

Crystal and Molecular Structure of a 1 : 1 Complex of Potassium Perchlorotriphenylmethide and 18-Crown-6 (1,4,7,10,13,16-Hexaoxacyclooctadecane)

C. MIRAVITLLES*, E. MOLINS, and X. SOLANS**

UEI de Recursos y Materiales del Instituto 'Jaime Almera' de Investigaciones Geológicas (CSIC), c/ Alcarria, s/n. Aptdo Correos 30102, Barcelona, Spain

G. GERMAIN and J. P. DECLERCQ

Laboratoire de Chimie-Physique et de Cristallographie, Université de Louvain, 1 place Louis Pasteur, B1348 Louvain-la-Neuve, Belgium

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Abstract. $(C_6Cl_5)_3 C^- K^+$, $C_{12}H_{24}O_6$ is monoclinic, space group $P2_1$ with $Z = 2$, $a = 10.491(2)$, $b = 18.016(7)$, $c = 11.670(6)$ Å, $\beta = 103.11(3)^\circ$, $V = 2148(1)$ Å³, final $R = 0.039$ for 2339 observed reflections at room temperature. The overall shape of the perchlorotriphenyl free radical is given by the angles between the mean planes of each ring (around 70°). The K^+ ion lies at the centre of the 18-membered macrocyclic ring.

Key words: Crystal structure, single crystal, crown ethers, free radical.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. 82012 (19 pages).

1. Introduction

Ballester and co-workers [1] have synthesized a series of new molecular complexes of perchlorotriphenylmethide with crown ethers and alkali metal cations. The properties of these compounds justify a systematic crystal structure analysis by X-ray diffraction.

2. Experimental

Single crystals suitable for investigation by X-ray methods were grown from methylene chloride by slow evaporation of the solvent. Accurate cell dimensions were determined by the least-squares fit to the angular settings of 15 reflections on a Syntex diffractometer which was also used for the intensity measurements. Crystal data are given in Table I. Intensities were collected in the θ - 2θ scan mode with graphite monochromated $MoK\alpha$ radiation. Some 3298 reflections were recorded up to $2\theta = 47^\circ$. Three monitor reflections were measured after every 60 reflections. These intensities dropped by an average of 3% over the period of data collection. Data were corrected for Lorentz and polarization effects but not for absorption and extinction. Some 2339 independent reflections were classified as observed with $I > 2.5\sigma(I)$; $\sigma(I)$ was derived from counting statistics.

* Author for correspondence.

** Dpto. Cristalografía y Mineralogía, Universidad de Barcelona, Spain.

Table I. Crystal data

$(\text{C}_6\text{Cl}_5)_3 \text{C}^- \text{K}^+, \text{C}_{12}\text{H}_{24}\text{O}_6$	
Monoclinic $P2_1$	$M_r = 798.85 + 264.19$
$a = 10.491(2) \text{ \AA}$	$Z = 2$
$b = 18.016(7) \text{ \AA}$	$F(000) = 1064$
$c = 11.670(6) \text{ \AA}$	$D_c = 1.644 \text{ Mg m}^{-3}$
$\beta = 103.11(3)^\circ$	$\mu(\text{MoK}\alpha) = 11.042 \text{ cm}^{-1}$
$V = 2148(1) \text{ \AA}^3$	$\lambda = 0.71069 \text{ \AA}$

Table II. Atomic fractional coordinates for non-hydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) and equivalent isotropic thermal parameters (e.s.d.'s are in parentheses)

Atom	x/a	y/b	z/c	BEQ	Atom	x/a	y/b	z/c	BEQ
C1	2262(8)	3916(6)	4227(8)	2.60	C40	1215(15)	7041(8)	1959(16)	8.68
C2	1929(9)	3863(6)	2945(7)	2.53	C41	1841(16)	6903(8)	958(15)	8.87
C3	2511(10)	3361(6)	2317(8)	3.22	O42	1896(7)	7557(5)	294(7)	7.26
C4	2208(12)	3308(7)	1089(10)	4.52	C43	2411(15)	7452(9)	-735(12)	8.48
C5	1327(12)	3810(9)	457(10)	4.83	C44	2544(17)	8179(9)	-1261(13)	8.47
C6	724(12)	4318(8)	1023(10)	4.21	O45	3438(8)	8620(5)	-516(6)	6.50
C7	967(10)	4333(6)	2232(9)	3.02	C46	3847(15)	9238(10)	-1073(13)	8.12
C8	2485(9)	4651(5)	4755(8)	2.25	C47	4624(16)	9764(10)	-153(15)	8.78
C9	3289(9)	5203(6)	4397(8)	2.89	O48	3793(6)	10001(4)	558(7)	6.04
C10	3522(11)	5875(6)	4949(10)	3.47	C49	4374(14)	10550(8)	1357(12)	7.02
C11	3052(10)	6035(6)	5926(9)	3.14	C50	3492(13)	10735(6)	2109(12)	6.68
C12	2262(10)	5526(6)	6318(9)	2.89	O51	3337(6)	10126(4)	2819(6)	5.36
C13	1952(9)	4854(5)	5710(8)	2.55	C52	2517(13)	10281(7)	3585(12)	6.13
C14	2397(11)	3261(6)	4985(9)	2.80	C53	2578(12)	9649(7)	4397(10)	6.06
C15	3385(10)	3203(6)	6032(9)	2.93	H37A	314(11)	824(6)	463(9)	9.39
C16	3473(10)	2619(7)	6803(9)	2.64	H37B	186(10)	843(6)	510(9)	9.39
C17	2598(11)	2023(6)	6553(10)	3.50	H38A	36(10)	786(6)	329(8)	9.39
C18	1637(10)	2050(6)	5495(11)	3.12	H38B	135(10)	733(6)	431(9)	9.39
C19	1542(9)	2653(7)	4762(8)	2.79	H40A	115(10)	663(6)	246(9)	9.39
C120	3763(3)	2795(2)	3080(3)	5.26	H40B	34(11)	721(6)	166(9)	9.39
C121	2961(4)	2666(3)	381(3)	8.40	H41A	273(11)	663(6)	118(9)	9.39
C122	1001(4)	3805(3)	-1071(3)	8.40	H41B	122(9)	656(6)	37(9)	9.39
C123	-418(4)	4928(2)	215(3)	7.14	H43A	347(11)	721(6)	-37(9)	9.39
C124	61(3)	4922(2)	2904(3)	5.17	H43B	176(10)	710(6)	-131(9)	9.39
C125	4059(3)	5001(2)	3263(3)	4.62	H44A	159(11)	847(6)	-149(9)	9.39
C126	4554(3)	6517(2)	4491(3)	5.03	H44B	273(10)	808(6)	-199(10)	9.39
C127	3413(3)	6876(2)	6660(3)	4.93	H46A	436(10)	911(6)	-174(9)	9.39
C128	1645(3)	5718(2)	7544(3)	4.45	H46B	312(11)	949(6)	-132(9)	9.39
C129	798(3)	4301(2)	6126(2)	3.64	H47A	503(11)	1011(6)	-64(9)	9.39
C130	4600(2)	3872(2)	6354(2)	3.94	H47B	538(11)	945(6)	50(10)	9.39
C131	4673(3)	2596(2)	8088(2)	4.62	H49A	528(11)	1028(6)	181(9)	9.39
C132	2686(3)	1286(2)	7518(3)	6.25	H49B	468(10)	1095(7)	79(9)	9.39
C133	554(3)	1308(2)	5191(3)	4.49	H50A	278(10)	1090(6)	161(9)	9.39
C134	220(3)	2666(2)	3567(3)	4.65	H50B	385(9)	1108(6)	269(8)	9.39
K35	7333(3)	3810 ^a	8402(2)	4.32	H52A	289(10)	1072(6)	419(9)	9.39
O36	2076(6)	8998(4)	3750(5)	4.67	H52B	146(11)	1039(6)	305(9)	9.39
C37	2193(13)	8334(8)	4424(11)	6.67	H53A	216(10)	965(6)	488(9)	9.39
C38	1411(12)	7737(7)	3702(13)	6.62	H53B	358(11)	951(5)	483(9)	9.39
O39	1930(7)	7593(4)	2699(7)	6.25					

^a Not refined, fix the origin on the axis.

The structure was solved by direct methods applying the straightforward running of MULTAN-80 [2]. The *E*-map based on the phases set with highest figure of merit established positions for 30 atoms. After two successive electron density maps the remaining non-hydrogen atoms were located. The refinement of the structure model was done by isotropic full matrix least-squares methods [SHELX-76 [3]] and led to $R = 0.13$. Anisotropic refinements of this model converged at $R = 0.05$. At this stage, 16 H-atoms were located from a difference Fourier synthesis and the remainder were introduced in calculated positions. The last stage of refinement was carried out with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for all H-atoms. There were 2339 observed reflections contributing to the final $R = 0.039$, $R_w = 0.033$ ($R_w = [\sum_w (\Delta F)^2 / \sum_w F_0^2]^{1/2}$ where $w = 1.2709 / (\sigma^2(F) + 0.000139 F^2)$). Form factors for all atoms were taken from the *International Tables for X-ray Crystallography* [4]. In the final difference Fourier map calculated after the last cycle there were no peaks $> 0.18 e \text{ \AA}^{-3}$. The atomic coordinates are listed in Table II.

3. Discussion of Results

A general perspective view of the complex with the atom numbering is shown in Figure 1. Figures 2a and 2b show the bond lengths and bond angles. The bond lengths and bond angles in the three pentachlorophenyl groups do not differ significantly from those values obtained in other structures containing this group (mean value of C—C = 1.39(2)Å;

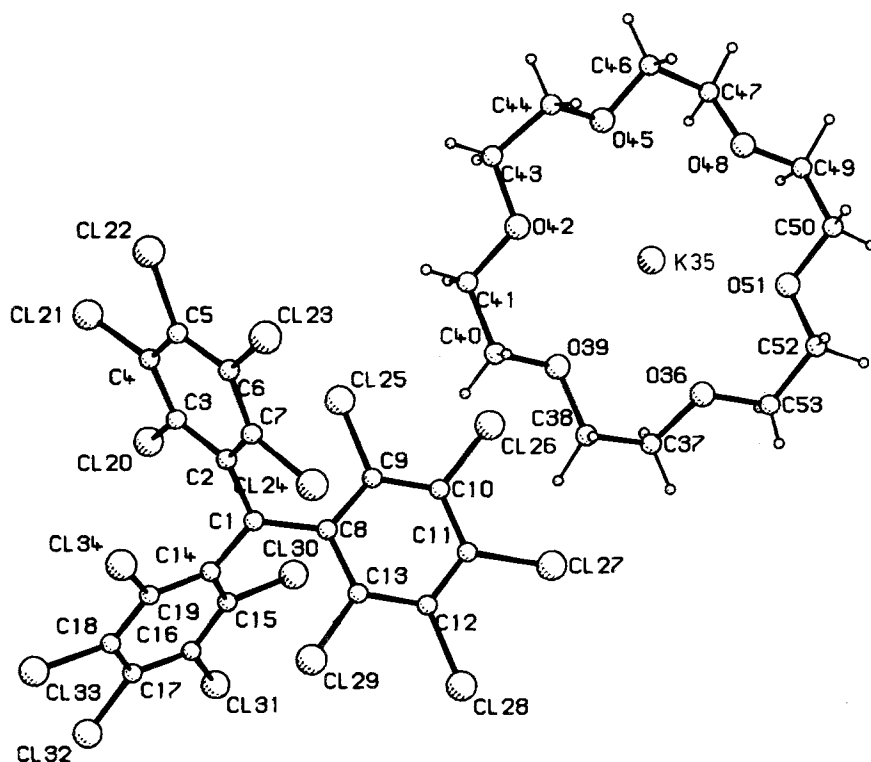


Fig. 1. Perspective view of the molecule with the atom numbering.

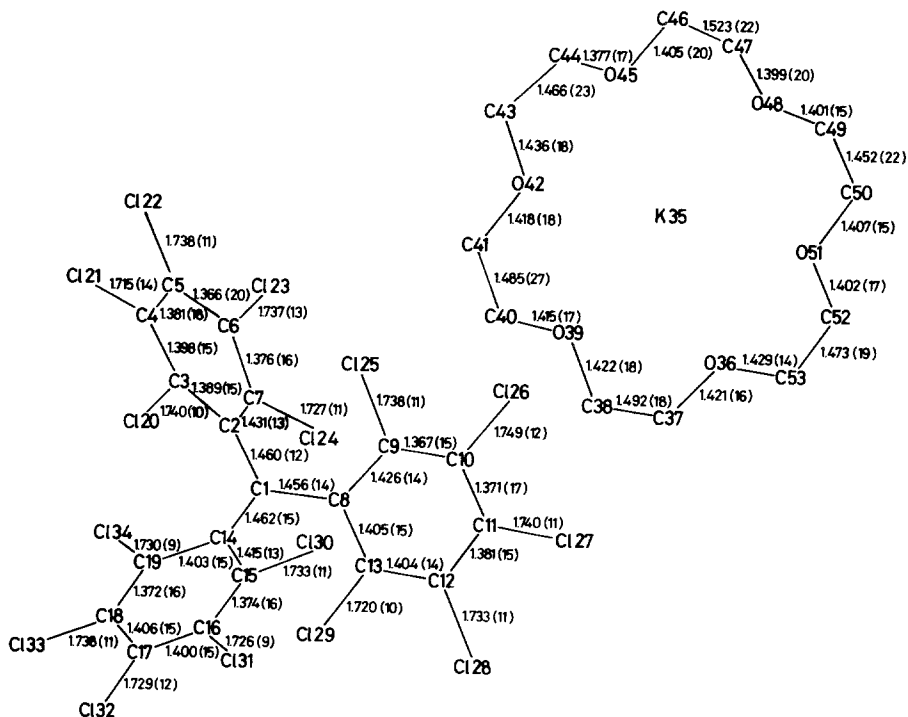
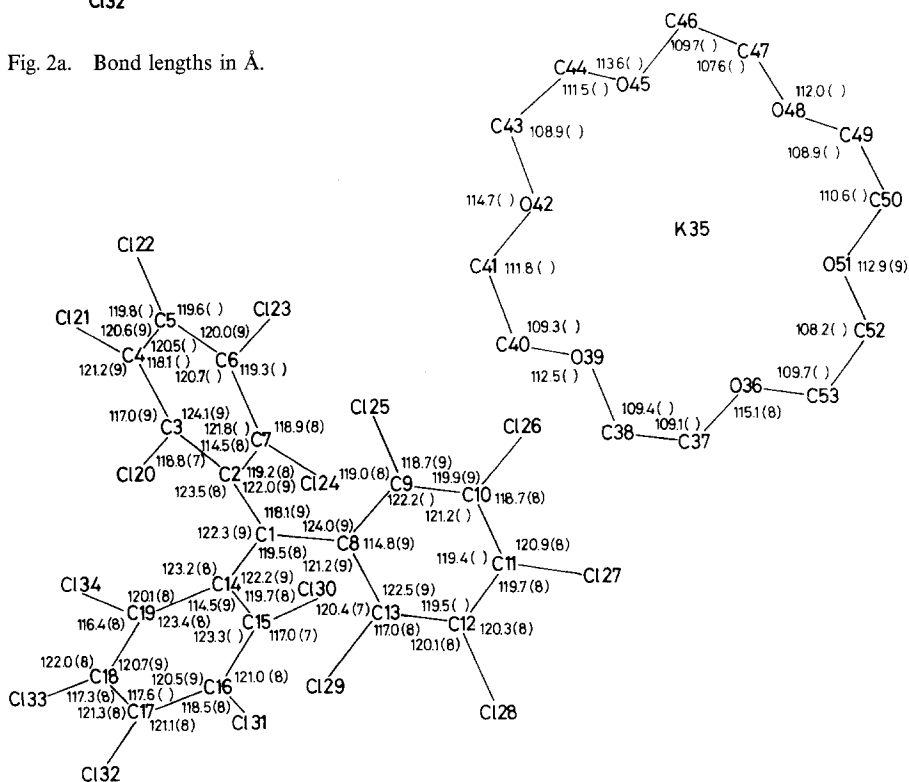


Fig. 2a. Bond lengths in Å.

Fig. 2b. Bond angles in $^{\circ}$. The blank e.s.d.'s are in the range 1.0–1.3 $^{\circ}$.

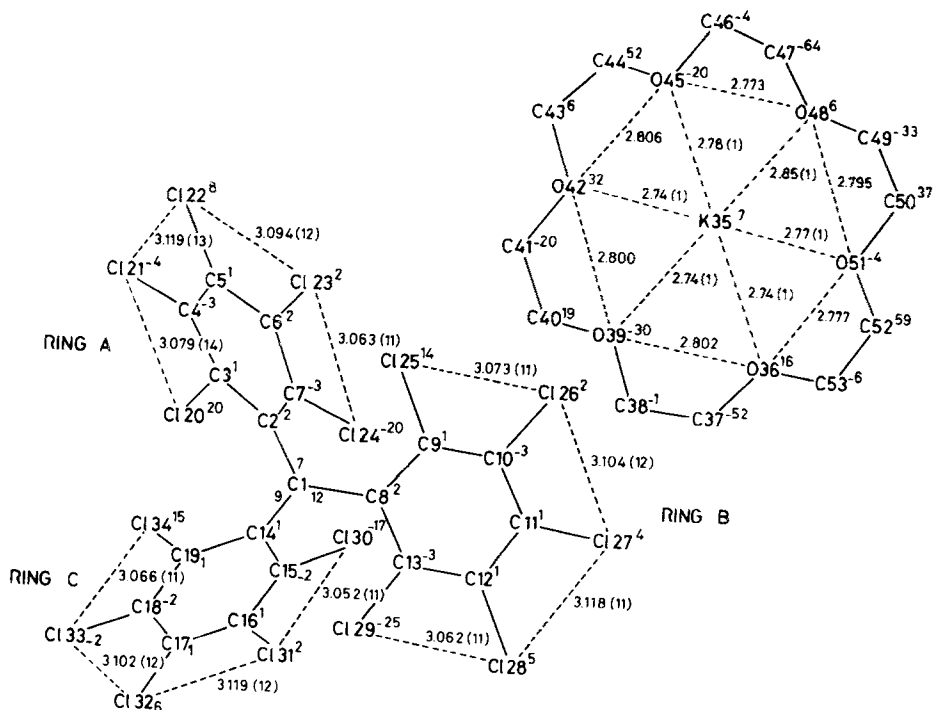


Fig. 3. Selected non-bonded distances and deviations of the atoms ($\times 10^2$) from least-squares mean planes indicated in Table III.

Table III. Selected least-squares planes and their r.m.s.d.'s

Plane	Atoms in the plane	r.m.s.d. (in Å)	Equation of plane
A	C(2) to C(7)	0.026	$7.8845x + 11.8822y - 2.1436z = 5.4641$
B	C(8) to C(13)	0.023	$7.1929x - 7.2562y + 5.0771z = 0.8105$
C	C(14) to C(19)	0.013	$-7.7838x + 8.2748y + 7.5152z = 4.5677$
D	C(1), C(2), C(8), C(14)	0.003	$10.4706x - 1.1153y - 2.7311z = 0.7828$
E	O(36), O(39), O(42), O(45), O(48), O(51)	0.208	$8.8457x + 6.0646y + 2.5330z = -0.5194$

C—Cl = 1.733(9)Å; C—C—C = 120.(3)°; C—C—Cl = 120.(2)° as in perchloro(5,10-diphenyldibenzo[*a,e*]pentalene) [5], decachlorobiphenyl [6], perchlorodiphenylnitroxide [7], perchloro(1-benzylidene-2,5-cyclohexadiene) [8] or in perchloro(1,2,3-triphenylnaphthalene) [9]. The C—Cl bond distances are in the range of the values given by Herbstein [10].

Figure 3 shows the non-bonded distances Cl...Cl in the free radical, the non-bonded O...O distances in the macrocyclic ring and the deviations of the atoms from least-squares mean planes defined by the C-atoms in each pentachlorophenyl group and by the O-atoms in the 18-crown-6.

The overall shape of the perchlorotriphenyl free radical is given by the angles between those planes ($\hat{AB} = 76(1)^\circ$, $\hat{BC} = 67(1)^\circ$ and $\hat{AC} = 75(1)^\circ$), the angles between these planes and the plane D determined by C(1)—C(2)—C(8)—C(14) (rmsd 0.3^{1/4}) ($\hat{AD} = 45(1)^\circ$, $\hat{BD} = 45(1)^\circ$, $\hat{CD} = 40(1)^\circ$) and the torsion angles which contain the C(1) atom. This shape

is a consequence of the internal overcrowding produced by the steric interactions between non-bonded Cl-atoms (the minimum Cl \cdots Cl non-bonded intermolecular distance is 3.89(1) Å). This also yields slight distortions from planarity in the perchlorotriphenyl rings.

The unpaired electron density is located equally between C(1)–C(2), C(1)–C(8) and C(1)–C(4) bonds, because this group forms a planar region and the bond distances are equivalent (1.46 Å), which correspond to shortened single bonds. This electronic distribution trends to close the bond angles C(3)–C(2)–C(7), C(9)–C(8)–C(13), and C(15)–C(14)–C(19) distorting the perchlorophenyl rings and compensating the remaining bond angles. This effect cannot be assigned to Cl \cdots Cl interactions because their distances are longer than 3.0 Å.

The degree of π -electron delocalization between the C(1) atom and the perchlorophenyl groups might be expected to be dependent on the twist angles, with the most delocalization occurring when the perchlorophenyl is coplanar with the mean plane of the four central C-atoms. However, in this free radical, the increasing of the twist angle does not correspond to a localization of the π -electron, and therefore to an increase of the bond distance [11].

The mean values of C–C and C–O bond lengths in the macrocyclic ring are 1.482(22) Å and 1.411(15) Å, respectively; these values should be compared with the electron diffraction reference values [12] of 1.523(3) and 1.423(3) Å. Systematic errors in the geometrical parameters of macrocyclic rings have been carefully discussed by Dunitz *et al.* [13].

The conformation of the 18-membered ring has an approximate D_{3d} symmetry. All torsion

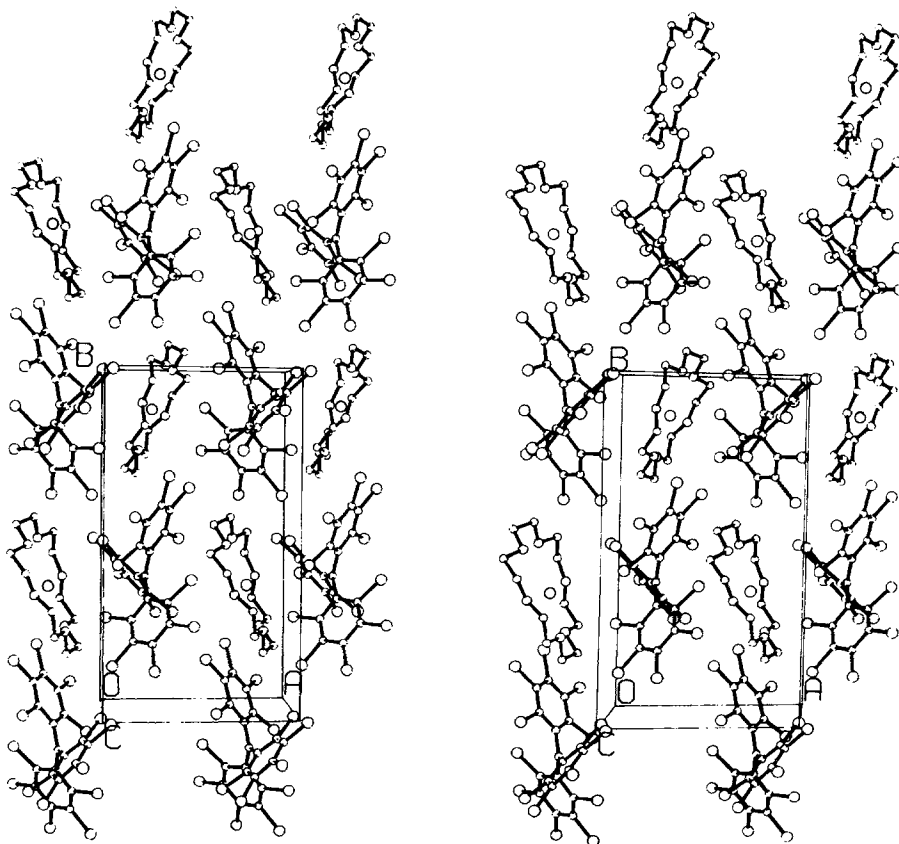
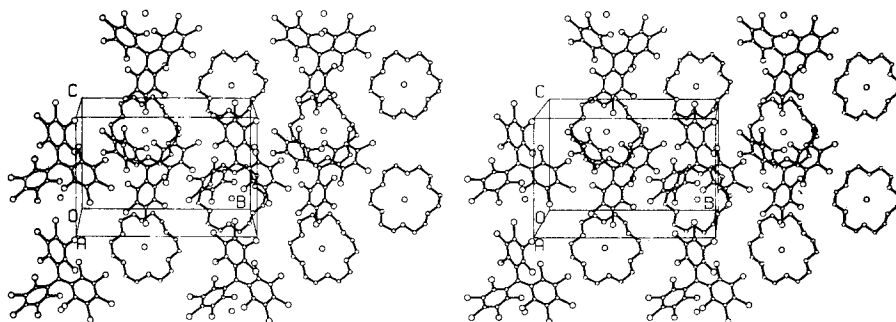


Fig. 4. Stereo drawing of the packing of the molecules viewed in the direction along the z -axis.

Table IV. Selected torsion angles ($^{\circ}$). Maximum e.s.d. is 1.0 $^{\circ}$

Macrocyclic 18 – Membered ring					Perchloro triphenyl				
C(53)	O(36)	C(37)	C(38)	169.2	C(8)	C(1)	C(2)	C(7)	-46.2
C(37)	O(36)	C(53)	C(52)	174.5	C(14)	C(1)	C(2)	C(3)	-45.4
O(36)	C(37)	C(38)	O(39)	62.7	C(2)	C(1)	C(8)	C(9)	-47.1
C(37)	C(38)	O(39)	C(40)	-178.7	C(14)	C(1)	C(8)	C(13)	-45.2
C(38)	O(39)	C(40)	C(41)	-178.0	C(2)	C(1)	C(14)	C(19)	-41.5
O(39)	C(40)	C(41)	O(42)	-58.8	C(8)	C(1)	C(14)	C(15)	-38.3
C(40)	C(41)	O(42)	C(43)	-176.0	C(1)	C(2)	C(3)	C(4)	180.0
C(41)	O(42)	C(43)	C(44)	-173.9	C(1)	C(2)	C(3)	C(120)	-3.4
O(42)	C(43)	C(44)	O(45)	63.7	C(1)	C(2)	C(7)	C(6)	175.2
C(43)	C(44)	O(45)	C(46)	164.8	C(1)	C(2)	C(7)	C(124)	-6.1
C(44)	O(45)	C(46)	C(47)	169.4	C(1)	C(8)	C(9)	C(10)	-177.0
O(45)	C(46)	C(47)	O(48)	-61.2	C(1)	C(8)	C(9)	C(125)	0.0
C(46)	C(47)	O(48)	C(49)	-173.6	C(1)	C(8)	C(13)	C(12)	172.9
C(47)	O(48)	C(49)	C(50)	-176.5	C(1)	C(8)	C(13)	C(129)	-11.0
O(48)	C(49)	C(50)	O(51)	65.7	C(1)	C(14)	C(15)	C(130)	-7.8
C(49)	C(50)	O(51)	C(52)	178.5	C(19)	C(14)	C(15)	C(16)	-2.9
C(50)	O(51)	C(52)	C(53)	-171.8	C(1)	C(14)	C(19)	C(18)	-177.4
O(51)	C(52)	C(53)	O(36)	-63.4	C(1)	C(14)	C(19)	C(134)	-2.0

angles about C—C bonds (Table IV) are close to 60 $^{\circ}$ (synclinal, sc) and C—O bonds are close to 180 $^{\circ}$ (antiplanar, ap). The six oxygen atoms are alternatively above and below their mean plane (Figure 3) and their projection in the plane defines an approximate hexagon of side 2.79 Å. The K $^{+}$ ion lies at the centre of the six-ligating oxygen atoms and at 0.07 Å from the mean plane defined by these atoms. The K $^{+}$...O distances are not equal (2.74–2.85 Å, average 2.77 Å) but are close to the sum of the van der Waals radii of O-atom and K $^{+}$ ion (2.73 Å). The minimum K $^{+}$...Cl distance is 3.44 Å. The packing of the molecules is shown in Figures 4 and 5 [14]. The shortest intermolecular distance is 3.45 Å (O(48)—Cl(23)).

Fig. 5. Stereo drawing of the packing of the molecules viewed in the direction along the x -axis.

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