Dimethylthallium(III) Complex of a Cylindrical Crown Ether: Molecular Structure of $[Tl(CH_3)_2(L)]ClO_4$†

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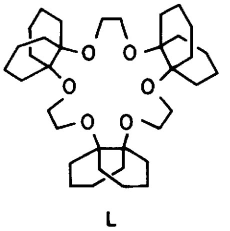
The complex $[Tl(CH_3)_2(L)]ClO_4$ was prepared from tridecalino-18-crown-6 {1,4,15,18,29,32-hexaoxaperhydro[4.4.4](4a,8a)naphthalenophane} (L) and dimethylthallium(III) perchlorate. The molecular structure has been determined by single-crystal *X*-ray diffraction methods. The O_6 hexagon of the crown ether is planar within 0.05 Å and the decalin moieties apparently construct a cylinder wall. The linear dimethylthallium(III) ion penetrates into the centre of the O_6 hexagon with six equal Tl–O bonds and the decalin walls are in contact with methyl groups of the dimethylthallium(III) ion.

In previous papers,[1–3] we have revealed that decalin (perhydronaphthalene) moieties incorporated into an 18-crown-6 system enhance the complexing ability as well as the complexing selectivity for a specific metal ion. We ascribed these properties to the embedding effect of the decalin moieties on a co-ordinated cation, by which the cation is buried deep in the lipophilic cylinder. The cation is shielded from attack by the solvent and/or the counter anion in the decomplexing process.[3] To obtain further information about the embedding effect of decalin moieties, we have now synthesized tridecalino-18-crown-6 (L) {1,4,15,18,29,32-hexaoxaperhydro[4.4.4](4a,8a)-naphthalenophane}, in which three decalin moieties are arranged alternately in expectation of a more efficient embedding effect by forming a cylindrical wall. In this paper, we wish to report the *X*-ray structure analysis of $[Tl(CH_3)_2(L)]ClO_4$. This complex is a good model for assessing the embedding effect of the decalin walls on the co-ordinated cation, since the determination of interatomic distances from the decalin walls to the methyl groups attached to Tl may clarify whether or not there is close contact between the decalin walls and the guest cation.

Experimental

Preparation of $[Tl(CH_3)_2(L)]ClO_4$.—A mixture of tridecalino-18-crown-6 (13.4 mg, 0.023 mmol), dimethylthallium(III) perchlorate (10.7 mg, 0.032 mmol), and propan-2-ol (1 cm³) was heated in a sealed glass ampoule at 105 °C for 4 d. The resulting precipitate was filtered off, washed with propan-2-ol, and dried *in vacuo* to give 17.5 mg (83%) of the complex which was recrystallized from dichloromethane–methanol (m.p. >300 °C) (Found: C, 49.45; H, 7.25. Calc. for $C_{38}H_{66}ClO_{10}Tl$: C, 49.45; H, 7.20%). The first crystal obtained from dichloromethane–methanol revealed many diffused streaks overlapping with the Bragg spots on the Weissenberg photographs. The second crystal obtained from dichloromethane–diisopropyl ether was rather unstable and powder rings were observed on the oscillation photograph after short time *X*-ray irradiation. A stable single crystal suitable for *X*-ray analysis was finally obtained from dichloromethane–acetonitrile.



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Crystal Data.—$C_{38}H_{66}ClO_{10}Tl$, $M = 922.76$, trigonal, space group $R\bar{3}c$, unit cell in hexagonal axes, $a = 12.502(3)$, $c = 42.675(14)$ Å, $U = 5776.5(21)$ Å³ (by least-squares refinement on diffractometer angles of 50 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 6$, $D_c = 1.591$ g cm^{-3}, μ(Mo-K_α) = 43.6 cm^{-1}, and $F(000) = 2\,832$. White crystals with approximate dimensions 0.13 × 0.15 × 0.20 mm.

Data Collection and Processing.—Intensity data were collected on a Rigaku automated four-circle diffractometer, θ–2θ scan, graphite monochromatized Mo-K_α radiation, 2 832 reflections measured ($0 < 2\theta < 60°$), 1 387 reflections observed [$|F_o| > 3\sigma(|F_o|)$]. Absorption correction not applied.

Structure Analysis and Refinement.—Systematic absences (*hkil*: $-h + k + l = 3n \pm 1$ and $\bar{h}0l$: $l = 2n + 1$) showed that the crystal belonged to the trigonal space group $R\bar{3}c$. In addition to these absences, the extra absence (*hkil*: $l = 2n + 1$) was clearly observed. From Patterson maps and a Z value of 6, the thallium atom was located at $0,0,\frac{1}{4}$ with D_3 molecular symmetry. The difference Fourier maps phased by the thallium atom showed the pseudo-mirror symmetry on plane c. Thus, the remaining non-hydrogen atoms were located with the aid of geometrical considerations. The structure was refined anisotropically by full-matrix least-squares methods. The R and R' values were 0.066 and 0.099 respectively. The weighting function applied was $w = (\sigma_c + 0.003|F_o|^2)^{-1}$, where σ_c was the standard deviation estimated from counting statistics. All computations were performed on an ACOS S850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University using the *X*-RAY SYSTEM.[4] Figures 1 and 2 were drawn using ORTEP.[5]

Results and Discussion

The title complex was easily prepared using a previously described method.[6] Irrespective of the steric hindrance of the

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† {1,4,15,18,29,32-Hexaoxaperhydro[4.4.4](4a,8a)naphthalenophane}-dimethylthallium(III) perchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates for the non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tl	0	0	0.25
O(1)	0.119 7(5)	0.258 4(6)	0.251 1(2)
C(1)	0.241 4(9)	0.302 1(8)	0.239 8(3)
C(2)	0.062 6(9)	0.330 2(7)	0.241 8(2)
C(3)	0.049 9(12)	0.321 8(11)	0.205 7(2)
C(4)	−0.032 8(12)	0.374 8(14)	0.194 1(3)
C(5)	0.162 5(12)	0.470 9(11)	0.288 9(3)
C(6)	0.142 6(10)	0.466 0(9)	0.252 9(3)
C(7)	0	0	0.200 8(4)
Cl	0	0	0
O(2)	0	0	−0.028 4(11)
O(3)	0.013 9(20)	0.117 0(20)	0.019 2(6)

Table 2. Selected bond distances and contact distances (Å), and bond angles(°)

Tl–O(1)	2.801(7)	Tl–C(7)	2.099(18)
O(1)–C(1)	1.419(13)	O(1)–C(2)	1.454(15)
C(1)–C(1′′′′′)	1.577(18)	C(2)–C(2′)	1.528(13)
C(2)–C(3)	1.547(13)	C(2)–C(6)	1.553(12)
C(3)–C(4)	1.562(25)	C(4)–C(5′)	1.581(18)
C(5)–C(6)	1.554(19)	C(5)–C(4′)	1.581(18)
C(3) ··· C(7)	3.757(14)		
C(7)–Tl–C(7′)	180	C(7)–Tl–O(1)	91.0(2)
O(1)–Tl–O(1′)	55.2(3)	O(1)–Tl–O(1′′′′′)	64.9(3)
Tl–O(1)–C(1)	106.9(6)	Tl–O(1)–C(2)	124.3(4)
C(1)–O(1)–C(2)	115.5(8)	C(1′′′′′)–C(1)–O(1)	108.0(9)
O(1)–C(2)–C(2′)	104.5(9)	O(1)–C(2)–C(3)	107.3(10)
O(1)–C(2)–C(6)	110.1(9)	C(2′)–C(2)–C(3)	112.3(8)
C(2′)–C(2)–C(6)	110.7(10)	C(3)–C(2)–C(6)	111.6(8)
C(2)–C(3)–C(4)	110.8(12)	C(3)–C(4)–C(5′)	110.7(14)
C(4′)–C(5)–C(6)	109.3(10)	C(5)–C(6)–C(2)	110.4(9)

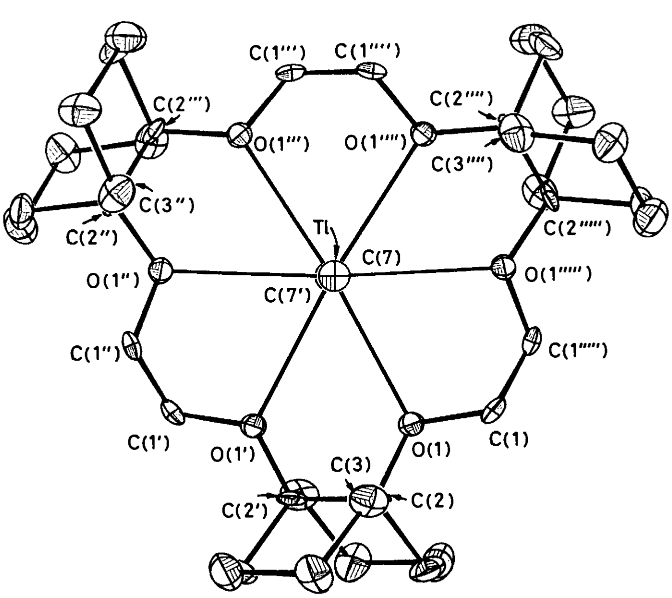

Figure 1. Top view of $[Tl(CH_3)_2(L)]^+$ with 30% probability ellipsoids

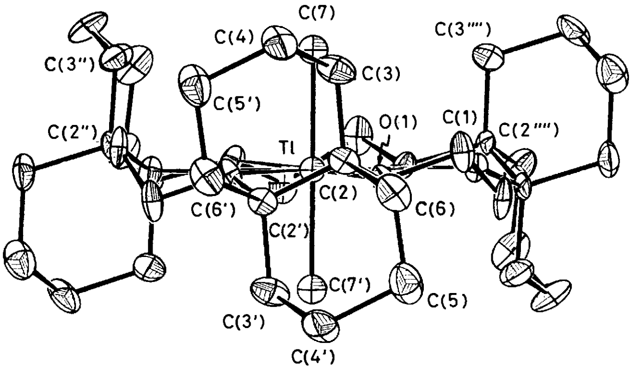

Figure 2. Side view of $[Tl(CH_3)_2(L)]^+$ with 30% probability ellipsoids

three decalin moieties and the rigidity of the crown ether ring, L gave the complex in 83% yield. The molecular structure was determined by *X*-ray diffraction techniques. The fractional atomic co-ordinates and the selected interatomic distances are listed in Tables 1 and 2 respectively. As the molecule has D_3 symmetry, only one sixth of it is crystallographically independent. The crystallographic C_3 axis passes through C(7), Tl, and C(7′), while C_2 passes through the midpoint of the C(2)–C(2′) bond, through Tl, and through the midpoint of the C(1′′′)–C(1′′′′) bond. The O_6 plane comprising the O(1), O(1′), O(1′′), O(1′′′), O(1′′′′), and O(1′′′′′) atoms is planar within 0.05 Å. The dimethylthallium(III) ion is nicely threaded through the cavity of L and the Tl atom lies on the centre of this O_6 plane. The six Tl–O distances are equivalent [2.801(7) Å] (Figure 1 and Table 2), indicating no difference between the co-ordination of the six oxygens. On the other hand, in other complexes formed between dimethylthallium(III) and 18-crown-6 derivatives, such as didecalino- and dibenzo-18-crown-6,* there are two types of Tl–O bonds and the O_6 hexagons of the crown ethers are widely elongated in the direction of the decalin or benzene moieties {didecalino-18-crown-6:[7] Tl–O(decalin) 2.818(17)—2.939(17) and Tl–$O(CH_2)_2$ 2.608(17)—2.677(18); dibenzo-18-crown-6:[8] Tl–O(benzene) 2.769(8)—2.818(11) and Tl–$O(CH_2)_2$ 2.694(10)—2.698(9) Å}. In addition, in the case of the dimethylthallium(III) complex of dicyclohexyl-18-crown-6,[9,†] the bond distances from thallium to the axial oxygens which are bonded to the cyclohexane moieties are longer than those to the equatorial ones [*cis,syn,cis* isomer: Tl–$O_{ax.}$ 2.805(5)—2.979(5) and Tl–O_{eq} 2.677(5)—2.782(5); *cis,anti,cis* isomer: Tl–O_{ax} 2.867(5) and Tl–O_{eq} 2.736(5) Å].

The dimethylthallium(III) ion is perpendicular to the O_6 plane because of the D_3 molecular symmetry. The three decalin moieties take chair forms and construct an apparent cylinder wall defined by the C(2)–C(3), C(2′′)–C(3′′), and C(2′′′′)–C(3′′′′) bonds. This cylinder is approximately perpendicular to the O_6 plane (84.8°). The dimethylthallium(III) ion is buried deep in the cylinder as shown in Figure 2. The distances from the decalin walls to the methyl group attached to Tl [C(3)–C(7), C(3′′)–C(7), and C(3′′′′)–C(7)] are 3.757(14) Å. Interestingly, these distances are shorter than the sum of the van der Waals radii of methyl and methylene groups (4.0 Å), indicating that the dimethylthallium(III) ion contacts with the cylinder of decalin walls by hydrophobic interaction. This effect may protect the complex from attack by the solvent and/or counter anion in the decomplexation process.[3]

The perchlorate anion lies on the three-fold rotoinversion axis (0,0,0) and exhibits packing disorder.

In conclusion, decalin moieties incorporated alternately into an 18-crown-6 system construct a lipophilic cylinder wall and, as a result, the co-ordinated cation is embedded in it.

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* 1,4,7,18,21,24-Hexaoxaperhydro[7.7](4a,8a)naphthalenophane and 6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclo-octadecin respectively.

† Icosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclo-octadecin.

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