THE MOLECULAR STRUCTURE OF $[TlCl_2(18\text{-crown-6})][TlCl_4]$

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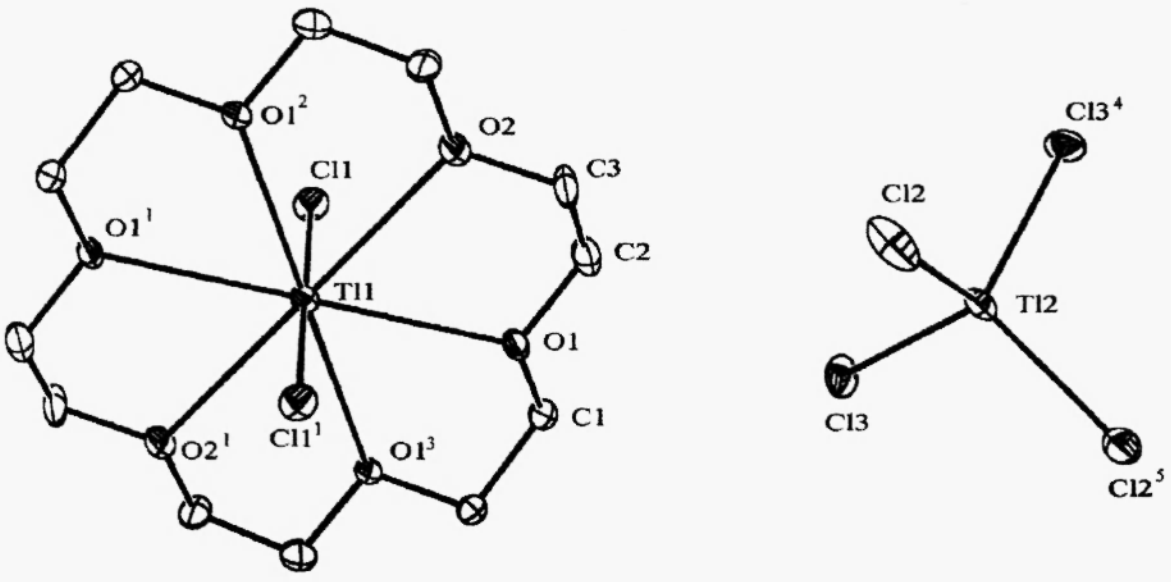

Figure 1. Molecular structure of $[TlCl_2(18\text{-crown-6})][TlCl_4]$. Selected bond lengths (Å) and angles(°): Tl(1)-Cl(1) 2.293(3), Tl(1)-O(1) 2.704(6), Tl(1)-O(2)2.709(6), Tl(2)-Cl(3) 2.400(4), Tl(2)-Cl(2) 2.415(4), O(1)-C(2) 1.39(1), O(1)-C(1) 1.43(1), O(2)-C(3) 1.43(1), C(2)-C(3) 1.50(1), Cl(1)-Tl(1)-O(2) 86.1(2), Cl(1)^1-Tl(1)-O(2) 93.9(2), Cl(1)-Tl(1)-O(1) 91.9(1), Cl(1)^1-Tl(1)-O(1) 88.1(1), Cl(3)-Tl(2)-Cl(2) 106.69(8), Cl(3)^4-Tl(2)-Cl(3) 113.6(2), Cl(2)-Tl(2)-Cl(2)^5 116.8(3), O(1)-Tl(1)-O(2) 60.01(14), Symmetry operator used to generate equivalent atoms: ^{1} –x, -y, -z+1; ^{2} –x, y, z; ^{3} x, -y, -z+1; ^{4} x, y, -z+1/2; ^{5} –x+1, y, z.

Comment

The thallium centre, Tl(1), in the compound has a slightly distorted hexagonal bipyramidal geometry and all the bond lengths to this centre are unexceptional. The other thallium centre, Tl(2), has a slightly distorted tetrahedral coordination environment. The cation has 2/m symmetery and the anion m2m symmetery. The overall geometry of the molecule is close to that seen in the isostructural compound, $[TlI_2(18\text{-crown-6})][TlI_4]$.[1]

Experimental

Preparation of $[TlCl_2(18\text{-crown-6})][TlCl_4]$:

18-crown-6 (0.40 g, 1.51 mmol), purified by recrystallisation from acetonitrile, was added in excess (*ca.* 1:1 equivalents) as an ethereal solution (20 cm^3) to a stirred solution of $TlCl_3$ (0.49 g, 1.58 mmol) cooled to –70 °C, also in ether (20 cm^3). The subsequent slurry was then allowed to warm to room temperature and stirred for a further 4 hours to yield a clear light yellow solution. Volatiles were removed *in-vacuo* and the resultant white solid recrystallised from THF (*ca.* 10 cm^3) to yield the title product as clear colourless prisms (0.53 g, 76 %), m.p. 194 °C (decomp.). ^{1}H NMR (400 MHz, CD_3CN, 300 K): δ 3.57 (br d, 24H, *c*-$(OC_2H_4)_6$, $^3J_{Tl}$ 8.2 Hz). ^{13}C NMR (100.6 MHz, CD_3CN, 300 K): δ 117.1 (s, *c*-$(C_2H_4O)_6$). MS APCI: *m/z* (%) 540 [(M-$TlCl_4$)$^+$, 100]. IR (Nujol) ν/cm^{-1}: 827 m, 972 m, 1106 m br, 1237 m, 1287 m sh, 1352 s sh. (Found: C, 16.39; H, 2.64. Calc. for $C_{12}H_{24}O_6Tl_2Cl_6$: C, 16.27; H, 2.73%).

Crystallography:

Table 1. Crystal data for [TlCl(18-crown-6)][TlCl$_4$]

Formula	$C_{12}H_{24}Cl_6O_6Tl_2$	Formula weight	885.75
Crystal system	orthorhombic	Crystal size, mm	0.40x0.30x0.20
Space Group	*Cmcm*	*a*, Å	12.246(2)
b, Å	9.103(2)	*c*, Å	22.342(4)
V, Å^3	2490.6(8)	*Z*	4
Diffractometer	CAD4	μ(Mo-K$_\alpha$), mm^{-1}	13.590
D_{calcd}, g cm^{-3}	2.362	*F*(000)	1632
θ_{max}, °	25.16	Reflns meas.	4736
Reflns unique	1196	Reflns with $I > 2\sigma(I)$	1038
$R(F^2)$, $R_w(F^2)$ (all data)	0.057, 0.125	ρ, e Å^{-3}	3.43 near Tl(2)
G.O.F	1.27	No. parameters	82
Absorp. correct. [2]	Difabs	Temp, K	150
Programs used	SHELX-97 [3], Ortep-3 [4]		
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.0785P)^2]$, where $P = (F_o^2+2F_c^2)/3$		
Deposition number	CCDC 169849		

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