Preparation and Crystal Structure of Quasi-cylindrical Crown Ether Complexes with Dimethyl- and Diethyl-thallium(III) Perchlorates†

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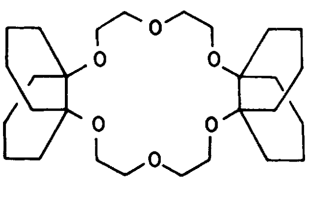
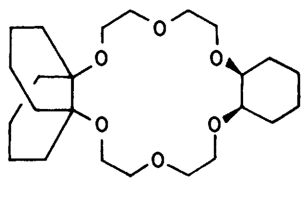
Complexes of quasi-cylindrical crown ethers with dimethyl- and diethyl-thallium(III) perchlorates have been prepared and their spin–spin coupling constants between the thallium nucleus and protons measured. The molecular structure of $[TlMe_2(L^1)]ClO_4$ {L^1 = 1,4,7,18,21,24-hexaoxaperhydro[7.7](4a,8a)naphthalenophane} has been determined by *X*-ray diffraction methods.

Although thousands of crown ethers have been synthesized and their complexes with spherical cations, such as alkali and alkaline-earth metal ions, have been widely investigated, little is known about the influence of topological changes of crown ethers on complexation with rod-like cations such as diorganothallium(III) ions. The present paper describes the preparation of quasi-cylindrical crown ether complexes with dimethyl- and diethyl-thallium(III) perchlorates and the structure determination of the complex $[TlMe_2(L^1)]ClO_4$.


L^1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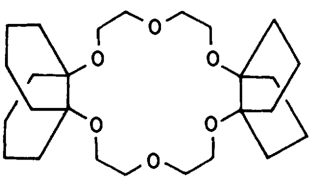
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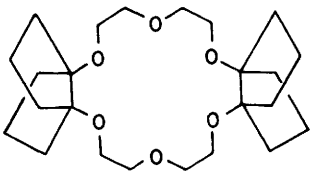
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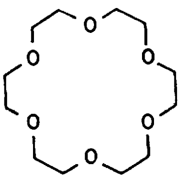
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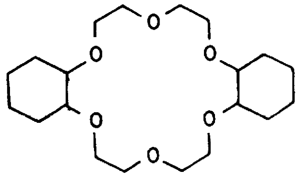
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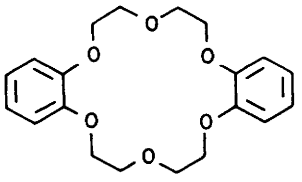
L^7

Results and Discussion

The desired complexes were easily obtained by a method similar to that described before.[1,2] Irrespective of the ring size of the constituent bicycloalkane, all the quasi-cylindrical crown ethers L^1—L^4 gave crystalline complexes with dimethylthallium(III) in good yield, as summarized in Table 1. With diethylthallium(III), bearing sterically bulkier groups, L^2, L^3, and L^4 gave complexes effectively, while L^1 did not form a complex at all even after a long reaction time, indicating that L^1 has selectivity for the molecular size of the guest molecule.

As shown in Table 2, ^1H n.m.r. spectra of these complexes show larger spin–spin coupling constants between the thallium nucleus and protons [$J(Tl–CH_3)$, $J(Tl–CH_2–CH_3)$, and $J(Tl–CH_2–CH_3)$] than those of L^5. In the case of L^2, the two methyl groups are not magnetically equivalent, as is observed in the complex *cis,syn,cis*-$[TlMe_2(L^6)][OC_6H_2(NO_2)_3\text{-}2,4,6]$.[1,3] It is well known that larger coupling constants reflect stronger co-ordination of ligands surrounding the thallium nucleus.[4] As a result, it is clear that thallium(III) ions are co-ordinated more strongly by the oxygen atoms of quasi-cylindrical crown ethers, L^1—L^4, than by those of L^5. From these data, we expect the thallium(III) ions to be situated in the centre of the quasi-cylindrical crown ethers.

The crystal structure analysis of $[TlMe_2(L^1)]ClO_4$ was performed to confirm the above reasoning. As shown in the Figure this complex has an approximate plane of symmetry, through O(2), O(5), and C(29)–Tl–C(30), analogous to the complex *cis,syn,cis*-$[TlMe_2(L^6)][OC_6H_2(NO_2)_3\text{-}2,4,6]$.[3] The Tl atom is situated in the O_6 plane [O(1)—O(6)] and the TlC_2 unit is perpendicular to this plane (88.7 and 87.2°). The bond angle of the TlC_2 unit is approximately linear (179°). The conformation of the two decalin moieties, forming side walls, takes a chair form; torsion angles, O(6)–C(1)–C(2)–O(1) and O(3)–C(7)–C(8)–O(4), are in a clockwise direction −56.3 and 56.2°, respectively. The C(1)–C(20), C(2)–C(16), C(7)–C(21), and C(8)–C(25) bonds are approximately perpendicular to the O_6 plane (87.6, 83.2, 82.8, and 85.5°, respectively). The distances of the methyl groups to the decalin wall are 3.81 from C(29) to C(16), 3.82 from C(29) to C(21), 3.85 from C(30) to C(20), and 3.97 Å from C(30) to C(25). These distances are slightly shorter than the sum of the van der Waals radii of two methyl groups (4.0 Å).

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† *Supplementary data available* (No. SUP 56562, 4 pp.): thermal parameters, least-squares plane data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical[a] (%) and other physical data for the complexes

Complex[b]	Yield (%)	C	H	M.p.[c]/°C
$[TlMe_2(L^5)]ClO_4$[d]	81	28.20 (28.10)	5.25 (5.05)	220—230 (d)
$[TlMe_2(L^2)]ClO_4$	65	41.30 (41.05)	6.50 (6.35)	219—221 (d)
$[TlMe_2(L^1)]ClO_4$	71	44.35 (44.25)	6.80 (6.70)	295—303 (d)
$[TlMe_2(L^3)]ClO_4$	67	43.05 (42.75)	6.55 (6.40)	258—286 (d)
$[TlMe_2(L^4)]ClO_4$	83	41.50 (41.15)	6.35 (6.10)	264—281 (d)
$[TlEt_2(L^5)]ClO_4$	81	30.80 (30.70)	5.45 (5.45)	>220
$[TlEt_2(L^2)]ClO_4$	88	42.55 (42.65)	6.85 (6.65)	195—229 (d)
$[TlEt_2(L^3)]ClO_4$	86	44.40 (44.25)	6.80 (6.70)	174—206 (d)
$[TlEt_2(L^4)]ClO_4$	68	42.85 (42.75)	6.60 (6.40)	180—230 (d)

[a] Calculated values are given in parentheses. [b] Recrystallized from acetone–light petroleum unless otherwise stated. [c] d = Decomposition. [d] Recrystallized from dichloromethane–n-hexane.

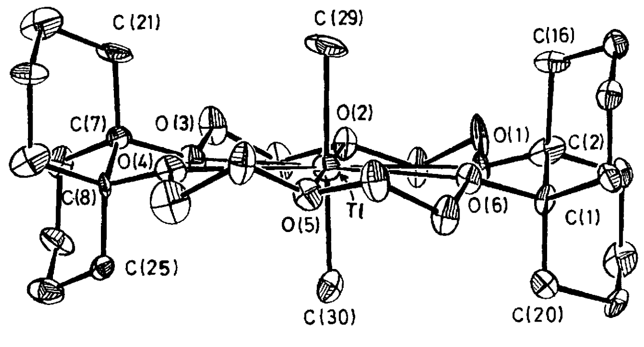

Figure. The structure of $[TlMe_2(L^1)]^+$

Table 2. Coupling constants (in Hz) and proton chemical shifts for the complexes

	$[TlMe_2(L)]ClO_4$	$[TlEt_2(L)]ClO_4$	
	$J(Tl\text{–}CH_3)$ (δ_H)[a]	$J(Tl\text{–}CH_2\text{–}CH_3)$ (δ_H)[b]	$J(Tl\text{–}CH_2\text{–}CH_3)$ (δ_H)[b]
$[TlMe_2]ClO_4$	400 (1.23)		
$[TlEt_2]ClO_4$		340 (1.92)[a]	611 (1.65)[a]
L^5	430 (0.89)	387 (1.61)[a]	636 (1.50)[a]
L^2	431 (1.01)	386 (1.70)	646 (1.49)
	437 (1.04)	401 (1.83)	648 (1.56)
L^1	434 (1.15)	*c*	*c*
L^3	437 (1.04)	400 (1.78)	646 (1.55)
L^4	440 (0.93)	410 (1.66)	647 (1.52)

[a] In CD_3CN, 100-MHz spectra. [b] In CD_3CN, 60-MHz spectra unless otherwise stated. [c] No complex was formed.

Table 3. Atomic co-ordinates, with estimated standard deviations in parentheses, for $[TlMe_2(L^1)]ClO_4$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Tl	0	0.24179(7)	0	C(15)	0.3214(23)	0.1721(31)	−0.1387(11)
O(1)	0.2177(12)	0.4067(19)	−0.0135(6)	C(16)	0.3041(23)	0.1996(30)	−0.0757(13)
O(2)	0.1951(15)	0.3191(22)	0.1079(7)	C(17)	0.3571(19)	0.5296(27)	−0.0665(11)
O(3)	−0.0362(13)	0.1846(22)	0.1182(7)	C(18)	0.2942(35)	0.7124(37)	−0.0709(18)
O(4)	−0.2269(12)	0.0768(20)	0.0087(8)	C(19)	0.1873(30)	0.7476(19)	−0.1213(13)
O(5)	−0.2004(15)	0.1673(22)	−0.1113(8)	C(20)	0.0741(20)	0.6108(28)	−0.1304(9)
O(6)	0.0343(13)	0.3041(21)	−0.1240(8)	C(21)	−0.0843(21)	−0.1303(30)	0.1223(16)
C(1)	0.1287(19)	0.4304(25)	−0.1300(8)	C(22)	−0.1749(38)	−0.2741(38)	0.1238(27)
C(2)	0.2505(21)	0.3918(26)	−0.0693(14)	C(23)	−0.3074(30)	−0.2381(26)	0.0627(13)
C(3)	0.3264(18)	0.4014(37)	0.0492(9)	C(24)	−0.3541(24)	−0.0471(31)	0.0681(13)
C(4)	0.2823(19)	0.4497(33)	0.1014(9)	C(25)	−0.3096(21)	0.2686(22)	0.0704(12)
C(5)	0.1598(22)	0.3380(37)	0.1646(10)	C(26)	−0.3281(24)	0.3151(35)	0.1325(16)
C(6)	0.0915(21)	0.1906(43)	0.1732(12)	C(27)	−0.1960(32)	0.2817(39)	0.1950(16)
C(7)	−0.1283(19)	0.0599(26)	0.1254(13)	C(28)	−0.1474(22)	0.1055(28)	0.1892(9)
C(8)	−0.2582(15)	0.0910(23)	0.0676(9)	C(29)	0.0818(25)	−0.0143(35)	0.0042(19)
C(9)	−0.3315(28)	0.0853(45)	−0.0518(12)	C(30)	−0.0761(25)	0.4984(30)	−0.0038(11)
C(10)	−0.2758(27)	0.0291(42)	−0.1079(15)	Cl	0.5473(9)	0.6119(14)	−0.1916(5)
C(11)	−0.1710(24)	0.1570(43)	−0.1685(14)	O(7)	0.4505(15)	0.4971(20)	−0.2197(8)
C(12)	−0.0953(23)	0.3042(40)	−0.1744(12)	O(8)	0.5996(15)	0.5987(19)	−0.1198(8)
C(13)	0.1476(23)	0.3908(30)	−0.1951(13)	O(9)	0.5808(15)	0.8323(21)	−0.1842(8)
C(14)	0.1935(26)	0.2122(31)	−0.1984(12)	O(10)	0.4596(20)	0.7498(15)	−0.1852(10)

Interestingly, bond distances from thallium to the oxygens O(1), O(3), O(4), and O(6), which are bonded to the decalin moieties, are much longer than those of the others (longer, 2.82—2.94; shorter, 2.61—2.68 Å). In the case of $[TlMe_2(L^6)][OC_6H_2(NO_2)_3\text{-}2,4,6]$, there are no significant differences between the bond distances from Tl to oxygens which are bonded to cyclohexane moieties and to those of the other oxygens (*cis,syn,cis* isomer: the former 2.68—2.98 and the latter 2.74—2.80 Å; *cis,anti,cis* isomer: the former 2.74—2.87 and the latter 2.76 Å, respectively).[3] Moreover, the longer distances are much longer and the shorter distances much shorter than those described in the complex $[TlMe_2(L^7)][OC_6H_2(NO_2)_3\text{-}2,4,6]$ (longer, 2.77—2.82; shorter 2.69—2.70 Å).[5] Consequently, the O_6 hexagon of $[TlMe_2(L^1)]^+$ is widely elongated in the direction of each decalin moiety. The steric effect of the decalin wall, as shown above, and the strong co-ordination of O(2) and O(5) might be the cause of the large spin–spin coupling observed (Table 2).

Table 4. Bond distances (Å) for $[TeMe_2(L^1)]ClO_4$

Tl–O(1)	2.842(14)	Tl–O(2)	2.608(17)
Tl–O(3)	2.818(17)	Tl–O(4)	2.890(18)
Tl–O(5)	2.677(18)	Tl–O(6)	2.939(17)
Tl–C(29)	2.170(42)	Tl–C(30)	2.150(28)
O(1)–C(2)	1.413(34)	O(1)–C(3)	1.450(32)
O(2)–C(4)	1.444(31)	O(2)–C(5)	1.451(34)
O(3)–C(6)	1.476(38)	O(3)–C(7)	1.457(33)
O(4)–C(8)	1.469(26)	O(4)–C(9)	1.400(39)
O(5)–C(10)	1.378(37)	O(5)–C(11)	1.419(38)
O(6)–C(1)	1.475(27)	O(6)–C(12)	1.445(35)
C(1)–C(2)	1.528(37)	C(1)–C(13)	1.556(31)
C(1)–C(20)	1.523(31)	C(2)–C(16)	1.630(42)
C(2)–C(17)	1.577(39)	C(3)–C(4)	1.459(39)
C(5)–C(6)	1.422(44)	C(7)–C(8)	1.538(34)
C(7)–C(21)	1.562(46)	C(7)–C(28)	1.541(38)
C(8)–C(24)	1.511(34)	C(8)–C(25)	1.500(33)
C(9)–C(10)	1.635(48)	C(11)–C(12)	1.451(46)
C(13)–C(14)	1.487(37)	C(14)–C(15)	1.556(38)
C(15)–C(16)	1.488(38)	C(17)–C(18)	1.566(47)
C(18)–C(19)	1.310(52)	C(19)–C(20)	1.596(40)
C(21)–C(22)	1.510(69)	C(23)–C(24)	1.588(43)
C(25)–C(26)	1.504(43)	C(27)–C(28)	1.491(43)

Experimental

^1H N.m.r. spectra were measured on JEOL JNM-PS-100 (100 MHz) and Hitachi R-600S (60 MHz) spectrometers, using $SiMe_4$ as internal standard and CD_3CN as solvent.

Preparation of Complexes.—Complexes were prepared by a method similar to that described before[1] in an appropriate solvent (propan-2-ol, acetone, or CD_3CN), and purified by recrystallization from acetone–light petroleum or dichloromethane–n-hexane.

Crystal Data.—$C_{30}H_{54}ClO_{10}Tl$, $M = 814.57$, monoclinic, $a = 11.075(3)$, $b = 7.753(2)$, $c = 22.052(7)$ Å, $\beta = 112.21(3)°$, $U = 1\,753$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 710\,69$ Å), space group Pc, $Z = 2$, $D_c = 1.54$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 47.8$ cm^{-1}, $F(000) = 824$; white needle of approximate dimensions 0.20 × 0.24 × 0.80 mm recrystallized from methanol.

Data Collection and Processing.—The data were collected on a Rigku automated four-circle diffractometer, θ—2θ scan, $0 < 2\theta < 55°$, graphite-monochromated Mo-K_α radiation, 4 257 unique reflections, 3 323 reflections with $I > 3\sigma(I)$. Absorption corrections were not applied.

Table 5. Selected bond angles (°) for $[TlMe_2(L^1)]ClO_4$

O(1)–Tl–O(2)	63.2(5)	O(2)–C(5)–C(6)	111(3)
O(2)–Tl–O(3)	63.3(6)	C(5)–C(6)–O(3)	108(3)
O(3)–Tl–O(4)	55.8(5)	C(6)–O(3)–C(7)	115(3)
O(4)–Tl–O(5)	61.7(6)	O(3)–C(7)–C(8)	106(2)
O(5)–Tl–O(6)	62.4(5)	C(7)–C(8)–O(4)	105(2)
O(6)–Tl–O(1)	54.2(5)	C(8)–O(4)–C(9)	117(3)
C(29)–Tl–C(30)	179(2)	O(4)–C(9)–C(10)	107(3)
		C(9)–C(10)–O(5)	104(3)
C(1)–C(2)–O(1)	108(3)	C(10)–O(5)–C(11)	111(3)
C(2)–O(1)–C(3)	116(2)	O(5)–C(11)–C(12)	112(3)
O(1)–C(3)–C(4)	110(3)	C(11)–C(12)–O(6)	112(3)
C(3)–C(4)–O(2)	110(3)	C(12)–O(6)–C(1)	118(2)
C(4)–O(2)–C(5)	115(2)	O(6)–C(1)–C(2)	102(2)

Structure Analysis and Refinement.—A Patterson function was used to determine the position of the thallium atom. The remaining atoms were located from Fourier maps. All the non-hydrogen atoms were refined anisotropically by block-diagonal least-square methods. R and R' values were 0.078 and 0.117, respectively. Atomic co-ordinates are given in Table 3, bond lengths in Table 4, and selected bond angles in Table 5.

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