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Structures of Complexes between Dimethylthallium Picrate and Two Isomers of Dicyclohexano-18-crown-6*

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Abstract

The crystal structures of complexes formed by dimethylthallium picrate with two isomers of dicyclohexano-18-crown-6 have shown that in both there are [Me$_2$Tl crown]$^+$ cations and picrate anions, the complex cations consisting of linear Me$_2$Tl entities normal to the plane through the six O atoms of the ligand and the Tl atom. For isomer *A*, *cis-cisoid-cis*-dicyclohexano-18-crown-6, the complex **A** is formed: [Tl(CH$_3$)$_2$(C$_{20}$H$_{36}$O$_6$)].C$_6$H$_2$N$_3$O$_7$, C$_{22}$H$_{42}$O$_6$-Tl$^+$.C$_6$H$_2$N$_3$O$_7^-$, M_r = 835·0, triclinic, $I\bar{1}$ (variation of $P\bar{1}$), $a = 11·359$ (2), $b = 19·772$ (3), $c = 14·904$ (2) Å, $\alpha = 95·55$ (1), $\beta = 90·65$ (1), $\gamma = 94·58$ (1)°, $V = 3320·5$ Å^3, $Z = 4$, $D_x = 1·670$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 49·8$ cm^{-1}, $F(000) = 1672$, $R = 0·036$ for 3067 reflections with above zero intensities. The cation has an approximate plane of symmetry through the dimethylthallium group and the O atoms in $-$CH$_2$$-O-CH_2-$ groups. This gives a different conformation for the ligand from that, with approximate 2 symmetry, in other complexes of isomer *A*. For isomer *B*, *cis-transoid-cis*-dicyclohexano-18-crown-6, the complex **B** is formed: [Tl(CH$_3$)$_2$(C$_{20}$H$_{36}$-O$_6$)].C$_6$H$_2$N$_3$O$_7$, C$_{22}$H$_{42}$O$_6$Tl$^+$.C$_6$H$_2$N$_3$O$_7^-$, M_r = 835·0, triclinic, $P\bar{1}$, $a = 8·137$ (2), $b = 8·205$ (3), $c = 13·201$ (3) Å, $\alpha = 94·16$ (2), $\beta = 96·71$ (2), $\gamma = 108·63$ (3)°, $V = 823·8$ Å^3, $Z = 1$, $D_x = 1·683$ g cm^{-3},

Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 50·1$ cm^{-1}, $F(000) = 418$, $R = 0·038$ for all 2142 (all observed) reflections. The Tl atom lies on, and the picrate anion is disordered about, centres of symmetry. The conformation of the ligand with $\bar{1}$ symmetry is the same as that found in the sodium complex. In both complexes, on each cyclohexane ring one O atom is axially and one equatorially substituted; these are at significantly different distances from the Tl atom, the former giving the longer bond. An explanation, applicable also to other complexes, is that of steric hindrance between the equatorial H atom on a cyclohexane carbon and a H atom of the macrocyclic ring.

Introduction

Comparison of the formation constants for dibenzo-18-crown-6 and the two isomers obtained by hydrogenation with *cis* substitution on the ring junctions shows that the *cis-cisoid-cis* isomer *A* has a higher value than the *cis-transoid-cis* isomer *B*. (Formulae are in Fig.1.) According to the cation and solvent, however, the value of the formation constant for dibenzo-18-crown-6 may be higher or lower than or between isomers *A* and *B* (Frensdorff, 1971; Izatt *et al.*, 1976). This is unexpected because O atoms attached to aliphatic C atoms are normally more electronegative than those attached to aromatic C atoms, consistent with the value for dibenzo-18-crown-6 being the lowest. Similar variations in formation constant are found for macrobicyclic compounds, the [222], [benzo 222] and [dibenzo 222] cryptands (Lehn, 1973) and Parsons'

macrobicyclic compounds with carbon bridgehead atoms (Parsons, 1978; Hanson, Parsons & Truter, 1979; Bandy, Parsons & Truter, 1981).

No kinetic measurements have been made of isomer A and isomer B with the same metallic cations. For isomer B and dibenzo-18-crown-6 the reaction with sodium in methanol was studied by Shchori, Jagur-Grodzinski & Shporer (1973); they found that the explanation for the difference in the stability constants, 4·8 times higher for the latter than for the former, lay in the rate of formation being 1·2 times faster and the rate of dissociation being 3·7 times slower for the dibenzo-18-crown-6 than for the dicyclohexyl compound. Other systems with cyclic ethers and with the bicyclic cryptands (Cox, Garcia-Rosas & Schneider, 1981) have all established the same pattern; discrimination arises from greater changes in the rate of decomplexation than those in the rate of formation. This suggests that structural investigation of the complexes may give an insight into the first stage of reaction in solution.

Crystal-structure determinations have been reported in full for the isomer B complex with diaquasodium bromide (Mercer & Truter, 1973), and in preliminary form for complexes of isomer A with lanthanum nitrate (Harman, Hart, Hursthouse, Moss & Raithby, 1976), barium thiocyanate monohydrate (Dalley, Smith, Izatt & Christensen, 1972) and uranium as the UCl_4^+ cation (de Villardi et al., 1978) and also for the uncomplexed ligands (Dalley, Smith, Larson, Christensen & Izatt, 1975). The coordinates are available through various sources enabling us to use them for comparison. The
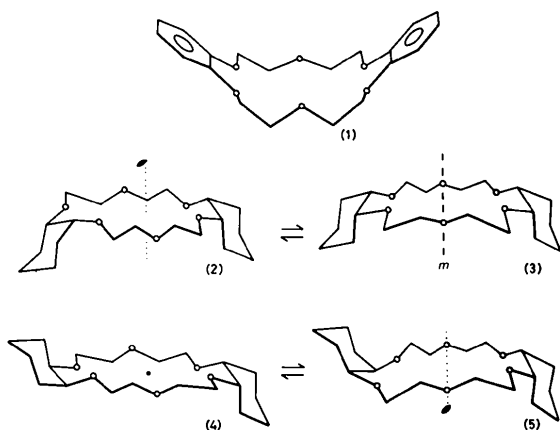
reported isolation of complexes formed from the same cation and anion, dimethylthallium picrate, by each of the dicyclohexano-18-crown-6 isomers, A and B (Kawasaki & Kitano, 1978), has provided the crystals for the present study with the additional interest that those authors had measured the ¹H NMR spectra in CDCl₃. A recent preliminary communication of the structure of dimethylthallium picrate complex with dibenzo-18-crown-6 (Henrick, Matthews, Podejma & Tasker, 1982) allows further comparison. A preliminary account of the crystal-structure determinations of the dimethylthallium picrate complexes, A (with isomer A) and B (with isomer B), has appeared (Hughes & Truter, 1982). We now give the experimental details and a discussion of the chemical significance.

Experimental

The fine yellow needles of both samples received from Dr Kawasaki (Kawasaki & Kitano, 1978) were recrystallized, A from acetone/petroleum ether, and B from acetone/2-propanol. The crystal of A selected for X-ray analysis had a flat needle shape, 0·03 × 0·11 × 0·24 mm. Crystals of B were rather thicker and larger, approximately square prisms; the selected crystal was 0·10 × 0·12 × 0·26 mm.

Preliminary photographs indicated that both crystals were triclinic, that A was most conveniently considered

Fig. 1. Structural formulae of dibenzo-18-crown-6 (1) and of dicyclohexano-18-crown-6 (2)–(5). The cis-cisoid-cis isomer, A, is shown diagrammatically with a twofold axis of symmetry in (2) and a plane of symmetry in (3); (2) and (3) are related by inversion of one cyclohexano ring, inversion of both converts (2) to its non-superimposable mirror image. The cis-transoid-cis isomer, B, is shown diagrammatically with a centre of symmetry in (4) and a twofold axis in (5); (4) and (5) are related by inversion of one cyclohexano ring. The symmetry specified is the maximum attainable; in all the crystal structures analysed to date (see text), the observed conformations have contained these symmetry elements either precisely or very closely.

Fig. 2. The [(CH₃)₂Tl(cis-cisoid-cis-dicyclohexano-18-crown-6, isomer A)]⁺ cation as found in the crystal structure of the picrate, A. The numbering of the non-hydrogen atoms and of some H atoms is shown. H atoms are numbered to correspond to the C atoms to which they are bonded.

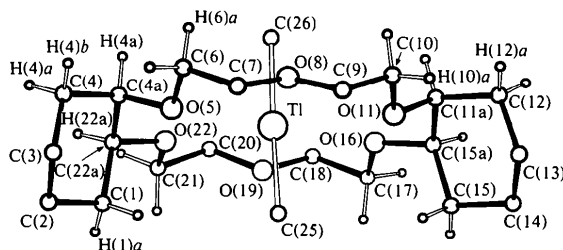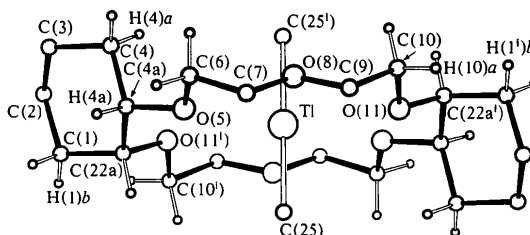Fig. 3. The [(CH₃)₂Tl(cis-transoid-cis-dicyclohexano-18-crown-6, isomer B)]⁺ cation as found in the crystal structure of the picrate, B. The numbering of the non-hydrogen atoms of the asymmetric unit, and a few of those at −x,−y,−z (distinguished by the Roman superscript i) is shown. Some H atoms are also shown with their designations.
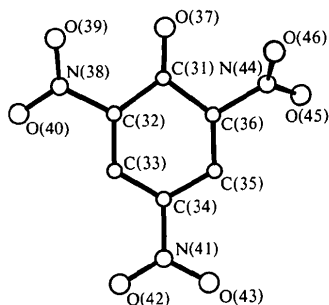
Fig. 4. The picrate anion of **A**. The atomic numbering scheme of the anions is the same in **A** and **B**.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for the refined atoms of* **A**

E.s.d.'s are in parentheses. U_{eq} [$= \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$] values are marked with a dagger.

	x	y	z	U_{iso}/U_{eq}
Tl	3134·3 (3)	2912·8 (2)	5221·2 (2)	42·1 (1)†
C(1)	1870 (8)	4280 (5)	7294 (6)	66 (3)
C(2)	2304 (9)	4701 (5)	8179 (7)	80 (3)
C(3)	3629 (8)	4717 (5)	8309 (6)	70 (3)
C(4)	4239 (9)	4955 (5)	7486 (6)	69 (3)
C(4a)	3844 (7)	4507 (4)	6633 (6)	52 (2)
O(5)	4093 (4)	3799 (2)	6677 (3)	45 (2)†
C(6)	5313 (7)	3701 (4)	6820 (6)	52 (2)
C(7)	5440 (8)	2964 (4)	6864 (6)	55 (2)
O(8)	5206 (4)	2607 (3)	5984 (3)	48 (2)†
C(9)	5393 (8)	1904 (4)	5944 (5)	53 (2)
C(10)	5251 (7)	1584 (4)	5008 (6)	56 (2)
O(11)	4053 (4)	1559 (3)	4730 (3)	45 (2)†
C(11a)	3848 (7)	1347 (4)	3785 (5)	49 (2)
C(12)	4250 (8)	632 (4)	3533 (6)	67 (3)
C(13)	3587 (9)	106 (6)	4034 (7)	85 (3)
C(14)	2268 (9)	112 (5)	3914 (8)	84 (3)
C(15)	1856 (8)	821 (4)	4137 (6)	61 (2)
C(15a)	2553 (7)	1330 (4)	3607 (6)	50 (2)
O(16)	2224 (4)	2017 (3)	3780 (3)	49 (2)†
C(17)	1053 (8)	2114 (4)	3497 (6)	57 (2)
C(18)	967 (8)	2863 (4)	3449 (6)	59 (2)
O(19)	1084 (5)	3205 (3)	4331 (3)	50 (2)†
C(20)	1064 (8)	3920 (4)	4329 (6)	60 (2)
C(21)	1140 (8)	4249 (5)	5286 (6)	68 (3)
O(22)	2219 (4)	4102 (3)	5670 (3)	51 (2)†
C(22a)	2561 (7)	4517 (4)	6499 (5)	50 (2)
C(25)	2092 (9)	2390 (5)	6126 (6)	62 (4)†
H(25)a	1771 (108)	2015 (41)	5695 (72)	245 (84)
H(25)b	2478 (74)	2204 (47)	6626 (42)	97 (37)
H(25)c	1454 (63)	2664 (47)	6337 (63)	124 (46)
C(26)	4215 (8)	3399 (5)	4288 (6)	60 (4)†
H(26)a	4948 (51)	3656 (41)	4492 (68)	114 (42)
H(26)b	3719 (75)	3705 (41)	4011 (69)	123 (46)
H(26)c	4290 (107)	2966 (31)	3949 (90)	241 (86)
C(31)	7701 (7)	3669 (4)	4893 (5)	48 (2)
C(32)	8177 (7)	3467 (4)	5730 (5)	50 (2)
C(33)	8477 (7)	2832 (4)	5849 (5)	47 (2)
C(34)	8384 (7)	2333 (4)	5146 (5)	48 (2)
C(35)	7971 (6)	2455 (4)	4301 (5)	41 (2)
C(36)	7687 (7)	3085 (4)	4198 (5)	48 (2)
O(37)	7316 (6)	4209 (3)	4777 (4)	75 (3)†
N(38)	8310 (6)	3972 (4)	6515 (5)	57 (3)†
O(39)	8366 (7)	4571 (4)	6413 (4)	92 (3)†
O(40)	8406 (7)	3775 (4)	7262 (5)	92 (3)†
N(41)	8712 (7)	1658 (4)	5277 (6)	62 (3)†
O(42)	9103 (7)	1544 (3)	6017 (5)	87 (3)†
O(43)	8603 (8)	1218 (3)	4640 (5)	94 (3)†
N(44)	7267 (8)	3226 (5)	3289 (5)	63 (3)†
O(45)	6465 (7)	2856 (5)	2931 (4)	94 (3)†
O(46)	7808 (9)	3686 (4)	2945 (5)	110 (4)†

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for the refined atoms of* **B**

The thallium atom, at the origin, and the picrate ion, disordered about ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$), were treated as having site occupancy factors of 0·5. E.s.d.'s are in parentheses.

U_{eq} values (defined in Table 1) are marked with an asterisk.

	x	y	z	U_{iso}/U_{eq}
Tl	0	0	0	47·0 (2)*
C(1)	1254 (12)	−892 (12)	−3683 (7)	72 (2)
C(2)	−297 (12)	−2466 (13)	−4120 (7)	76 (2)
C(3)	−185 (13)	−4018 (13)	−3642 (7)	77 (2)
C(4)	−10 (11)	−3738 (11)	−2479 (6)	67 (2)
C(4a)	1570 (10)	−2145 (10)	−2065 (6)	56 (2)
O(5)	1817 (7)	−1778 (7)	−965 (4)	56 (2)*
C(6)	2366 (12)	−3013 (12)	−433 (6)	67 (2)
C(7)	2978 (11)	−2277 (12)	668 (6)	67 (2)
O(8)	1522 (7)	−2033 (7)	1088 (4)	57 (2)*
C(9)	1973 (11)	−1450 (11)	2156 (6)	64 (2)
C(10)	392 (11)	−1250 (12)	2561 (7)	69 (2)
O(11)	58 (7)	207 (6)	2182 (6)	56 (2)*
C(22a)	1410 (10)	−558 (10)	2518 (5)	55 (2)
C(25)	2346 (12)	2140 (11)	229 (7)	70 (3)*
H(25)a	2965 (119)	1907 (133)	863 (43)	99 (34)
H(25)b	2031 (167)	3171 (108)	379 (81)	145 (53)
H(25)c	3053 (141)	2167 (170)	−318 (61)	157 (58)
C(31)	5005 (18)	2890 (16)	4003 (10)	49 (3)
C(32)	5138 (20)	4686 (19)	4189 (11)	53 (4)
C(33)	5059 (23)	5538 (18)	5079 (11)	64 (4)
C(34)	4875 (22)	4656 (20)	5924 (11)	58 (4)
C(35)	4838 (19)	2935 (17)	5867 (11)	55 (3)
C(36)	4868 (17)	2103 (15)	4944 (10)	47 (3)
O(37)	5021 (17)	2130 (20)	3184 (10)	71 (3)
N(38)	5420 (18)	5644 (20)	3305 (10)	63 (3)
O(39)	6166 (31)	5375 (31)	2584 (16)	134 (7)
O(40)	4507 (42)	6437 (43)	2977 (28)	209 (13)
N(41)	4832 (19)	5526 (21)	6890 (11)	69 (3)
O(42)	5055 (21)	7077 (25)	6978 (12)	93 (4)
O(43)	4902 (26)	4750 (24)	7658 (13)	110 (5)
N(44)	4805 (15)	331 (13)	4930 (9)	51 (3)
O(45)	5805 (22)	19 (27)	5601 (12)	94 (4)
O(46)	3717 (22)	−765 (23)	4334 (13)	100 (5)

as $I\bar{1}$ (or $I1$), and that **B** was either $P1$, or $P\bar{1}$ with centrosymmetry in the molecule.

Intensities were measured on an Enraf–Nonius CAD-4 diffractometer and were corrected by Lorentz, polarization, absorption and (slight) deterioration factors. For **A**, 3084 independent reflections ($1 \cdot 3 < \theta < 20°$) were measured; 2716 of these were considered observed, with $I > 2\sigma_I$, and 3067 had positive net intensities. For **B**, of 2142 independent reflections ($1 \cdot 3 < \theta < 22 \cdot 5°$) measured, none had $I \le 2\sigma_I$.

Both structures were solved from Patterson and electron-density maps, and showed distinct [Me$_2$Tl crown]$^+$ and picrate ions. The atomic numbering schemes are in Figs. 2, 3 and 4. Refinements, with *SHELX* (Sheldrick, 1976), showed both structures to be in the centrosymmetric space groups; in **B** the [Me$_2$Tl crown]$^+$ moiety is therefore centrosymmetric with the Tl on a centre of symmetry [at (0,0,0)], and the picrate ion is disordered about the centre at ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$).

For the refinement process, scattering curves were taken from *International Tables for X-ray Crystallog-*

raphy (1974). In **A**, the Tl, O, N and methyl C atoms were allowed anisotropic thermal parameters, and the H atoms of the crown ligand and picrate ion were constrained to ride, in geometrically ideal positions, on their bonded C atoms. The methyl-group H atoms, located in a difference map, were constrained towards a reasonable CH_3 group in the refinement process. The best weighting analysis was achieved with the refined weighting scheme $w = 1/[\sigma^2(F_o) + 0.000995\ F_o^2]$, and at convergence R and R' were 0.0358 and 0.0352 for 3067 reflections. Atomic coordinates are in Table 1.*

The refinement of **B** followed a similar course, except that some of the half-atoms of the disordered picrate ion had to be constrained (towards bond lengths derived from the structure of **A**) because the two possible sites for the ions were partly overlapping. No anisotropic motion was allowed for in the refinement of the parameters of the picrate ion. At convergence, R and R' were 0.0383 and 0.0391 for the 2142 reflections, with a weighting scheme $w = 1/[\sigma^2(F_o) + 0.002428\ F_o^2]$. Atomic coordinates are in Table 2.

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* Lists of stucture factors, anisotropic thermal parameters. H-atom parameters in idealized positions, the results of mean-plane calculations, some bond lengths and torsion angles and short intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38282 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Molecular-geometry programs were written and adapted by Owen (1981) and were run on a Prime 550 computer. This computer and the ICL System 4 in Rothamsted Experimental Station were used for all other computations.

Results

Both crystals contain complex cations and separate anions; as discussed below, the packing does not suggest that intermolecular forces would have a large effect on the cation geometry. The cations, shown in Figs. 2 and 3, consist of nearly, in **A**, or exactly, in **B**, linear dimethylthallium entities surrounded by, and normal to, six nearly coplanar O atoms of the ligands. The cyclohexane rings in **A** and **B** are all chair shaped, and on each there is one axially and one equatorially substituted O atom, the axial ones being O(5) and O(11) in **A**, O(11) and O(11^i)* in **B**, so that the conformations of the molecules correspond to forms (3) and (4) of Fig. 1. [Note that we refer to axial and equatorial substituents on the cyclohexane rings and have avoided in this paper referring to the coordination about Tl as 'axial' (to the methyl groups) and 'equatorial' (to the O atoms).]

Bond lengths and angles involving the Tl atoms are in Table 3. Selected torsion angles in the ligands are in

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* Symmetry code: (i) $-x, -y, -z$.

Table 3. *Bond lengths* (Å) *and angles* (°) *involving thallium atoms*

Complex	A	B		A
Tl—C(25)	2.097 (9)	2.113 (9)	Tl—C(26)	2.115 (8)
Tl—O(5)	2.805 (5)	2.736 (5)	Tl—O(16)	2.782 (5)
Tl—O(8)	2.737 (5)	2.762 (5)	Tl—O(19)	2.795 (5)
Tl—O(11)	2.979 (5)	2.867 (5)	Tl—O(22)	2.677 (5)

Angles a—Tl—b
Complex A

a	b C(26)	O(5)	O(8)	O(11)	O(16)	O(19)	O(22)
C(25)	177.5 (4)	89.2 (3)	93.2 (3)	84.2 (3)	90.9 (3)	89.6 (3)	93.8 (3)
C(26)		92.2 (3)	85.6 (3)	93.3 (3)	87.6 (3)	91.5 (3)	88.7 (3)
O(5)			62.4 (1)	121.6 (1)	178.8 (1)	120.3 (1)	59.7 (1)
O(8)				60.2 (1)	116.4 (2)	176.2 (1)	121.5 (2)
O(11)					57.2 (1)	117.6 (1)	177.6 (1)
O(16)						61.0 (1)	121.5 (2)
O(19)							60.8 (2)

Complex B

a	b C(25^i)	O(5)	O(8)	O(11)
C(25)	180	86.4 (3)	93.1 (3)	88.9 (3)
O(5)			60.4 (1)	121.3 (1)
O(8)				61.5 (1)

Angles at the coordinated oxygen atoms

	Complex A	Complex B		Complex A
Tl—O(5)—C(4a)	113.7 (4)	121.9 (4)	Tl—O(16)—C(15a)	123.3 (4)
Tl—O(5)—C(6)	110.8 (4)	118.4 (4)	Tl—O(16)—C(17)	115.4 (5)
Tl—O(8)—C(7)	112.8 (4)	113.2 (4)	Tl—O(19)—C(18)	112.1 (5)
Tl—O(8)—C(9)	115.9 (4)	113.1 (4)	Tl—O(19)—C(20)	109.5 (5)
Tl—O(11)—C(10)	109.2 (4)	110.2 (4)	Tl—O(22)—C(21)	120.9 (5)
Tl—O(11)—C(11a)	110.7 (4)	114.0 (4)*	Tl—O(22)—C(22a)	121.6 (4)

* In B, atom C(11a) is named C(22a^i).

Table 4. *Torsion angles* (°) *in the macrocyclic 18-crown-6 rings of* A *and* B

	A	B
C(22a)–C(4a)–O(5)–C(6)	–179 (1)	–167 (1)
O(22)–C(22a)–C(4a)–O(5)	–59 (1)	–60 (1)*
C(4a)–O(5)–C(6)–C(7)	179 (1)	167 (1)
O(5)–C(6)–C(7)–O(8)	69 (1)	63 (1)
C(6)–C(7)–O(8)–C(9)	176 (1)	176 (1)
C(7)–O(8)–C(9)–C(10)	–175 (1)	–179 (1)
O(8)–C(9)–C(10)–O(11)	–69 (1)	–71 (1)
C(9)–C(10)–O(11)–C(11a)	172 (1)	–179 (1)*
C(10)–O(11)–C(11a)–C(15a)	179 (1)	
C(10)–O(11)–C(22aⁱ)–C(4aⁱ)		179 (1)
O(11)–C(11a)–C(15a)–O(16)	64 (1)	
C(11a)–C(15a)–O(16)–C(17)	170 (1)	
C(15a)–O(16)–C(17)–C(18)	–163 (1)	
O(16)–C(17)–C(18)–O(19)	–67 (1)	
C(17)–C(18)–O(19)–C(20)	177 (1)	
C(18)–O(19)–C(20)–C(21)	178 (1)	
O(19)–C(20)–C(21)–O(22)	61 (1)	
C(20)–C(21)–O(22)–C(22a)	165 (1)	
C(21)–O(22)–C(22a)–C(4a)	–159 (1)	

* In B, atoms O(22) and C(11a) are named O(11ⁱ) and C(22aⁱ).

Table 4; other lengths and angles for the ligands and for the picrate anions have been deposited.* The C—C bond lengths range from 1·472 (11) Å for C(4a)—C(22a) to 1·544 (14) Å for C(1)—C(2) in A, and from 1·486 (14) Å for C(2)—C(3) to 1·527 (11) Å for C(1)—C(22a) in B. These extremes are all within the cyclohexane rings and can be compared with 1·532 (2) Å for cyclohexane in the gas phase (Bastiansen, Fernholt, Seip, Kambara & Kuchitsu, 1973); in A, the two C—C bonds at the ring junctions may be significantly shorter, 1·47 (1) and 1·49 (1) Å, but the bond in B, 1·51 (1) Å, is not. Comparison of the four complexes with other metals is similarly inconclusive. The torsion angles within the cyclohexane rings range from ±52·1 (10) to ±59·5 (10)° in A and from ±55·5 (11) to ±58·8 (9)° in B, compared with ±55·0° in cyclohexane (Beagley, 1978). C—O distances range from 1·410 (11) Å for O(22)—C(21) to 1·459 (10) Å for O(5)—C(4a) in A and from 1·420 (10) Å for O(11)—C(10) to 1·439 (9) Å for O(5)—C(4a) in B with no significant trend for axial or equatorial substitution.

Discussion

Conformation

For B the results are comparable with those for the sodium bromide complex (Mercer & Truter, 1973) in which linear H_2O—Na—OH_2 occupies a crystallographic centre of symmetry surrounded by isomer B in the same conformation as that found here. This can be approximated as having all the C—O—C—C torsion angles *trans* and the O—C—C—O alternately + and —

gauche (Table 4). It is one of the conformations attainable from form (4) of Fig. 1. The structure of the uncomplexed isomer B (Dalley et al., 1975) is also derived from (4); it has a centre of symmetry but a different conformation having two *trans* O—C—C—O torsion angles (Dobler, 1981).

For A the six O atoms are coplanar within ±0·19 Å (e.s.d. 0·005 Å) and the Tl atom is not significantly out of this plane [0·003 (2) Å].* It is displaced from their mass centre by 0·072 (2) Å towards O(5). This off-setting of the Tl atom is the main deviation from a plane of symmetry through O(8), O(19), C(25) and C(26) corresponding to form (3) of Fig. 1. As Table 4 shows, the 18-crown-6 ring here also has alternating signs for the gauche O—C—C—O torsion angles around the ring.

Kawasaki & Kitano (1978) found that the ¹H NMR spectrum showed that decomplexation was slow on the NMR time scale. Inversion of the cyclohexano rings was shown by ¹³C NMR (Randall & Rosenberg, 1971) to be taking place in solution even in the presence of sodium. Mercer & Truter (1973) noted that this was consistent with isomers A and B having *cis* substitution at the ring junctions because inversion converts a pair of axial and equatorial O atoms into a pair of equatorial and axial respectively, still geometrically suitably placed for coordination. In contrast, *trans* substitution gives two equatorial O atoms suitable for chelation, but inversion gives a pair of axial O atoms. Coxon, Laidler, Pettman & Stoddart (1978) discussed the complex-forming properties of substituted 18-crown-6 rings in terms of the possibility of attaining the 'all gauche conformation', i.e. that with all O—C—C—O torsion angles gauche as exhibited by both the isomers with dimethylthallium. The greater stability of the *cis* isomers was attributed to the ability to retain this conformation on inversion of the cyclohexane rings. [In this approach, forms (2) and (5) were seen as transient intermediates between stable forms related by inversion of both rings.] One of the *trans* forms can attain this conformation of the 18-crown-6 ring, but only with one set of conformations of the cyclohexane rings. Coxon et al. (1978) were primarily interested in crown ethers as acceptors of hydrogen bonds. However, 18-crown-6 itself does not always adopt the 'all gauche' form as a recipient of hydrogen bonds (Knochel, Kopf, Oehler & Rudolph, 1978; Bandy, Truter, Wingfield & Lamb, 1981). Further, the 'all gauche' arrangement is not found for the other three metal complexes of isomer A which all have the conformation derived from form (2) of Fig. 1 and have +,+,−,+,+,− or −,−,+,−,−,+ as the sequence of gauche torsion angles for the O—C—C—O bonds.

Our calculations show that in the Ba complex (Dalley, 1971; Dalley et al., 1972), the ion is 0·59 Å

* See deposition footnote.

* See deposition footnote.

Table 5. Comparison of M—O bond lengths in complexes of dicyclohexano-18-crown-6 (Å)

M	Isomer	Form (Fig. 1)	M—O$_{ax}$	M—O$_{eq}$	M—O$_{cent}$	Reference[*]
Tl	A	3	2·805, 2·979 (5)	2·677, 2·782 (5)	2·737, 2·795 (5)	This work
La	A	2	2·85, 2·87	2·62, 2·63	2·73, 2·75	Harman et al. (1976)[a]
Ba	A	2	2·91	2·79	2·82	Dalley et al. (1972)[b]
U	A	2	2·63–2·68	2·40–2·47	2·54–2·57	de Villardi et al. (1978)[c]
Tl	B	4	2·867 (5)	2·736 (5)	2·762 (5)	This work
Na	B	4	2·967 (4)	2·682 (4)	2·676 (4)	Mercer & Truter (1973)

[*] Values calculated from coordinates supplied by (a) Hursthouse (1981); (b) Dalley (1971); (c) Cambridge Crystallographic Data Centre, University Chemical Laboratories, Cambridge, England.

from the mean plane through the O atoms towards the 'open' side from which it is coordinated by two isothiocyanate anions; on the other, the 'closed', side, i.e. between the two cyclohexane rings, it is coordinated by one water molecule. In the La complex (Harman et al., 1976; Hursthouse, 1981), the O atoms are less nearly coplanar, the deviation range being +0·36 to −0·54 Å, the effect being that the La atom is +0·47 Å from this plane on the open side where it is coordinated by two nitrate anions; on the closed side it is coordinated by one nitrate ion, the O atoms on this side giving longer La—O bonds noted by Harman et al. (1976). There is a similar effect for the complex 2[UCl$_3$ isomer A]$^+$.UCl$_6^{2-}$ (de Villardi et al., 1978), whereby there are two independent cations; both have U out of the plane towards two chloride ions, the third chloride being on the closed side.[*]

The more puckered ring in the form (2) is correlated with a closer approach of the two cyclohexane rings. The shortest C···C distance is C(1) to C(15) in our compound **A**, 7·91 (1) Å; it is 7·86 Å in the Ba complex, and 7·65 Å for the La compound. Form (2) also allows higher coordination numbers on the open side. The uncomplexed isomer A also crystallizes in form (2) but with a different conformation having two trans O—C—C—O bonds.

A recent molecular-mechanics treatment of 18-crown-6 and its alkali-metal complexes (Wipff, Weiner & Kollman, 1982) gives, with the assumption of a charge of −0·3 e on each O atom, good agreement with the experimental angles for the uncomplexed molecule (Dunitz & Seiler, 1974), including a C—C—O—C torsion angle of about 155°, without the need to invoke crystal packing forces. As the corresponding angle is 87° in uncomplexed isomer B (Dobler, 1981), clearly the cyclohexano substituents have a profound effect; it is not surprising that the macrocyclic ring of Wipff et al. (1982) constrained to C_2 symmetry, like isomer A, also differs in a pair of torsion angles, calculated gauche, observed (Dobler, 1981) trans. The conformation with an opposite pair of O—C—C—O torsion

[*] Calculated from coordinates supplied by the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Cambridge, England.

angles fixed at 0° was calculated to give better interaction than the 'all gauche' form, with K$^+$, Rb$^+$ and Cs$^+$, because it affords six good interactions; this is the arrangement of torsion angles corresponding to dibenzo-18-crown-6. Even if it is the six coplanar O atoms, rather than the 'all-gauche' conformation which is preferred, isomer A would still be expected to have the conformation as found in **A**, not that based on (2).

From the metal–oxygen distances (Table 5), it does not appear that the radius of the cation determines the conformation of isomer A. The important factors could be the charge on the cation and the coordinating tendency of the anions [the three complexes of form (2) are all complexed ion pairs], or the critical factor may be the shape of the polyatomic cation, e.g. (TlMe$_2$)$^+$.

Metal–ligand distances

Mercer & Truter (1973) suggested that the different metal–oxygen distances for the three independent Na—O distances with isomer B, and Ba—O distances with isomer A, might depend upon the orientation of M—O relative to the plane of the C—O—C group and the bisector of its angle; they expected that the metal occupying a position to complete a trigonal arrangement would be closer than one in a tetrahedral position. Now that more compounds have been studied, the striking feature is the consistent pattern of M—O bond lengths. As shown in Table 5, they are significantly longer to the axial than to the equatorial O atoms. This may arise from a steric hindrance in closing the 'bite' at the ring junctions, and making the six O atoms approximately coplanar and equidistant from a point. The steric hindrance postulated is between the equatorial H atom on a carbon next to the one bearing the axial O atom and one of the H atoms in a CH$_2$ group of the macrocyclic ring. For **A**, the values of H···H distances are H(4)b···H(6)b 2·07 and H(12)a···H(10)a 2·10 Å. For **B**, the corresponding atoms are H(1^i)b··· H(10)a at 2·07 Å. We calculated the corresponding H···H distances in the isomer B–sodium complex (2·22 Å) and the isomer A– lanthanum complex (1·89 Å), to be shorter than any other inter- or intramolecular H···H distance in these

complexes. The persistence of the phenomenon, even in the other forms, suggests that the effect is real. Its presence in solution may explain the field anisotropy observed in a ^{13}C NMR investigation of the lanthanum complex (Catton, Harman, Hart, Hawker & Moss, 1978). Similar short contacts were noted in the potassium perchlorate complex of the macrobicyclic polyether (Fig. 5); at each of the two cyclohexano substituents, the $K \cdots O_{axial}$ distance was significantly larger than the $K \cdots O_{equatorial}$ distance (Bandy & Truter, 1982).

As can be deduced from the Tl—O—C angles in Table 3, the equatorial O atoms have their three neighbours more nearly coplanar, corresponding to approximately trigonal bonding, than the axial and central oxygen atoms for which the O → M directions are approximately along tetrahedral directions.

In the preliminary report on dimethylthallium dibenzo-18-crown-6 picrate, Henrick et al. (1982) depicted an arrangement of the ligand similar to that in its complexes with sodium bromide (Bush & Truter, 1971), and potassium iodide (Aldoshin, D'yachenko, Tkachev & Atovmyan, 1981; Myskiv et al., 1980), i.e. nearly coplanar O atoms with both benzene rings on one side, as in form (1) of Fig. 1. The dimethylthallium complex, however, contrasts with the alkali-metal ones in having significantly different metal–oxygen bond lengths, viz 2·787 (9) Å to O atoms on the aromatic rings, and 2·696 (9) Å to the purely aliphatic O atoms; the mean of all six is 2·76 (9) Å, the same as the mean value for the potassium complexes, and slightly more than that of the sodium complexes, 2·72 Å.

The Tl—C bond lengths in A, Table 3, are not significantly different from each other or from that in B or in the dibenzo-18-crown-6 complex (Henrick et al., 1982). The average value 2·11 (1) Å agrees with that suggested by Chow & Britton (1975) who made an extensive study of dimethylthallium compounds. Values from the 14 compounds in the Cambridge Crystallographic Database (1981) range from 2·02 to 2·18 Å with differences of up to 0·1 Å between the two bonds in one structure. C—Tl—C angles, not constrained by
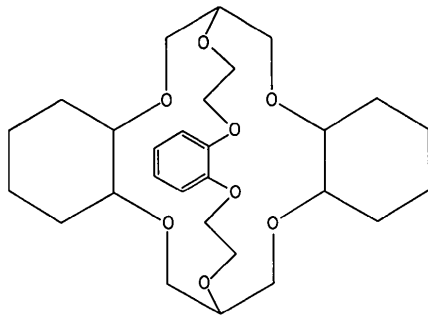
crystallographic symmetry, range from 163·7 to 178·6°. A smaller angle is found as a bend away from a chelate group. The C(25)—Tl—C(26) angle in A, 177·5 (4)°, is not significantly different from linear (the most probable value is not 180°). An 18-crown-6 ring can be regarded as providing six chelate groups, each giving a five-membered ring with the metal.

The 18-crown-6 macrocyclic ethers are the first recorded dimethylthallium compounds having six ligand O atoms. All the Tl—O bond lengths are longer than the two previously found to O atoms of chelating anions (Chow & Britton, 1975), but the remaining coordination in other systems is in shared contacts which range in length from 2·67 to 2·95 Å or more.

Interionic contacts

In both crystals, contacts between neighbouring moieties are at typical van der Waals distances, principally between the picrate atoms and C atoms of the crown ligand.*

Although the two methyl groups in the crystal of (dibenzo-18-crown-6)dimethylthallium picrate are not equivalent, Henrick et al. (1982) note that they did not give separate ^{1}H NMR signals in solution. For the isomer A complex, the two methyl groups are magnetically distinguishable in solution (Kawasaki & Kitano, 1978). In the crystal, C(25), on the closed side, is inserted between C(1) and C(15) at distances of 3·99 (1) and 4·07 (1) Å, while C(26) has no contacts with the outer atoms of the cyclohexane rings. In B, where the two methyl groups are equivalent, C(25) makes a single contact, 4·06 (1) Å to C(4^i). The closest intermolecular neighbours of the methyl groups in both A and B appear to be O atoms of picrate ions: in A, $C(25) \cdots O(42)$ (of the anion at $x - 1$, y, z) is 3·66 (1) Å, and $C(26) \cdots O(45)$ (of the anion of Table 1) is 3·45 (1) Å; in B, $C(25) \cdots O(43)$ (of the anion at $1 - x$, $1 - y$, $1 - z$) is 3·63 (2) Å.

In the picrate ion of A, the para-nitro group is coplanar with the benzene ring, but the ortho groups are rotated out of this plane by 18·9 (4) and 55·0 (3)°. Each anion is surrounded by four cationic groups (and vice versa) in an approximately planar, square arrangement; the planes roughly overlap, ca 7·5 Å apart up c. Thus there is no close stacking of the picrate ions. The angle between the normals to the plane through the six crown O atoms and the benzene ring plane is 34·2 (3)°.

The bond lengths of the disordered picrate ions in B were constrained to the values found in A. The para-nitro group in B, too, is roughly coplanar with the benzene ring [the angle of rotation is 4 (5)°], but the ortho groups are rotated by 40 (2) and 52 (1)°. In this crystal, where the cations lie on centres of symmetry at (0,0,0) and the anions are disordered about centres at

Fig. 5. Macrobicyclic polyether studied by Bandy & Truter (1982); Bandy, Parsons & Truter (1981).

* See deposition footnote.

$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, each cation is surrounded by eight anions (and *vice versa*) in an approximately cubic arrangement. Parallel picrate ions are not close stacked but separated by the length of the *a* axis which is approximately parallel to the normal to the picrate ring plane. This normal is 35·5 (6)° from the normal to the mean plane through the six crown O atoms.

A possible explanation for the differences in formation constants for alkali-metal complexes of isomers *A* and *B*, and the even more marked difference for three isomers of the bicyclic compound shown in Fig. 5 (Bandy, Parsons & Truter, 1981), is that the H atoms at the ring junctions are slightly electropositive. If so, it might be manifested by formation of C–H···O hydrogen bonds; we found, however, that the ring-junction C···O and H···O distances were no shorter than others of the same kind, so these crystal structures do not support that hypothesis.

An alternative explanation lies in the relative accessibility of the metal or the O atoms to the solvent for the first stage in the decomplexation process. However, the metal atoms are well enclosed with no intermolecular contacts less than 4·0 Å. Despite the difference in orientation of the cyclohexano rings in A and B, O atoms of the same type (*i.e.* axial, equatorial or 'central') appear to have very similar environments in the two crystals. The closest intermolecular contacts involving the O atoms are at distances 0·5 Å greater than the sum of van der Waals radii.

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