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Structure of a 1:2 Complex between *rel*-(1*S*,2*R*,16*S*,18*R*,32*S*,33*R*,47*S*,49*R*)-3,6,9,12,15,19,22,25,28,31,34,37,40,43,46,50,53,56,59,62-Icosaoxapentacyclo-[31.29.1.1^{2,32}.0^{16,49}.0^{18,47}]dohexacontane and Potassium Picrate, $C_{44}H_{80}O_{20}.2[K(C_6H_2N_3O_7)]$

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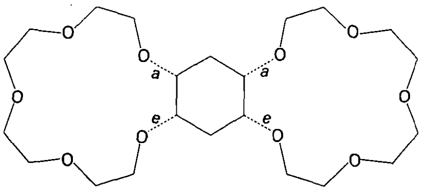
Abstract. $M_r = 1463·6$, monoclinic, $P2_1/c$, $a = 9·170\,(1)$, $b = 16·089\,(1)$, $c = 22·846\,(1)$ Å, $\beta = 92·797\,(7)°$, $U = 3367$ Å^3, $Z = 2$, $D_m = 1·43$, $D_x = 1·44$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 2·32$ cm^{-1}, $F(000) = 1544$, room temperature, $R = 0·064$ for 3054 observations [$I > 2\sigma(I)$]. The two K$^+$ ions are each coordinated to ten O atoms of the ligand. The complex cation contains a centre of symmetry, and 'wraps up' the K$^+$ cations to the exclusion of the anions.

Introduction. The polyether ligand (I) (Fig. 1) named in the title was the unexpected product of an attempted synthesis of the 'clam' ligand (II). Full details of the synthesis and the rearrangement which occurred to produce (I) will be reported elsewhere (Parsons, 1983). The structure determination reported here identified the ligand as (I), and shows it is capable of 'wrapping up' two K$^+$ cations to the exclusion of the picrate anions, in a similar way to that found in the KI complex of dibenzo-30-crown-10 (Bush & Truter, 1972).



(II)

Experimental. Orange crystal, 0·28 × 0·30 × 0·56 mm, Enraf–Nonius CAD-4 diffractometer; 18 reflections with 9° < θ < 16° used to refine the unit-cell parameters; 4251 reflections collected in the *hkl* and $\bar{h}kl$ octants, $2\theta \leq 44°$, ω–2θ scans; two control reflections measured every 2 h, no significant change in I over the data collection; 4126 unique reflections, $R_{\text{Int}} = 0·025$, 3054 with $I > 2\sigma(I)$ classed as observed; index range h −9 to 9, k 0 to 16, l 0 to 23; no absorption correction applied; structure solved using multisolution direct methods (Sheldrick, 1976), and developed by successive Fourier difference maps and least-squares refinements minimizing $\sum w(\Delta F)^2$. The numbering schemes for (I) and the picrate anion are shown in Fig. 1. The H atoms were numbered according to the atom to which they are bonded; those on (I) were included in calculated positions (C—H = 0·098 Å) and given a common isotropic temperature factor, which refined to 0·123 (4) Å^2; the two on the anion were treated similarly and their U_{iso} refined to 0·078 (4) Å^2. All the non-H atoms were assigned anisotropic temperature factors. The parameters were split into two blocks for the final refinements, one containing all the atoms of (I), the other the atoms of the picrate anion. The parameters for the K$^+$ ion were refined every cycle, with the atoms of blocks 1 and 2 being refined in alternate cycles; final $(\Delta/\sigma)_{\max} = 0·13$, $wR = 0·065$, $w \propto 1/\sigma^2(F_o)$. The large temperature factors provide evidence for disorder in atoms C(7), C(8) and C(57)–C(61), but discrete sites for alternative conformations could not be found on difference Fourier maps; final $\Delta\rho$ excursions $\leq 0·5$ e Å^{-3} [near C(58)] and $\geq -0·48$ e Å^{-3}; scattering factors calculated using an analytical approximation (*International Tables for X-ray Crystallography*, 1974).

Discussion. The final atomic parameters are in Table 1,* and a stereopair (Johnson, 1971) of the complex cation is shown in Fig. 2. Bond lengths and torsion angles are shown in Table 2.

The two halves of the complex cation are related by a crystallographic centre of symmetry at ($\frac{1}{2}$,0,$\frac{1}{2}$), so the asymmetric unit is composed of half a molecule of (I) and one K(picrate). Each K$^+$ is coordinated to ten O atoms from (I) with K—O in the range 2·822—3·195 Å.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles and deviations of atoms from the plane of the C atoms of the anion have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38946 (22 pp). Copies may be obtained through The Execution Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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This is a wider range of values than has been found in the potassium complexes with benzo-15-crown-5 (Mallinson & Truter, 1972), dibenzo-30-crown-10 (Bush & Truter, 1972) or (II) (Owen, 1983). The K^+ is entirely surrounded by the ten O atoms, with the O—CH_2—CH_2—O chain forming the 'seam of a tennis ball' as in the dibenzo-30-crown-10 complex. *M*—O (axial) distances have been found to be longer than *M*—O (equatorial) distances in several complexes of cyclic polyethers containing cyclohexano rings [see, for example, Hughes & Truter (1983) and references therein]. Here, the K—O distances involving each chelating pair of O atoms on a cyclohexano ring follow this trend. The coordination around K^+ is of irregular shape, and the K···K distance within the complex is 7·382 (2) Å.

The bond lengths and angles within (I) are as expected, except where disorder has led to shortening of the bond lengths and increase of the angles. The torsion angles are close to the expected ± *gauche* for C—C bonds and *trans* for C—O bonds, except where disorder is present, and around the bonds C(14)—O(15), C(49)—O(50), C(52)—O(53), O(53)—C(54) (see Table 2). Non-bonded distances within the complex cation are all longer than the sum of the van der Waals radii, as are the distances between complex cations. The isomer of the ligand is confirmed as *cis-syn-cis* around each cyclohexano ring as expected from the synthetic method.

Distances between cations and anions are also greater than the sum of the van der Waals radii, except for O(74)*a*···H(17)*a* at 2·47 Å. This is probably of no significance since the H atom is in a calculated position and the O is undergoing considerable anisotropic thermal motion.

Table 1. *Fractional coordinates* ($\times 10^4$) *and* U_{eq} *values* ($Å^2 \times 10^3$) *for the non-hydrogen atoms*

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

	x	*y*	*z*	U_{eq}
K	4086 (1)	−471·6 (1)	6520·1 (5)	54·1 (4)
O(3)	6188 (3)	−1692 (2)	6071 (1)	55 (1)
C(4)	6140 (7)	−2435 (4)	6422 (2)	83 (3)
C(5)	6330 (7)	−2231 (4)	7040 (3)	90 (3)
O(6)	5134 (6)	−1841 (3)	7239 (2)	101 (2)
C(7)	5217 (16)	−1711 (6)	7839 (4)	242 (10)
C(8)	5015 (11)	−1083 (7)	8091 (3)	136 (5)
O(9)	4953 (4)	−315 (3)	7809 (2)	87 (2)
C(10)	6132 (9)	175 (6)	7992 (3)	128 (4)
C(11)	6370 (8)	845 (4)	7598 (3)	98 (3)
O(12)	6447 (4)	581 (3)	7018 (2)	81 (2)
C(13)	7043 (6)	1163 (4)	6646 (3)	84 (3)
C(14)	6885 (5)	885 (4)	6033 (2)	71 (2)
O(15)	5416 (3)	813 (2)	5808 (1)	50 (1)
C(16)	4563 (5)	1563 (3)	5791 (2)	51 (2)
C(17)	5193 (6)	2292 (3)	5462 (2)	67 (2)
C(18)	5259 (6)	2166 (3)	4799 (2)	61 (2)
C(47)	3791 (5)	1876 (3)	4545 (2)	54 (2)
C(48)	3236 (5)	1116 (3)	4860 (2)	47 (2)
C(49)	3094 (5)	1335 (3)	5503 (2)	48 (2)
O(50)	2426 (3)	670 (2)	5800 (1)	55 (1)
C(51)	1162 (5)	902 (4)	6105 (2)	64 (2)
C(52)	1513 (6)	1392 (3)	6655 (2)	68 (2)
O(53)	2411 (4)	925 (2)	7063 (1)	68 (1)
C(54)	1748 (8)	680 (4)	7583 (3)	91 (3)
C(55)	749 (7)	−9 (5)	7510 (3)	92 (3)
O(56)	1477 (4)	−712 (3)	7286 (2)	85 (2)
C(57)	492 (9)	−1344 (6)	7093 (3)	125 (4)
C(58)	797 (13)	−1705 (6)	6636 (5)	237 (8)
O(59)	1485 (5)	−1324 (4)	6190 (3)	151 (3)
C(60)	1296 (8)	−1550 (7)	5615 (5)	195 (6)
C(61)	2267 (7)	−1948 (5)	5345 (3)	105 (3)
O(62)	3678 (3)	−1582 (2)	5364 (1)	61 (1)
O(71)	−743 (4)	6952 (2)	4894 (2)	74 (1)
O(72)*a*	−878 (5)	6375 (3)	5993 (2)	99 (2)
O(72)*b*	1049 (5)	5843 (4)	6352 (2)	136 (3)
O(74)*a*	4014 (4)	4191 (2)	5152 (2)	98 (2)
O(74)*b*	4019 (5)	4427 (3)	4217 (2)	105 (2)
O(76)*a*	1138 (5)	7045 (3)	3551 (2)	121 (2)
O(76)*b*	−954 (6)	6534 (3)	3647 (2)	122 (2)
N(72)	303 (5)	6057 (3)	5939 (2)	66 (2)
N(74)	3568 (5)	4551 (3)	4703 (3)	74 (2)
N(76)	297 (6)	6611 (3)	3800 (2)	73 (2)
C(71)	177 (5)	6396 (3)	4871 (2)	47 (2)
C(72)	809 (5)	5916 (3)	5359 (2)	46 (2)
C(73)	1898 (5)	5342 (3)	5299 (2)	50 (2)
C(74)	2443 (5)	5181 (3)	4764 (2)	49 (2)
C(75)	1934 (5)	5614 (3)	4274 (2)	54 (2)
C(76)	848 (5)	6173 (3)	4330 (2)	48 (2)

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses and selected torsion angles* (°) (*e.s.d.'s* 0·5–1·5°)

Primed atoms are related to the positions in Table 1 by the symmetry operation 1 −*x*, −*y*, 1 −*z*. C(18)′, C(47)′ and O(62)′ are shown as C(1), C(2) and O(19), respectively, in Fig. 1.

K–O(3)	2·969 (3)	C(48)–C(49)	1·523 (6)
K–O(6)	2·885 (4)	C(49)–O(50)	1·422 (6)
K–O(9)	3·023 (4)	O(50)–C(51)	1·431 (6)
K–O(12)	2·934 (4)	C(51)–C(52)	1·505 (8)
K–O(15)	2·933 (3)	C(52)–O(53)	1·427 (7)
K–O(50)	2·855 (3)	O(53)–C(54)	1·416 (7)
K–O(53)	3·022 (4)	C(54)–C(55)	1·442 (10)
K–O(56)	3·057 (4)	C(55)–O(56)	1·422 (9)
K–O(59)	2·822 (6)	O(56)–C(57)	1·417 (10)
K–O(62)	3·195 (4)	C(57)–C(58)	1·238 (14)
		C(58)–O(59)	1·368 (13)
O(3)–C(4)	1·442 (7)	O(59)–C(60)	1·366 (12)
O(3)–C(47)′	1·438 (6)	C(60)–C(61)	1·279 (12)
C(4)–C(5)	1·452 (9)	C(61)–O(62)	1·421 (8)
C(5)–O(6)	1·361 (8)	O(71)–C(71)	1·233 (6)
O(6)–C(7)	1·386 (10)	O(72)*a*–N(72)	1·209 (7)
C(7)–C(8)	1·181 (15)	O(72)*b*–N(72)	1·190 (7)
C(8)–O(9)	1·393 (12)	O(74)*a*–N(74)	1·231 (8)
O(9)–C(10)	1·386 (10)	O(74)*b*–N(74)	1·220 (9)
C(10)–C(11)	1·428 (11)	O(76)*a*–N(76)	1·203 (7)
C(11)–O(12)	1·397 (8)	O(76)*b*–N(76)	1·190 (8)
O(12)–C(13)	1·394 (8)	N(72)–C(72)	1·443 (7)
C(13)–C(14)	1·470 (9)	N(74)–C(74)	1·458 (6)
C(14)–O(15)	1·424 (6)	N(76)–C(76)	1·469 (7)
O(15)–C(16)	1·436 (6)	C(71)–C(72)	1·452 (7)
C(16)–C(17)	1·523 (7)	C(71)–C(76)	1·451 (7)
C(16)–C(49)	1·515 (7)	C(72)–C(73)	1·372 (6)
C(17)–C(18)	1·533 (7)	C(73)–C(74)	1·367 (8)
C(18)–C(47)	1·514 (7)	C(74)–C(75)	1·381 (7)
C(18)–O(62)′	1·417 (6)	C(75)–C(76)	1·353 (7)
C(47)–C(48	1·520 (7)		

C(18)′–C(47)′–O(3)–C(4)	74	C(47)–C(48)–C(49)–C(16)	−62
C(47)′–O(3)–C(4)–C(5)	172	C(16)–C(49)–O(50)–C(51)	111
O(3)–C(4)–C(5)–O(6)	72	C(49)–O(50)–C(51)–C(52)	−73
C(4)–C(5)–O(6)–C(7)	174	O(50)–C(51)–C(52)–O(53)	−61
C(5)–O(6)–C(7)–C(8)	130	C(51)–C(52)–O(53)–C(54)	−112
O(6)–C(7)–C(8)–O(9)	−14	C(52)–O(53)–C(54)–C(55)	76
C(7)–C(8)–O(9)–C(10)	−113	O(53)–C(54)–C(55)–O(56)	58
C(8)–O(9)–C(10)–C(11)	162	C(54)–C(55)–O(56)–C(57)	−168
O(9)–C(10)–C(11)–O(12)	−52	C(55)–O(56)–C(57)–C(58)	140
C(10)–C(11)–O(12)–C(13)	−164	O(56)–C(57)–C(58)–O(59)	−32
C(11)–O(12)–C(13)–C(14)	−172	C(57)–C(58)–O(59)–C(60)	−151
O(12)–C(13)–C(14)–O(15)	64	C(58)–O(59)–C(60)–C(61)	−106
C(13)–C(14)–O(15)–C(16)	62	O(59)–C(60)–C(61)–O(62)	−54
C(14)–O(15)–C(16)–C(49)	177	C(60)–C(61)–O(62)–C(18)′	164
C(49)–C(16)–C(17)–C(18)	−53	C(61)–O(62)–C(18)′–C(47)′	−158
O(15)–C(16)–C(49)–O(50)	56	O(62)–C(18)′–C(47)′–O(3)	51
C(48)–C(49)–C(16)–C(17)	58		
C(16)–C(17)–C(18)–C(47)	50	O(72)*a*–N(72)–C(72)–C(71)	21
C(17)–C(18)–C(47)–C(48)	−53	O(74)*a*–N(74)–C(74)–C(73)	−1
C(18)–C(47)–C(48)–C(49)	60	O(76)*a*–N(76)–C(76)–C(75)	−62

The anions show the usual geometry of picrates, the two oxygens of the *ortho* nitro groups are rotated out of the plane of the rest of the molecule, the *para* nitro group remaining almost coplanar. In this case, the torsion angles (Table 2) about the C—N bonds are 21 and −62° for the *ortho* positions, and −1° for the *para*. However, the very anisotropic thermal parameters found for the nitro O atoms indicate there is considerable torsional vibration occurring about the C—N bonds. The C—C bond lengths to C(71), to which the phenolic O is attached, are systematically longer than the other C—C bonds in the benzene ring as is common for these anions.

The anion is stacked parallel to and 3·33 Å from another at $-x$, $1-y$, $1-z$ with considerable overlap when viewed perpendicular to the plane of the benzene ring, C(72) being almost over the centre of the second anion. A third anion at $1-x$, $1-y$, $1-z$ is also parallel, but only the *para* nitro groups overlap, with O(74)*a*···N(74)′ at 3·01 Å as the closest atoms.

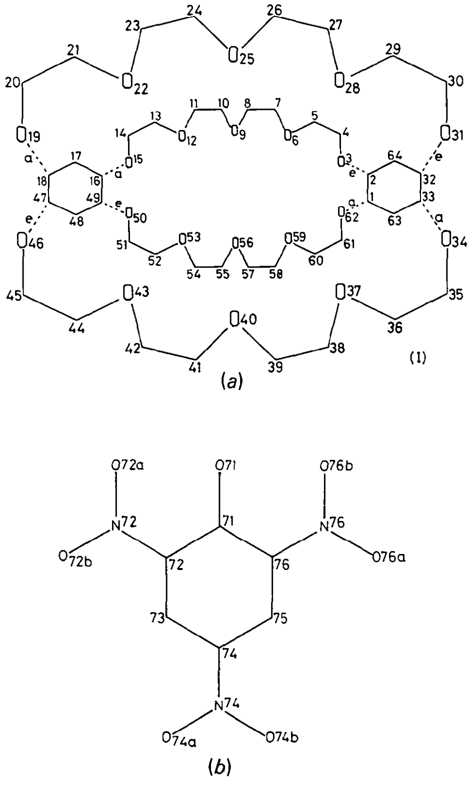

Fig. 1. (*a*) Molecule of (I) showing the atomic numbering scheme. Atoms O(3)–C(18) and C(47)–O(62), which surround one K$^+$, were chosen as the asymmetric unit. (*b*) The picrate anion showing the atomic numbering scheme.

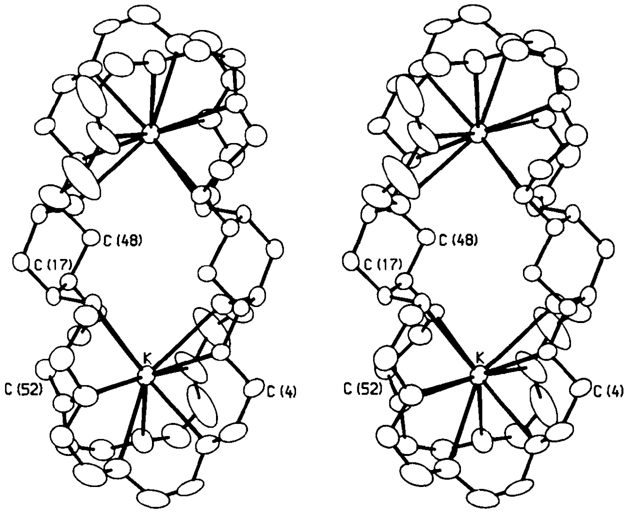

Fig. 2. Stereopair of the complex cation. Atoms are represented by their 30% thermal ellipsoids.

The crystal structure is determined by the packing of discrete complex cations centred around ($\frac{1}{2}$, 0, $\frac{1}{2}$) and ($\frac{1}{2}$, $\frac{1}{2}$, 0) with the anions filling channels down the crystal *a* axis at (x, 0, 0) and (x, $\frac{1}{2}$, $\frac{1}{2}$).

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