–N$_\beta$ angles between 116° and 121°. All inter-ligand angles are close to 90° which indicates stereochemical inactivity of the lone electron pair at germanium.[14]

Table 1 Bond lengths D / Å in the salt-like homoleptic azides the type (WCC)^+_n[E(N$_3$)$_{3n}$]$^{n-}$, E = Ge, Sn; n = 1, WCC = PPh$_4^+$; n = 2, WCC = N(PPh$_3$)$_2^+$

E, n	E–N$_\alpha$	N$_\alpha$–N$_\beta$	N$_\beta$–N$_\gamma$	ΔNN$_{av}$^{a}	
Ge, 1	1.984(3)-2.011(2)	1.206(4)-1.213(4)	1.140(4)-1.148(4)	6.6(5)^b	^{c}
Ge, 2	1.969(2)-1.980(3)	1.210(4)-1.214(3)	1.143(3)-1.151(3)	6.5(4)	^{d}
Sn, 1	2.193(3)-2.262(3)	1.189(6)-1.203(4)	1.143(5)-1.163(6)	4.6(17)	^{c}
Sn, 2	2.117(3)-2.134(2)	1.182(3)-1.213(3)	1.111(4)-1.148(3)	5.7(10)	^{e}

^{a} ΔNN = Σ$_{i=1}^n$ [d(N$_\alpha$-N$_\beta$)$_i$ − d(N$_\beta$-N$_\gamma$)$_i$]/n, s = [(1/(n − 1) Σ$_{i=1}^n$ (ΔNN$_i$ − ΔNN$_{av}$)^2]$^{0.5}$ in parentheses, ^{b} s << σ, error estimated by σ = [Σ$_{i=1}^n$(σ_i / N)^2]$^{0.5}$; ^{c} this work; ^{d} ref. (1b); ^{e} ref. (15).

This structural feature has been found in the valence isoelectronic complexes of Ge$_2$(μ-pz*)$_3^+$ GeCl$_3^-$ [11f] and pilocarpine-

trichlorogermanate hemihydrate.[11g] The Ge–N$_\alpha$ bonds of **3b** are shorter than those of tetracoordinate Ge(II) azides 2.088(6)-2.094(7) Å (Fig. 1), longer than those of the homoleptic Ge(IV) azide PPN$_2$Ge(N$_3$)$_6$ (**5c**, Tab. 1) and rather within the range of previously investigated, tricoordinate Ge(II) azides (1.969-2.047(2) Å, Table 1). All other bond lengths and angles are close to those of **5c** (Table 1). The crystallographic structure of Ge(N$_3$)$_3^-$ is consistent with one of the geometries predicted by DFT (*vide supra*).
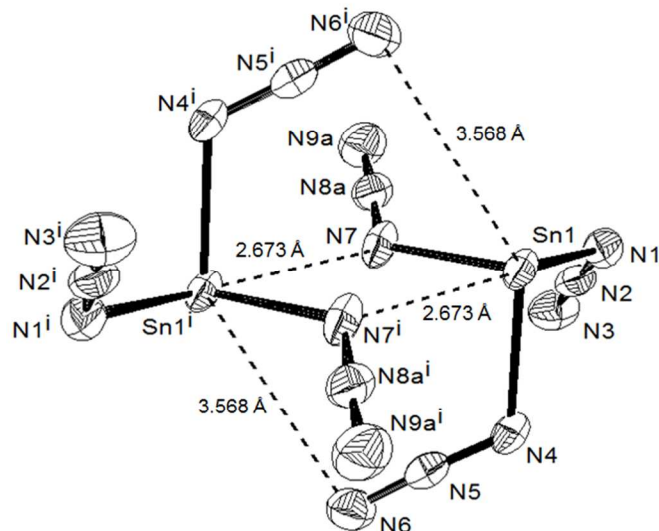
Figure 3 Thermal ellipsoid plot (50%) of {Sn$_2$(N$_3$)$_6$}$^{2-}$ in crystals of PPh$_4$Sn(N$_3$)$_3$ (**4b**). Bond lengths [Å] Sn-N1 2.262(3), Sn-N4 2.193(3), Sn-N7 2.207(3), 2.674(3), N1-N2 1.203(4), N2-N3 1.148(5), N4-N5 1.200(5), N5-N6 1.143(5), N7-N8 1.185(5), 1.193(5), N8-N9 1.157(6), 1.168(6) Sn^i-N6 3.567(4), angles [°] N1-Sn-N4 88.35(12), N4-Sn-N7 89.14(13), N1-Sn-N7 88.59(12), N2-N1-Sn 123.6(3), N5-N4-Sn 119.4(2), N8-N7-Sn 128.2(9), 120.2(8), N7-Sn-N7 68.32(16), Sn-N7-Sn 111.68(18).

Single crystalline needles of **4b** were obtained and investigated with the methods used for **3b**.† The asymmetric unit of **4b** also contains a E(N$_3$)$_3^-$ moiety; however, the packing is at variance with **3b**, which allows Sn(N$_3$)$_3^-$ to interact *via* two long E···N$_\alpha$ bonds and form {Sn(N$_3$)$_3$}$_2^{2-}$ dimers (Fig. 3). The interaction involves asymmetric $\mu_{1,1}$-N$_3$ bridges with short (2.207(3) Å) and long (2.674(3) Å)
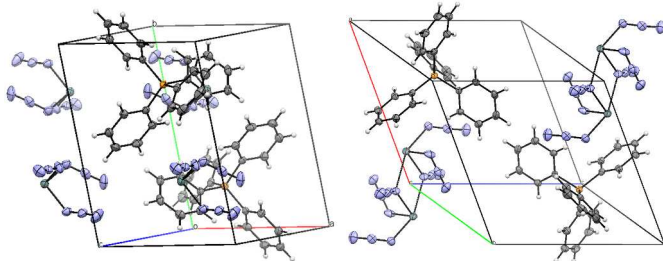

Figure 4 Packing diagrams of PPh$_4$Ge(N$_3$)$_3$ (**3b**, left) and PPh$_4$Sn(N$_3$)$_3$ (**4b**, right); H (bright grey), C (dark grey), N (light blue), P (orange), Ge and Sn (turquoise).

Sn-N$_\alpha$ bonds, the latter being considerably shorter than the sum of the van-der-Waals radii (3.72 Å).[16] Weak intermolecular interactions have been observed previously between neutral Sn-(^{n}Pr$_2$ATI)N$_3$ complexes (*vide supra*),[4b] where a slightly longer Sn···N$_\alpha$ bond (2.87 Å) was found. The sum of bond angles involving the bridging N$_\alpha$ indicates planarity and effective sp^2 hybridisation. As in the crystal of **3b**, the primary E(II)-N$_\alpha$

bonds are significantly longer (2.193(3)-2.262(3) Å) than those found in the homoleptic E(IV) azide **6** (2.125 Å).[15]The potential for dimerisation was studied by DFT using the geometry of {E(N$_3$)$_2$($\mu_{1,1}$-N$_3$)}$_2^{2-}$ in crystalline **4b** as a starting point. Optimisation results in separate anions devoid of covalent interionic interactions in the case of Ge(N$_3$)$_3^-$, whereas a dimeric structure was found for Sn(N$_3$)$_3^-$ that resembles the molecular structure in the crystal. Estimates of the basis set superposition error for the solution phase were obtained from BSSE calculations[26] in the gas phase. After BSSE correction, {Sn(N$_3$)$_2$($\mu_{1,1}$-N$_3$)}$_2^{2-}$ was found to be at least 4 kcal mol^{-1} less stable than two monomers, rendering the existence of a dimer in solution highly unlikely.

According to differential scanning calorimetry measurements (Fig. S12, 13), compound **3b** decomposes in two exothermic processes with $\Delta H = -270$ and -467 J g^{-1}).[F4] Remarkably, step 1 occurs at temperatures ($T_{on}^{ex1} = 99$ °C) that are drastically below the decomposition onset of the related, hypervalent azide **5c** ($T_{on}^{ex1} = 256$ °C),[1b] whereas step 2 sets in at $T_p^{ex2} = 310$ °C, which is nearly identical with the temperature found in 5c (312 °C).[F3] Furthermore, the molar enthalpies of step 2 (-251 *vs*. -482 kJ mol^{-1}) scale approximately with the complex charge; however, step 1 releases much less energy than expected (145 kJ mol^{-1}, **3b** *vs*. 705 kJ mol^{-1}, **5c**). This phenomenon is still under investigation. Further experiments show that heating of **3b** at 150 °C produces PPh$_4$N$_3$, which suggests that the release of N$_3^-$ initiates the decomposition of
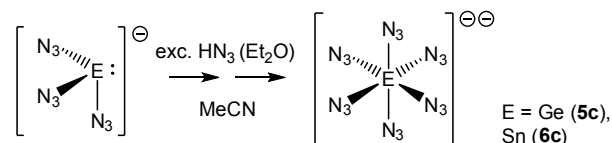
Scheme 2 Oxidation of the tri(azido) complexes **3b** and **5b**.

Ge(N$_3$)$_3^-$. The tin homologue **4b** melts at $T_{on} = 115$°C and decays at 215°C and 308°C and thus behaves as expected relative to **6c**.[15] No sensitivity was noted during preparation and analysis of compounds **3b** and **4b** on the stated reaction scale. The material remains unchanged when struck by a hammer. Upon lighting up, it burns rapidly with an orange flame leaving black residues.

In solution, Ge(N$_3$)$_3^-$ and Sn(N$_3$)$_3^-$ react with hydrazoic acid leading to a precipitate with the IR ν_{as}(N$_3$) absorptions characteristic for Ge(N$_3$)$_6^{2-}$ and Sn(N$_3$)$_6^{2-}$ complexes, respectively, which can be verified by comparison with spectra of the fully characterized salts **5c**, **6c** (Scheme 2, Figs. S13,14).

Conclusions

The first low-valent homoleptic azido complexes of Group 14 have been synthesized and fully characterised. The preparative approach to salt-like compounds containing these complexes has been demonstrated on a 0.2-0.7 g scale for a range of weakly coordinating cations and involves chloro(azido) species, ECl$_x$(N$_3$)$_y^-$. Unlike their hypervalent E(N$_3$)$_6^{2-}$ analogues and despite the presence of innocent cations, the new class of compounds is highly reactive, exhibiting low thermal stability and a propensity to oxidation. Crystallographic analysis revealed that in the solid state, E(N$_3$)$_3^-$ complexes of Group 14 may dimerise *via* azido ligand bridges. Neither of the low-valent coordination centres exhibits a stereochemically active lone electron pair. DFT calculations correctly predict the dimerisation and suggest furthermore that the dimers are unstable in polar solvents.

Notes and references

[a] Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK.

† Crystallographic data: **3b**, CCDC 1030032, $C_{24}H_{20}GeN_9P$, 538.07 g mol^{-1}, $P\bar{1}$, $a = 7.7712(2)$, $b = 11.4711(4)$, $c = 14.2003(4)$ Å, $\alpha = 93.278$ (2), $\beta = 99.357(2)$, $\gamma = 100.865(2)°$, $Z = 2$, $V = 1221.59(6)$ Å^3, $D_c = 1.463$ g cm^{-3}, $T = 120(2)$ K, $F(000) = 548$, $R_1 = 0.0376$ (316 param.), $wR_2 = 0.0807$, GOOF = 1.090. **3c**, $P\,2_1$, $a = 10.7640(11)$, $b = 12.732(2)$, $c = 25.713(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.682(12)°$, $D_c = 1.414$ g cm^{-3}, $T = 180(2)$ K, extensive disorder of $Ge(N_3)_3^-$ part (see SI and ref. 10). **4b**, CCDC 1030031, $C_{24}H_{20}N_9PSn$, $M = 584.15$ g mol^{-1}, $P\bar{1}$, $a = 10.7560(6)$, $b = 11.0605(6)$, $c = 12.3540(7)$ Å, $\alpha = 91.668(4)$, $\beta = 108.414(4)$, $\gamma = 116.545(3)°$, $Z = 2$, $V = 1222.11(12)$ Å^3, $D_c = 1.587$ g cm^{-3}, $T = 100(2)$ K, $F(000) = 584$, $R_1 = 0.0521$ (334 param.), $wR_2 = 0.1020$, GOOF = 1.053.

‡ Electronic Supplementary Information (ESI) available: Spectra, thermograms, full crystallographic data and computational details. See DOI: 10.1039/c000000x/

F1 $GeCl_3^-$ (refs. 9,11) and $SnCl_3^-$ salts (refs. 11c,e-g) with various organic counter ions have been reported previously.

F2 All attempts to crystallize compound **3a** have been futile.

F3 This step is assigned tentatively to the thermolysis of $PPN(N_3)$ and PPh_4 (N_3) since enthalpies and onset temperatures are comparable with those of genuine samples of these salts: PPh_4N_3, mp = 250°C, $T_{on}^{ex} = 291$°C, ref. 15.

F4 estimated error approx. ±10%.

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