Thallium Macrocyclic Chemistry: Synthesis and Crystal Structures of $[Tl([18]aneN_2S_4)]PF_6$ and $[Tl([18]aneS_6)]PF_6$ ($[18]aneN_2S_4$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane, $[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) †

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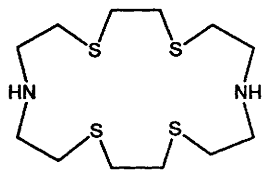
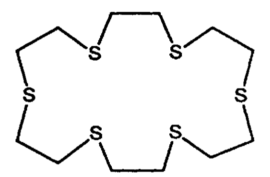
Reaction of $TlPF_6$ with 1 molar equivalent of L (L = $[18]aneN_2S_4$ or $[18]aneS_6$) in refluxing MeCN followed by addition of diethyl ether affords the 1:1 complex $[TlL]PF_6$ in high yield. The complex $[Tl([18]aneN_2S_4)]PF_6$ crystallises in the triclinic space group $P\bar{1}$ with a = 9.733(6), b = 9.775(6), c = 11.370(8) Å, α = 102.68(4), β = 92.35(4), γ = 95.05(5)° and Z = 2. The structure shows the thallium(I) ion occupying the 'cradle' formed by the macrocycle and bound *via* an $[N_2S_2 + S_2]$ donor set, Tl–S(4) 3.1299(13), Tl–S(13) 3.1445(13), Tl–N(7) 2.834(4), Tl–N(16) 2.992(4), Tl···S(1) 3.4778(15) and Tl···S(10) 3.4739(14) Å. This leaves the top face of the metal centre exposed, except for long-range interactions with two further thioether donor atoms from adjacent $[Tl([18]aneN_2S_4)]^+$ cations, Tl···S(1′) 3.643(1) (related by 1 − *x*, 1 − *y*, 1 − *z*), Tl···S(10″) 3.676(1) Å (related by 1 − *x*, 1 − *y*, −*z*), and one F atom of the PF_6^- counter-ion, Tl···F(1) 3.326(4) Å. The complex $[Tl([18]aneS_6)]PF_6$ crystallises in the monoclinic space group $P2_1/c$ with a = 11.0279(13), b = 18.617(5), c = 10.8568(13) Å, β = 96.876(13)° and Z = 4. The structure shows Tl^I interacting with all six macrocyclic thioether donors; two of those interactions, Tl–S(1) 3.164(5) and Tl–S(13) 3.205(7) Å, being considerably shorter than the other four, Tl···S(4) 3.370(5), Tl···S(7) 3.315(6), Tl···S(10) 3.347(7) and Tl···S(16) 3.356(6) Å. There are additional long-range interactions with two further thioether donors from adjacent $[Tl([18]aneS_6)]^+$ cations, Tl···S(7′) 3.689(6) (related by −*x*, 1 − *y*, 1 − *z*) and Tl···S(16″) 3.688(6) Å (related by 1 − *x*, 1 − *y*, 1 − *z*). There is also a long-range contact with one F atom of the PF_6^- counter-ion, Tl···F(6) 3.052(24) Å.



$[18]aneN_2S_4$



$[18]aneS_6$

We have been studying the co-ordination chemistry of the thioether macrocyclic ligands $[9]aneS_3$ (1,4,7-trithiacyclononane), $[14]aneS_4$ (1,4,8,11-tetrathiacyclotetradecane), $[15]aneS_5$ (1,4,7,10,13-pentacyclopentadecane), $[18]aneS_6$ (1,4,7,10,13,16-hexathiacyclooctadecane)[1] and the mixed thia–aza macrocycles $[18]aneN_2S_4$ (1,4,10,13-tetrathia-7,16-diazacyclooctadecane) and $Me_2[18]aneN_2S_4$ (7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane)[2] with transition-metal ions. These studies were initiated in an attempt to understand the relationships between the stereochemical and redox characteristics of these systems. As a result, we have shown that macrocyclic ligands are very efficient at stabilising discrete one-electron transfers. Thus, for example, mononuclear palladium-(I) and -(III) species are stabilised by co-ordination to $Me_2[18]aneN_2S_4$ and $[18]aneN_2S_4$ respectively,[3] while the complexes $[Rh([9]aneS_3)_2]^{3+}$ and $[Rh([18]aneS_6)]^{3+}$ both exhibit chemically reversible Rh^{III}–Rh^{II} and Rh^{II}–Rh^{I} redox couples.[4] More recently, we have extended these studies to include d^{10} metal ions such as Cu^I,[5] Ag^I[6] and Au^I,[7] and, for example, we are now able to prepare the unique series $[Au([9]aneS_3)_2]^{n+}$ (n = 1–3).[1,7] In contrast, there have been very few reports on complexation of main-group elements with these ligands.[8–13] Wieghardt and co-workers[8] have reported the structure of $[Pb([9]aneS_3)_2(OClO_3)_2]$ which shows a distorted square-antiprismatic geometry involving two facially bound $[9]aneS_3$ ligands, Pb–S 3.015(5), 3.084(4) and 3.129(5) Å, with monodentate perchlorate ions completing the co-ordination sphere, Pb–O 2.719(15) and 2.720(15) Å. The structures of $[(AlMe_3)_4([14]aneS_4)]$ and $[AlMe_3([12]aneS_4)]$ ($[12]aneS_4$ = 1,4,7,10-tetrathiacyclododecane) have been reported:[9] the former shows an exocyclic geometry in which one $AlMe_3$ fragment is bound to each S-donor, Al–S 2.512(2)–2.531(2) Å, generating a tetrahedral stereochemistry at each Al^{III} centre; in contrast the geometry at Al^{III} in $[AlMe_3([12]aneS_4)]$ is trigonal bipyramidal with $[12]aneS_4$ bridging $AlMe_3$ units, Al–S 2.718(3) and 3.052(3) Å. We have reported the structure of $[Tl([9]aneS_3)]PF_6$,[10] while more recently Willey *et al.*[12] have described the first examples of thioether crown complexation to $BiCl_3$ and $SbCl_3$ fragments. Izatt *et al.*[13] have studied the effects which partial substitution of S for O have upon binding of alkali

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Bond lengths (Å), angles and torsion angles (°) with estimated standard deviations (e.s.d.s) for [Tl([18]aneN$_2$S$_4$)]$^+$

Tl···S(1)	3.4778(15)	S(1)–C(2)	1.837(6)	C(6)–N(7)	1.481(7)	C(12)–S(13)	1.815(5)
Tl–S(4)	3.1299(13)	S(1)–C(18)	1.825(6)	N(7)–C(8)	1.461(7)	S(13)–C(14)	1.817(6)
Tl–N(7)	2.834(4)	C(2)–C(3)	1.528(8)	C(8)–C(9)	1.543(8)	C(14)–C(15)	1.523(8)
Tl···S(10)	3.4739(14)	C(3)–S(4)	1.804(6)	C(9)–S(10)	1.823(5)	C(15)–N(16)	1.459(7)
Tl–S(13)	3.1445(13)	S(4)–C(5)	1.816(6)	S(10)–C(11)	1.818(6)	N(16)–C(17)	1.465(7)
Tl–N(16)	2.992(4)	C(5)–C(6)	1.512(8)	C(11)–C(12)	1.529(8)	C(17)–C(18)	1.521(8)
S(1)–Tl–S(4)	62.78(4)	S(10)–Tl–S(13)	62.28(3)	S(4)–C(5)–C(6)	115.0(4)	C(11)–C(12)–S(13)	110.7(4)
S(1)–Tl–N(7)	116.83(9)	S(10)–Tl–N(16)	115.04(9)	C(5)–C(6)–N(7)	112.6(5)	Tl–S(13)–C(12)	102.73(17)
S(1)–Tl–S(10)	172.43(3)	S(13)–Tl–N(16)	65.15(9)	Tl–N(7)–C(6)	110.5(3)	Tl–S(13)–C(14)	102.92(18)
S(1)–Tl–S(13)	110.22(4)	Tl–S(1)–C(2)	105.61(19)	Tl–N(7)–C(8)	119.3(3)	C(12)–S(13)–C(14)	100.71(25)
S(1)–Tl–N(16)	60.02(9)	Tl–S(1)–C(18)	101.62(19)	C(6)–N(7)–C(8)	112.9(4)	S(13)–C(14)–C(15)	114.3(4)
S(4)–Tl–N(7)	66.74(9)	C(2)–S(1)–C(18)	101.6(3)	N(7)–C(8)–C(9)	112.8(4)	C(14)–C(15)–N(16)	112.7(5)
S(4)–Tl–S(10)	111.30(3)	S(1)–C(2)–C(3)	112.4(4)	C(8)–C(9)–S(10)	115.0(4)	Tl–N(16)–C(15)	110.5(3)
S(4)–Tl–S(13)	65.90(4)	C(2)–C(3)–S(4)	111.8(4)	Tl–S(10)–C(9)	97.91(18)	Tl–N(16)–C(17)	120.7(3)
S(4)–Tl–N(16)	77.11(9)	Tl–S(4)–C(3)	104.11(19)	Tl–S(10)–C(11)	105.79(18)	C(15)–N(16)–C(17)	114.1(4)
N(7)–Tl–S(10)	62.15(9)	Tl–S(4)–C(5)	100.79(19)	C(9)–S(10)–C(11)	103.29(25)	N(16)–C(17)–C(18)	113.1(5)
N(7)–Tl–S(13)	79.30(9)	C(3)–S(4)–C(5)	99.0(3)	S(10)–C(11)–C(12)	112.9(4)	S(1)–C(18)–C(17)	113.7(4)
N(7)–Tl–N(16)	137.22(12)						

C(18)–S(1)–C(2)–C(3)	−129.6(4)	C(5)–C(6)–N(7)–C(8)	71.2(6)	C(11)–C(12)–S(13)–C(14)	176.7(4)
C(2)–S(1)–C(18)–C(17)	74.2(5)	C(6)–N(7)–C(8)–C(9)	161.8(4)	C(12)–S(13)–C(14)–C(15)	72.3(4)
S(1)–C(2)–C(3)–S(4)	67.8(5)	N(7)–C(8)–C(9)–S(10)	64.4(5)	S(13)–C(14)–(15)–N(16)	68.2(5)
C(2)–C(3)–S(4)–C(5)	−179.2(4)	C(8)–C(9)–S(10)–C(11)	77.8(4)	C(14)–C(15)–N(16)–C(17)	77.6(6)
C(3)–S(4)–C(5)–C(6)	78.1(4)	C(9)–S(10)–C(11)–C(12)	−124.2(4)	C(15)–N(16)–C(17)–C(18)	163.5(5)
S(4)–C(5)–C(6)–N(7)	65.3(6)	S(10)–C(11)–C(12)–S(13)	67.5(4)	N(16)–C(17)–C(18)–S(1)	64.1(6)

Table 2 Atomic coordinates with e.s.d.s for [Tl([18]aneN$_2$S$_4$)]PF$_6$

Atom	*x*	*y*	*z*
Tl	0.384 560(20)	0.415 130(20)	0.237 070(20)
S(1)	0.375 21(14)	0.363 11(15)	0.529 68(14)
C(2)	0.249 1(6)	0.477 7(6)	0.603 1(5)
C(3)	0.231 2(6)	0.601 4(5)	0.543 6(5)
S(4)	0.150 03(14)	0.543 65(13)	0.393 15(12)
C(5)	0.149 4(6)	0.713 6(5)	0.353 2(5)
C(6)	0.286 5(6)	0.771 8(5)	0.317 0(5)
N(7)	0.330 9(5)	0.684 9(4)	0.203 9(4)
C(8)	0.247 8(6)	0.695 8(5)	0.097 0(5)
C(9)	0.319 2(5)	0.645 9(5)	−0.021 4(5)
S(10)	0.346 61(14)	0.459 56(14)	−0.056 99(12)
C(11)	0.176 8(6)	0.373 1(5)	−0.115 7(5)
C(12)	0.123 4(5)	0.262 7(5)	−0.047 6(5)
S(13)	0.087 85(14)	0.345 73(13)	0.105 69(12)
C(14)	0.017 9(6)	0.193 5(5)	0.159 4(5)
C(15)	0.124 8(6)	0.096 0(5)	0.182 1(5)
N(16)	0.222 3(5)	0.160 3(4)	0.284 2(4)
C(17)	0.166 8(6)	0.162 3(6)	0.402 4(5)
C(18)	0.278 4(6)	0.189 6(5)	0.504 6(5)
P	0.622 22(15)	0.026 49(14)	0.230 77(14)
F(1)	0.622 4(4)	0.191 3(3)	0.240 1(3)
F(2)	0.561 9(4)	0.044 2(4)	0.360 8(3)
F(3)	0.621 9(4)	−0.139 8(3)	0.221 2(4)
F(4)	0.774 5(4)	0.050 6(4)	0.293 4(4)
F(5)	0.683 5(4)	0.009 3(4)	0.101 1(3)
F(6)	0.469 0(4)	0.002 4(4)	0.169 6(4)

metals and Tl^{I}, Pb^{II}, Ag^{I} and Hg^{II} in a range of mixed thia–oxa crowns. The results show that such macrocycles form much more stable complexes with Ag^{I} and Hg^{II} than with Tl^{I} and Pb^{II}. However, no structural data are as yet available for these complexes.

We report herein the synthesis and single-crystal X-ray structures of [Tl([18]aneN$_2$S$_4$)]PF$_6$ and [Tl([18]aneS$_6$)]PF$_6$, which incorporate potentially hexadentate ligands.

Results and Discussion

Treatment of TlPF$_6$ with 1 molar equivalent of L (L = [18]aneN$_2$S$_4$ or [18]aneS$_6$) in refluxing MeCN for 30 min affords a colourless solution from which a white solid can be obtained upon addition of diethyl ether. Infrared spectroscopy and microanalytical data are consistent with the formulation of the products as [TlL]PF$_6$. Fast atom bombardment mass spectrometry of the complexes shows molecular ion peaks (M^+) at *m*/*z* 531 and 565 assigned to [Tl([18]aneN$_2$S$_4$)]$^+$ and [Tl([18]aneS$_6$)]$^+$ respectively. In order to define the nature of the interaction between the macrocyclic ligand and the metal ion, and the conformation adopted by the macrocycle, single-crystal X-ray structure determinations were undertaken for both complexes.

Colourless crystals of [Tl([18]aneN$_2$S$_4$)]PF$_6$ were grown by slow evaporation from a solution of the complex in MeCN. A single-crystal structure determination shows (Fig. 1, Tables 1 and 2) the thallium(I) ion occupying a 'cradle' formed by the [18]aneN$_2$S$_4$ ligand. The metal ion appears to be bound *via* an [N$_2$S$_2$ + S$_2$] donor set, Tl–S(4) 3.1299(13), Tl–S(13) 3.1445(13), Tl–N(7) 2.834(4), Tl–N(16) 2.992(4) Å, Tl···S(1) 3.4778(15) and Tl···S(10) 3.4739(14) Å. The shorter Tl–S and Tl–N bond lengths are less than the sum of the formal ionic radii (1.50 + 1.84 = 3.34 Å for Tl–S, 1.12 + 1.84 = 2.96 Å for Tl–N),[14] consistent with a significant degree of covalency in the bonding for the primary co-ordination sphere. Furthermore, the lone pairs on all six macrocyclic donor atoms are clearly directed towards the central metal ion, with the methylene chains of the macrocycle all directed towards one side of the metal ion. The top face of the thallium(I) ion is therefore exposed except for two further, long-range interactions with thioether donors from adjacent [Tl([18]aneN$_2$S$_4$)]$^+$ cations, Tl···S(1′) 3.643(1) (related by 1 − *x*, 1 − *y*, 1 − *z*) and Tl···S(10″) 3.676(1) Å (related by 1 − *x*, 1 − *y*, −*z*). This cation–cation cross-linking results in infinite double columns of cations running along the *c* axis. There is also a very long-range interaction of the thallium(I) centre with one F atom of the PF$_6^-$ counter ion, Tl···F 3.326(4) Å. The packing diagram for the complex is shown in Fig. 2. The unusual 'cradle'-like conformation adopted by the macrocycle in this complex probably reflects the considerable size mismatch between [18]aneN$_2$S$_4$ and the large thallium(I) ion, and the stereochemical preferences of Tl^{I} for relatively high co-ordination numbers. The bond angles around Tl^{I} are extremely acute as a consequence of the long thallium-donor bond lengths.

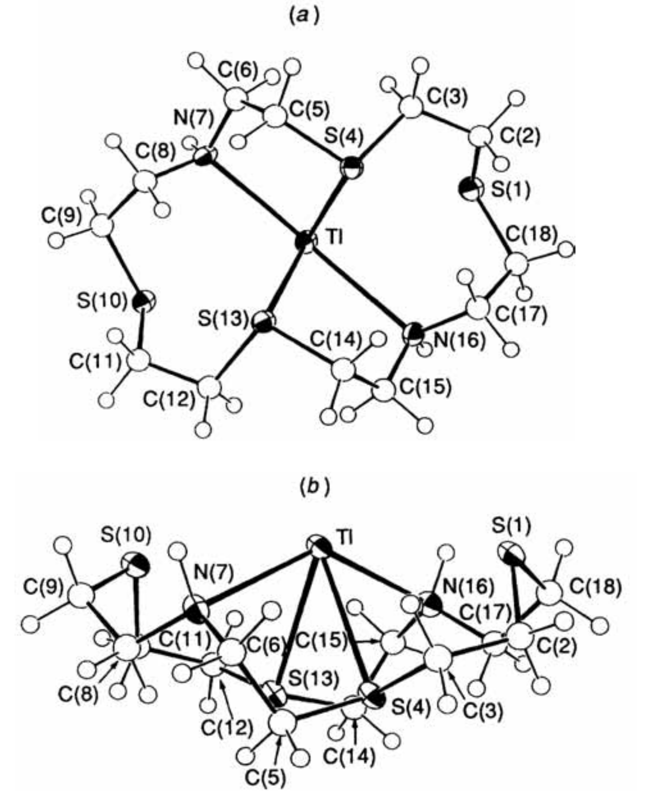

Fig. 1 (*a*) View of the structure of [Tl([18]aneN$_2$S$_4$)]$^+$ with numbering scheme adopted. (*b*) Orthogonal view of [Tl([18]aneN$_2$S$_4$)]$^+$ showing the conformation of the macrocycle

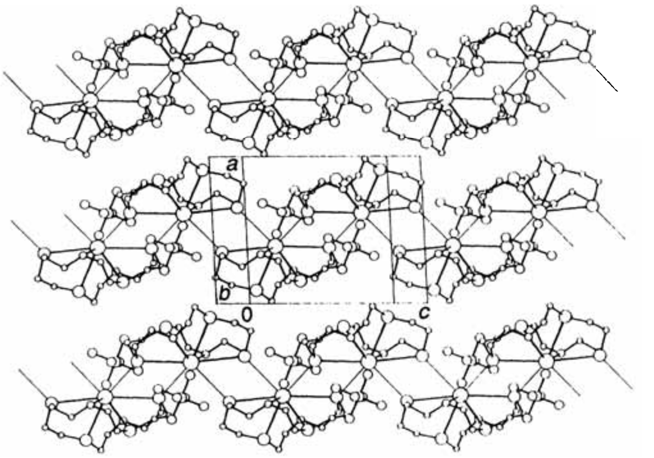

Fig. 2 Packing diagram of [Tl([18]aneN$_2$S$_4$)]PF$_6$

Previously, we have shown that, upon co-ordination to a large metal ion such as Ag^{I}[16] and Hg^{I},[15] [18]aneN$_2$S$_4$ tends to bind through all six donor atoms, but distorts tetrahedrally in order to accommodate the inherent stereochemical and size mismatch between the metal ion and the ligand cavity. Thus, structural studies show that for the octahedral complexes *rac*-[M([18]aneN$_2$S$_4$)]$^{n+}$ there is a direct correlation between the degree of tetrahedral distortion and the ionic radius of the metal centre.[2] It appears however that in [Tl([18]aneN$_2$S$_4$)]$^+$ the metal ion is too large even for this, and we observe a new conformation for co-ordinated [18]aneN$_2$S$_4$. Significantly, the ^{13}C DEPT (distortionless enhancement of polarisation transfer) NMR spectrum (CD$_3$CN) of [Tl([18]aneN$_2$S$_4$)]PF$_6$ exhibits only three carbon resonances at 298 K, δ 51.66, 36.05 and 35.89, consistent with a time-averaged or fluxional species in solution.

We wished to compare the above structure of [Tl([18]aneN$_2$S$_4$)]$^+$ with its homoleptic thioether analogue. Slow evaporation from a solution of [Tl([18]aneS$_6$)]PF$_6$ in MeCN gave crystals of suitable quality for X-ray analysis. The structure shows (Fig. 3, Tables 3 and 4) the [Tl([18]aneS$_6$)]$^+$ cation adopting a very similar stereochemistry to that observed for [Tl([18]-

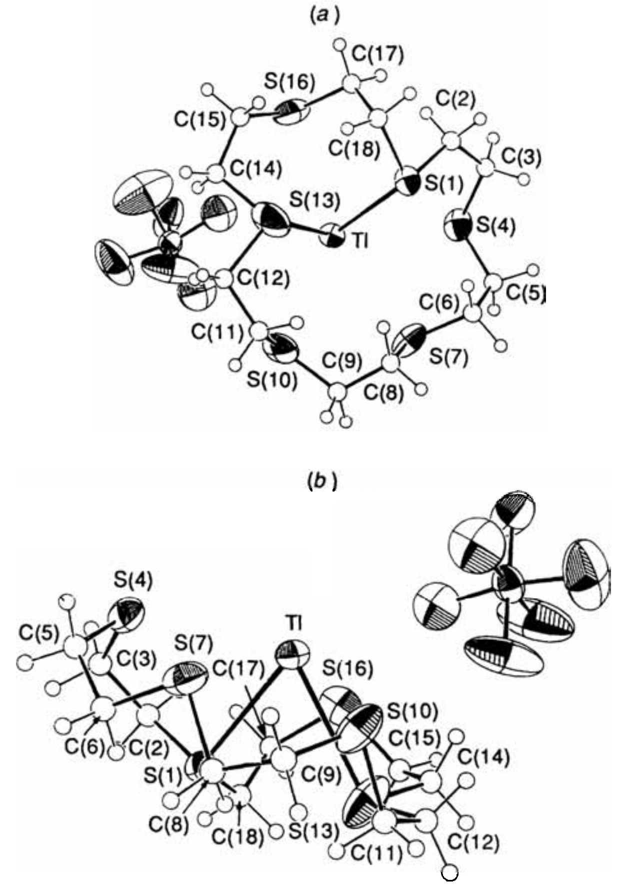

Fig. 3 (*a*) View of the structure of [Tl([18]aneS$_6$)]PF$_6$ with numbering scheme adopted. (*b*) Orthogonal view of [Tl([18]aneS$_6$)]PF$_6$ showing the conformation of the macrocycle

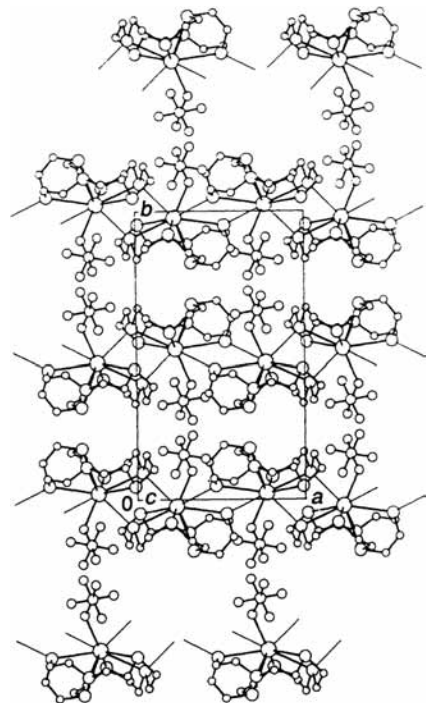

Fig. 4 Packing diagram of [Tl([18]aneS$_6$)]PF$_6$

Table 3 Bond lengths (Å), angles and torsion angles (°) with e.s.d.s for [Tl([18]aneS_6)]$^+$

Tl–S(1)	3.164(5)	Tl–S(13)	3.205(7)	C(5)–C(6)	1.50(3)	C(14)–C(15)	1.52(4)
Tl ··· S(4)	3.370(5)	Tl ··· S(16)	3.356(6)	C(6)–S(7)	1.796(24)	C(15)–S(16)	1.790(25)
Tl ··· S(7)	3.315(6)	S(1)–C(18)	1.789(19)	C(12)–S(13)	1.82(3)	S(16)–C(17)	1.806(19)
Tl ··· S(10)	3.347(7)	S(4)–C(5)	1.802(23)	S(13)–C(14)	1.78(3)	C(17)–C(18)	1.47(3)
S(1)–Tl–S(4)	63.27(12)	Tl–S(1)–C(2)	102.6(9)	Tl–S(7)–C(6)	104.4(8)	C(12)–S(13)–C(14)	93.2(13)
S(1)–Tl–S(7)	82.81(13)	Tl–S(1)–C(18)	110.2(6)	Tl–S(7)–C(8)	100.0(9)	S(13)–C(14)–C(15)	108.0(18)
S(1)–Tl–S(10)	105.72(15)	Tl–S(1)–C(2′)	114.8(8)	Tl–S(7)–C(8′)	111.9(25)	C(14)–C(15)–S(16)	116.2(17)
S(1)–Tl–S(13)	66.34(15)	C(2)–S(1)–C(18)	89.5(11)	C(6)–S(7)–C(8)	94.0(12)	Tl–S(16)–C(15)	108.4(8)
S(1)–Tl–S(16)	65.65(13)	C(18)–S(1)–C(2′)	105.6(10)	C(6)–S(7)–C(8′)	112.4(26)	Tl–S(16)–C(17)	103.5(6)
S(4)–Tl–S(7)	61.59(13)	S(1)–C(2)–C(3)	121.1(21)	S(7)–C(8)–C(9)	103.6(18)	C(15)–S(16)–C(17)	102.9(10)
S(4)–Tl–S(10)	121.16(15)	C(2)–C(3)–S(4)	117.5(22)	C(8)–C(9)–S(10)	114.9(19)	S(16)–C(17)–C(18)	116.6(13)
S(4)–Tl–S(13)	128.47(16)	Tl–S(4)–C(3)	106.8(10)	Tl–S(10)–C(9)	109.6(9)	S(1)–C(18)–C(17)	116.9(14)
S(4)–Tl–S(16)	105.76(13)	Tl–S(4)–C(5)	107.7(7)	Tl–S(10)–C(11)	105.3(7)	S(1)–C(2′)–C(3′)	124.4(24)
S(7)–Tl–S(10)	59.66(16)	Tl–S(4)–C(3′)	114.6(15)	C(9)–S(10)–C(11)	94.3(11)	S(4)–C(3′)–C(2′)	115(3)
S(7)–Tl–S(13)	102.55(16)	C(3)–S(4)–C(5)	106.8(13)	S(10)–C(11)–C(12)	113.2(16)	S(7)–C(8′)–C(9′)	119(6)
S(7)–Tl–S(16)	147.93(14)	C(5)–S(4)–C(3′)	80.6(16)	C(12)–C(11)–S(10′)	101.9(18)	C(8′)–C(9′)–S(10′)	114(6)
S(10)–Tl–S(13)	63.88(18)	S(4)–C(5)–C(6)	119.7(16)	C(11)–C(12)–S(13)	107.2(18)	C(11)–S(10′)–C(9′)	95(3)
S(10)–Tl–S(16)	121.96(16)	C(5)–C(6)–S(7)	107.2(16)	Tl–S(13)–C(12)	109.2(9)		
S(13)–Tl–S(16)	60.51(16)			Tl–S(13)–C(14)	102.7(9)		

C(18)–S(1)–C(2)–C(3)	−171.9(24)	C(5)–C(6)–S(7)–C(8)	−169.4(17)	C(11)–C(12)–S(13)–C(14)	163.7(18)
C(2)–S(1)–C(18)–C(17)	60.9(17)	C(5)–C(6)–S(7)–C(8′)	170(3)	C(12)–S(13)–C(14)–C(15)	174.6(18)
C(2′)–S(1)–C(18)–C(17)	82.2(17)	C(6)–S(7)–C(8)–C(9)	−176.6(18)	S(13)–C(14)–C(15)–S(16)	60.2(21)
C(18)–S(1)–C(2′)–C(3′)	−155.4(27)	C(6)–S(7)–C(8′)–C(9′)	64(6)	C(14)–C(15)–S(16)–C(17)	−123.2(18)
S(1)–C(2)–C(3)–S(4)	36(3)	S(7)–C(8)–C(9)–S(10)	−69.6(21)	C(15)–S(16)–C(17)–C(18)	65.4(16)
C(2)–C(3)–S(4)–C(5)	−106.1(23)	C(8)–C(9)–S(10)–C(11)	−85.3(20)	S(16)–C(17)–C(18)–S(1)	65.3(17)
C(3)–S(4)–C(5)–C(6)	89.2(20)	C(9)–S(10)–C(11)–C(12)	160.7(18)	S(1)–C(2′)–C(3′)–S(4)	33(4)
C(3′)–S(4)–C(5)–C(6)	87.8(23)	S(10)–C(11)–C(12)–S(13)	−75.4(19)	S(7)–C(8′)–C(9′)–S(10′)	40(8)
C(5)–S(4)–C(3′)–C(2′)	−120(3)	S(10′)–C(11)–C(12)–S(13)	7.8(21)	C(8′)–C(9′)–S(10′)–C(11)	99(6)
S(4)–C(5)–C(6)–S(7)	65.5(20)	C(12)–C(11)–S(10′)–C(9′)	176(3)		

Table 4 Atomic coordinates with e.s.d.s for [Tl([18]aneS_6)]PF_6

Atom	*x*	*y*	*z*
Tl	0.234 11(6)	0.522 83(4)	0.396 93(5)
S(1)	0.332 9(4)	0.678 4(3)	0.470 6(4)
S(4)	0.199 6(5)	0.579 9(3)	0.685 2(4)
S(7)	−0.031 1(5)	0.594 5(3)	0.445 9(5)
S(10)	0.013 2(6)	0.546 3(5)	0.160 8(5)
S(13)	0.306 5(5)	0.614 6(5)	0.166 8(4)
S(16)	0.530 0(4)	0.548 2(3)	0.364 7(5)
C(2)	0.399 6(24)	0.666 6(21)	0.631 7(13)
C(3)	0.323(3)	0.643 4(19)	0.730(3)
C(5)	0.058 8(19)	0.629 8(14)	0.676 1(19)
C(6)	0.009 1(21)	0.665 0(13)	0.556 2(19)
C(8)	−0.055(3)	0.655 1(16)	0.314 7(23)
C(9)	−0.099 5(24)	0.605 9(15)	0.206 9(22)
C(11)	0.074 2(21)	0.611 8(11)	0.059 1(19)
C(12)	0.201 3(20)	0.593 4(18)	0.029 8(23)
C(14)	0.427 0(20)	0.563 0(17)	0.115 8(22)
C(15)	0.541 0(19)	0.574 4(16)	0.207 8(18)
C(17)	0.568 1(16)	0.629 9(11)	0.450 5(15)
C(18)	0.482 9(16)	0.690 2(11)	0.426 6(16)
C(2′)	0.346(3)	0.698 2(17)	0.635 4(11)
C(3′)	0.261(5)	0.669 4(17)	0.723(4)
C(8′)	−0.117(6)	0.628(6)	0.302(5)
C(9′)	−0.053(4)	0.679(5)	0.222(8)
S(10′)	0.106(3)	0.656 8(19)	0.209 8(23)
P	0.279 1(4)	0.343 1(3)	0.145 5(4)
F(1)	0.333 5(11)	0.276 4(8)	0.219 9(10)
F(2)	0.227 0(12)	0.409 5(8)	0.069 4(16)
F(3)	0.409 4(16)	0.356 9(10)	0.103 1(21)
F(4)	0.258 2(17)	0.294 0(10)	0.029 0(13)
F(5)	0.153 4(23)	0.329 6(17)	0.192(3)
F(6)	0.327 8(20)	0.400 4(15)	0.247 0(19)
F(7)	0.230(3)	0.357 4(20)	0.272 7(16)
F(8)	0.143 6(14)	0.315 3(18)	0.118(3)

aneN_2S_4)]$^+$, with the macrocycle in a 'cradle'-like conformation. In [Tl([18]aneS_6)]$^+$ the metal ion interacts with all six macrocyclic donor atoms, with two Tl–S bond lengths much shorter, Tl–S(1) 3.164(5) and Tl–S(13) 3.205(7) Å, than the other four, Tl ··· S(4) 3.370(5), Tl ··· S(7) 3.315(6), Tl ··· S(10) 3.347(7) and Tl ··· S(16) 3.356(6) Å. These six macrocyclic donors all lie on one side of the thallium(I) ion, with two much longer intermolecular Tl ··· S interactions on the other side, Tl ··· S(7′) 3.689(6) (related by −*x*, 1 − *y*, 1 − *z*) and Tl ··· S(16″) 3.688(6) Å (related by 1 − *x*, 1 − *y*, 1 − *z*). One F atom of the PF_6^- counter-ion also interacts at long range with the Tl^I, Tl ··· F(6) 3.052(24) Å. The packing diagram for the complex is shown in Fig. 4.

We have observed similar long Tl–S bond distances and acute S–Tl–S angles (*ca.* 68°) for the complex [Tl([9]aneS_3)]$^+$ in which the trithia macrocycle is bound facially to the metal ion, Tl–S 3.114(3), 3.092(3) and 3.110(3) Å. Additonally, a thioether donor of an adjacent cation makes a long contact, Tl ··· S′ 3.431(3), linking [Tl([9]aneS_3)]$^+$ cations to form infinite helices.[10] Wieghardt *et al.*[16] have reported the structure of the related complex [Tl(Me$_3$[9]aneN_3)]$^+$ (Me$_3$[9]aneN_3 = 1,4,7-trimethyl-1,4,7-triazacyclonane), which shows the triaza macrocycle binding facially to the thallium centre, Tl–N 2.59(2), 2.60(1) and 2.63(1) Å, with PF_6^- counter ions bridging between the cations, Tl ··· F 3.23(1)–3.54(2) Å. These Tl–N bond distances are considerably shorter than those in [Tl([18]aneN_2S_4)]$^+$, suggesting that the macrocyclic configuration plays a significant role in determining the stereochemistry and metal–donor distances in the complex.

The results described herein reveal that the intra- and intermolecular contacts present in [Tl([18]aneN_2S_4)]PF_6 and [Tl([18]aneS_6)]PF_6 lead to very similar overall geometries for the two complexes. The very long metal–donor bond lengths and acute angles at Tl^I illustrate the severity of the size mismatch between the metal-ion radius and the macrocyclic cavity size in these systems.

Experimental

Infrared spectra were measured as KBr and CsI discs using a Perkin Elmer 598 spectrometer over the range 200–4000 cm^{-1}, electronic spectra in quartz cells using a Perkin Elmer Lambda 9 spectrophotometer and electron-impact mass spectra on a Kratos MS902 spectrometer. Fast-atom bombardment (FAB) mass spectra in a 3-nitrobenzyl alcohol matrix, were recorded on a Kratos MS 50TC spectrometer. Microanalyses were carried out by the University of Edinburgh Chemistry Department microanalytical service. Proton and ^{13}C NMR spectra were run on Bruker WP200 (operating at 200.13 and 50.32 MHz respectively) and JEOL FX90Q (operating at 89.55 and 22.49 MHz respectively) spectrometers.

Synthesis of [Tl([18]aneN$_2$S$_4$)]PF$_6$.—The salt TlPF$_6$ (40 mg, 0.123 mmol) was added to a solution of [18]aneN$_2$S$_4$ (43 mg, 0.123 mmol) in MeCN (10 cm^3). The reaction mixture was refluxed for 30 min to give a colourless solution. The volume of solvent was reduced to 5 cm^3 and diethyl ether was added to afford a white precipitate which was recrystallised from MeCN–Et$_2$O and dried *in vacuo*. Yield 79% (Found: C, 21.3; H, 3.95; N, 4.10; S, 18.6. Calc. for $C_{12}H_{26}F_6N_2PS_4Tl$: C, 21.3; H, 3.90; N, 4.15; S, 19.0%). FAB mass spectrum: *m/z* 531; calc. for [^{205}Tl([18]aneN$_2$S$_4$)]$^+$ (M^+) *m/z* 531. NMR (CD$_3$CN, 298 K): ^{1}H (200.13 MHz), δ 2.96 (s, 8 H), 2.91 (m, 8 H) and 2.81 (m, 8 H); ^{13}C DEPT (50.32 MHz), δ 51.66 (NCH$_2$, 4C), 36.05 (SCH$_2$, 4C) and 35.89 (SCH$_2$, 4C). IR (KBr disc): 3260m, 2940w, 2910m, 2865w, 2820m, 2740w, 1480w, 1470m, 1445vs, 1420m, 1380w, 1340w, 1295m, 1210m, 1175w, 1130m, 1000m, 940m, 840vs, 780m, 760w, 710w, 640m and 555vs cm^{-1}.

Structure Determination of [Tl([18]aneN$_2$S$_4$)]PF$_6$.—*Crystal data.* $C_{12}H_{26}N_2S_4Tl^+PF_6^-$, M = 675.87, triclinic, space group $P\bar{1}$, a = 9.733(6), b = 9.775(6), c = 11.370(8) Å, α = 102.68(4), β = 92.35(4), γ = 95.05(5)°, U = 1049 Å^3 [from 2θ values of 30 reflections measured at ±ω (2θ = 30–32°, $\bar{\lambda}$ = 0.710 73 Å)], Z = 2, D_c = 2.139 g cm^{-3}, T = 150 K, colourless block, 0.39 × 0.39 × 0.58 mm, μ = 8.285 mm^{-1}, F(000) = 652.

Data collection and processing. Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-Kα X-radiation, T = 150 K, ω–2θ scans using the learnt-profile method,[17] 2692 unique data (R_{int} = 0.0156), (2θ$_{max}$ 45°, h −10 to 10, k −10 to 10, l 0–12), semiempirical absorption correcton applied, giving 2633 reflections with $F \geqslant 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed.

Structure solution and refinement. The Tl atom was located by a Patterson synthesis. Iterative cycles of least-squares refinement and Fourier difference syntheses located all non-H atoms.[18] At isotropic convergence, final corrections (minimum 0.864, maximum 1.188) for absorption effects were applied using DIFABS.[19] Non-H atoms were then refined (by least squares on F)[18] with anisotropic thermal parameters, with H atoms included at fixed, calculated positions. At final convergence R, R' = 0.0278, 0.0396 respectively, S = 0.981 for 237 refined parameters and the final ΔF synthesis showed no peak above 1.15 e Å^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,358F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.05. Selected bond lengths, angles and torsion angles are given in Table 1. Fractional atomic coordinates are listed in Table 2.

Synthesis of [Tl([18]aneS$_6$)]PF$_6$.—Procedure as for [Tl([18]aneN$_2$S$_4$)]PF$_6$, using TlPF$_6$ (39 mg, 0.112 mmol) and [18]aneS$_6$ (40 mg, 0.111 mmol). Yield 72% (Found: C, 20.1; H, 3.45; S, 26.8. Calc. for $C_{12}H_{24}F_6PS_6Tl$]: C, 20.3; H, 3.40; S, 27.1%). FAB mass spectrum: *m/z* 565; calc. for [^{205}Tl([18]aneS$_6$)]$^+$ (M^+) *m/z* 565. NMR (CD$_3$CN, 298 K): ^{1}H (89.55 MHz), δ 2.96 (CH$_2$, 24 H); ^{13}C (22.49 MHz), δ 31.65 (SCH$_2$). IR (KBr disc): 2920m, 2900m, 1415vs, 1400(sh), 1290w, 1255m, 1215w, 1190m, 1150w, 1020w, 925w, 840vs(br), 740m, 710w, 695w, 680m, 660w, 620w, 555vs and 480m cm^{-1}.

Structure Determination of [Tl([18]aneS$_6$)]PF$_6$.—*Crystal data.* $C_{12}H_{24}S_6Tl^+PF_6^-$, M = 709.96, monoclinic, space group $P2_1/c$, a = 11.0279(13), b = 18.617(5), c = 10.8568(13) Å, β = 96.876(13)°, U = 2213 Å^3 [from 2θ values of 18 reflections measured at ±ω (2θ = 22–24°, $\bar{\lambda}$ = 0.710 73 Å)], Z = 4, D_c = 2.131 g cm^{-3}, T = 150 K, colourless triangular plate, 0.35 × 0.31 × 0.04 mm, μ = 8.035 mm^{-1}, F(000) = 1368.

Data collection and processing. The above procedure yielded 4302 data of which 2678 were unique (R_{int} = 0.0529), 2θ$_{max}$ 45°, h −11 to 11, k −6 to 20, l 0–11), semiempirical absorption correction applied, giving 2297 reflections with $F \geqslant 4\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed.

Structure solution and refinements. The above procedure was employed. At isotropic convergence, final corrections (minimum 0.845, maximum 1.276) for absorption effects were applied using DIFABS. During refinement, some disorder was identified in the macrocycle and in the PF$_6^-$ anion. The macrocyclic disorder was modelled partially by constraining the C–C (1.52 Å) and C–S (1.83 Å) bond lengths in the disordered regions S(1) to S(4), S(7) to C(11) and C(14) to C(15). This gave rise to two alternative, equally likely, sites for C(2) and C(3) and two alternative conformations for the linkage from S(7) to C(11) in the ratio 0.837(1):0.163(1). All subsequent discussion will refer to the major [0.837(1)] component. Partial F atom occupancies were also employed for the PF$_6^-$ counter ion, such that there was a total of six F atoms around the P atom. Anisotropic thermal parameters were refined for Tl, S, P and all fully occupied F atoms, with H atoms included at fixed, calculated positions. At final convergence R, R' = 0.0670, 0.0880 respectively, S = 1.163 for 193 refined parameters and in the final ΔF synthesis the largest peak of 1.82 e Å^{-3} lay close to Tl. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,265F^2$ gave satisfactory agreement analyses and in the final cycle (Δ/σ_{max}) was 0.06. Atomic scattering factors were inlaid,[18] or taken from ref. 20. Molecular geometry calculations utilised CALC[21] and the Figures were produced by ORTEP II.[22] Selected bond lengths, angles and torsion angles are given in Table 3, fractional atomic coordinates in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517; A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1.
2 G. Reid and M. Schröder, *Chem. Soc. Rev.*, 1990, **19**, 239.
3 G. Reid, A. J. Blake, T. I. Hyde and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1988, 1397; A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1990, 3363.
4 A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1988, 1861; G. Reid and M. Schröder, unpublished work.
5 N. Atkinson, A. J. Blake, M. G. B. Drew, G. Forsyth, A. J. Lavery, G. Reid and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1989, 984; A. J. Blake, A. J. Holder and M. Schröder, *Polyhedron*, 1990, **9**, 2919; A. J. Blake, G. Reid and M. Schröder, unpublished work.
6 A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1991, 615; A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde and M. Schroder, *Polyhedron*, 1989, **8**, 513; A. J. Blake, R. O. Gould, G. Reid and M. Schroder, *J. Chem. Soc., Chem. Commun.*, 1990, 974.
7 A. J. Blake, R. O. Gould, J. A. Greig, A. J. Holder, T. I. Hyde and M. Schroder, *J. Chem. Soc., Chem. Commun.*, 1989, 876; A. J. Blake, J. A. Greig, A. J. Holder, T. I. Hyde and M. Schröder, *Angew. Chem.*, 1990, **102**, 203; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 197.
8 H.-J. Kuppers, K. Wieghardt, B. Nuber and J. Weiss, *Z. Anorg. Allg. Chem.*, 1989, **577**, 155.

9 G. H. Robinson and S. A. Sangokoya, *J. Am. Chem. Soc.*, 1988, **110**, 1494; G. H. Robinson, H. Zhang and J. L. Atwood, *Organometallics*, 1987, **6**, 887.

10 A. J. Blake, J. A. Greig and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1991, 529.

11 K. Wieghardt, M. Kleine-Boymann, B. Nuber and J. Weiss, *Inorg. Chem.*, 1986, **25**, 1654.

12 G. R. Willey, M. T. Lakin, M. Ravindran and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1991, 271; G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 591.

13 R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshaw, N. K. Dalley, T. E. Jensen and B. L. Haymore, *Inorg. Chim. Acta*, 1978, **30**, 1 and refs. therein.

14 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

15 A. J. Blake, G. Reid and M. Schröder, *Polyhedron*, 1990, **9**, 2931.

16 K. Wieghardt, M. Kleine-Boymann, B. Nuber and J. Weiss, *Inorg. Chem.*, 1986, **25**, 1309.

17 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

18 G. M. Sheldrick, SHELX 76, program for crystal structure refinement, University of Cambridge, 1976.

19 N. Walker and D. Stuart, DIFABS, program for empirical absorption corrections, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

20 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

21 R. O. Gould and P. Taylor, CALC, program for molecular geometry calculations, University of Edinburgh, 1985.

22 P. D. Mallinson and K. W. Muir, ORTEP II, interactive version, *J. Appl. Crystallogr.*, 1985, **18**, 51.

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