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A Ternary Complex of 1,3-Xylyl-18-crown-5,* *tert*-Butylammonium Perchlorate and Dichloromethane

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Abstract. $C_{16}H_{24}O_5 \cdot C_4H_{12}N^+ \cdot ClO_4^- \cdot CH_2Cl_2$, $M_r = 554.91$, monoclinic, $P2_1$, $a = 11.582$ (1), $b = 12.396$ (2), $c = 9.281$ (1) Å, $\beta = 91.59$ (1)°, $V = 1332.0$ (5) Å³, $Z = 2$, $D_x = 1.383$ g cm⁻³, $\mu(Mo K\alpha) = 4.0$ cm⁻¹, $F(000) = 588$, $T = 187$ K, final $R = 3.4\%$ for 2154 observed reflections. The crown-*tert*-butylammonium cation complex is of the 'nesting' type: the aryl group of the crown ether and the cation are on the same face of the crown. The $-NH_3^+$ group is hydrogen-bonded to three next-nearest-neighbour O atoms of the macrocycle, which has approximate D_{3d} symmetry. On the opposite face of the ring one Cl of dichloromethane forms a close contact with the $-NH_3^+$ group [$Cl \cdots N^+ 3.554$ (3) Å] through the cavity of the ring and also with the intra-annular CH of the aryl group [$C \cdots Cl 3.827$ (4) Å].

Introduction. As part of a study of the complexing properties of crown ethers (Reinhoudt, de Boer, Uiterwijk & Harkema, 1985, and references therein), the complex of 1,3-xylyl-18-crown-5 with *tert*-butylammonium perchlorate was prepared in dichloromethane solution. Upon standing the solution at room temperature, a crystalline complex was obtained and a structure determination was undertaken.

* IUPAC name: 5,6,8,9,11,12,14,15,16,17-decahydro-4,7,10,13,16-pentaaxabenzol[ab]cyclooctadecene.

Experimental. 1,3-Xylyl-18-crown-5 and *tert*-butylammonium perchlorate were prepared according to literature procedures (Reinhoudt, Gray, Smit & Veenstra, 1976; Kyba, Helgeson, Madan, Gokel, Tarnowski, Moore & Cram, 1977, respectively). Slow evaporation of the solvent from 0.08 *M* 1,3-xylyl-18-crown-5 and 0.16 *M* *tert*-butylammonium perchlorate in dichloromethane solution yielded the crystalline material. D_m not determined.

Intensities measured at 187 K on a Philips PW 1100 diffractometer (Mo $K\alpha$ radiation, graphite monochromator). Lattice parameters determined by least squares from 25 reflections ($4.5^\circ < \theta < 8^\circ$). Total of 2606 reflections up to $\theta = 25^\circ$ ($-13 \leq h \leq 13$, $0 \leq k \leq 14$, $0 \leq l \leq 11$) measured in the $\theta/2\theta$ scan mode (scan speed 0.05° s⁻¹, scan width 1.8°); 2154 reflections considered observed [$I > 3\sigma(I)$]. The intensity variation of 3 standard reflections, measured every hour, was less than 3%. No absorption correction. Structure solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined with a local block-diagonal version of *ORFLS* (Busing, Martin & Levy, 1962). Weights for each reflection in the refinement (on F) calculated from $w = |\sigma(F_o) + 0.01|F_o|^{-2}$, $\sigma(F_o)$ being the e.s.d., based on counting statistics, of the observed structure factor. Scattering factors taken from *International Tables for X-ray Crystallography* (1974) for the non-H atoms and from Stewart, Davidson &

Simpson (1965) for the H atoms. All but one H atoms were located on difference Fourier maps in the course of refinement. The position of the last H atom was calculated and included in the refinement. The total number of parameters refined was 460: scale factor, isotropic extinction parameter (final value 3×10^{-6}), position parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. Refinement resulted in final values of $R = 3.4\%$ and $wR = 3.8\%$; in the last cycle $(\Delta/\sigma)_{\max} = 0.6$. Largest peak on final difference Fourier map $0.4 \text{ e } \text{Å}^{-3}$, located near a Cl atom. The structure revealed a ternary complex of 1,3-xylyl-18-crown-5, *tert*-butylammonium perchlorate and dichloromethane.

Discussion. Final atomic positional parameters are given in Table 1 for non-H atoms*. The numbering of these atoms is shown in Fig. 1 (drawn with *ORTEP*, Johnson, 1965). Bond distances, bond angles and torsion angles in the macrocycle are given in Table 2, from which it is clear that the ring has approximate D_{3d} symmetry (conformation $ag^+a \text{ } ag^-a \text{ } ag^+a \text{ } ag^-a \text{ } ag^+a \text{ } ag^-a$). The stereoscopic view (Johnson, 1965) of the complex, in Fig. 2, reveals the hydrogen bonding between the $-\text{NH}_3^+$ group and next-nearest-neighbour O atoms of the macrocycle, with $\text{N}\cdots\text{O}$ distances of 3.000 (4), 2.931 (4) and 3.043 (4) Å and $\text{N}-\text{H}\cdots\text{O}$ angles of 175 (3), 169 (4) and 179 (2)°, respectively. From Fig. 2 and Table 1 it can be seen that the structure contains a pseudomirror plane through crown, cation and anion; the dichloromethane breaks this symmetry.

The distance between the N atom and the best mean plane of C(1) and the five O atoms of the macrocycle is 1.15 Å, which is larger than the values reported for complexes of 18-crown-6 in the D_{3d} conformation with ammonium cations. In the complexes of 18-crown-6 with ammonium bromide (Nagano, Kobayashi & Sasaki, 1978), benzylammonium thiocyanate (Bovill, Chadwick, Sutherland & Watkin, 1980) and methylammonium perchlorate (Trueblood, Knobler, Lawrence & Stevens, 1982) the distances between the N atom and the mean plane of the six ring O atoms are 1.00, 0.86 and 0.84 Å, respectively. The larger distance in the case of the 1,3-xylyl-18-crown-5-*tert*-butylammonium perchlorate complex is probably caused by the loss of one favourable $\text{N}^+\cdots\text{O}$ interaction between the cation and the crown, in which a C—O—C unit has been replaced by an aryl group. van der Waals repulsion between the *tert*-butyl group and the crown may also

play a role. Maud, Stoddart & Williams (1985) indeed report a large distance of 1.15 Å for the complex of 18-crown-6 and phenacylammonium hexafluorophosphate, which shows steric interaction between crown and cation.

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for non-H atoms

No y parameter was fixed, because in the block-diagonal least-squares refinement the origin is effectively fixed by the atoms in the unrefined blocks.

	x	y	z	$U_{\text{eq}}^*(\text{Å}^2)$
C(1)	2762 (3)	3635 (4)	6644 (4)	27 (1)
C(2)	3771 (3)	3087 (3)	6953 (4)	28 (1)
C(3)	4882 (3)	3537 (5)	6438 (4)	37 (1)
O(4)	4872 (2)	3452 (3)	4892 (3)	31 (1)
C(5)	5849 (4)	3975 (4)	4313 (5)	37 (1)
C(6)	5833 (3)	3825 (4)	2702 (5)	35 (1)
O(7)	4838 (2)	4357 (2)	2124 (3)	34 (1)
C(8)	4788 (3)	4387 (4)	586 (4)	32 (1)
C(9)	3799 (3)	5061 (4)	127 (4)	31 (1)
O(10)	2739 (2)	4591 (2)	549 (3)	28 (1)
C(11)	1802 (4)	5285 (4)	225 (5)	32 (1)
C(12)	702 (4)	4814 (4)	692 (4)	33 (1)
O(13)	704 (2)	4765 (2)	2237 (3)	32 (1)
C(14)	-345 (3)	4352 (4)	2765 (5)	35 (1)
C(15)	-321 (3)	4416 (4)	4372 (4)	34 (1)
O(16)	612 (2)	3801 (2)	4937 (3)	32 (1)
C(17)	635 (4)	3777 (5)	6486 (4)	37 (2)
C(18)	1691 (3)	3207 (3)	6987 (4)	29 (1)
C(19)	1665 (4)	2240 (4)	7715 (4)	35 (1)
C(20)	2671 (4)	1719 (4)	8076 (4)	38 (1)
C(21)	3721 (4)	2119 (4)	7687 (4)	35 (1)
N(22)	2675 (3)	3228 (3)	3127 (4)	22 (1)
C(23)	2547 (3)	2062 (3)	2729 (4)	26 (1)
C(24)	3607 (4)	1723 (4)	1953 (6)	45 (2)
C(25)	1487 (4)	1950 (4)	1771 (6)	45 (2)
C(26)	2411 (6)	1435 (4)	4115 (5)	51 (2)
Cl(27)	3378 (1)	5940 (1)	4032 (1)	61 (1)
Cl(28)	1793 (1)	6722 (1)	6162 (2)	69 (1)
C(29)	2080 (5)	6560 (5)	4316 (6)	51 (2)
Cl(30)	7817 (1)	3508 (1)	8964 (1)	25 (1)
O(31)	7759 (3)	3869 (3)	7488 (3)	48 (1)
O(32)	8858 (2)	2921 (2)	9206 (3)	43 (1)
O(33)	6852 (2)	2843 (3)	9224 (3)	46 (1)
O(34)	7797 (2)	4428 (2)	9888 (3)	41 (1)

* Defined according to Willis & Pryor (1975).

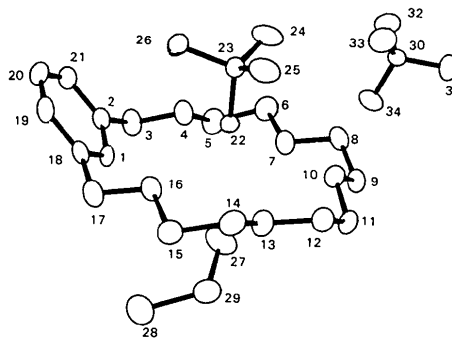


Fig. 1. Atom numbering in the title complex; H atoms have been omitted for clarity.

* Lists of structure factors, anisotropic thermal parameters for the non-H atoms, positional and isotropic thermal parameters for the H atoms and complete lists of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42579 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

An interesting aspect of the present structure is the fact that it is a ternary complex in which the crown is 'sandwiched' by the cation and one dichloromethane solvent molecule. Reinhoudt, den Hertog & de Jong (1981) have reported a similar structure for the ternary complex of 5-bromo-1,3-xylyl-18-crown-5, *tert*-butylammonium hexafluorophosphate and chloroform. Both

complexes adopt a 'nesting' conformation with the *tert*-butylammonium cation and the aryl group on the same face of the macrocycle. On the other face of the ring a solvent molecule is complexed. The nature of the interaction between the crown-cation complex and the nearest Cl atom of this solvent molecule has to be clarified.

There is a close contact between the Cl and the intra-annular CH of the aryl group [C...Cl distance 3.827 (4) Å and C-H...Cl angle 166 (3)°]. The H...Cl distance of 2.97 (4) Å is approximately equal to the sum of the van der Waals radii of H and Cl, but it seems doubtful to denote this as a hydrogen bond, for two reasons. Firstly, an aromatic C atom is not likely to be a hydrogen-bond donor and, secondly, C-H...Cl contacts involve Cl⁻ ions rather than Cl atoms, as was reported by Taylor & Kennard (1982) in a survey of C-H...X hydrogen bonds. Therefore the C-H...Cl interaction will be weak. On the other hand there is a close contact between the Cl atom and the -NH₃⁺ of the cation. The Cl...N⁺ distance is 3.554 (3) Å, which is 0.37 Å larger than the sum of the van der Waals radius of Cl (1.75 Å) and the ionic radius of NH₄⁺ (1.43 Å), due to the separation of the dichloromethane and the cation by the crown. It seems likely there is some ion-dipole interaction between the cation and the dichloromethane through the cavity of the crown.

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°)

C(1)-C(2)	1.375 (5)	C(17)-C(18)	1.476 (6)
C(2)-C(3)	1.494 (6)	C(18)-C(19)	1.393 (5)
C(3)-O(4)	1.439 (4)	C(18)-C(19)	1.377 (6)
O(4)-C(5)	1.423 (5)	C(19)-C(20)	1.365 (6)
C(5)-C(6)	1.507 (6)	C(20)-C(21)	1.371 (6)
C(6)-O(7)	1.420 (5)	C(21)-C(2)	1.382 (6)
O(7)-C(8)	1.428 (4)	C(23)-N(22)	1.499 (5)
C(8)-C(9)	1.471 (6)	C(23)-C(24)	1.501 (6)
C(9)-O(10)	1.424 (5)	C(23)-C(25)	1.503 (6)
O(10)-C(11)	1.411 (5)	C(23)-C(26)	1.514 (6)
C(11)-C(12)	1.477 (6)	Cl(27)-C(29)	1.715 (6)
C(12)-O(13)	1.434 (5)	Cl(28)-C(29)	1.766 (5)
O(13)-C(14)	1.419 (5)	Cl(30)-O(31)	1.441 (3)
C(14)-C(15)	1.492 (6)	Cl(30)-O(32)	1.420 (3)
C(15)-O(16)	1.411 (5)	Cl(30)-O(33)	1.415 (3)
O(16)-C(17)	1.437 (5)	Cl(30)-O(34)	1.428 (3)
C(18)-C(1)-C(2)	121.4 (4)	C(17)-C(18)-C(19)	122.8 (4)
C(1)-C(2)-C(3)	118.9 (3)	C(18)-C(19)-C(20)	120.1 (4)
C(2)-C(3)-O(4)	108.0 (3)	C(19)-C(20)-C(21)	121.4 (4)
C(3)-O(4)-C(5)	111.0 (3)	C(20)-C(21)-C(2)	119.5 (4)
O(4)-C(5)-C(6)	109.3 (3)	C(21)-C(2)-C(1)	119.0 (4)
C(5)-C(6)-O(7)	107.8 (4)	C(21)-C(2)-C(3)	122.0 (4)
C(6)-O(7)-C(8)	113.5 (3)	N(22)-C(23)-C(24)	108.2 (3)
O(7)-C(8)-C(9)	108.3 (3)	N(22)-C(23)-C(25)	107.9 (3)
C(8)-C(9)-O(10)	111.0 (3)	N(22)-C(23)-C(26)	107.3 (3)
C(9)-O(10)-C(11)	110.9 (3)	C(24)-C(23)-C(25)	110.9 (4)
O(10)-C(11)-C(12)	111.2 (4)	C(24)-C(23)-C(26)	111.8 (4)
C(11)-C(12)-O(13)	109.4 (3)	C(25)-C(23)-C(26)	110.6 (4)
C(12)-O(13)-C(14)	112.5 (3)	Cl(27)-C(29)-Cl(28)	112.9 (3)
O(13)-C(14)-C(15)	109.5 (3)	O(31)-Cl(30)-O(32)	109.1 (2)
C(14)-C(15)-O(16)	109.6 (4)	O(31)-Cl(30)-O(33)	109.1 (2)
C(15)-O(16)-C(17)	112.1 (3)	O(31)-Cl(30)-O(34)	108.8 (2)
O(16)-C(17)-C(18)	108.5 (3)	O(32)-Cl(30)-O(33)	110.2 (2)
C(17)-C(18)-C(1)	118.7 (3)	O(32)-Cl(30)-O(34)	110.0 (2)
C(1)-C(18)-C(19)	118.4 (4)	O(33)-Cl(30)-O(34)	109.7 (2)
Torsion angles in the macrocycle			
C(18)-C(1)-C(2)-C(3)	174.4 (3)	C(9)-O(10)-C(11)-C(12)	-178.6 (3)
C(1)-C(2)-C(3)-O(4)	-68.5 (3)	O(10)-C(11)-C(12)-O(13)	67.3 (3)
C(2)-C(3)-O(4)-C(5)	173.5 (4)	C(11)-C(12)-O(13)-C(14)	178.1 (4)
C(3)-O(4)-C(5)-C(6)	177.5 (3)	C(12)-O(13)-C(14)-C(15)	-175.0 (3)
O(4)-C(5)-C(6)-O(7)	64.1 (3)	O(13)-C(14)-C(15)-O(16)	-60.1 (3)
C(5)-C(6)-O(7)-C(8)	173.0 (4)	C(14)-C(15)-O(16)-C(17)	-176.3 (4)
C(6)-O(7)-C(8)-C(9)	-173.5 (3)	C(15)-O(16)-C(17)-C(18)	-174.8 (3)
O(7)-C(8)-C(9)-O(10)	-64.1 (3)	O(16)-C(17)-C(18)-C(1)	61.5 (4)
C(8)-C(9)-O(10)-C(11)	174.7 (3)	C(17)-C(18)-C(1)-C(2)	173.4 (3)

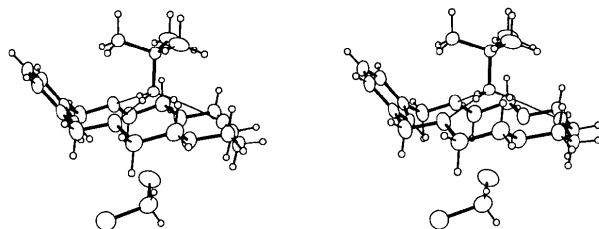


Fig. 2. Stereoscopic view of the complex, showing hydrogen bonds (thin lines) between the macrocycle and the *tert*-butylammonium cation; the perchlorate anion is not shown.

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