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Synthesis and structural features of the first thallium(I) selenoether derivatives

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The first evidence for thallium(I) complexes involving selenoether ligands is presented, together with the structure determinations for the 1D chain species [Tl{MeSe(CH_2)$_3$SeMe}]PF_6 and the 3D network species [Tl{MeSe(CH_2)$_2$SeMe}]PF_6.

While a wide range of middle and late transition metal complexes with selenoether ligands has been reported over the last two decades or so,[1,2] examples involving elements from the p-block are rare[3] and are limited almost exclusively to complexes involving the elements Sn(IV), As(III), Sb(III) and Bi(III).[4] There are no structurally characterised bi- or polydentate selenoether complexes involving Group 13 Lewis acids.

We have been interested in the structural features displayed by thio-, seleno- and telluro-ether complexes involving the Group 15 acceptors MX_3 (M = As, Sb, Bi; X = Cl, Br, I) and have identified a wide range of unusual structures from discrete species through 1-, 2- and 3-D networks. While the M–thioether and M–selenoether bonds usually take the form of weak, secondary interactions, we have noted that in Bi(III) complexes the Bi–Se and particularly Bi–Te interactions appear to be stronger than for Bi–S. Thus the bond lengths are essentially invariant with chalcogen.

Thallium(I) exhibits rather similar properties to Bi(III) insofar as it is a large, soft, polarisable ion which can adopt high coordination numbers and irregular stereochemistries.[5] There are no structural reports on bi- or poly-thioether complexes of thallium, however a small number of thiacrown complexes are known, including [Tl([9]aneS_3)]PF_6, [Tl([18]aneS_6)]PF_6, [Tl([18]aneN_2S_4)]PF_6 and [Tl([24]aneS_8)]PF_6 ([18]aneS_6 = 1,4,7,10,13,16-hexathiacyclooctadecane, [18]aneN_2S_4 = 7,16-diaza-1,4,10,13-tetrathiacyclooctadecane, [24]aneS_8 = 1,4,7,10,13,16,19,22-octathiacyclotetracosane).[6–8] We describe here our attempts to investigate the chemistry of Tl(I) with diselenoether ligands.

Reaction of MeSe(CH_2)$_n$SeMe (n = 2 or 3) with one molar equivalent of $TlPF_6$ in refluxing MeCN for *ca* 30 min gave a colourless solution. Concentration *in vacuo* afforded a white precipitate, together with a few colourless crystals. The solids were filtered, washed with hexane and dried *in vacuo*. ^1H NMR spectra show resonances indicative of extensively dissociated ligand, while IR spectra showed peaks associated with ionic PF_6^- as well as weak features associated with the diselenoether.

An X-ray structure determination on the crystals obtained from the MeSe(CH_2)$_3$SeMe–$TlPF_6$–MeCN system shows these to have stoichiometry [Tl{MeSe(CH_2)$_3$SeMe}]PF_6. The structure of this species shows† (Fig. 1(a)) the Tl(1), P(1) and C(3) atoms occupying crystallographic two-fold sites. The Tl(I) centre is coordinated linearly (Se(1)–Tl(1)–Se(1b) 179.9(1)°) to two Se atoms from different ligands, Tl–Se 3.390(1) Å. The second Se atom on each ligand then coordinates to an adjacent Tl(I) giving an infinite 1D chain in which the diselenoethers adopt an S-shaped conformation. This Se_2 donor set at each Tl(I) centre is supplemented by a series of ten long range Tl···F contacts involving four distinct PF_6^- anions, two of the anions provide two F contacts from one edge, while the other two provide three F's from a triangular face of the PF_6^- octahedron. The Tl···F contacts lie approximately at right angles to the direction of the [Tl{MeSe(CH_2)$_3$SeMe}]$^+$ chains, Tl···F 3.14(2)–3.24(2) Å (Fig. 1(b)) and each F atom bridges two neighbouring Tl centres, therefore crosslinking the parallel chains.

A crystal structure determination on a crystal from the MeSe(CH_2)$_2$SeMe–$TlPF_6$–MeCN system reveals the species to be [Tl{MeSe(CH_2)$_2$SeMe}]PF_6. In this species† each Tl(I) centre is coordinated to four Se atoms from different diselenoethers, giving a distorted tetrahedral geometry, Tl–Se 3.2769(8)–3.5058(8) Å. It is interesting that each Se atom uses its second lone pair to coordinate to an adjacent Tl centre, therefore generating a 3D network containing Tl_2Se_2 rhomboids (Fig. 2(a)). This is the first structural evidence for this doubly bridging coordination mode in diselenoether ligand chemistry. The anions in this species occupy the channels within the cationic 3D framework, providing five weak Tl···F contacts per Tl centre, from three PF_6^- anions, one of which interacts *via* the three F's from a triangular face, while the other two interact *via* a single F atom each, Tl···F 2.993(5)–3.302(5) Å (Fig. 2(b)). This combination leads to a nine-coordinate geometry at each Tl centre. When one considers that the diselenoethers in these two complexes differ only by a single methylene fragment in the

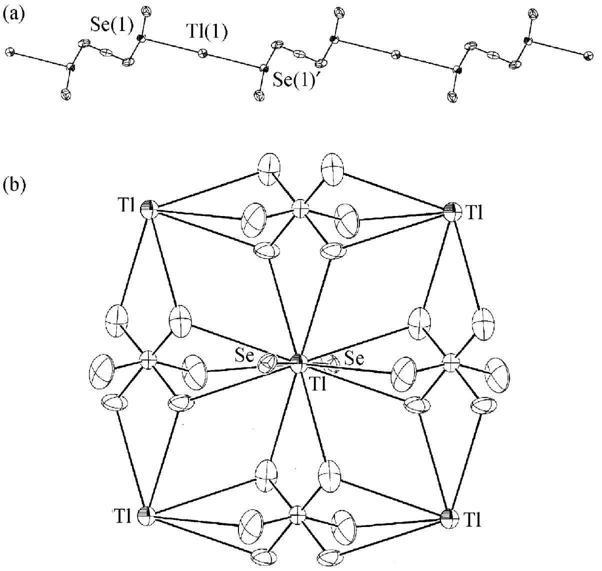

Fig. 1 (a) View of a portion of the infinite 1D chain structure of the [Tl{MeSe(CH_2)$_3$SeMe}]$^+$ cation with atom numbering scheme; 40% probability ellipsoids are shown. (b) View down the *c*-axis showing the long Tl···F contacts (only the two Se atoms coordinated to the central Tl are shown, the C and H atoms and all other Se atoms are omitted for clarity). Selected bond lengths: Tl(1)–Se(1) 3.390(1), Tl(1)···F(1)′ 3.16(3), Tl(1)···F(2)′ 3.14(2), Tl(1)···F(3) 3.23(2), Tl(1)···F(1)″ 3.24(2), Tl(1)···F(2)′ 3.19(3) Å. The symmetry related atom Se(1)′ is generated by the symmetry operation $-x, -y, 1 - z$; Se(2)′ by the operation $1 + x, y, z$; Se(2)′ by the operation $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; F(2)′, F(3)′, F(4)′, F(6)′ by the operation $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; F(5)′ by the operation $-x, -y, 1 - z$.

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backbone, they display suprisingly different structural features. The Tl–Se distances in the new complexes are significantly longer than the sum of the covalent radii for Tl and Se (2.72 Å), although they and the Tl···F distances are comparable to the Tl–S and Tl···F bond distances identified within the few known Tl(I) thiacrown complexes *e.g.* [Tl([9]aneS$_3$)]PF$_6$: *d*(Tl–S) = 3.092(3)–3.431(3), *d*(Tl···F) = 3.246(8)–3.389(8);[6] [Tl([18]-aneS$_6$)]PF$_6$: *d*(Tl–S) = 3.164(5)–3.370(5) Å.[7]

Microanalyses consistently reveal low %C and %H for these two compounds despite several modifications of the reaction conditions, *e.g.* changing the solvent, changing the anion to ClO$_4^-$ *etc.* We conclude therefore that in solution the complexes are extensively dissociated and upon concentrating the reaction solution a mixture of the selenoether complex and the inorganic TlPF$_6$ salt co-precipitate.

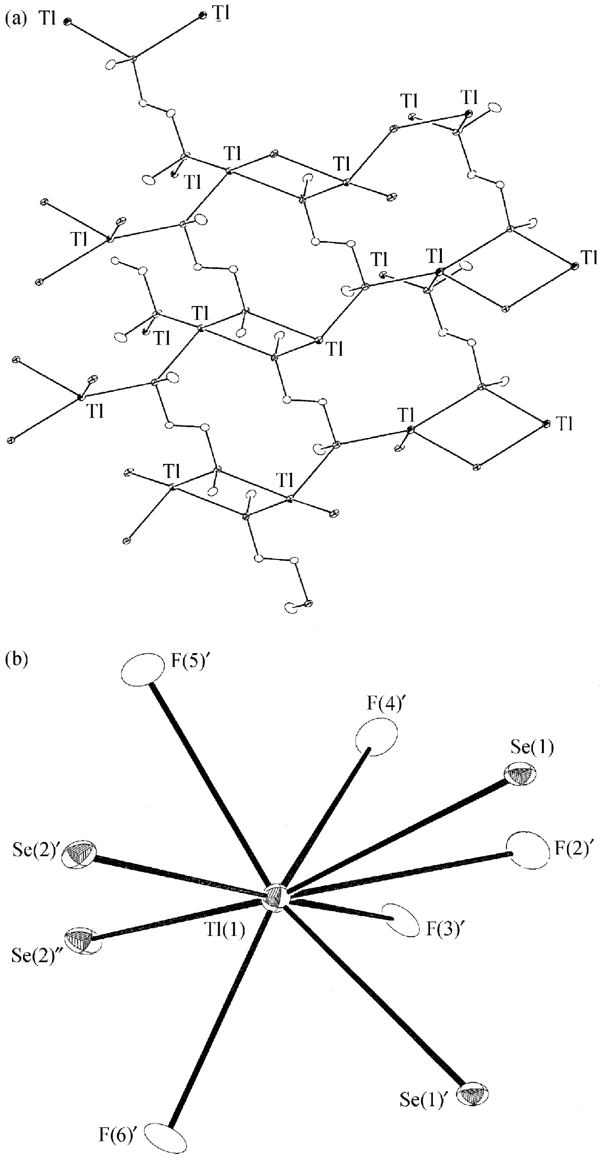

Fig. 2 (a) View down the *b*-axis of a section of the 3D structure identified for [Tl{MeSe(CH$_2$)$_2$SeMe}]$^+$; 40% probability ellipsoids are drawn. Selected bond lengths: Tl(1)–Se(1) 3.5058(8), Tl(1)–Se(1)′ 3.3333(7), Tl(1)–Se(2)′ 3.3142(8), Tl(1)–Se(2)′ 3.2769(8), Tl(1)···F(2)′ 3.231(5), Tl(1)···F(3)′ 3.302(5), Tl(1)···F(4)′ 3.048(5), Tl(1)···F(5)′ 2.993(5), Tl(1)···F(6)′ 2.995(5) Å; (b) view showing the immediate coordination environment at a single Tl centre (with numbering scheme adopted). Note that Se(1)′ is generated by the symmetry operation $-x$, y, $-z$.

We have also investigated the reaction of TlPF$_6$ with other selenoether ligands, including the solid PhSe(CH$_2$)$_2$SePh. However, following a 30 min reflux in MeCN with TlPF$_6$, and subsequent concentration of the mixture *in vacuo*, a yellow solid which was shown by ^{77}Se NMR and by a unit cell determination to be the diselenide, PhSeSePh, was isolated. We note that PhSe(CH$_2$)$_2$SePh does not itself decompose in refluxing MeCN over even 1 h, thus it appears that the TlPF$_6$ salt promotes the decomposition of the diselenoether.

These results show that within the heavy p-block elements a range of unusual coordination environments are possible and that even for simple chalcogenoether ligands the structures depend significantly upon the particular ligand employed.

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Notes and references

† *Crystal data* for [Tl{MeSe(CH$_2$)$_3$SeMe}]PF$_6$: C$_5$H$_{12}$F$_6$PSe$_2$Tl (M_r = 579.40), monoclinic, space group *C*2, a = 7.9081(3), b = 7.9111(3), c = 10.4005(4) Å, β = 101.932(1)°, V = 636.62(4) Å^3, Z = 2, D_c = 3.022 g cm^{-3}, μ(MoKα) = 18.551 cm^{-1}, T = 120 K, R = 0.0404, R_w = 0.0530 for 81 parameters against 737 reflections with $I > 2\sigma(I)$ out of 1314 unique reflections. Some disorder was evident in the half PF$_6^-$ anion in the asymmetric unit (P atom occupying a two-fold site). This was modelled reasonably satisfactorily using split occupanices, giving a major component involving F(1)–F(3) with 75% occupancy and a minor component involving F(4)–F(6) with 25% occupancy. The discussion within the text refers to the major component. Otherwise structure solution and refinement were routine.[9–11]

Crystal data for [Tl{MeSe(CH$_2$)$_2$SeMe}]PF$_6$: C$_4$H$_{10}$F$_6$PSe$_2$Tl (M_r = 565.38), monoclinic, space group $P2_1/n$, a = 7.3370(2), b = 9.0243(3), c = 17.8221(4) Å, β = 92.311(2)°, V = 1179.06(5) Å^3, Z = 4, D_c = 3.185 g cm^{-3}, μ(MoKα) = 20.028 cm^{-1}, T = 120 K, R = 0.0372, R_w = 0.0380 for 127 parameters against 2271 reflections with $I > 2\sigma(I)$ out of 2828 unique reflections. Structure solution and refinement were routine.[9,10,12]

CCDC 195979 and 195980. See http://www.rsc.org/suppdata/cc/b2/b209729j/ for crystallographic data in CIF or other electronic format.

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