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X-ray Structure of 18-Crown-6–$KClO_4$ at Room Temperature and 20 K

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Abstract

$(C_{12}H_{24}O_6)K^+.ClO_4^-$, $M_r = 402.87$, monoclinic, $P2_1/n$, $F(000) = 848.0$. At 295 K: $a = 8.299$ (2), $b = 15.012$ (2), $c = 15.267$ (2) Å, $\beta = 103.15$ (1)°, $V = 1852.2$ Å^3, $D_x = 1.445$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 42.39$ cm^{-1}, final $R = 0.052$, $wR = 0.042$ for 2793 reflections having $F > 2\sigma(F)$. At 20 K: $a = 8.251$ (1), $b = 14.757$ (2), $c = 15.057$ (3) Å, $\beta = 105.33$ (1)°, $V = 1768.1$ Å^3, $D_x = 1.510$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 4.99$ cm^{-1}, final $R = 0.027$, $wR = 0.030$ for 2034 reflections with $F > 2\sigma(F)$. The final displacement parameters, expressed in U_{eq} values for the 20 K structure, are approximately one order of magnitude smaller compared with the 295 K data. The average C—O and C—C bond lengths in the crown ether are 1.417 (5)/1.428 (5) and 1.486 (7)/1.496 (3) Å at 295/20 K. Since the usual shortening of the endocyclic C—C bond is present even at 20 K, it can scarcely be a thermal effect as has been previously discussed. In the 1:1 complex of the (18-crown-6)K^+ cation and the perchlorate anion the potassium ion is coordinated to the six O atoms of the crown and to two perchlorate anions on opposite sides of the crown, which are related *via* the glide plane. The potassium cation is only 0.141 (1)/0.236 (1) Å away from the least-squares plane through the six O atoms of the crown.

Introduction

The structures of more than 40 crown-ether potassium complexes of the 18-crown-6 type have been investigated so far (Cambridge Structural Database, September 1989 release; Allen *et al.*, 1979; Patz, 1990), covering a wide variety of anions. In a number of cases, the potassium is located exactly in the center of the crown, though different positions above the crown have also been observed. It is an interesting question, as to whether the nature of the anion *e.g.*, its hardness or softness, affects the conformation of the macrocycle and the position of the cation in relation to the crown center. In contrast to the known structure of 18-crown-6–KSCN (Dunitz, Dobler, Seiler & Phizackerley, 1974), which has a very soft anion and the potassium located at an inversion center in the macrocycle, the present structure is representative of one in which the anion, ClO_4^-, is very hard.

While the room-temperature structure investigation was in progress, a diffractometer with a double-stage helium cryostat became available (Zobel, Dreissig & Luger, 1990; Zobel, Luger & Dreissig, 1991), allowing diffraction experiments at temperatures as low as 15 K. In order to gain experience with this diffractometer and to obtain precise structural data of a crown ether for the first time at a very low temperature we repeated the data collection at 20 K.

Experimental

At room temperature

Crystallization was from dichloromethane. A crystal of size 0.57 × 0.4 × 0.25 mm was mounted on a Stoe four-circle diffractometer controlled by a DEC MicroPDP-11 computer. Lattice parameters were obtained from least-squares refinement of the setting angles of 50 reflections with $40 < 2\theta < 60$°. Two octants of independent reflections were measured in ω–2θ scan mode, up to $(\sin\theta/\lambda)_{max} = 0.582$ Å^{-1}, using Ni-filtered Cu $K\alpha$ radiation. 3457 reflections were collected, of which 410 were unobserved with $F_o < 2\sigma(F_o)$. The h, k, l range was 0 to 9, 0 to 17 and −17 to 17, respectively. Three standard reflections measured every 90 min showed insignificant statistical intensity variations. Lorentz–polarization and absorption corrections were applied. The structure solution was easily obtained by direct methods using *SHELXS*86 (Sheldrick, 1985, 1986). Conventional full-matrix least-squares refinement of atomic positional and displacement parameters, scale factor and an isotropic extinction parameter was carried out using the *XTAL* system

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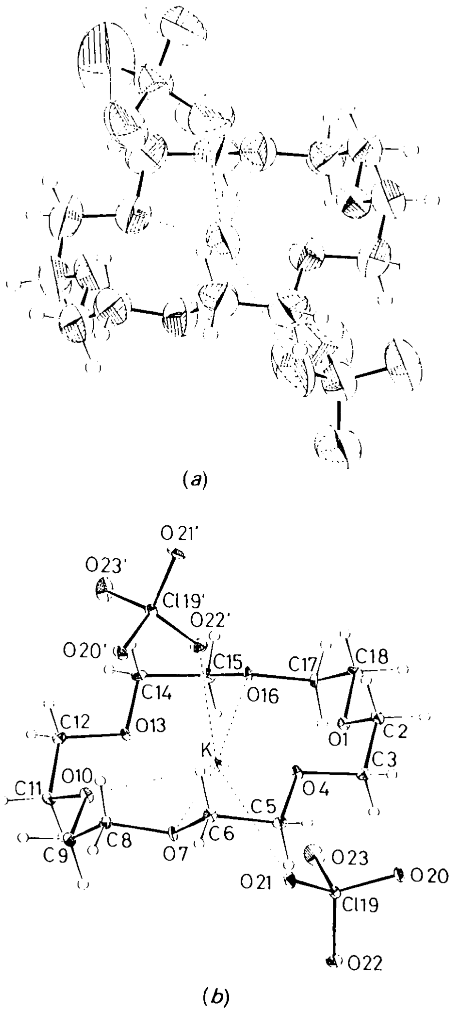
(Stewart & Hall, 1987). The quantity $\sum[w(|F_o| - |F_c|)^2]$ was minimized, unobserved reflections were included if $|F_c| > |F_o|$.

All non-H atoms were refined with anisotropic displacement parameters and all H atoms, located in difference Fourier maps, were refined with isotropic displacement parameters.

Final $R = 0.052$ and $wR = 0.042$, based on 2793 reflections and 314 variables, goodness of fit $S = 5.36$, $w = 1/\sigma^2(F)$, $\sigma^2(F)$ values from counting statistics, max. $(\Delta/\sigma) = 0.03$, largest peak in final difference map = 0.48, largest trough = 0.36 e Å^{-3}. Atomic scattering factors for non-H atoms were taken from Cromer & Mann (1968), H-atom scattering factors from Stewart, Davidson & Simpson (1965).


(a)

(b)

Fig. 1. *ORTEP* representations (Johnson, 1976) of the title complex at (*a*) 295 and (*b*) 20 K. Displacement ellipsoids are plotted at the 50% probability level. K$^+$···O coordination contacts are shown as dotted lines.

At 20 K

A Huber four-circle diffractometer (400 mm ∅, type 5042) with an offset χ-circle was used, controlled by a MicroVAX II with an inhouse-designed single-board computer based on the 68008 processor as interface. The low-temperature device was a double-stage closed-cycle helium cryostat (Air products, DE 202). The crystal (size 0.4 × 0.4 × 0.55 mm) was fixed with araldite glue on a Be needle on the cold head of the second stage [for details of crystal mounting and temperature control see Zobel & Luger (1990)]. Lattice parameters were obtained from least-squares refinement of 31 reflections with $40 < 2\theta < 50°$. Two octants of independent reflections were measured in the ω–2θ scan mode, up to $(\sin\theta/\lambda)_{\max} = 0.53$ Å^{-1}, using Nb-filtered Mo $K\alpha$ radiation. The number of reflections was 2216, of which 182 were unobserved with $F_o < 2\sigma(F_o)$. The h, k, l range was -8 to 0, -15 to 0 and -15 to 15. Three standard reflections measured every 90 min showed insignificant statistical intensity variations. Lorentz and polarization corrections were applied, no correction for absorption. Conventional full-matrix least-squares refinement of atomic positional and displacement parameters and one scale factor was executed with *XTAL* (Stewart & Hall, 1987), using the room-temperature structure as input. Further refinement procedures were as described for the room-temperature structure. Final $R = 0.027$, $wR = 0.031$, $S = 3.40$, based on 2034 observed reflections and 313 variables. Max. $(\Delta/\sigma) = 0.02$, largest peak/trough in final difference map 0.5/0.2 e Å^{-3}.

Discussion

Final atomic coordinates and equivalent isotropic displacement factors (Hamilton, 1959) are given in Table 1.* The atomic numbering scheme and the molecular conformation are shown in Fig. 1. Bond lengths and angles are given in Tables 2 and 3, and torsion angles of the macrocycle are shown in Table 4. As can be seen from Fig. 1 and Table 1, the displacement parameters for the 20 K structure are approximately an order of magnitude smaller compared with the room-temperature data. For the U_{eq} values, the ratio between room and low temperature is in the range 7.0–9.3 for the non-H crown atoms and 9.0–10.4 for the ClO$_4^-$ anion.

As expected, the ClO$_4^-$ oxygens have rather large displacement factors at room temperature; moreover, their internal difference is substantial, ranging from

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54628 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* (Å^2 × 10^2; *first line of every atom room temperature*; *second line* 20 K)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.2008 (3)	0.8955 (1)	0.5658 (1)	6.63 (8)
	0.1916 (2)	0.8952 (1)	0.5615 (1)	0.73 (6)
C(2)	0.3578 (6)	0.9178 (3)	0.5524 (3)	7.4 (2)
	0.3536 (4)	0.9191 (2)	0.5537 (2)	0.9 (1)
C(3)	0.4152 (6)	0.8468 (3)	0.4987 (3)	7.2 (1)
	0.4128 (4)	0.8477 (2)	0.4992 (2)	0.8 (1)
O(4)	0.4418 (3)	0.7679 (1)	0.5514 (1)	6.43 (8)
	0.4400 (2)	0.7665 (1)	0.5520 (1)	0.76 (6)
C(5)	0.5051 (6)	0.6968 (3)	0.5075 (3)	7.5 (2)
	0.5032 (4)	0.6944 (2)	0.5069 (2)	0.8 (1)
C(6)	0.5262 (5)	0.6175 (3)	0.5683 (3)	7.6 (2)
	0.5292 (4)	0.6135 (2)	0.5694 (2)	0.8 (1)
O(7)	0.3691 (3)	0.5816 (1)	0.5677 (1)	6.58 (8)
	0.3679 (2)	0.5747 (1)	0.5655 (1)	0.73 (6)
C(8)	0.3798 (6)	0.5096 (3)	0.6285 (3)	7.6 (2)
	0.3842 (4)	0.5015 (2)	0.6294 (2)	0.9 (1)
C(9)	0.2117 (6)	0.4765 (3)	0.6272 (3)	8.2 (2)
	0.2127 (4)	0.4665 (2)	0.6258 (2)	0.9 (1)
O(10)	0.1291 (3)	0.5445 (1)	0.6652 (2)	7.59 (9)
	0.1280 (2)	0.5362 (1)	0.6619 (1)	0.89 (6)
C(11)	−0.0280 (6)	0.5194 (3)	0.6784 (3)	8.1 (2)
	−0.0279 (4)	0.5087 (2)	0.6770 (2)	0.8 (1)
C(12)	0.0776 (6)	0.5878 (3)	0.7377 (3)	8.1 (2)
	−0.0744 (4)	0.5781 (2)	0.7386 (2)	0.8 (1)
O(13)	0.1011 (3)	0.6709 (2)	0.6916 (2)	6.71 (8)
	0.0994 (2)	0.6635 (1)	0.6924 (1)	0.75 (6)
C(14)	−0.1361 (6)	0.7399 (3)	0.7488 (3)	8.5 (2)
	0.1305 (4)	0.7333 (2)	0.7517 (2)	0.8 (1)
C(15)	−0.1657 (5)	0.8240 (3)	0.6964 (3)	8.2 (2)
	0.1658 (4)	0.8203 (2)	0.6988 (2)	1.0 (1)
O(16)	−0.0153 (3)	0.8538 (1)	0.6780 (1)	6.57 (8)
	−0.0150 (2)	0.8501 (1)	0.6790 (1)	0.73 (6)
C(17)	−0.0321 (6)	0.9312 (3)	0.6226 (3)	7.3 (2)
	−0.0421 (4)	0.9281 (2)	0.6202 (2)	0.8 (1)
C(18)	0.1340 (6)	0.9607 (2)	0.6139 (3)	7.4 (2)
	0.1238 (4)	0.9613 (2)	0.6114 (2)	0.8 (1)
Cl(19)	−0.0629 (1)	0.77221 (5)	0.35655 (6)	7.20 (3)
	0.05345 (9)	0.77506 (4)	0.35206 (4)	0.72 (2)
O(20)	0.0205 (3)	0.8488 (2)	0.3354 (2)	9.6 (1)
	0.0245 (2)	0.8564 (1)	0.3298 (1)	0.98 (6)
O(21)	0.0488 (5)	0.7146 (2)	0.4109 (2)	13.9 (2)
	0.0735 (3)	0.7154 (1)	0.4070 (1)	1.16 (6)
O(22)	0.1386 (5)	0.7272 (2)	0.2789 (2)	15.5 (2)
	0.1378 (3)	0.7294 (1)	0.2678 (1)	1.38 (7)
O(23)	0.1761 (5)	0.7977 (3)	0.4051 (3)	20.7 (3)
	−0.1728 (3)	0.7975 (1)	0.4034 (1)	2.02 (7)
K(1)	0.16072 (9)	0.71980 (4)	0.61119 (5)	6.67 (3)
	0.15192 (8)	0.71446 (4)	0.60310 (4)	0.70 (2)

0.096 (1) Å^2 for O(20) to 0.207 (3) Å^2 for O(23). Obviously, the Cl—O bond lengths are correlated with the U_{eq} values, whereby, as usual, increasing displacement parameters cause decreasing lengths. For the 20 K structure the internal differences between perchlorate oxygen displacement parameters still exist and the trend from O(20) to O(23) remains the same. However, the Cl—O bonds, now significantly longer [average 1.443 (2) Å as compared to 1.393 (15) Å at room temperature], are no longer correlated with the displacement parameters and show internal agreement.

In the 18-crown-6 ring, the average room-temperature C—O and C—C bond lengths are 1.417 (5) and 1.486 (7) Å, respectively. They are slightly longer at 20 K: 1.428 (5) and 1.496 (3) Å. The value for C—O is that of a normal C—O single bond as also found, for example, in carbohydrates (Jeffrey, Pople, Binkley & Vishweshwara, 1978), or in the low-temperature phase of 1,4-dioxane (Buschmann, Müller & Luger, 1986*a*,*b*). However, the average C—C length shows, at both temperatures, the usual shortening (below 1.50 Å) as already observed in a number of other crown ethers (Dunitz & Seiler, 1974; Maverick, Seiler, Schweizer & Dunitz, 1980; Goldberg, 1975; van Eerden, Harkema & Feil, 1990; Luger, Denner, Cerny, Jindrich & Trnka, 1991). This so-called macrocyclic C—C shortening effect (Shoham, Lipscomb & Olsher, 1983) has been intensively discussed, especially whether this shortening is a thermal effect of the crown macrocycle (van Eerden *et al.*, 1990). The results of the 20 K structure analysis show this to be definitely not true. The average value of 1.496 (3) Å at this very low temperature is even shorter (by 0.016 Å) than the mean C—C length reported for uncomplexed 18-crown-6 at 100 K (Marverick *et al.*, 1980) and is considerably shorter than the average value of 1.53 Å reported for C_{sp^3}—C_{sp^3} bond lengths obtained from other diffractometer data (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

Table 2. *Bond lengths* (Å), *with e.s.d.'s in parentheses*

O(22)′ is symmetry related to O(22) by $-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$.

	295 K	20 K		295 K	20 K
O(1)—C(2)	1.405 (5)	1.417 (4)	O(1)—C(18)	1.410 (5)	1.433 (4)
C(2)—C(3)	1.488 (6)	1.494 (4)	C(3)—O(4)	1.421 (5)	1.423 (3)
O(4)—C(5)	1.423 (5)	1.432 (4)	C(5)—C(6)	1.496 (6)	1.500 (4)
C(6)—O(7)	1.408 (5)	1.436 (4)	O(7)—C(8)	1.415 (5)	1.429 (3)
C(8)—C(9)	1.477 (7)	1.494 (4)	C(9)—O(10)	1.425 (5)	1.429 (4)
O(10)—C(11)	1.415 (6)	1.423 (4)	C(11)—C(12)	1.487 (7)	1.497 (4)
C(12)—O(13)	1.423 (5)	1.428 (3)	O(13)—C(14)	1.426 (5)	1.430 (4)
C(14)—C(15)	1.485 (6)	1.499 (4)	C(15)—O(16)	1.413 (5)	1.424 (4)
O(16)—C(17)	1.425 (5)	1.433 (3)	C(17)—C(18)	1.483 (7)	1.493 (5)
Cl(19)—O(20)	1.416 (3)	1.443 (2)	Cl(19)—O(21)	1.395 (3)	1.449 (2)
Cl(19)—O(22)	1.385 (3)	1.443 (2)	Cl(19)—O(23)	1.377 (5)	1.443 (2)
K(1)—O(1)	2.767 (2)	2.775 (2)	K(1)—O(4)	2.786 (3)	2.793 (2)
K(1)—O(7)	2.874 (3)	2.876 (2)	K(1)—O(10)	2.787 (2)	2.796 (2)
K(1)—O(13)	2.825 (3)	2.854 (2)	K(1)—O(16)	2.810 (3)	2.834 (2)
K(1)—O(21)	2.988 (4)	2.848 (2)	K(1)—O(22)′	2.832 (3)	2.748 (2)

Table 3. *Bond angles* (°), *with e.s.d.'s in parentheses*

	295 K	20 K
C(2)—O(1)—C(18)	113.4 (3)	112.4 (2)
O(1)—C(2)—C(3)	109.5 (3)	108.8 (2)
C(2)—C(3)—O(4)	108.2 (3)	108.2 (2)
C(3)—O(4)—C(5)	112.6 (3)	112.6 (3)
O(4)—C(5)—C(6)	108.0 (4)	107.7 (3)
C(5)—C(6)—O(7)	108.8 (3)	108.3 (2)
C(6)—O(7)—C(8)	111.5 (3)	110.6 (3)
O(7)—C(8)—C(9)	109.3 (3)	108.5 (2)
C(8)—C(9)—O(10)	107.1 (3)	107.0 (2)
C(9)—O(10)—C(11)	114.3 (3)	114.2 (2)
O(10)—C(11)—C(12)	107.1 (3)	107.2 (2)
C(11)—C(12)—O(13)	109.3 (4)	109.3 (2)
C(12)—O(13)—C(14)	111.0 (3)	111.0 (2)
O(13)—C(14)—C(15)	108.6 (4)	109.1 (2)
C(14)—C(15)—O(16)	109.3 (4)	108.5 (2)
C(15)—O(16)—C(17)	113.8 (3)	112.0 (2)
O(16)—C(17)—C(18)	109.2 (3)	108.8 (2)
O(1)—C(18)—C(17)	108.8 (3)	108.5 (2)
O(20)—Cl(19)—O(21)	110.2 (2)	109.8 (1)
O(20)—Cl(19)—O(22)	110.6 (2)	109.0 (1)
O(20)—Cl(19)—O(23)	109.0 (2)	110.1 (1)
O(21)—Cl(19)—O(22)	108.5 (2)	109.0 (1)
O(21)—Cl(19)—O(23)	107.2 (3)	109.0 (1)
O(22)—Cl(19)—O(23)	111.4 (3)	109.9 (1)

Table 4. *Dihedral angles* (°), *with e.s.d.'s in parentheses*

	295 K	20 K
C(18)—O(1)—C(2)—C(3)	−178.1 (3)	−178.8 (2)
C(2)—O(1)—C(18)—C(17)	179.0 (3)	−177.1 (2)
O(1)—C(2)—C(3)—O(4)	−66.6 (4)	−67.5 (3)
C(2)—C(3)—O(4)—C(5)	−177.0 (3)	−177.8 (2)
C(3)—O(4)—C(5)—C(6)	−179.4 (3)	179.1 (2)
O(4)—C(5)—C(6)—O(7)	73.9 (4)	75.3 (3)
C(5)—C(6)—O(7)—C(8)	−176.2 (3)	−175.4 (2)
C(6)—O(7)—C(8)—C(9)	178.3 (2)	177.3 (2)
O(7)—C(8)—C(9)—O(10)	−67.8 (4)	−67.4 (3)
C(8)—C(9)—O(10)—C(11)	−173.1 (3)	−170.6 (2)
C(9)—O(10)—C(11)—C(12)	166.4 (3)	164.0 (2)
O(10)—C(11)—C(12)—O(13)	65.5 (4)	63.2 (3)
C(11)—C(12)—O(13)—C(14)	−175.4 (3)	−175.2 (2)
C(12)—O(13)—C(14)—C(15)	−177.9 (3)	−176.7 (2)
O(13)—C(14)—C(15)—O(16)	−69.7 (4)	−68.8 (3)
C(14)—C(15)—O(16)—C(17)	176.0 (3)	173.9 (2)
C(15)—O(16)—C(17)—C(18)	175.4 (3)	173.6 (2)
O(16)—C(17)—C(18)—O(1)	66.2 (4)	67.4 (3)

Table 5. *Results of rigid-body thermal motion analysis* (*L and T relative to Cartesian crystal frame*), *with e.s.d.'s in parentheses*

(*a*) Libration and translation tensors (deg^2, Å^2 × 100)

	295 K			20 K		
ClO$_4$						
L	104 (16)	90 (8)	12 (9)	6 (4)	6 (2)	−2 (2)
		359 (17)	−17 (10)		30 (4)	−3 (3)
			133 (16)			19 (4)
T	9.0 (3)	−1.4 (2)	−0.7 (2)	0.58 (9)	0.11 (6)	−0.09 (6)
		5.5 (3)	0.1 (2)		0.52 (9)	0.00 (7)
			6.5 (3)			0.73 (9)
Crown						
L	6 (2)	−1.1 (6)	0 (1)	−0.4 (5)	0.1 (2)	0.5 (3)
		7 (2)	0 (1)		−1.0 (6)	0 (2)
			9.9 (8)			0.6 (3)
T	6.3 (2)	0.2 (2)	0.3 (3)	0.63 (7)	0.01 (5)	0.2 (1)
		4.9 (2)	0.0 (2)		0.60 (6)	0.05 (6)
			5.0 (5)			1.1 (2)

(*b*) Transformation matrices from crystal system to Cartesian crystal system (coordinates, Å)

8.29900	0	−3.47326	8.25080	0	−3.98074
0	15.012	0	0	14.757	0
0	0	14.86667	0	0	14.52126

(*c*) Corrected bond distances (Å) (crown, 295 K)

O(1)—C(2)	1.408	O(1)—C(18)	1.414
C(2)—C(3)	1.491	C(3)—O(4)	1.424
O(4)—C(5)	1.426	C(5)—C(6)	1.498
C(6)—O(7)	1.413	O(7)—C(8)	1.417
C(8)—C(9)	1.481	C(9)—O(10)	1.428
O(10)—C(11)	1.419	C(11)—C(12)	1.491
C(12)—O(13)	1.427	O(13)—C(14)	1.430
C(14)—C(15)	1.488	C(15)—O(16)	1.417
O(16)—C(17)	1.428	C(17)—C(18)	1.486

(*d*) Corrected bond distances (Å) (ClO$_4$)

	295 K	20 K
Cl(19)—O(20)	1.469	1.447
Cl(19)—O(21)	1.485	1.457
Cl(19)—O(22)	1.469	1.451
Cl(19)—O(23)	1.485	1.452

Rigid bodies have been fitted to the individual displacement parameters of the crown and the ClO$_4^-$ ion (Schomaker & Trueblood, 1968). The rigid body of the crown shows translational and librational motions without any preferred direction. The corrected average room-temperature C—O and C—C bond lengths are 1.421 (7) and 1.489 (6) Å. Because of the small librations no reasonable libration tensor for the rigid body of low-temperature crown has been found (negative diagonal elements, see Table 5). The ClO$_4^-$-anion rigid body has very large librational motions whereas the translational motions are of the same order of magnitude as those of the crown. The average corrected ClO$_4^-$ bond lengths are 1.477 (9) (room temperature) and 1.452 (4) Å (20 K). The overcorrected values of the room-temperature ClO$_4^-$ anion may hint at the inadequacy of the rigid-body model for this group.

The conformation of the 18-membered macrocycle is that of the typical 'crown' arrangement with almost undistorted symmetry D_{3d}. This is realized by the usual O—C—C—O torsion angles, which are close to a +*sc* or −*sc* (*gauche*) conformation and an *ap* (*trans*) conformation along the C—O bonds (see Table 4). The potassium ion is located inside the cavity formed by the macrocycle as can be seen from its distance of 0.141 (1) Å [0.236 (1) Å at 20 K] from the least-squares plane through the six O atoms of the crown. It coordinates with the six crown oxygens [K$^+$···O distances from 2.767 (2) to 2.876 (2) Å, averages 2.803 (35)/2.821 (36) Å at 295/20 K] and with one O atom each of two perchlorate anions, namely O(21) and O(22)′, where O(22)′ belongs to a ClO$_4^-$ unit which is symmetry related by $-\frac{1}{2}+x$, $\frac{3}{2}-y$, $-\frac{1}{2}+z$.

The small displacement of the potassium ion from the exact cavity center is in the direction of O(21), which is further away from the cation than O(22)′ [K···O(21) = 2.988 (4)/2.848 (2) Å and K···O(22)′ = 2.832 (3)/2.748 (2) Å]. Thus, this displacement can be interpreted as a compensation of the K···O$_{\text{perchlorate}}$ distances. In 18-crown-6–KNCS the potassium ion lies exactly on the crystallographic inversion center of the six O atoms of the crown (Dunitz *et al.*, 1974). In the potassium triphenyltin derivative of 18-crown-6, where the cation interacts with the π system of one of the phenyl rings the potassium ion is 0.139 Å from the oxygen least-squares plane (Birchall & Vetrone, 1988). It ought to be noted that these cation displacements are smaller than the maximum distances of the crown O atoms defining the least-squares plane, being 0.293 Å in the title compound and 0.195 Å in the triphenyltin derivative. The distances of potassium from the least-squares plane in 18-crown-6–K.BiCl$_3$(NCS) (Fan, Xu, Zhou & Yu, 1988) and 18-crown-6–potassium picrate (Barnes & Collard, 1988) lie in significantly different ranges, being 0.671 and 0.892 Å, respectively.

The packing of the 18-crown-6 perchlorate complex is shown in Fig. 2, viewed along [100]. The only intermolecular contacts are, as already mentioned, K···O(21) and K···O(22)′ interactions that stabilize the crystal.

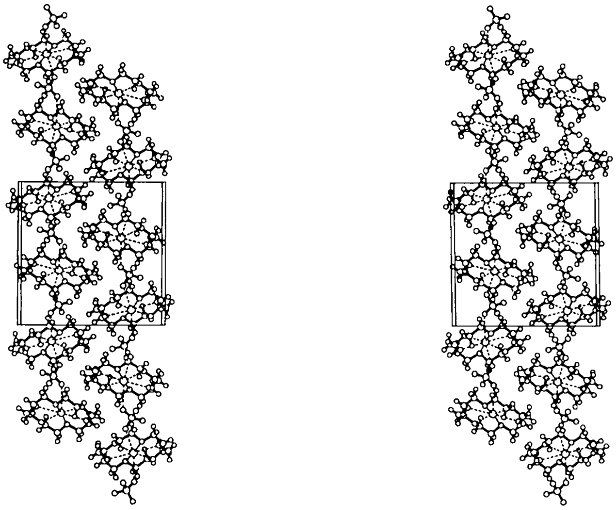

Fig. 2. Packing diagram of the title complex, viewed down the *a* axis (*SCHAKAL* representation, Keller, 1980).

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Structure of Liquid Benzyl Alcohol at 293 K

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Abstract

The experimental intermolecular function of the electron density distribution was determined by X-ray scattering from a liquid sample and compared with the corresponding theoretical functions calculated for the most probable assumed models of the alcohol structure. The best fitting theoretical curve for the intermolecular distribution function was assumed. The model describes the nearest surroundings of an alcohol molecule and determines the mutual arrangement of the planes of the benzene rings. It only

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