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#### Key indicators

Single-crystal X-ray study  
T = 164 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$   
Disorder in solvent or counterion  
R factor = 0.079  
wR factor = 0.213  
Data-to-parameter ratio = 14.3

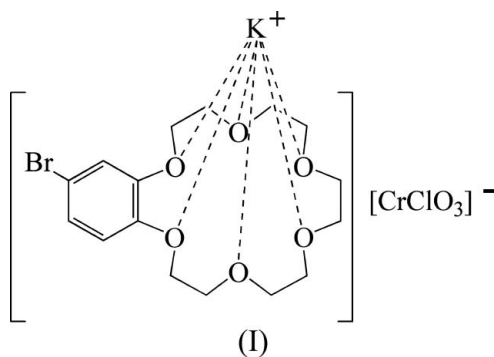
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## (4-Bromobenzo-18-crown-6)potassium chlorochromate

In the structure of the title compound, (18-bromo-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine)potassium chlorotrioxochromate,  $[\text{K}(\text{C}_{16}\text{H}_{23}\text{BrO}_6)][\text{CrClO}_3]$ , the K atom is coordinated equatorially by six macrocycle O atoms and axially by two O atoms of two anions. In the crystal structure, polymeric chains are formed in the [001] direction.

#### Comment

Complexes of aliphatic, mono- and dicycloaliphatic CEs (CE = crown ether) are easily crystallized from acid aqueous solutions and we have determined several crystal structures of these compounds (Kotlyar *et al.*, 2004*a,b*; Kotlyar, Zubatyuk, Zhigalko *et al.*, 2004; Kotlyar *et al.*, 2005*a*). Pure crystalline complexes of benzo- and dibenzo-CE with halogenochromates were obtained for the first time by mixing ethyl acetate solutions of the inorganic salt and ligand at room or increased temperature (Kotlyar *et al.*, 2000). Thus, the complexes of isomeric [3.3]-, [2.4]- and [1.5]-dibenzo-18-crown-6 with potassium chlorochromate were synthesized in the ratio 1:1, and the crystal structure of [1.5]-dibenzo-18-crown-6 with potassium chlorochromate was reported by us recently (Kotlyar *et al.*, 2005*b*). Furthermore, we are interested in the influence of certain aromatic ring substituents (F, Br,  $\text{NO}_2$ ,  $\text{NH}_2$  *etc.*) on the crystal structures of benzo- and dibenzo-CE.

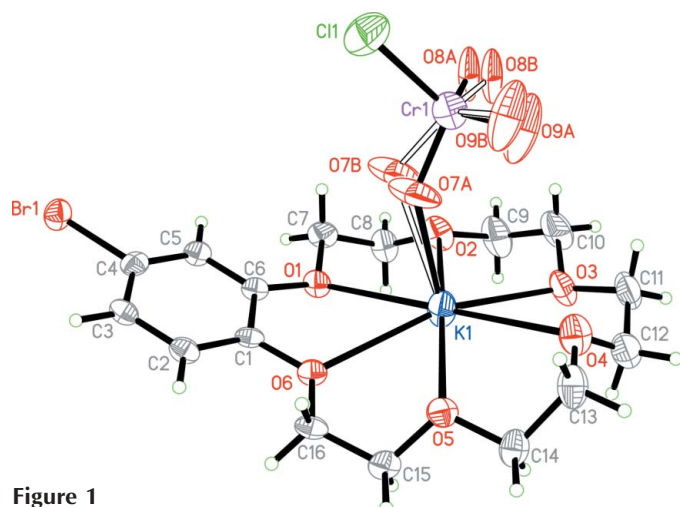


We report here the crystal structure of the title complex, (I), obtained by mixing  $\text{KCrO}_3\text{Cl}$  and CE ethyl acetate solutions in a 1:1 ratio at room temperature. The title compound is the complex formed by a K cation with one crown ether molecule and a chlorochromate anion (Fig. 1). In the molecule, a K atom is coordinated equatorially by six macrocycle O atoms, and axially by atom O7 of one anion and atom O9 of a symmetry-related anion. In the crystal structure, molecules form polymeric chains in the [001] direction (Fig. 2). The macrocycle has a crown-like conformation. The O—C—C—O

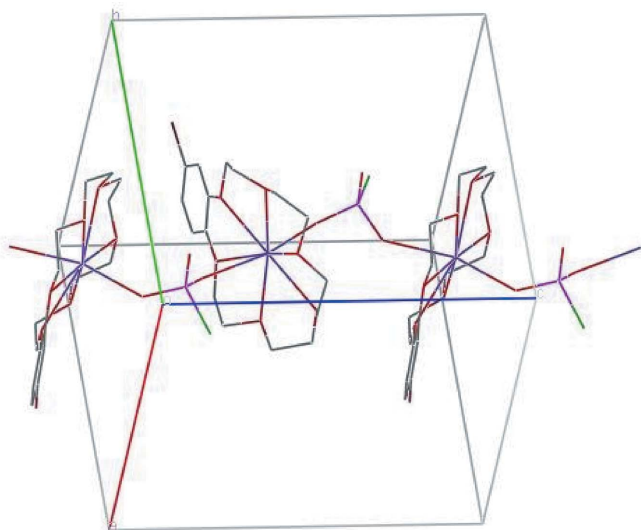
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**Figure 1**  
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. One disorder component of the anion is shown with open bonds.



**Figure 2**  
A line drawing showing part of a one-dimensional chain of the title compound. H atoms have been omitted and only one component of the disordered anion is shown.

fragments have alternating  $+sc$  and  $-sc$  conformations (Table 1). Atoms O1, O2, O5, O6 and K1 form a plane, and atoms O3 and O4 are displaced from this plane by 0.68 (1) and  $-0.31$  (1) Å, respectively. Typical for this type of molecule is a repulsion between the aromatic ring and the atoms of the macrocycle, which gives short intramolecular contacts, e.g.  $H5 \cdots C7 = 2.51$  Å [sum of van der Waals radii = 2.87 Å (Zefirov & Zorky, 1995)],  $H5 \cdots H7b = 2.09$  Å (sum of van der Waals radii = 2.34 Å),  $H2 \cdots C16 = 2.49$  Å,  $H2 \cdots H16a = 2.17$  Å,  $H7b \cdots C5 = 2.60$  Å,  $H16a \cdots C2 = 2.66$  Å and  $H16b \cdots C2 = 2.84$  Å. Close contacts between H atoms are also observed in the macrocycle, e.g.  $H12b \cdots H13b = 2.21$  Å and  $H14a \cdots H15a = 2.32$  Å. Atoms O7, O8 and O9 of the anion are disordered over two sites (denoted by the label suffixes A and B), with equal occupancies, as a result of rotational disorder

about the Cr1–Cl1 bond. In the crystal structure, there are close intermolecular contacts:  $Br1 \cdots Cl1(x, \frac{1}{2} - y, \frac{1}{2} + z) = 3.40$  Å (sum of van der Waals radii = 3.87 Å),  $Br1 \cdots H10b(2 - x, 1 - y, 1 - z) = 3.14$  Å (sum of van der Waals radii = 3.23 Å),  $Br1 \cdots H13a(1 - x, 1 - y, 1 - z) = 3.11$  Å,  $Br1 \cdots H16a(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z) = 3.18$  Å,  $H16b \cdots C3(1 - x, 1 - y, 1 - z) = 2.77$  Å,  $Cl1 \cdots H10a(2 - x, -\frac{1}{2} - y, \frac{1}{2} - z) = 3.02$  Å.

## Experimental

The title complex, (I), was prepared in 78% yield (10.1 g) according to the previously described procedure (Kotlyar *et al.*, 2005b), by mixing ethyl acetate solutions of potassium chlorochromate (4.0 g, 22.9 mmol) and 4-bromobenzo-18-crown-6 (8.97 g, 22.9 mmol) at room temperature. Transparent yellow crystals of (I) suitable for X-ray analysis were obtained by evaporation of a dichloromethane solution [m.p. 435–437 K (decomposition)]. Analysis calculated for  $C_{16}H_{23}BrClCrO_9$ : C 33.97, H 4.10, Cr 9.19%; found: C 34.05, H 4.11, Cr 9.25%. The crystals are soluble in dichloromethane, chloroform, dimethyl sulfoxide and dimethyl formamide, less soluble in acetone and 1,4-dioxane, and practically insoluble in benzene and toluene.

### Crystal data

$[K(C_{16}H_{23}BrO_6)][CrClO_3]$   
 $M_r = 565.79$   
Monoclinic,  $P2_1/c$   
 $a = 11.102$  (3) Å  
 $b = 14.930$  (4) Å  
 $c = 13.552$  (3) Å  
 $\beta = 94.676$  (18)°  
 $V = 2238.8$  (10) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.679$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 12 reflections  
 $\theta = 2$ –25°  
 $\mu = 2.64$  mm<sup>-1</sup>  
 $T = 164$  (2) K  
Plate, yellow  
0.50 × 0.50 × 0.20 mm

### Data collection

Siemens P3/PC diffractometer  
 $\omega$ -2 $\theta$  scans  
Absorption correction: analytical (Alcock, 1970)  
 $T_{min} = 0.352$ ,  $T_{max} = 0.620$   
4083 measured reflections  
3875 independent reflections  
2598 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.105$   
 $\theta_{max} = 25.1^\circ$   
 $h = -10 \rightarrow 13$   
 $k = 0 \rightarrow 17$   
 $l = -16 \rightarrow 16$   
2 standard reflections  
every 98 reflections  
intensity decay: 5%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.079$   
 $wR(F^2) = 0.213$   
 $S = 1.05$   
3875 reflections  
271 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1318P)^2 + 1.9879P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 2.00$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.83$  e Å<sup>-3</sup>

**Table 1**  
Selected geometric parameters (Å, °).

K1–O7A	2.591 (11)	K1–O1	2.774 (4)
K1–O2	2.722 (4)	K1–O4	2.798 (4)
K1–O5	2.737 (4)	K1–O3	2.802 (4)
K1–O9A <sup>i</sup>	2.741 (3)	K1–O6	2.815 (4)
K1–O9B <sup>i</sup>	2.772 (3)	K1–O7B	2.867 (12)
O6–C1–C6–O1	–0.1 (6)	O3–C11–C12–O4	–67.0 (7)
O1–C7–C8–O2	–65.7 (6)	O4–C13–C14–O5	–66.5 (6)
O2–C9–C10–O3	67.9 (7)	O5–C15–C16–O6	62.2 (5)

Symmetry codes: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

All H atoms were placed in calculated positions, with C—H distances of 0.95 and 0.99 Å. They were included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . In the disordered anion values of the Cr—O bond lengths were all restrained to 1.600 (1) Å and values of anisotropic displacement parameters of equivalent O atoms were constrained to be equal. No restraints were applied to the K—O distances involving the anion, and hence the disorder of O7A/O7B has led to differences between the bond lengths K1—O7A and K1—O7A (Table 1). The bond lengths for typical K—O distances in related compounds are 2.55–3.32 Å (Kotlyar *et al.*, 2004, 2004b, 2005a).

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1991); software used to prepare material for publication: *SHELXL97*.

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