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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$
R factor = 0.067
wR factor = 0.180
Data-to-parameter ratio = 15.8

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

Bis(*cis*-cyclohexano-12-crown-4)potassium chlorochromate

The crystal structure of the title compound, bis(*cis*-dodecahydro-1,4,7,10-benzotetraoxacyclododecin)potassium chlorochromate, $[\text{K}(\text{C}_{24}\text{H}_{44}\text{O}_8)][\text{CrClO}_3]$, contains two independent isomeric sandwich-type complexes of a potassium cation, each with two crown ether ligands, and two independent chlorochromate anions. The crown ethers have head-to-head and head-to-tail orientations with respect to one another.

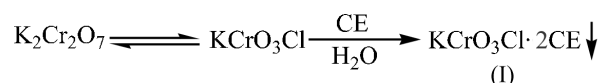
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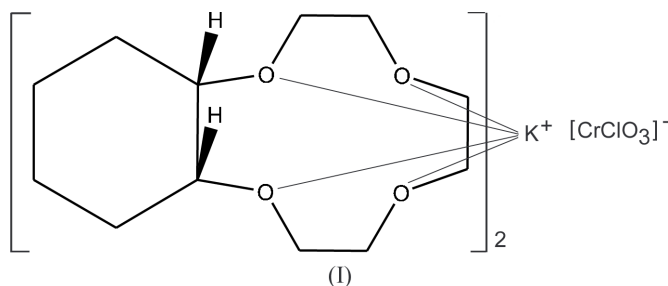
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Comment

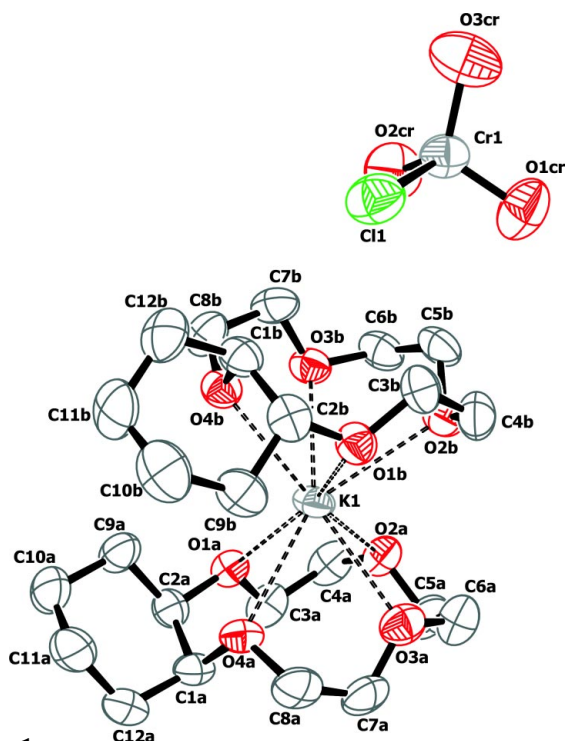
Chromium(VI) complexes with aliphatic, cycloaliphatic, benzo- and dibenzocrown ethers (CEs) with ratios of 1:1 or 1:2 were obtained for the first time by us (Kotlyar *et al.*, 1987, 1989, 2000; Fedorova *et al.*, 1989, 1990) and proved themselves to be new mild and selective oxidants of alcohols (Kamalov *et al.*, 2003) and cyclic acetals (Akbalina *et al.*, 2002). The structures of the synthesized complexes could not be determined for some time because of the inability to obtain crystals of the necessary quality, and this report is the first devoted to their X-ray structure analysis. We have found that, in a solution of potassium dichromate and hydrochloric acid at room temperature, some CEs (including *cis*-cyclohexano-12-crown-4) immediately form crystalline complexes with only one component of the equilibrium mixture, with potassium chlorochromate KCrO_3Cl :



We have obtained the *cis*-cyclohexano-12-crown-4- KCrO_3Cl complex, (I), in the ratio 2:1.



The asymmetric unit contains four cyclohexano-12-crown-4 molecules (*A*, *B*, *C* and *D*), two potassium cations and two chlorochromate anions. The molecular structure of the two independent ion pairs of the title compound are shown in Figs. 1 and 2. Selected bond distances and angles are given in Table 1. Each cation forms a sandwich structure with two CE


Figure 1

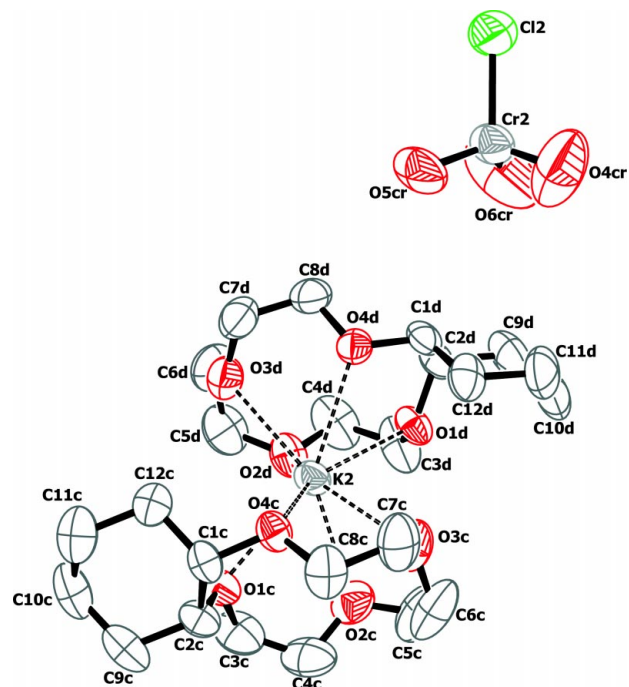
View of one ion pair of the title compound formed by the crown ether molecules *A* and *B*. Atoms are shown with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

ligands. In the complex of the ion K1, ligands *A* and *B* have a head-to-head orientation. Nevertheless, this arrangement does not lead to steric repulsion between cyclohexyl fragments. In the complex formed by ion K2, ligands *C* and *D* have a head-to-tail orientation.

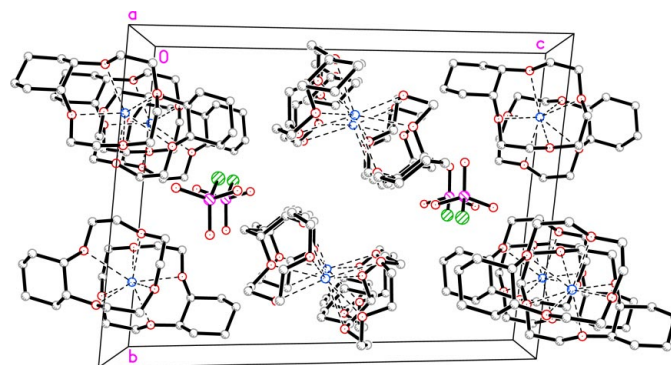
All of the macrocycles have crown-like conformations, with the ether O atoms oriented towards the cations. The cyclohexane rings are *cis*-fused, the H1–C1–C2–H2 torsion angles being 55, 55, –57 and –56° for molecules *A*, *B*, *C* and *D*, respectively. Such conformations of the CE molecules result in steric repulsion between axial H atoms, which are oriented towards the center of the macrocycle. The H···H distances range from 2.17 to 2.34 Å, as shown in Table 2. In the crystal structure, chlorochromate anions are located in the cavities formed by the complex cations, as shown in Fig. 3.

Experimental

To a stirred solution of potassium dichromate (319.8 mg, 1.1 mmol) in distilled water (5 ml) and 13 *M* hydrochloric acid (1 ml) at room temperature was added *cis*-cyclohexano-12-crown-4 (1000 mg, 4.3 mmol), and an orange precipitate was obtained immediately. This was filtered off, washed with diethyl ether (3 ml), dried at reduced pressure and then heated at 313 K to constant weight. Yield 46% (630 mg). Transparent pale-yellow–orange crystals suitable for X-ray investigation [m.p. 385–387 K (decomposed)] were obtained by evaporation of a methylene chloride solution. Analysis calculated for C₂₄H₄₄ClCrKO₁₁: C 45.25, H 6.83, Cl 5.46, Cr 8.10%; found: C 45.36, H 6.78, Cl 5.40, Cr 8.02%. The crystals are soluble in methylene chloride, dimethylsulfoxide and dimethylformamide, and slightly soluble in chloroform, acetone and ethyl acetate.


Figure 2

View of the other ion pair of the title compound formed by the crown ether molecules *C* and *D*. Atoms are shown with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.


Figure 3

Packing diagram of the title compound, viewed along the *a* axis.

Crystal data

[K(C₂₄H₄₄O₈)] [CrClO₃]
M_r = 635.14
 Triclinic, *P*1̄
a = 10.244 (3) Å
b = 15.246 (5) Å
c = 20.302 (6) Å
 α = 94.58 (2)°
 β = 101.00 (2)°
 γ = 95.88 (3)°
V = 3080.3 (16) Å³

Z = 4
D_x = 1.370 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 12–15°
 μ = 0.65 mm^{−1}
T = 293 (2) K
 Block, pale yellow–orange
 0.4 × 0.2 × 0.2 mm

Data collection

Siemens *P3* diffractometer
 θ –2 θ scans
 11 441 measured reflections
 10 794 independent reflections
 6314 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.026
 θ _{max} = 25.1°

h = 0 → 12
k = −18 → 18
l = −24 → 23
 2 standard reflections
 every 98 reflections
 intensity decay: 5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.180$
 $S = 1.03$
 10794 reflections
 685 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0997P)^2 + 0.8411P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.72 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.73 \text{ e } \text{\AA}^{-3}$

Table 1Selected geometric parameters (\AA , $^\circ$).

K1—O1A	2.761 (3)	K2—O1C	2.823 (3)
K1—O2A	2.831 (3)	K2—O2C	2.721 (4)
K1—O3A	2.698 (3)	K2—O3C	2.789 (4)
K1—O4A	2.759 (3)	K2—O4C	2.801 (3)
K1—O1B	2.759 (3)	K2—O1D	2.854 (3)
K1—O2B	2.765 (3)	K2—O2D	2.802 (3)
K1—O3B	2.691 (3)	K2—O3D	2.760 (4)
K1—O4B	2.849 (3)	K2—O4D	2.734 (3)
O1A—C3A—C4A—O2A	63.9 (5)	O3A—C7A—C8A—O4A	64.5 (5)
O1B—C3B—C4B—O2B	63.0 (5)	O3B—C7B—C8B—O4B	62.8 (5)
O1C—C3C—C4C—O2C	-62.6 (6)	O3C—C7C—C8C—O4C	-60.4 (6)
O1D—C3D—C4D—O2D	-65.3 (6)	O3D—C7D—C8D—O4D	-61.8 (6)
O2A—C5A—C6A—O3A	59.1 (6)	O4A—C1A—C2A—O1A	54.1 (4)
O2B—C5B—C6B—O3B	60.9 (5)	O4B—C1B—C2B—O1B	54.6 (4)
O2C—C5C—C6C—O3C	-56.6 (9)	O4C—C1C—C2C—O1C	-56.1 (5)
O2D—C5D—C6D—O3D	-57.4 (7)	O4D—C1D—C2D—O1D	-54.9 (5)

Table 2Selected interatomic distances (\AA).

H1AA...H3AB	2.27	H2CA...H4CA	2.17
H3AB...H5AB	2.24	H4CA...H6CA	2.34
H5AB...H7AB	2.19	H6CA...H8CA	2.26
H7AB...H1AA	2.32	H8CA...H2CA	2.28
H1BA...H3BB	2.25	H2DA...H4DA	2.25
H3BB...H5BB	2.22	H4DA...H6DA	2.21
H5BB...H7BB	2.17	H6DA...H8DA	2.23
H7BB...H1BA	2.32	H8DA...H2DA	2.29

All H atoms were placed in calculated positions and included in the refinement in the riding-model approximation; C—H = 0.97–0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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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