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Homoleptic poly(nitrato) complexes of Group 14 stable at ambient conditions

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Abstract. Using a novel approach in homoleptic nitrate chemistry, the previously unknown hexanitrato complexes $Si(NO_3)_6^{2-}$ (**1c**), $Ge(NO_3)_6^{2-}$ (**2c**) as well as $Sn(NO_3)_6^{2-}$ (**3c**) were synthesised from the element tetranitrates as salt-like compounds which were isolated and characterised using ^{1}H, ^{13}C, ^{14}N and ^{29}Si NMR and IR spectroscopies, elemental and thermal analyses and single crystal XRD. All hexanitrates are moderately air sensitive at 298 K and possess greater thermal stability toward NO_2 elimination than their charge-neutral tetranitrato congeners as solids and in solution. The complexes adopt distorted octahedral coordination frameworks with geometries that are highly symmetric (**3c**) or deformed (**1c**, **2c**) depending on the degree of steric congestion of the ligand sphere. As opposed to the κ^2O,O' coordination mode reported for $Sn(NO_3)_4$ previously,[1] all nitrato ligands of **3c** coordinate in κ^1O mode. Two experimentally observed and four additional geometric isomers of $Si(NO_3)_6^{2-}$ were identified as minima on the PES using DFT calculations at the B3LYP/6-311+G(d,p) level.

Introduction

Nitrogen and oxygen-rich nitric acid esters and other covalently bound nitrates are highly endothermic compounds. The covalent character of $E–ONO_2$ bonds causes a significant lowering of the activation barrier for the elimination of NO_2 in comparison to the NO_3^- ion in salts. Intriguingly, polynitrato *complexes* occupy a place between these extremes. Such complexes and in particular the metal-containing species with bidentate nitrate ligand coordination, are powerful oxidising agents which is exemplified by the capability of $Ti(NO_3)_4$ to set alkanes on fire.[2] It has been shown previously that the thermal decomposition pathway of transition metal nitrato complexes leads to metals or metal oxides and involves multiple reaction steps in which highly reactive nitryl radicals, $NO_3^{\cdot}$, or NO_2 are released depending on the coordination mode of the nitrato ligands.[2] It has been demonstrated that the anionic homoleptic nitrato complexes in the compounds $(NO)Au(NO_3)_4$, $(NO)_2Pd(NO_3)_6$ and $(NO)_2Pt(NO_3)_6$ [3] in which the nitrato ligands prevail in a monodentate mode produce metal in chemical vapour deposition (CVD) processes, whereas the compound $(NO_2)Ga(NO_3)_4$,[4] in which a larger coordination centre permits agostic coordination of the nitrato ligand, generates gallium oxide deposits. Consequently, metal nitrates are considered in CVD applications for the growth of C,H-free deposits.[4] The properties of complexes of

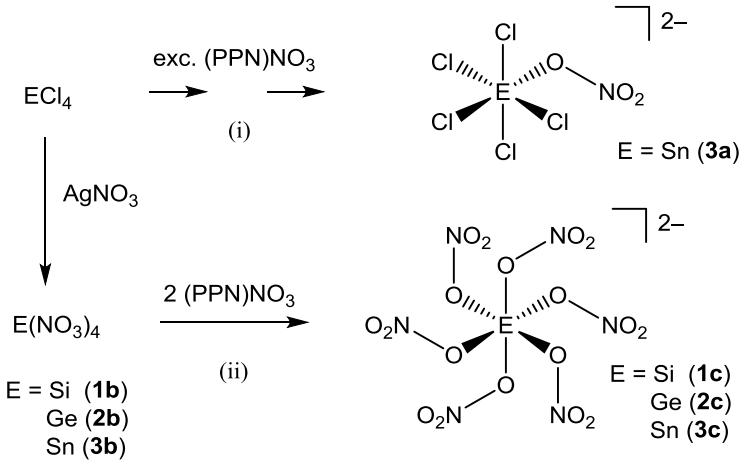
semimetallic *p*-block and *d*-block elements are related where the former possess, however, lower oxidation potentials and less labile NO_3 ligands. Polynitrato complexes of light *p*-block elements are interesting species that may act as unusual energetic materials and as novel precursors for well-defined E, N, O deposits. Such complexes are, however, not well-researched and many potentially viable complexes of elements with lesser metallic character are still unknown.

Traditionally, polynitrato complexes have been synthesised by the reaction of either N_2O_4 or N_2O_5 with metal halides.[5] This method affords group 13, 14 and 15 polynitrato complexes of the type $E(NO_3)_4$ (E = Sn, **3b**[6]), $E(NO_3)_4^-$ (E = B,[7, 8] Al,[9-13] Ga[14,15]), $E(NO_3)_5^{2-}$ (E = Al[10,16-20]) and $E(NO_3)_6^{q-}$ (E = Sn, q = 2;[21] Al,[22,23] Bi,[24] q = 3). Attempts to synthesise $Pb(NO_3)_6^{2-}$, $Ge(NO_3)_6^{2-}$ or $Ge(NO_3)_4$ (**2b**) using this method, however, failed and afforded GeO_2 and $Pb(NO_3)_2$, respectively, instead.[25] An alternative preparative method for polynitrates involving silver nitrate as a NO_3 group transfer reagent afforded **1b** from $SiCl_4$ in MeCN-Et_2O solution.[26] While data on homoleptic group 13 nitrato complexes and in particular those of B, Al and Ga and that of Sn(IV) (*vide supra*) is available, very little is known on complexes of the lighter group 14 elements Si and Ge. Data available thus far for group 14 nitrates suggest that poly(nitrato) silicon and germanium complexes are likely to be insufficiently stable to allow their isolation at r.t. – a notion which could be rationalised by estimating the degree of ionicity of the Si–O and Ge–O bonds in hypothetical $E(NO_3)_x^{(4-x)-}$ complexes which should be less than that of the E–O bonds of the related and well-characterised complexes $Al(NO_3)_4^-$, $Ga(NO_3)_4^-$ and $Sn(NO_3)_4$ (**3b**). In these compounds the trigonal geometry of the NO_3 group is severely distorted through the shortening of the terminal N-O bonds and the lengthening of the N–O bond that links to the centre (E) *via* E–ONO_2 bridges. In group 14, **3b** [1,27,28] and the salt-like compounds $(Cat)_2Sn(NO_3)_6$, Cat = Et_4N^+,[21] Cs^+ [25] remain the only characterised *homoleptic* nitrates. To the best of our knowledge, reported structures featuring any Si−ONO_2 or Ge−ONO_2 motifs are the nitric acid silyl-ester $O_2NO{-}SiMe_2\{C(SiMePh_2)(SiMe_3)_2\}$[29] and the five-coordinate nitrato complex $Si(NO_3\text{-}\kappa^1O)\{O{-}C(Me){=}CH{-}C(Me){=}N{-}C_6H_4{-}S\text{-}\kappa^3N,O,S)\}Ph$,[30] while $SiMe_2(NO_3)_2$ and the Lewis acid base adduct $Si(NO_3)_4{\cdot}2py$ are the only characterised poly(nitrato) silicon compounds.[26] $Si(NO_3)_4$ (**1b**, *vide infra*) is proposed as an intermediate for the preparation of $Si(NO_3)_4{\cdot}2py$; however, no spectroscopic evidence of its formation is available. $Si(NO_3)_4{\cdot}2py$ is highly thermolabile and releases nitrogen oxides readily at r.t. Although the germanium nitrates $GeMe_3(NO_3)$ and $GeMe_2(NO_3)_2$[27, 28, 31] have been reported, no reference has been made to either $Ge(NO_3)_4$ (**2b**) or $Ge(NO_3)_6^{2-}$. Due to these findings,

covalent nitrates have been considered *a priori* unstable and their synthesis a considerable challenge.

This paper reports the first synthesis and the full characterisation of homoleptic silicon and germanium nitrates including the experimentally determined molecular structures $E(NO_3)_6^{2-}$, E = Si, Ge or Sn. Detailed structural and reactivity studies reveal how the binding mode of the nitrato ligand affects stability and chemical properties of this class of compounds. Density functional theory methods were employed to evaluate the energetics of conformational isomers of $Si(NO_3)_6^{2-}$ complexes.

Results and Discussion



Scheme 1. Synthesis of the homoleptic nitrato complexes of silicon, germanium and tin. $(PPh_3)_2N^+$ (PPN^+) are counter ions to charged complexes.

In the exploration of potential routes for the synthesis of the hexanitrato complexes of silicon, germanium and tin, two approaches were taken. In a direct approach (*i*), a suitable halide is allowed to react with a large excess of nitrate salt of a non-coordinating cation avoiding the intermediate formation of the highly reactive charge-neutral tetranitrates. This method is akin to the synthesis of the related hexaazido complexes.[32-46] The indirect approach (*ii*) involves the *in situ* formation of tetranitrates, which are then "trapped" by Lewis acid-base reactions with nitrate anions.

The feasibility of the Cl^- / NO_3^- ligand exchange in approach (*i*) was tested by the reaction of tin(IV) chloride with an excess of NO_3^- ions (Scheme 1). The nitrato complexes of this element were deemed to be the thermally least labile target species. The addition of $(PPN)NO_3$ to a solution of $SnCl_4$ in Ar-saturated acetonitrile at 60°C causes a brown

colouration of the protective gas which indicates the formation of NO_2. The formation of NO_2 was confirmed by the presence of a band at 1740 cm^{-1} characteristic for NO stretches in the *in situ* IR spectra of the reaction solution. Moderately air sensitive, colourless, block-shaped crystals grow in the concentrated reaction solution below –20°C and these were investigated by single crystal X-ray diffraction. The structure solution revealed that the mixed-ligand complex in the salt $(PPN)_2[SnCl_5(NO_3)]$ (**3a**) had formed as one of the reaction products. The molecular structure of the $SnCl_5(NO_3)^{2-}$ complex in **3a** is shown in Fig. 1; complete structural details are given in the SI. Briefly, $SnCl_5(NO_3)^{2-}$ adopts a distorted octahedral geometry with a long Sn–Cl bond (2.58 Å) *trans* to the nitrato ligand and two short Sn–Cl bonds (2.41 Å) due to the variation in the *trans* influence of chloro and nitrato ligands. The nitrato ligand binds through one oxygen atom ($d_{Sn–O}$ = 2.16 Å) which is located off the Sn–Cl_{trans} axis. A Sn–O–N angle of 133° implies that a second oxygen atom is drawn close to the coordination centre $d(Sn\cdots O) \approx 3.1$ Å. Due to the type of disorder in the tin-containing part of the crystal it is clear that the observed diffraction pattern cannot be caused by a disordered solid solution containing an equal distribution of $SnCl_6^{2-}$ and $Sn(NO_3)_2Cl_4^{2-}$. Heating an acetonitrile solution containing **3a** and a tenfold molar excess of $(PPN)NO_3$ to 60 °C led to a brown solution from which no products other than $(PPN)_2[SnCl_5(NO_3)]$ and $(PPN)NO_3$ were obtained. The absence of a nitrate-rich stannate indicates that these complexes tend to decompose upon release of NO_2 under the conditions needed to bring about ligand exchange using nitrate salts with weakly coordinating cations. Therefore, the Cl / NO_3 ligand exchange cannot be driven to completion in a hexacoordinate tin complex under this regime.

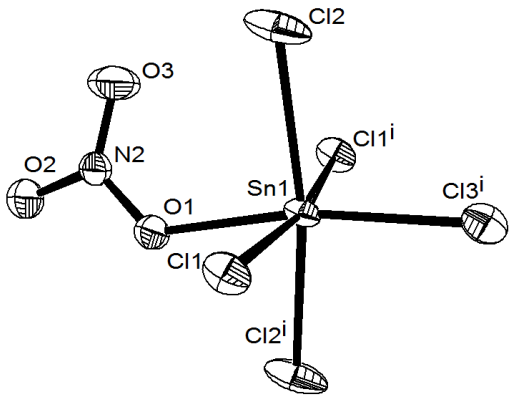


Figure 1. Thermal ellipsoid plot of one component of the disordered structure of $[SnCl_5(NO_3)]^{2-}$ in compound **3a** at 100 K. Ellipsoids are set to 50% probability. Selected bond lengths [Å] and angles [°]: Sn1-Cl1 2.423(15), Sn1-Cl2 2.357(15), Sn1-Cl3 2.395(3), Sn1-O1 2.155(4), O1-N2 1.287(9), O2-N2 1.240(13), O3-N 21.217(11); Sn1-O1-N2 128.8(7), Cl1-Sn1-Cl1 169.79(3), Cl1-Sn1-Cl2 91.89(5), Cl1-Sn1-O1 87.89(10), Cl2-Sn1-O1 79.27(16), Cl2-Sn-Cl2 170.20(3), Cl2-Sn1-Cl3 95.31(8), O3-N2-O2 121.2(7), O3-N2-O1 121.4(11), O2-N2-O1

117.3(9). Atomic coordinates denoted with superscript (i) were generated by inversion symmetry from the asymmetric unit.

Exploring route (*ii*), tin tetranitrate (**3b**) that was obtained from the reaction of $SnCl_4$ with $AgNO_3$,[1] was allowed to react with $(PPN)NO_3$ in an acetonitrile solution at 0°C. I*n situ* IR spectroscopy revealed a reaction that causes the bands due to the characteristic N–O stretch of **3b** at 1556 cm^{-1} to disappear while bands of a new NO_3 species appeared at lower wavenumbers (e.g. 1547 cm^{-1}). A colourless crystalline solid was obtained from the reaction mixture, which according to ^{1}H, ^{13}C, ^{31}P and ^{14}N NMR and IR spectra, elemental analysis, and X-ray diffraction data is identifiable as the hexanitratostannate(2−) $(PPN)_2Sn(NO_3)_6$ (**3c**).

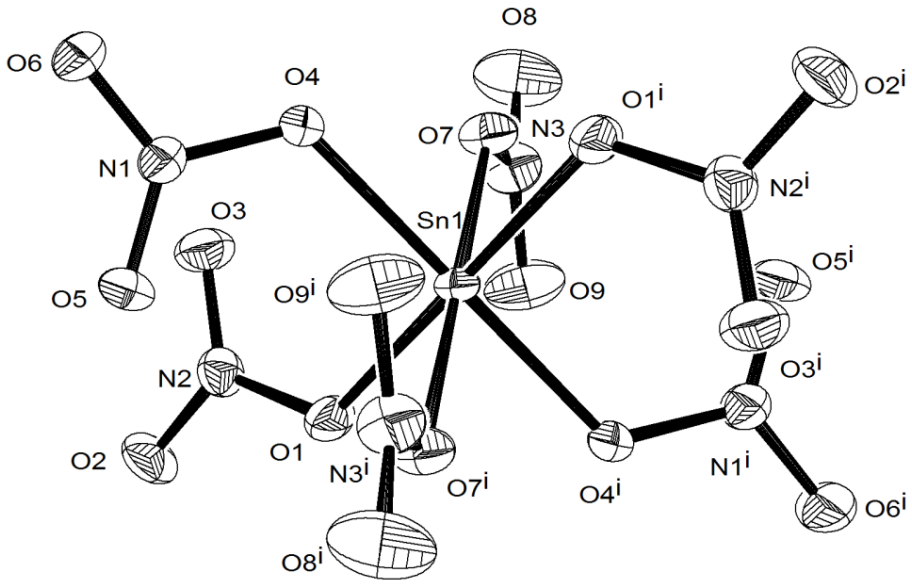


Figure 2. Thermal ellipsoid plot of the hexa(nitrato)stannate(2−) complex in $(PPN)_2Sn(NO_3)_6 \cdot 2MeCN$ (**3c·2MeCN)** at 100 K. Ellipsoids are set to 50% probability. Selected bond lengths [Å] and angles [°]: Sn1-O1 2.0624(17), Sn1-O7 2.0706(16), Sn-O4 2.0831(16), O1-Sn1-$O1^i$ 180, O1-Sn1-O7 80.79(7), O1-Sn1-O7 99.21(7), O7-Sn1-$O7^i$ 180, O1-Sn1-O4 78.79(6), O1-Sn1-O4 101.21(6), O7-Sn1-O4 79.17(7), O7-Sn1-O4 100.83(7); Sn1 occupies an inversion centre. Atomic coordinates denoted with superscript (i) were generated by inversion symmetry from the asymmetric unit.

The anionic part of the crystal structure of **3c** (Fig. 2) consists of a D_{3d} symmetric tin(IV) complex in which six nitrato ligands coordinate *via* comparably long Sn–O bonds (d(Sn–O) = 2.0624(17)-2.0831(16) Å) which are, intriguingly, on average shorter than those found in $Sn(NO_3)_4$ (**3b**, 2.151(7)-2.195(7) Å) even though the number of coordinated nitrato ligands is smaller in the latter. The octahedral SnO_6 coordination framework in **3c** is elongated along one C_3 axis. The distortion is caused by crowding of the ligand sphere due to the essentially covalent nature of the coordinative bonds which appear to involve sp^2 hybridisation of the ligating oxygen and therefore require a non-linear ligand coordination (Sn–O–N angles of 120° required, 121.9(1)-123.0(1)° observed). This coordination angle brings six additional

potential ligators into closer proximity of the centre and causes additional Sn···NO_3 interactions (d(Sn···O) = 3.105 to 3.121 Å) which elongate the SnO_6 octahedron along the axis normal to the face defined by O1, O4 and O7 and reduce the adjacent O–Sn–O bond angles from their ideal value of 90° down to 78.79(6)-80.79(7)° (see Fig. 2, caption and Table 1). Hence the κ^1O-NO_3 coordination mode of the nitrato ligands in **3c** is in stark contrast to the bidentate κ^2O,O'-NO_3 mode found in **3b** which possesses an eight-coordinate Sn centre (see ref. 1 for the crystallographically determined structure of **3b**). Compound **3c** is moderately air sensitive and soluble in CH_2Cl_2 and MeCN. No decomposition was detected over 15 minutes in a MeCN solution at temperatures of up to 35-40°C. A comparison of solution IR spectra with those obtained from nujol suspension indicate that $Sn(NO_3)_6^{2-}$ does not dissociate into $Sn(NO_3)_4$ in solution.

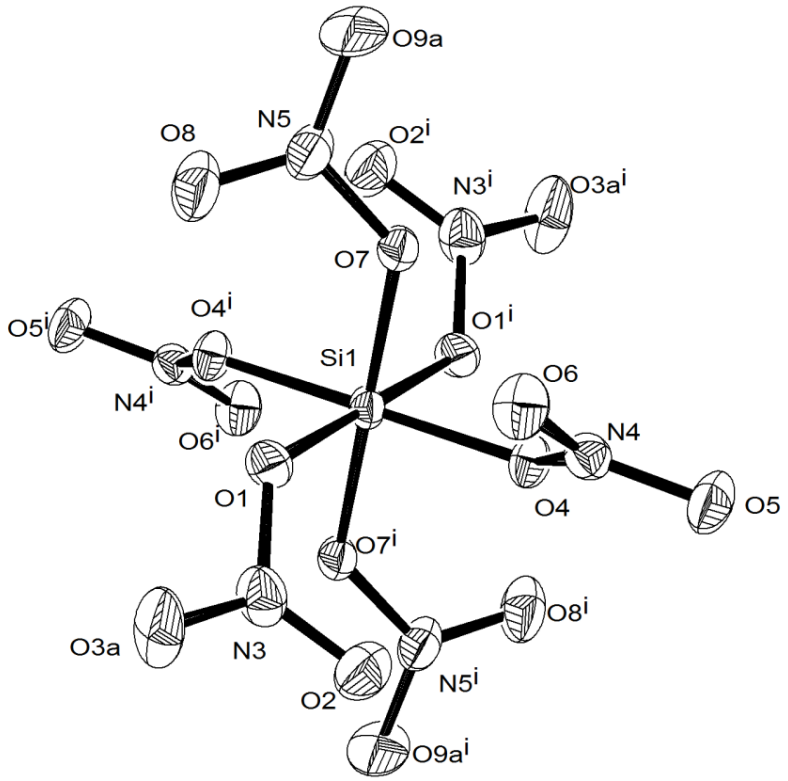


Figure 3. Thermal ellipsoid plot of one component of the two crystallographically independent hexa(nitrato)silicate(2–) complexes in crystals of **1c** at 100 K. Ellipsoids are set to 50% probability. Selected bond lengths [Å] and angles [°]: Si1-O1 1.7875(16), Si1-O4 1.7936(14), Si1-O7 1.7689(15), Si2-O16 1.7785(16), Si2-O10 1.773(15), Si2-O13 1.8053(15); O1-Si1-O1 180, O1-Si1-O4 96.13(7), O1-Si1-O4^i 83.87(7), O4-Si1-O4 180, O1-Si1-O7 90.78(7), O1-Si1-O7^i 89.22(7), O4-Si1-O7 88.19(7), O4-Si1-O7^i 91.81(7), O7-Si1-O7^i 180, O16-Si2-O16^i 180, O16-Si2-O10 87.52(7), O16-Si2-O10^i 92.48(7), O10-Si2-O10^i 180, O16-Si2-O13 89.14(7), O16-Si2-O13^i 90.86(7), O10-Si2-O13 82.27(7), O10-Si2-O13^i 97.73(7), O13-Si2-O13^i 180. Disorder in N-O groups is accounted for by a 1:1 disorder model for two independent NO_3 ligands in which the positions of the terminal O atoms are split and geometry and thermal motion related to each other by suitable SADI, SIMU and DELU restraints. Atomic coordinates denoted with superscript (i) were generated by inversion symmetry from the asymmetric unit.

Previous work led to the suggestion that the classical N_2O_5 / EX_n method used for binary nitrates is unsuitable for the synthesis of the unknown germanium tetranitrate, $Ge(NO_3)_4$ (**2b**), as attempts to prepare **2b** led to GeO_2.[23] We have instead applied the method used for the *in situ* generation of the lighter congener, $Si(NO_3)_4$ (**1b**), with the intention to obtain a Lewis acid precursor and facilitate a reaction of **2b** with nitrate anions under conditions similar to those for **3c**. It was found that $GeCl_4$ reacts with $AgNO_3$ in MeCN solution at r.t. causing the immediate precipitation of AgCl. An acetonitrile adduct, $Ge(NO_3)_4 \cdot MeCN$ (**2b.MeCN**), remains after evaporation of the filtered, colourless reaction solution. While the colourless, waxy **2b.MeCN** melts under decomposition at 30-35ºC releasing a brown gas, the gas evolution in MeCN solutions at r.t. becomes noticeable in the protective atmosphere of the storage vessel after at least 6 h. **2b** has characteristic NO_2 absorption bands in the IR spectrum at 1618 and 1558 cm^{-1} and 1286 cm^{-1}. Based on interpretations of infrared spectra of nitrato complexes in the cited literature, these bands are assigned to the asymmetric and symmetric N–O bond stretching vibrations $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively. MeCN solutions of **2b** react with $(PPN)NO_3$ in an analogous fashion to **3b**, generating the salt $(PPN)_2[Ge(NO_3)_6]$ (**2c**), which was isolated as colourless, less air sensitive crystals that are stable at ambient temperature. The preparation of the highly thermolabile $Si(NO_3)_4$ (**1b**) involved $SiCl_4$ that had to be dissolved in diethyl ether in order to bring about the reaction with $AgNO_3$. Using acetonitrile as the solvent resulted in no precipitation of AgCl over the period of several hours. The same method described for **2c** and **3c** was then used to convert (**1b**) into $(PPN)_2[Si(NO_3)_6]$ (**1c**), which shows no decomposition over several months at a temperature of −28 °C, though the crystals begin to discolour within few hours at ambient temperature. The application of method (*i*) to synthesise **1c** resulted in the type of decomposition observed for **3c**. The structures of the salts **1c** (Fig. 3) and **2c** (Fig. 4) were also determined by single crystal X-ray diffraction studies.

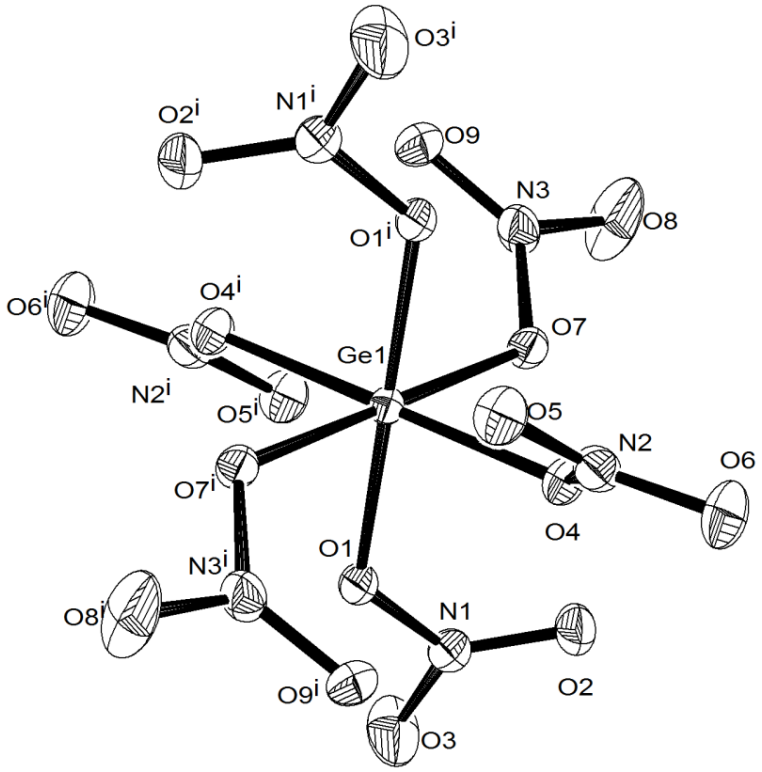


Figure 4. Thermal ellipsoid plot of one crystallographically independent hexanitrato germanate(2–) complex in crystals of **2c** at 100 K. Ellipsoids are set to 50% probability. Selected bond lengths [Å] and angles [°]: Ge1-O7 1.8918(12), Ge1-O1 1.8944(13), Ge1-O4 1.9166(12), Ge2-O10 1.8794(13), Ge2-O16 1.8988(13), Ge2-O13 1.9062(12); O7-Ge1-O7^{i} 180, O7-Ge1-O1 86.43(5), O7-Ge1-O1^{i} 93.57(5), O1-Ge1-O1^{i} 180, O7-Ge1-O4 99.69(5), O7-Ge1-O4^{i} 80.31(5), O1-Ge1-O4 91.60(5), O1-Ge1-O4^{i} 88.40(5), O4-Ge1-O4^{i} 180, O10-Ge2-O10^{i} 180, O10-Ge2-O16 91.47(6), O10-Ge2-O16^{i} 88.53(6), O16-Ge2-O16^{i} 180, O10-Ge2-O13 92.59(6), O10-Ge2-O13^{i} 87.41(6), O16-Ge2-O13 82.37(6), O16-Ge2-O13^{i} 97.63(6), O13-Ge2-O13^{i} 180. Atomic coordinates denoted with superscript (i) were generated by inversion symmetry from the asymmetric unit.

A comparison of the structural parameters derived from the X-ray diffraction studies reveals a number of interesting trends (Table 1). Even though all hexa(nitrato)complexes $E(NO_3)_6^{2-}$ (E = Si, Ge, Sn) possess strict inversion symmetry and therefore all *trans*- ligand pairs are in the *anti*-conformation (*vide infra*), the relative orientation of the ligand pairs differ and this results in different complex geometries. While those in **1c** and **2c** can be approximated by C_{2h} point group symmetry, in **3c** an orientation close to D_{3d} is adopted. Consequently, the coordination centre in the former complexes is not in the planes spanned by all individual NO_3 ligands. A comparison of the inter-ligand O–E–O bond angles reveals deviations from 90° that increase in the series $Si(NO_3)_6^{2-}$, $Ge(NO_3)_6^{2-}$, $Sn(NO_3)_6^{2-}$ causing extended distortions of the [EO_6] framework (*vide supra*). The average E-O-N angles, however, narrow in this series and get very close to the value required for sp^2 hybridised oxygen in **3c**. The change of angle is interpreted in terms of increased crowding of the ligand spheres. All E-O bonds are long in comparison with most four-coordinate complexes and this is ascribed to the typical bond-elongating effect upon hyper-coordination. More subtle changes are noticeable

in the intra-ligand bonds where the internal N–O bonds are much longer, and the external N–O bonds slightly shorter than those of the uncoordinated NO_3^- ion. All intramolecular Sn-O distances to the *endo* terminal oxygen atoms, *d*(E···O), are 0.5 to 0.6 Å shorter than the sum of the van der Waals radii.[47]

Table 1. Characteristic bond length ranges [Å] and angles [°] in the $E(NO_3)_n]^{(4-n)2-}$ complexes of **1c-3c** (n = 6) and **1b** (n = 4)

	d(E-O) [a]	*d*(E···O) [b]	d(O-N)$_{int}$	d(O-N)$_{term}$	<(E-O-N)	<(O-E-O) [c]	
1c	1.769(2)-1.805(2)	3.082-3.174	1.342(2)-1.352(2)	1.204(2)-1.235(4)	127.2(2)-130.6(2)	82.27(7)-97.73(7)	XRD [d]
1c (S_6)	1.809	3.172	1.342	1.216, 1.224	131.5	87.2, 92.8	DFT [e]
1c (C_{2h})	1.802, 1.818	3.136, 3.204	1.338, 1.347	1.212-1.225	129.4, 133.3	83.5-96.5	DFT [e]
1c (C_{2h})	1.798, 1.814	3.125, 3.195	1.342, 1.346	1.213-1.220	129.0, 133.1	83.6-96.4	DFT [e,f]
1b (S_4)	1.667	2.901	1.462	1.185, 1.200	122.5	117.9	DFT [e,f]
2c	1.879(2)-1.917(2)	3.094-3.193	1.338(2)-1.356(2)	1.201(2)-1.223(3)	122.9(1)-128.1(1)	82.4(1)-99.7(1)	XRD [d]
3c	2.062(2)-2.083(2)	3.105-3.121	1.329(2)-1.334(3)	1.207(3)-1.225(2)	121.9(1)-123.0(1)	78.8(1)-101.2(1)	XRD [d]
NO_3^-	-	-	-	1.226(3)-1.268(3)	-	-	XRD [d,e]

[a] e.s.d.s < 0.002 are rounded up, [b] sum of van der Waals radii E,O / Å: 3.62 (E = Si); 3.63 (E = Ge), 3.69 (E = Sn);[47,48] [c] all *trans* O-E-O angles equal 180°; [d] determined crystallographically, [e] density functional theory at the B3LYP/6-311+G(d,p) level, [f] PCM (MeCN); [g] obtained from $(PPN)NO_3 \cdot MeCN$, crystallographic data can be found in the SI.

Thermogravimetric analyses of compounds **1c-3c** (TGA, Fig. 5) suggest the operation of a three-stage thermolysis process. The onset of decomposition of **1c** occurs at T_{on1} = 138°C (stage I, 12.7 % mass loss) and is followed by the stages II (T_{on2} = 257°C, 2.0 %) and III (T_{on3} = 398°C). The mass loss up to 300 °C integrates to 14.8%. Similar observations were made with **2c** where T_{on1} was found to be only slightly higher (145°C, 12.0 %) whereas the onset for stage II occurred at the same temperature within the accuracy of measurement (T_{on2} = 260°C, 4.2 %). The mass loss regime of compound **3c·2MeCN** is analogous to that of **1c** and **2c** with the exception of crepitation occurring at T_{on} = 93°C and the onset temperatures for stages I and II being higher (204°C and 303°C). The elevated onset temperature for thermal decomposition are remarkable given the thermal sensitivity of the polynitrato complexes formed during Cl^- / NO_3^- ligand exchange reactions (*vide supra*). The thermal reactivity is reflected in differential scanning calorimetry traces which indicate the exothermic nature of stage I (Fig. 5). Furthermore, heating crystals of **1c** or **2c** to 160°C under a dynamic vacuum releases brown gas. A comparison of IR spectra of the yellow, glassy residues left behind

with those of a genuine sample indicate that $(PPN)NO_3$ is formed at this temperature. Only the residue of **1c** shows additional signatures of a species bearing nitrato ligands.

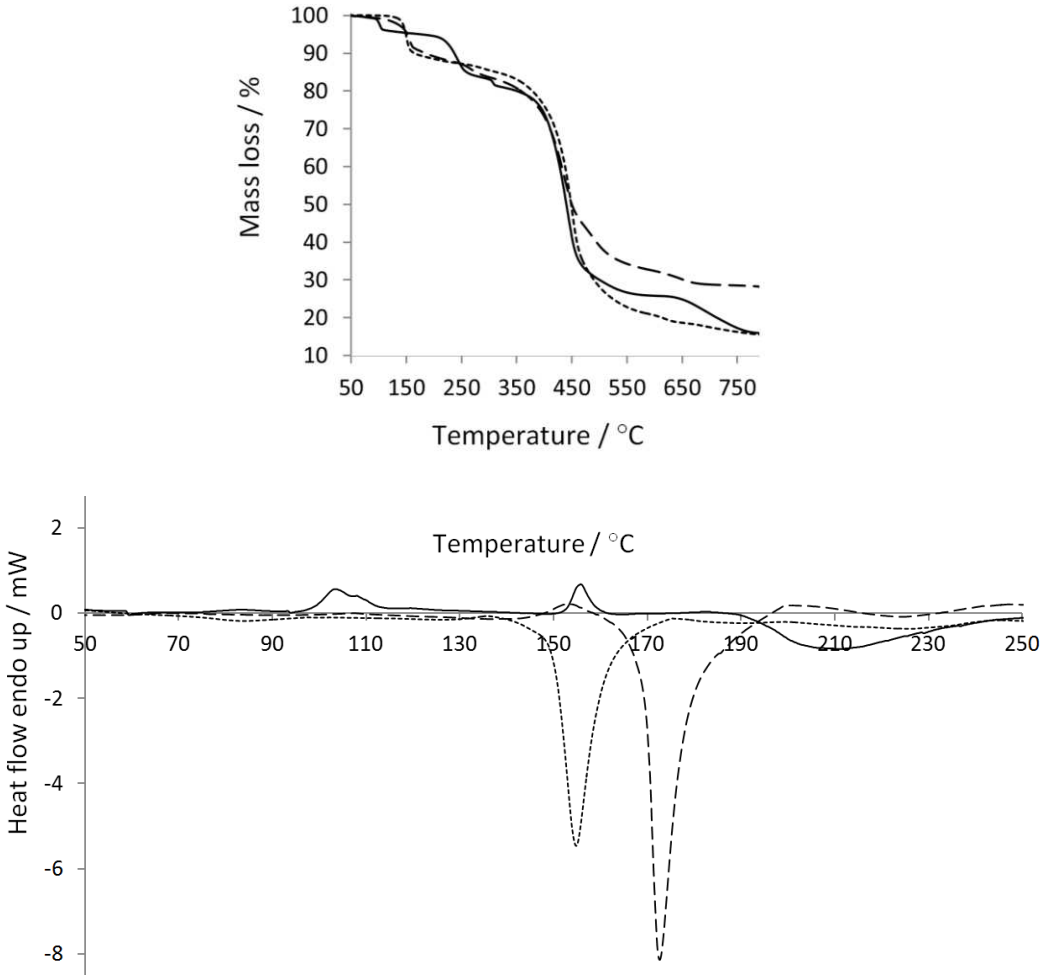


Figure 5. Thermogravimetric (top) and calorimetric traces (bottom) of the $(PPN)_2E(NO_3)_6$ salts **1c** (E = Si, - - -), **2c** (E = Ge, – – –) and **3c**·**2MeCN** (E = Sn, ——) obtained with heating rates of 10 K min^{-1}.

The available data can be interpreted tentatively in terms of NO_2 and O_2 gas release assuming that by completing stage II the decomposition reaction $(PPN)_2E(NO_3)_6 \rightarrow 2(PPN)NO_3 + EO_n + 4NO_2 + (1 - n/2)O_2$ is complete. This scheme reproduces the observed mass losses very well (**1c**, n = 2, Δm / (%) = 14.8 predicted, 14.6 observed; **2c**, n = 0, 16.3, 16.3; **3c**, n = 1, 14.8, 14.9) and implies the formation of SiO_2, Ge and SnO, respectively. Furthermore, all stage I mass losses are commensurate with the release of approximately four molar equivalents of NO_2 (**1c**, Δm / (%) = 12.4 predicted, 12.7 observed; **2c**, 12.0, 12.1; **3c**, 12.0, 11.7).

Density functional theory calculations at the B3LYP/6-311+g(d,p) level on both $Si(NO_3)_6^{2-}$ and $Si(NO_3)_4$ systems offer explanations for the increased thermal stability of the six-coordinate in comparison to four-coordinate nitrato complexes. A large difference was found

in the internal bonds N-O which are 0.1 Å longer in **1b** (see Table 1) and in charge distribution where less negative charge is distributed over the NO_3 ligands in **1b**. These changes have the effect of increasing the strength of the terminal N-O bonds and this is reflected in the vibrational frequencies $\nu_{as}(NO_2)$ which is more than 100 cm^{-1} higher in **1b** (see experimental part and DFT results, table 2). These characteristics position the structure of **1b** closer to the transition state for NO_2 elimination than **1c**. An in-depth investigation revealed that six isomers of hexa(nitrato)silicate complex are likely to have stable geometries (Fig. 6). These isomers differ primarily in their relative *trans*-(O_2NO)-E-(ONO_2) ligand conformations which were found to be *syn*, *syn*, *syn* (C_3), *syn*, *syn*, *anti* (C_2), *syn*, *anti*, *anti* (C_S) and *anti*, *anti*, *anti* (C_{2h}, S_6 and D_{3d}) (point group symbols in parentheses).

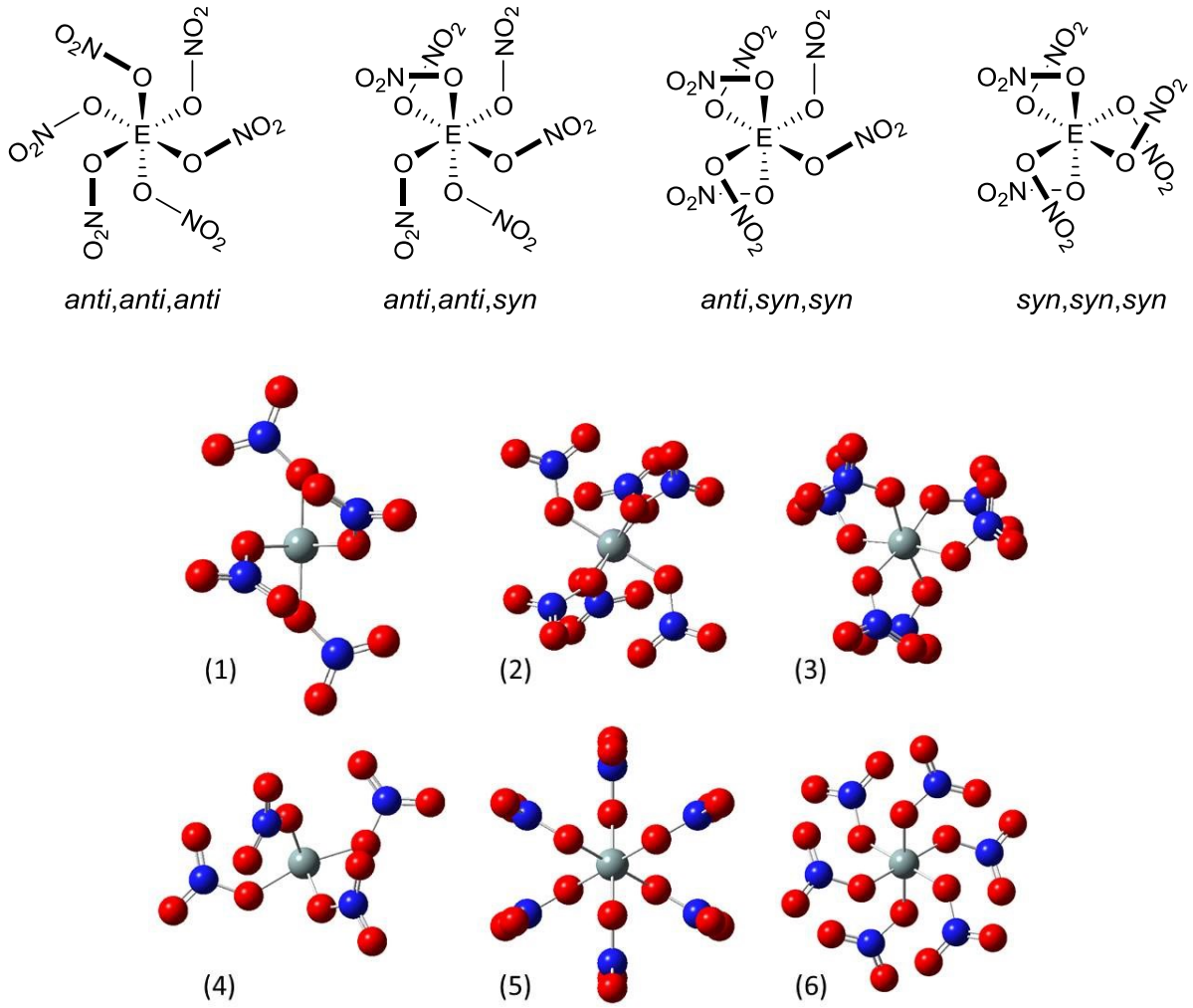


Figure 6. Stereo projections of the *syn* / *anti* conformers of $Si(NO_3)_6^{2-}$ (top, labels denote relative orientation of the *trans*-pairs) and ball-and-stick diagrams (bottom) of the optimised geometries obtained from DFT calculations at the B3LYP/6-311+g(d,p) level with the PCM model (MeCN) and the following start geometries applied: C_{2h} (1), C_2 (2), C_3 (3), C_s (4), D_{3d} (5) and S_6 (6) (blue, N; red, O; grey, Si).

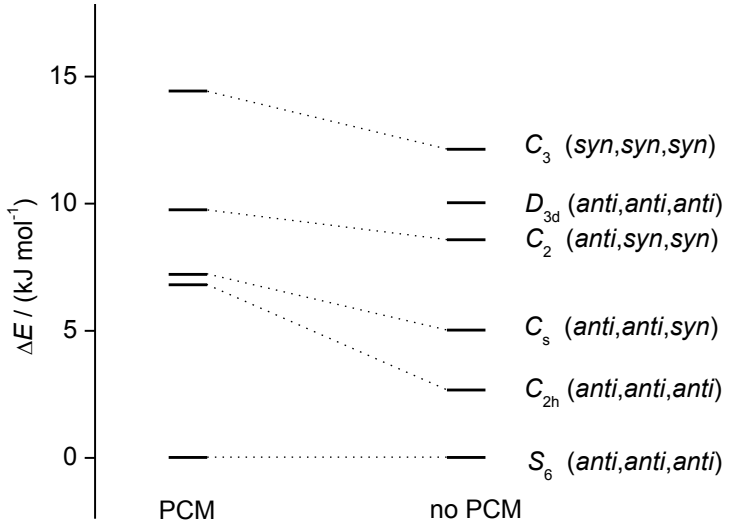


Figure 7. Total energies (0 K) relative to the lowest-energy isomer of the optimised geometries at the B3LYP/6-311+g(d,p) level. In the polarisable continuum model (PCM with MeCN as solvent, left), the D_{3d} symmetric conformer is not a minimum on the PES.

With the exception of the D_{3d} symmetry, for which one imaginary frequency was found, all conformer models lead also to stable minima upon taking account of solvent (MeCN) within the polarisable continuum model (PCM). From a comparison of the energies (Fig. 7 and Table 2), a clear trend emerges that inversely correlates total energy with the number of *anti*-configured *trans*-ligands.

Table 2. Total energies E_{tot} / (kJ mol^{-1}) [a] of the $Si(NO_3)_6^{2-}$ species relative to the S_6 symmetric conformer and the frequencies of the fundamental $\nu_{as}(NO_2)$ N-O bond stretching vibrations ν_1 to ν_6.

Isomer		E_{tot}	E_{tot} [b]	ν_1 [c]	ν_2	ν_3	ν_4	ν_5	ν_6
C_3	*syn*, *syn*, *syn*	12.12	14.41	1591 (1)	1585 (13)	1585 (10)	1568 (1697)	1568 (1669)	1567 (1724)
C_2	*anti*, *syn*, *syn*	8.56	9.74	1591 (54)	1579 (13)	1577 (629)	1575 (808)	1571 (444)	1570 (3068)
C_s	*anti*, *anti*, *syn*	5.01	7.20	1591 (155)	1585 (727)	1579 (63)	1570 (274)	1569 (3776)	1566 (29)
C_{2h}	*anti*, *anti*, *anti*	2.65	6.79	1583 (0)	1583 (1590)	1578 (0)	1576 (17)	1564 (3360)	1560 (0)
S_6 [d]	*anti*, *anti*, *anti*	0.00	0.00	1581 (703)	1577 (0)	1577 (0)	1576 (0)	1575 (2106)	1575 (2117)
D_{3d}	*anti*, *anti*, *anti*	10.02	12.35 [e]	1589 (0)	1578 (86)	1578 (92)	1567 (4909)	1566 (0)	1566 (0)

[a] at the B3LYP/6-311+g(d,p) level, [b] a polarisable continuum model was applied with MeCN as the solvent, [c] frequency / (cm^{-1}), intensity / (km mol^{-1}) in parentheses, [d] C_3 and C_i symmetric start geometries revert to S_6 symmetry, [e] imaginary frequency at −24 cm^{-1}.

Clearly, any *syn*-configuration increases internal energy and is therefore thermodynamically disfavoured. Even though the PCM model appears to increase the energetic preference for the S_6 conformer, all energies are within a narrow band that stretches over less than 15 kJ mol^{-1}.

^{14}N NMR spectra of the hexanitrato complexes were recorded in dichloromethane-d_2. All spectra show at least three resonance lines attributable to NO_3 groups at δ (^{14}N) / ppm ≈ −7 ($\Delta\nu_{½}$ = 87 Hz), −44 ($\Delta\nu_{½}$ = 85 Hz) (**1c**), −13 ($\Delta\nu_{½}$ = 22 Hz), −34 ($\Delta\nu_{½}$ = 65 Hz), −40 ($\Delta\nu_{½}$ = 50 Hz) (**2c**) and −13 ($\Delta\nu_{½}$ = 88 Hz), −29 ($\Delta\nu_{½}$ = 82 Hz) (**3c**, also MeC*N* at −136.0, $\Delta\nu_{½}$ = 90 Hz). These signals are thought to arise from $E(NO_3)_6^{2-}$ as well as the solvent-induced dissociation into $E(NO_3)_{6-x}^{(2-x)-}$ and NO_3^- anions. This interpretation is supported by the predicted ^{14}N shielding parameters obtained from the DFT (*vide supra*) calculations using the optimised structures of candidate species within the PCM model in CH_2Cl_2. For the silicon species the calculated chemical shifts relative to $MeNO_2$ are δ(^{14}N) / ppm = −7 ppm (NO_3^-) and −43 ($Si(NO_3)_6^{2-}$), −52 ($Si(NO_3)_4(NCMe)_2$), −78 ($Si(NO_3)_4$) and −157 (MeCN) which allows the assignment of the peaks found in the solution of **1c** to NO_3^- and $Si(NO_3)_6^{2-}$, respectively.

Conclusion

A synthetic route has been demonstrated leading to the previously unreported oxygen-rich, hypercoordinate, homoleptic nitrato complexes of silicon and germanium. The direct approach using $(PPN)NO_3$ and the tetrachloride fails to accomplish complete ligand exchange. Instead, a two-step process *via* the thermolabile tetranitrates gave the salt-like compounds containing the sought-after hexanitrato complexes. This approach avoids the use of dry, NO_2-free N_2O_5 required previously in the synthesis of polynitrates. As the size of the central *p*-block atom increases (Si < Ge < Sn), the complexes adopt an increasingly distorted octahedral geometry and the nitrato ligands adopt a κ^1O / κ^2O,O' hybrid coordination mode akin to transition metal nitrato complexes. DFT calculations reveal the likely existence of rotamers due to the *syn* or *anti* arrangement of pairs of *trans*-nitrato ligands of which two types are observed in the solid state. The complex rotamer in which all nitrato ligands adopt *trans* configuration has the lowest energy at 0 K. The hypercoordinate $E(NO_3)_6^{2-}$ complexes show greater thermal stability than either the related tetracoordinate $E(NO_3)_4$ nitrates or hexacoordinate chloro(nitrato) complexes. The stability gap between tetranitrato and hexanitrato species has been rationalised by comparison of structural parameters obtained from DFT. The thermal decomposition of the new hexanitrato complexes has been

interpreted in terms of NO_2 / O_2 loss accompanied with the deposition of the corresponding oxide (Si, Sn) or metal (Ge) based on the observed mass losses under controlled heating. The proof that homoleptic polynitrates of the lighter group 14 elements Si and Ge can be stabilised under ambient conditions and the noted possibility of their controlled thermally induced decomposition at elevated temperatures opens up an opportunity to study decomposition mechanisms of such energetic species and use the same synthetic method to a more diverse range of polynitrato species.

Experimental

Standard Schlenk tube, vacuum line and glove box techniques were employed throughout. NMR spectra were recorded on a Bruker Avance 250 MHz (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$) or 400 MHz (solution ^{14}N, $^{29}Si\{^{1}H\}$ MAS at 10 kHz) spectrometers run by TopSpin software. TGA, DSC measurements and elemental analyses were obtained at the Centre for Chemical Instrumentation and Analytical Services at Sheffield, using a Perkin Elmer 2400 CHNS/O series II elemental analyser, a Perkin-Elmer thermographic analyser (20 ml min^{-1} N_2 protective gas) and Pyris 1 differential scanning calorimeter (both run at heating rate 10 K min^{-1}). DSC samples were prepared under argon and loaded into sealed, stainless steel, high pressure capsules (V_{int} = 30 μL) with Au-plated copper seals, which can operate up to 400°C and 150 bar. Onset temperatures and mass losses were calculated using the data analysis tools within instrument software. FTIR spectra were recorded between NaCl windows in the range 500-4000 cm^{-1} using a Bruker Tensor 27 FTIR spectrometer running OPUS software, at a resolution of 2 cm^{-1}. The spectra obtained from nujol suspensions contained a number of very weak bands, which are not reported. Single crystal X-ray diffraction measurements for the structures of **3a·2MeCN**, **1c**, **2c**, **3c** and (PPN)NO_3·MeCN were recorded on a Bruker Kappa diffractometer equipped with CCD area detector and Oxford Cryosystems NHelix cryostat. Data were collected and integrated using APEX2 and Bruker SAINT, respectively. Absorption correction was applied using SADABS (APEX2). All structures were solved by direct methods (SHELXS-97) and refined using SHELXL-2014 within the Shelxtl software suite. H atoms were included on idealised positions (riding model) with the thermal parameters H_{iso} = 1.2U_{eq}(pivot atom). The synthesis of **1b** was adapted from a previous report.[26] $SiCl_4$, $GeCl_4$ and $SnCl_4$ (all obtained from Aldrich) were stirred over dry Na_2CO_3 and purified by trap-to-trap condensation. $AgNO_3$ (Engelhard) was used without further purification. (PPN)NO_3 was prepared from (PPN)Cl according to a published procedure[49,50] and confirmed to be of high purity (elem. anal. calcd. for $C_{36}H_{30}N_2O_3P_2$, 600.57 g mol^{-1}, C,

72.00; H, 5.04; N, 4.66, found C, 71.92; H, 4.87; N, 4.51%). The pre-dried solvents (Grubbs)[51] MeCN, Et_2O and CD_2Cl_2 were stored over CaH_2 and purified by trap-to-trap condensation prior to use. Filtration was carried out using stainless steel cannulas fitted with 24 mm glass microfiber filters (VWR).

Caution! *Although no violent reactions were encountered by us, appropriate safety measures need to be taken in attempts to prepare oxygen-rich covalent polynitrates. Filter residues other than those of the PPN salts should not be allowed to dry in the air or in* vacuo *and should be discarded into dilute, aqueous sodium hydroxide.*

I*n situ* generation of $Si(NO_3)_4$ (1b), modified from reference 24. A Schlenk tube containing a mixture of $SiCl_4$ (0.250 g, 1.47 mmol) in diethyl ether (5 ml) was immersed in a cold bath at –40°C. After the ethereal solution had attained the bath temperature, a cold solution (–40°C) of $AgNO_3$ (1.03 g, 6.06 mmol) in acetonitrile was added rapidly, upon which AgCl is produced as a white, suspended solid. Immediately after the addition was completed, the Schlenk tube was immersed in liquid nitrogen and then allowed to warm again up to –40°C. The resultant suspension was then rapidly filtered and the filtrate collected by a second Schlenk tube containing diethyl ether (5 ml) precooled to –40°C which resulted in further precipitation of white solid. This step was repeated until no further precipitation occurred. The finally resulting colourless solution was cooled further down to –60°C and the diethyl ether removed at this temperature under a dynamic vacuum which affords an acetonitrile solution of $Si(NO_3)_4$ (**1b**). Solutions of **1b** were used immediately for the synthesis of **1c**. IR (MeCN, Et_2O (1:1), cm^{-1}) ν = 1667sh (HNO_3), 1662m, 1617m, 1493w, 1353s, 1297s, 1153s, 1133s, 1115s.

Synthesis of $Ge(NO_3)_4$ (2b). $GeCl_4$ (0.35 ml, 3.1 mmol) was dissolved in acetonitrile (3 ml) in a Schlenk tube and treated with a solution of $AgNO_3$ (2.12 g, 12.5 mmol) in acetonitrile at room temperature resulting in an immediate white precipitate, AgCl. The solution was allowed to stir for 2 h at ambient temperature and then filtered. The colourless, filtrate was collected and the majority of the solvent removed under dynamic vacuum. The evaporation residue consisted of a colourless, gel-like solid containing germanium tetranitrate (**2b**). IR (nujol, cm^{-1}) ν = 3224w, 3189w, 3165w, 3006m, 2300s, 2272s, 2253m, 1574s, 1550s, 1445s, 1428m, 1414m, 1367m, 1323s, 1307s, 1283s, 1032m, 948s, 819w, 786m, 763m, 709w, 692m; (MeCN, cm^{-1}) ν = 1667 (HNO_3) 1618 m, 1558 m, 1286 s.

Synthesis of $Sn(NO_3)_4$ (3b). The procedure for **2b** was also applied to the preparation of **3b** from $SnCl_4$. IR (Nujol, cm^{-1}) ν = 2920s, 2852s, 2294m, 2253s, 1645s, 1433vs, 1377vs, 1038s, 952m, 919s, 842m, 725m, 689w; (MeCN, cm^{-1}) ν = 1667 (HNO_3), 1592w, 1554s, 1285s.

Preparation of $(PPN)_2Si(NO_3)_6$ (1c). The solution of **1b**, containing approximately 1.5 mmol of **1b**, was allowed to warm to –40°C and transferred via cannula to a colourless solution of $(PPN)NO_3$ (1.77 g, 2.95 mmol) in acetonitrile at the same temperature resulting in a clear, pale green reaction solution and stirred for 1 h. This solution was placed under a dynamic vacuum until all acetonitrile had been evaporated leaving an off-white solid. The solid was washed with cold acetonitrile at –40°C and then dissolved by adding approximately 5 ml acetonitrile and raising the temperature to ambient temperature. Colourless, block-shaped crystals of **1c** were obtained upon reducing the temperature to –28°C within 24 h. The crystals were isolated by filtration, washing (cold acetonitrile) and drying under high vacuum, 0.568 g, 0.384 mmol, 24% with respect to $SiCl_4$. Solid **1c** is moderately air sensitive and decomposes in air at r.t. within *ca*. 0.5 h. Elem. anal. calcd. for $C_{72}H_{60}N_8O_{18}P_4Si$ (1477.29 g mol^{-1}): C, 58.54; H, 4.09; N, 7.59%; found: C, 58.37; H, 3.84; N, 7.70%. DSC, T_{on}^{ex1} = 146°C, T_p^{ex1} = 154°C, ΔH^1= –93 J g^{-1}, T_{on}^{ex2} = 276°C, T_p^{ex2} = 301°C, ΔH^2= –791 J g^{-1}. IR (Nujol cm^{-1}) ν = 3164w, 1623m, 1589m, 1569vs, 1484s, 1344s, 1322vs, 1293vs, 1287vs, 1274vs, 1267vs 1185w, 1154w, 1117vs, 1072w, 1036w, 998m, 977vs, 950s, 930vs, 824m, 798w, 752s, 724vs, 695vs, 547vs. ^{1}H-NMR (CD_2Cl_2, 250 MHz) δ [ppm] = 7.65 (m, 4H), 7.45 (m, 26H). $^{14}N\{^1H\}$ NMR (CD_2Cl_2, 29 MHz) δ [ppm] = –7.3 (rel. int. 1, $\Delta\nu_{½}$ = 87 Hz), –43.8 (rel. int. 1.5, $\Delta\nu_{½}$ = 85 Hz). $^{29}Si\{^1H\}$ NMR (MAS, 10 kHz) δ [ppm] = 198.4, 198.9.

Synthesis of $(PPN)_2Ge(NO_3)_6$ (2c). The gel (**2b**) was re-dissolved in acetonitrile and added to a solution of $(PPN)NO_3$ (3.19 g, 5.31 mmol) in acetonitrile. The resulting reaction solution was allowed to stir for 1 h, after which the solvent was evaporated to dryness in *vacuo* resulting in an off-white solid. The solid was washed with cold acetonitrile and then dissolved in warm (55°C) acetonitrile. Precipitation of the salt **2c** was induced by slow reduction of the solution temperature to –28°C within 24 h. Colourless, block-shaped crystals were obtained by filtration, washing and drying in *vacuo*, 1.849 g, 1.22 mmol, 40% with respect to $GeCl_4$, elem. anal. calcd. for $C_{72}H_{60}GeN_8O_{18}P_4$ (1521.79 g mol^{-1}): C, 56.83; H, 3.97; N, 7.36%; found: C, 56.43; H, 3.91; N, 6.90%. IR (Nujol, cm^{-1}) ν = 3055m, 1561vs, 1464m, 1298 vs, 1291vs, 1278s, 1272vs, 1183m, 1116vs, 998m, 959vs, 953vs, 725vs, 691vs,

532vs. T_{on}^{ex1} = 168°C, T_p^{ex1} = 172°C, ΔH^1 = –61 J g^{-1}, T_{on}^{ex2} = 294°C, T_p^{ex2} = 301°C, ΔH^2= –685 J g^{-1}. ^{1}H NMR (CD_2Cl_2, 250 MHz) δ [ppm] = 7.65 (m, 4H), 7.45 (m, 26H). ^{14}N{^{1}H} NMR (CD_2Cl_2, 29 MHz) δ [ppm] = –12.7 (rel. int. 1.0, $\Delta\nu_{½}$ = 22 Hz), –34.0 (rel. int. 1.0, $\Delta\nu_{½}$ = 65 Hz), –39.7 (rel. int. 2.0, $\Delta\nu_{½}$ = 50 Hz)].

Synthesis of $(PPN)_2Sn(NO_3)_6$·2MeCN (3c·2MeCN). The same procedure was applied to the preparation of **2c** and **3c·2MeCN**. Colourless, block-shaped crystals (1.174 g, 0.712 mmol, 64% with respect to $SnCl_4$. Elem. anal. calcd. for $C_{76}H_{66}N_{10}O_{18}P_4Sn$ (1650.02 g mol^{-1}): C, 55.32; H, 4.03; N, 8.49%; found: C, 55.09; H, 3.81; N, 8.06%; m.p. 204-206°C. DSC, T_{on}^{endo} = 94°C, T_p^{endo} = 103°C, ΔH^{endo} = 12.4 J g^{-1}, T_{on}^{ex1} = 182°C, T_p^{ex1} = 221°C, ΔH^{ex1} = –583 J g^{-1}; T_{on}^{ex2} = 276°C, T_p^{ex2} = 281°C, ΔH^{ex2}= –367 J g^{-1}. IR (Nujol, cm^{-1}) ν = 3063m, 2249w, 1589m, 1547vs, 1544vs, 1541vs, 1538vs, 1462s, 1297vs, 1290vs, 1280vs, 1272vs, 1182m, 1115s, 1026m, 969vs, 964vs, 745s, 723vs, 690vs. ^{1}H NMR (CD_2Cl_2, 250MHz): δ [ppm] = 7.65 (m, 4H), 7.45 (m, 26H), 2.10 (s, 6H, C*H*$_3$CN); ^{14}N NMR (CD_2Cl_2, 29 MHz) δ [ppm] = –12.6 (rel. int. 0.35, $\Delta\nu_{½}$ = 88 Hz), –29.3 (rel. int. 1.0, $\Delta\nu_{½}$ = 82 Hz), –136.0 (rel. int. 1.0, CH_3C*N,* $\Delta\nu_{½}$ = 90 Hz).

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Supporting information containing crystallographic and computational details, IR and NMR spectra and TA traces is available free of charge from the ACS website at DOI: …. Crystallographic data for this paper (CCDC 1479375, **1c**; 1479376, **3c·2MeCN**; 1479377, **2c**; 1479378, **3a**; 1481642, (PPN)NO_3·MeCN) can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

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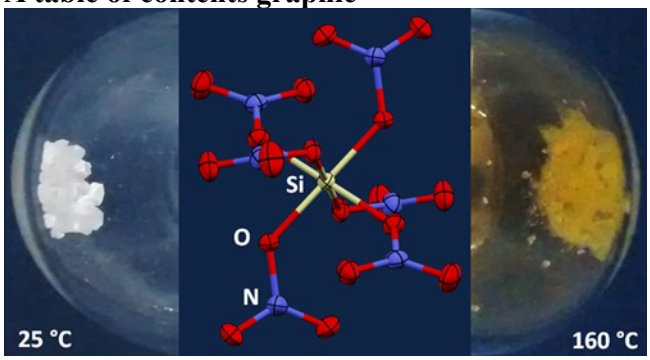

Synopsis

The novel homoleptic nitrato complexes $Si(NO_3)_6^{2-}$, $Ge(NO_3)_6^{2-}$ and $Ge(NO_3)_4$ were synthesised and characterised and the structures of the hexanitrates including that of $Sn(NO_3)_6^{2-}$ determined crystallographically. The new $E(NO_3)_6^{2-}$ complexes are surprisingly thermally stable and unreactive in contrast to the related tetranitrates. DFT calculations were employed to investigate their distorted octahedral coordination geometry