([1.5]Dibenzo-18-crown-6)potassium chlorochromate

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The title compound, (6,7,9,10,12,13,15,16-octahydrodibenzo-[b,e]-1,4,7,10,13,16-hexaoxacyclooctadecine)potassium chlorochromate, [K($C_{20}H_{24}O_6$)][$CrClO_3$], is the complex formed by a K^+ cation with one crown ether molecule and a chlorochromate anion. The cation is displaced from the mean plane of the ether O atoms by 0.849 (2) Å towards the anion. It forms coordination bonds with all of the O atoms of the crown ether, as well as with the disordered O and Cl atoms of the anion.

Comment

There are three possible isomers of dibenzo-18-crown-6, namely [3.3]dibenzo-18-crown-6, (I), [2.4]dibenzo-18-crown-6, (II) and [1.5]dibenzo-18-crown-6, (III), which differ in terms of the positions of the aromatic rings. With regard to the ability of these crown ether (CE) molecules to form complexes with cations and neutral guest molecules, the [1.5]dibenzo-18-crown-6 molecule, (III), is, in our opinion, the most interesting. In particular, it has the shortest distance between benzene rings of only one bridging O atom. Restricted rotation around the C_{ar}—O bonds may result in selectivity in complex formation, which was recently confirmed by us (Kotlyar, Fonari *et al.*, 2005; Ganin *et al.*, 2005).

(I)   (II)   (III)

(IV)
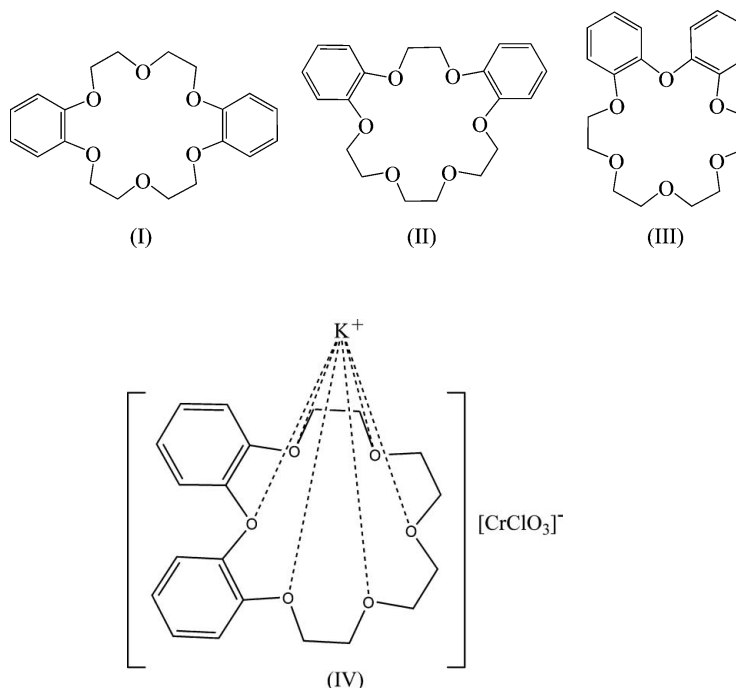
We now report the crystal structure of the title complex, (IV), of [1.5]dibenzo-18-crown-6 with potassium chlorochromate (Fig. 1), obtained by mixing $KCrO_3Cl$ and CE ethyl acetate solutions in a 1:1 ratio at room temperature.
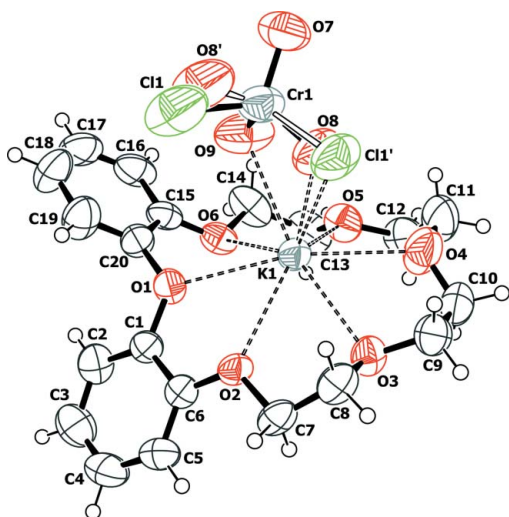
Figure 1
A view of (IV), with displacement ellipsoids drawn at the 50% probability level. The minor disorder component of the anion is indicated by primed atoms.

The CE molecule in (IV) possesses the crown-like conformation, which is somewhat strained due to the presence of the two benzene rings. The C1—O1 and C20—O1 bonds are geometrically non-equivalent. The C20—O1—C1—C2 torsion angle of 3.9 (7)° implies the existence of electronic conjugation between the lone pairs of the O atom and the π system of the C1–C6 ring. The C1—O1 bond has a *syn*-clinal conformation with respect to the C15–C20 benzene ring [C1—O1—C20—C19 = 72.1 (6)°], so the conjugation of this ring with the lone pairs of atom O1 is disrupted. Nevertheless, the C1—O1 and C20—O1 bond lengths are practically the same (Table 1). This could be caused by elongation of the C1—O1 bond due to the presence of a short C20···H2 intramolecular contact of 2.54 Å (van der Waals radius sum for C and H = 2.86 Å; Zefirov & Zorky, 1989). The C2—C1—C20—C19 pseudo-torsion angle in (IV) of 62.3 (5)° is somewhat smaller than that in the free [1.5]dibenzo-18-crown-6 ligand (89.3°; Kotlyar, Fonari *et al.*, 2005). Based on this fact, we can suggest that the complexation probably leads to some flattening of the Ar–O–Ar fragment.

The K$^+$ cation is coordinated by all six O atoms of the CE molecule. The K—O(ether) bond distances are within the range 2.744 (4)–2.975 (4) Å (Table 1). The bridging O atom between the benzene rings, O1, lies opposite atom O4. The cation is displaced from the mean plane of the CE O atoms by 0.849 (2) Å toward the anion, due to the formation of bonds with the anion.

The anion is disordered over two positions [occupancy ratio 0.729 (8):0.271 (8)] as a result of rotation around the bisector of the O7—Cr1—O9 bond angle. The minor disorder component of Cl1 (marked Cl1′ in Fig. 1) lies near atom O8, and consequently atom O8′ lies near atom Cl1. In contrast with previously reported structures of CE complexes with potassium chlorochromate (Kotlyar, Zubatyuk, Shishkin *et al.*, 2004; Kotlyar, Zubatyuk, Zhygalko *et al.*, 2004; Kotlyar, Zubatyuk *et al.*, 2005), the Cl atom of the anion also participates in the formation of complex (IV).

Experimental

To a stirred solution of potassium chlorochromate (241 mg, 1.38 mmol) in dry ethyl acetate (10 ml) at room temperature was added a solution of [1.5]dibenzo-18-crown-6 (497 mg, 1.38 mmol) in dry ethyl acetate (7 ml). The reaction mixture was stirred for 10 min and the yellow–orange precipitate which formed was filtered off, washed with cold ethyl acetate (2 ml) and diethyl ether (2 ml), dried at reduced pressure and heated at 313 K to constant weight (yield 65%, 480 mg). Transparent yellow crystals of (IV), suitable for X-ray investigation [m.p. 417–420 K (decomposition)], were obtained by evaporation of a dichloromethane solution. Analysis, calculated for $C_{20}H_{24}O_9ClCrK$: C 44.90, H 4.52, Cl 6.63, Cr 9.72%; found: C 44.99, H 4.38, Cl 6.56, Cr 9.60%. The crystals are soluble in dichloromethane, dimethyl sulfoxide, dimethyl formamide and acetone, and sparingly soluble in chloroform.

Crystal data

$[K(C_{20}H_{24}O_6)][CrClO_3]$	$Z = 2$
$M_r = 534.94$	$D_x = 1.490$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.139$ (3) Å	Cell parameters from 24
$b = 10.649$ (4) Å	reflections
$c = 12.138$ (3) Å	$\theta = 12$–16°
$\alpha = 95.34$ (3)°	$\mu = 0.81$ mm^{-1}
$\beta = 94.11$ (2)°	$T = 295$ (2) K
$\gamma = 113.05$ (2)°	Block, yellow
$V = 1192.3$ (7) Å^3	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Siemens $P3/PC$ diffractometer	$\theta_{max} = 25.1°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 12$
Absorption correction: none	$k = -12 \rightarrow 11$
4317 measured reflections	$l = -14 \rightarrow 14$
4067 independent reflections	2 standard reflections
2703 reflections with $I > 2\sigma(I)$	every 98 reflections
$R_{int} = 0.069$	intensity decay: 3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1033P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.068$	$+ 1.1342P]$
$wR(F^2) = 0.197$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.003$
4067 reflections	$\Delta\rho_{max} = 0.76$ e Å^{-3}
296 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

K1—O1	2.753 (3)	K1—O8	2.922 (15)
K1—O2	2.899 (3)	K1—O9	2.784 (5)
K1—O3	2.810 (3)	K1—Cl1′	3.197 (14)
K1—O4	2.744 (4)	C1—O1	1.385 (5)
K1—O5	2.791 (4)	C20—O1	1.388 (5)
K1—O6	2.975 (4)		
C1—O1—C20	118.6 (4)	C10—O4—C11	116.9 (5)
C6—O2—C7	116.5 (4)	C13—O5—C12	114.7 (5)
C9—O3—C8	113.0 (4)	C15—O6—C14	116.9 (4)
C20—O1—C1—C2	3.9 (7)	O5—C13—C14—O6	61.6 (7)
C1—O1—C20—C19	72.1 (6)	C6—O2—C7—C8	−65.5 (6)
O2—C7—C8—O3	−63.3 (5)	C15—O6—C14—C13	−176.9 (4)
O3—C9—C10—O4	−174.6 (4)	C7—O2—C6—C1	−174.6 (4)
O4—C11—C12—O5	64.3 (7)	C14—O6—C15—C20	−167.8 (4)

The disordered atoms which occupy neighbouring sites (O8′ and Cl1, and O8 and Cl1′) were constrained to have the same U^{ij}

components and their site occupancies were constrained to sum to unity. The Cr1—O8 and Cr1—O8′ bond lengths were restrained to 1.59 (1) Å. All H atoms were placed in calculated positions and included in the refinement in the riding-model approximation, with C—H distances of 0.97 and 0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *P3/PC* (Siemens, 1989); cell refinement: *P3/PC*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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