Notes

Thallium Thioether Chemistry. Synthesis and Crystal Structure of [Tl([9]aneS$_3$)]PF$_6$ ([9]aneS$_3$ = 1,4,7-Trithiacyclononane), showing Infinite Helices of [Tl([9]aneS$_3$)]$^+$ Fragments†

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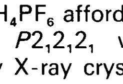
Treatment of TlNO$_3$ with an excess of 1,4,7-trithiacyclononane ([9]aneS$_3$) in MeCN followed by addition of NH$_4$PF$_6$ affords the 1 : 1 complex [Tl([9]aneS$_3$)]PF$_6$, which crystallises in the orthorhombic space group $P2_12_12_1$ with a = 7.7655(11), b = 8.3767(18), c = 20.838(4) Å and Z = 4 as determined by X-ray crystallography. The structure shows the trithia ligand bound facially to the Tl$^{\rm I}$ centre, Tl–S(1) 3.114(3), Tl–S(4) 3.092(3) and Tl–S(7) 3.110(3) Å. A secondary interaction between the thallium and S(7′) {in a neighbouring [Tl([9]aneS$_3$)]$^+$ unit at $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z)$}, Tl–S(7′) 3.431(3) Å, gives overall [3 + 1] thioether co-ordination at Tl$^{\rm I}$. These contacts between cations related by the 2_1 screw axis parallel to a link [Tl([9]aneS$_3$)]$^+$ fragments to form infinite helices running in that direction. Further secondary interactions occur between the Tl$^{\rm I}$ centre and the fluorines of three different PF$_6^-$ counter ions, Tl···F(2) 3.228(8), Tl···F(4) 3.389(8), Tl···F(3) 3.246(8) and Tl···F(5) 3.272(9) Å, to give formally an eight-co-ordinate metal complex.

The co-ordination chemistry of the facially pre-organised trithia crown 1,4,7-trithiacyclononane ([9]aneS$_3$) is dominated by complexation to transition-metal ions.[1–4] More recently, this work has been extended to the study of the co-ordination and redox chemistry of [9]aneS$_3$ and related thioether crowns with d^{10} metal centres, particularly Cu$^{\rm I}$,[5,6] Ag$^{\rm I}$,[6,7] Au$^{\rm I}$,[8] Zn$^{\rm II}$, Cd$^{\rm II}$[9] and Hg$^{\rm II}$.[10] The complexation of other Main Group metal ions including Pb$^{\rm II}$,[9] Al$^{\rm III}$ [11] and In$^{\rm III}$ [12] with thioether macrocycles has been reported. For example, Wieghardt and co-workers[9] reported the complexation of Pb$^{\rm II}$ with [9]aneS$_3$ to afford the eight-co-ordinate complex [Pb([9]aneS$_3$)$_2$(OClO$_3$)$_2$]. This complex shows a distorted square anti-prismatic structure incorporating two facially co-ordinated [9]aneS$_3$ ligands and two monodentate ClO$_4^-$ ligands to give an overall S$_6$O$_2$ donation at Pb$^{\rm II}$ [Pb–S 3.015(5), 3.084(4) and 3.129(5); Pb–O 2.719(15) and 2.720(15) Å[9]]. In addition, the synthesis of [InCl$_3$([9]aneS$_3$)] has been described briefly.[12] We have been interested in developing the chemistry of thioether macrocycles with p-block metal ions, and report herein the synthesis and structure of [Tl([9]aneS$_3$)]PF$_6$.



[9]aneS$_3$

Results and Discussion

Treatment of TlNO$_3$ with an excess of [9]aneS$_3$ in a minimum amount of MeCN under reflux for 1 h gave a pale yellow solution from the initially colourless solution of the starting materials. Addition of NH$_4$PF$_6$ afforded, on cooling, a yellow-brown product which could be recrystallised from MeCN–Et$_2$O. The IR spectrum of the complex confirmed the presence of [9]aneS$_3$ and PF$_6^-$ counter ion, while the fast atom bombardment (FAB) mass spectrum in 3-nitrobenzyl alcohol (noba) shows a molecular peak at m/z 385 with the correct isotopic distribution for [^{205}Tl([9]aneS$_3$)]$^+$. Elemental analysis confirmed the stoicheiometry of the complex. The ^{1}H NMR spectrum of [Tl([9]aneS$_3$)]PF$_6$ in CD$_3$CN shows a broad resonance at δ 3.06; metal-free [9]aneS$_3$ shows a sharper resonance at δ 3.08 under the same conditions. The ^{13}C NMR spectrum in CD$_3$CN shows a triplet resonance at 33.80 ppm, while metal-free [9]aneS$_3$ shows a triplet resonance at 31.21 ppm.

In order to establish the connectivity and stereochemistry of [Tl([9]aneS$_3$)]PF$_6$ in the solid state, single crystals were grown by vapour diffusion of Et$_2$O into a solution of the complex in MeCN. A single crystal X-ray structure determination on [Tl([9]aneS$_3$)]PF$_6$ confirms the co-ordination of [9]aneS$_3$ to the Tl$^{\rm I}$ centre. Selected bond lengths, angles and torsion angles are given in Table 1, and fractional atomic coordinates in Table 2. The trithia ligand is bound facially to the metal centre, Tl–S(1) 3.114(3), Tl–S(4) 3.092(3) and Tl–S(7) 3.110(3) Å (Fig. 1). These are the longest bond lengths to [9]aneS$_3$ for any metal ion measured thus far.[1] Nevertheless the Tl–S bond lengths are less than the sum of the formal ionic radii of S and Tl$^{\rm I}$ (1.50 + 1.84 = 3.34 Å),[13] suggesting substantial covalency in the Tl–S bonding. The S–Tl–S angles, S(1)–Tl–S(4) 67.57(7), S(1)–Tl–S(7) 67.31(7) and S(4)–Tl–S(7) 67.52(7)°, are substantially narrower than those observed in complexes of [9]aneS$_3$ with smaller metal ions[1] and reflect the relatively long Tl–S distances in the [Tl([9]aneS$_3$)]$^+$ moiety. In addition to primary co-ordination of the three thioether S-donors to Tl$^{\rm I}$, there is a secondary interaction between the thallium and S(7′) {in a neighbouring [Tl([9]aneS$_3$)]$^+$ moiety at $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z)$}, Tl–S(7′) 3.431(3) Å. This gives an overall [3 + 1] thioether co-ordination at Tl$^{\rm I}$. Since

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† (1,4,7-Trithiacyclononane-κS,^{1},S^4,S^7)thallium(I) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations (e.s.d.s) in parentheses

Tl–S(1)	3.114(3)	C(3)–S(4)	1.821(11)
Tl–S(4)	3.092(3)	S(4)–C(5)	1.781(11)
Tl–S(7)	3.110(3)	C(5)–C(6)	1.529(15)
S(1)–C(2)	1.818(12)	C(6)–S(7)	1.814(11)
S(1)–C(9)	1.832(12)	S(7)–C(8)	1.806(12)
C(2)–C(3)	1.509(16)	C(8)–C(9)	1.492(17)
S(1)–Tl–S(4)	67.57(7)	Tl–S(4)–C(5)	102.0(4)
S(1)–Tl–S(7)	67.31(7)	C(3)–S(4)–C(5)	103.9(5)
S(4)–Tl–S(7)	67.52(7)	S(4)–C(5)–C(6)	118.0(8)
Tl–S(1)–C(2)	102.9(4)	C(5)–C(6)–S(7)	113.3(7)
Tl–S(1)–C(9)	111.0(4)	Tl–S(7)–C(6)	110.6(4)
C(2)–S(1)–C(9)	102.9(6)	Tl–S(7)–C(8)	103.8(4)
S(1)–C(2)–C(3)	117.5(8)	C(6)–S(7)–C(8)	104.2(5)
C(2)–C(3)–S(4)	113.6(8)	S(7)–C(8)–C(9)	118.3(8)
Tl–S(4)–C(3)	111.8(4)	S(1)–C(9)–C(8)	114.9(8)
C(9)–S(1)–C(2)–C(3)	−57.2(10)	S(4)–C(5)–C(6)–S(7)	−56.8(10)
C(2)–S(1)–C(9)–C(8)	128.3(9)	C(5)–C(6)–S(7)–C(8)	129.2(8)
S(1)–C(2)–C(3)–S(4)	−56.6(11)	C(6)–S(7)–C(8)–C(9)	−58.8(10)
C(2)–C(3)–S(4)–C(5)	130.9(8)	S(7)–C(8)–C(9)–S(1)	−53.7(11)
C(3)–S(4)–C(5)–C(6)	−54.9(9)		

Table 2 Atomic coordinates with e.s.d.s in parentheses

	x	*y*	*z*
Tl	1.036 56(6)	0.027 91(5)	0.050 540(20)
S(1)	0.982 8(4)	0.118 9(4)	0.194 05(12)
C(2)	1.180 5(16)	0.224 0(16)	0.213 9(5)
C(3)	1.225 0(14)	0.369 9(14)	0.174 7(5)
S(4)	1.238 2(3)	0.331 5(4)	0.088 88(13)
C(5)	1.110 5(14)	0.485 4(13)	0.054 1(5)
C(6)	0.924 6(12)	0.503 5(13)	0.077 2(5)
S(7)	0.798 1(4)	0.323 0(4)	0.067 84(12)
C(8)	0.701 9(13)	0.292 7(15)	0.145 8(6)
C(9)	0.818 4(15)	0.274 4(15)	0.202 3(6)
P	0.507 4(4)	0.328 3(3)	0.373 81(13)
F(1)	0.491 6(10)	0.420 8(10)	0.308 2(3)
F(2)	0.565 1(10)	0.488 7(9)	0.408 0(4)
F(3)	0.526 2(12)	0.240 4(10)	0.440 6(4)
F(4)	0.703 4(9)	0.292 6(12)	0.359 4(4)
F(5)	0.313 0(10)	0.368 7(12)	0.389 6(5)
F(6)	0.453 1(13)	0.171 2(9)	0.338 9(5)

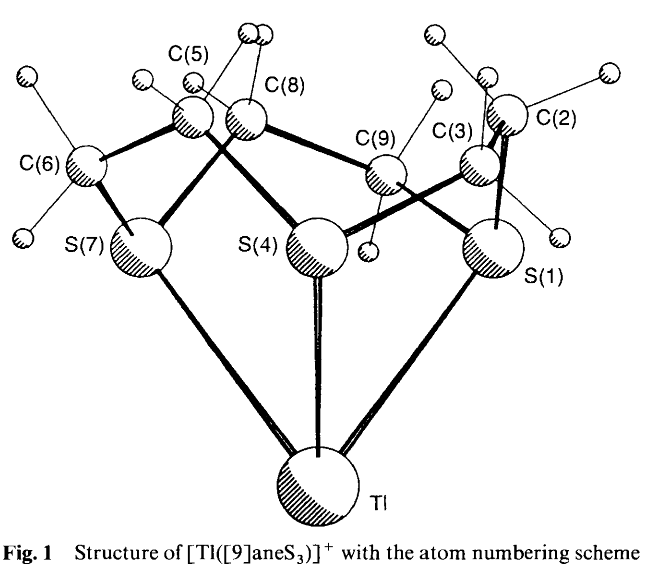

Fig. 1 Structure of [Tl([9]aneS$_3$)]$^+$ with the atom numbering scheme adopted

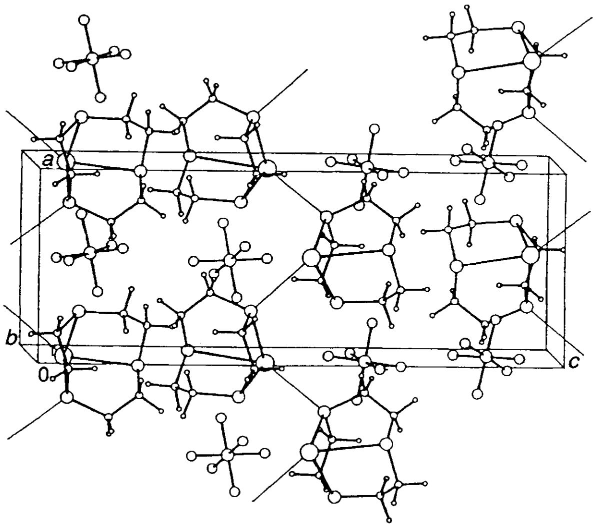

Fig. 2 A view of the structure of [Tl([9]aneS$_3$)]PF$_6$ showing the helices formed by Tl • • • S contacts

S(7′) is related to S(7) by a 2_1 ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$) screw axis parallel to *a*, the solid-state structure of [Tl([9]aneS$_3$)]PF$_6$ is particularly unusual, and consists of infinite helices of [Tl([9]aneS$_3$)]$^+$ units (Fig. 2). Further secondary interactions between the Tl$^{\text{I}}$ centre and fluorines of three PF$_6^-$ counter ions are observed: to F(2) and F(4) at ($2 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$); to F(3) at ($1\frac{1}{2} - x$, $-y$, $z - \frac{1}{2}$) and to F(5) at ($1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$). The Tl • • • F distances are 3.228(8), 3.389(8), 3.246(8) and 3.272(9) Å respectively: details of the geometry of the intermolecular contacts are given in Table 3. Formally, therefore, the Tl$^{\text{I}}$ centre can be regarded as eight-co-ordinate. The space group $P2_12_12_1$ is enantiomorphous and there is a very significant anomalous difference between the two hands of the structure, the hand chosen being favoured by *ca.* 0.03 in terms of the *R* value.

It is useful to compare the structure of [Tl([9]aneS$_3$)]PF$_6$ with that of [Tl(Me$_3$[9]aneN$_3$)]PF$_6$ (Me$_3$[9]aneN$_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane).[14] Similar acute angles at Tl$^{\text{I}}$ are observed in both, reflecting the distance between Tl$^{\text{I}}$ and the centre of the facially co-ordinated ligands. However, whereas the solid-state structure of [Tl([9]aneS$_3$)]PF$_6$ shows thioether S atoms bridging between Tl$^{\text{I}}$ ions to afford a helical structure, the N-donors in [Tl(Me$_3$[9]aneN$_3$)]PF$_6$ do not act as bridges. This is consistent with the presence of two lone pairs of electrons on each S-donor compared with one on each N-donor of a tertiary amine ligand. In [Tl(Me$_3$[9]aneN$_3$)]PF$_6$, bridging between the cations is achieved *via* the PF$_6^-$ counter ions only.[14] Bridging of individual thioether S atoms between metal centres is still rare.[6,15] In [Tl([9]aneS$_3$)]PF$_6$ the affinity of Tl$^{\text{I}}$ for thioether S-donors corresponds to the relative softness of the two centres and the covalency in their bonding.

Experimental

Infrared spectra were measured as KBr discs using a Perkin-Elmer 598 spectrometer over the range 200—4000 cm^{-1}. Microanalyses were performed by the Edinburgh University Chemistry Department microanalytical service. Mass spectra were run by electron impact on a Kratos MS 902 and by fast atom bombardment on a Kratos MS 50TC spectrometer. Proton and ^{13}C NMR spectra were recorded at 200 and 50.32 MHz respectively on a Bruker WP200 spectrometer.

Synthesis of [Tl([9]aneS$_3$)]PF$_6$.—Thallium(I) nitrate (0.133 g, 0.5 mmol) was treated with [9]aneS$_3$ (0.10 g, 0.566 mmol) in refluxing MeCN (5 cm^3) for 1 h. The solution was cooled and an excess of NH$_4$PF$_6$ added. The resulting white precipitate was collected, recrystallised from MeCN–Et$_2$O and dried *in vacuo*. Yield = 73% (Found: C, 13.4; H, 2.25; N, 0.0. Calc. for

Table 3 Intermolecular contacts

(*a*) Type S–Tl···C–D

Atoms				Symmetry			
S	Tl	C	D	C, D	B···C/Å	A–B···C/°	B···C–D/°
S(1)	Tl	S(7)	Tl	$\frac{1}{2} + x, \frac{1}{2} - y, -z$	3.431(3)	132.90(7)	123.96(9)
S(4)			C(6)			65.58(7)	95.4(4)
S(7)			C(8)			98.43(7)	117.0(4)
S(1)	Tl	F(2)	P	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.228(8)	84.05(14)	118.5(4)
S(4)						61.92(14)	
S(7)						128.35(14)	
S(1)	Tl	F(3)	P	$1\frac{1}{2} - x, -y, z - \frac{1}{2}$	3.246(8)	145.80(14)	158.4(5)
S(4)						145.89(16)	
S(7)						122.86(16)	
S(1)	Tl	F(4)	P	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.389(8)	71.97(15)	111.0(4)
S(4)						91.94(15)	
S(7)						138.86(15)	
S(1)	Tl	F(5)	P	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.272(9)	67.82(17)	163.5(5)
S(4)						131.07(17)	
S(7)						77.62(17)	

(*b*) Type S···Tl···F

	Symmetry	F	Symmetry	S···Tl···F/°
S(7)	$\frac{1}{2} + x, \frac{1}{2} - y, -z$	F(2)	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	70.26(14)
		F(3)	$1\frac{1}{2} - x, -y, z - \frac{1}{2}$	80.40(15)
		F(4)	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	104.90(15)
		F(5)	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	156.02(17)

(*c*) Type F···Tl···F′

F	Symmetry	F′	Symmetry	F···Tl···F/°
F(2)	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	F(3)	$1\frac{1}{2} - x, -y, z - \frac{1}{2}$	105.21(20)
		F(4)	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	38.90(19)
		F(5)	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	130.66(21)
F(3)	$1\frac{1}{2} - x, -y, z - \frac{1}{2}$	F(4)	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	94.45(20)
		F(5)	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	82.09(22)
F(4)	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	F(5)	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	92.65(21)

$C_6H_{12}F_6PS_3Tl$: C, 13.6; H, 2.25; N, 0.0%). IR spectrum (KBr disc): 3000–2920w, 1445w, 1420(sh), 1410m, 830s and 555s cm^{-1}. FAB mass spectrum (noba): *m*/*z* 385, calc. for [^{205}Tl([9]-aneS$_3$)]$^+$ 385 (with correct isotopic distribution). NMR spectra (CD$_3$CN, 298 K): ^{1}H (200 MHz), δ 3.06 (s, CH$_2$); ^{13}C (50.32 MHz), δ 33.80 ppm (CH$_2$).

Structure Determination of [Tl([9]aneS$_3$)]PF$_6$.—*Crystal data.* $C_6H_{12}F_6PS_3Tl$, *M* = 529.6, orthorhombic, space group $P2_12_12_1$, $a = 7.7655(11)$, $b = 8.3767(18)$, $c = 20.838(4)$ Å, $U = 1355.5$ Å^3 [from 2θ values of 56 reflections measured at $\pm\omega(2\theta = 24\text{–}26^\circ$, $\bar{\lambda} = 0.710\ 73$ Å)], $Z = 4$, $D_c = 2.595$ g cm^{-3}, $T = 293$ K, pale yellow-brown tablet, 0.54 × 0.39 × 0.19 mm, $\mu = 12.64$ mm^{-1}, $F(000) = 984$.

Data collection and processing. Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-Kα X-radiation, ω–2θ scans with ω scan width (1.05 + 0.347 tan θ)°, 2245 data measured (2θ$_{max}$ 45°, *h* −8 to 8, *k* 0–9, *l* 0–22), 1752 unique (R_{int} = 0.025), semi-empirical absorption correction (min. and max. transmission factors 0.0286 and 0.0621 respectively), giving 1691 reflections with $F \geqslant 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed.

Structure solution and refinement. A Patterson synthesis located the Tl atom and iterative cycles of least-squares refinement and difference Fourier synthesis located all non-H atoms: these were then refined anisotropically, while H atoms were included in fixed, calculated positions.[16] At final convergence *R*, *R*′ = 0.0294, 0.0379 respectively, *S* = 1.045 for 155 refined parameters and the final Δ*F* synthesis showed no peak above 1.39 e Å^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\ 169F^2$ gave satisfactory agreement analyses, $(\Delta/\sigma)_{max}$ in the final cycle was 0.02, and a secondary extinction parameter refined to 1.50(13) × 10^{-7}. (The alternative hand was rejected since its refinement converged to *R* = 0.0633, with errors on refined parameters twice those for the correct enantiomorph.)

Atomic scattering factors were inlaid,[16] or taken from ref. 17. Molecular geometry calculations utilised CALC[18] and Figs. 1 and 2 were produced by PLUTO.[19]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Acknowledgements

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