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(18-Crown-6)potassium chlorochromate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.014 Å
R factor = 0.082
wR factor = 0.253
Data-to-parameter ratio = 15.7

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

The crystal structure of the title compound, (1,4,7,10,13,16-hexaoxacyclooctadecane-κ^6O)potassium chlorochromate(VI), $[K(C_{12}H_{24}O_6)][CrClO_3]$, contains a K^+ cation, complexed with one crown ether molecule, and a chlorochromate anion. The cation is located within the mean plane of the ether O atoms, approximately in the centre of the macrocyclic cavity, and bonded to them with K—O distances in the range 2.785 (5)–2.836 (5) Å. In the crystal structure, polymeric chains of the type K^+–CrO_3^-–K^+ are formed.

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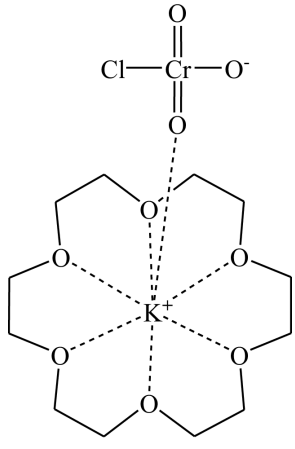
Comment

Recently, we have synthesized the complexes of *cis*-cyclohexano-12-crown-4 in the ratio 2:1, *cis*-cyclohexano-18-crown-6 and *cis-syn-cis*-dicyclohexano-18-crown-6 in the ratio 1:1, with potassium chlorochromate, and reported their crystal structures (Kotlyar, Zubatyuk, Shishkin *et al.*, 2004*a*,*b*; Kotlyar, Zubatyuk, Zhigalko *et al.*, 2004). We have established that 18-crown-6, similar to the above-mentioned crown ethers (CE), in a solution of potassium dichromate and hydrochloric acid at room temperature, where the dichromate–chlorochromate equilibrium is taking place, immediately and almost quantitatively forms a stable crystalline complex with only one component of the equilibrium mixture, namely potassium chlorochromate, $KCrO_3Cl$. We now report the crystal structure of the title complex, (I) (Fig. 1), of 18-crown-6 with potassium chlorochromate, obtained in the ratio 1:1.



(I)

$$K_2Cr_2O_7 \underset{H_2O}{\overset{2\ HCl}{\rightleftharpoons}} 2\ KCrO_3Cl \xrightarrow[H_2O]{2\ CE} 2\ (KCrO_3Cl\cdot CE)\downarrow$$

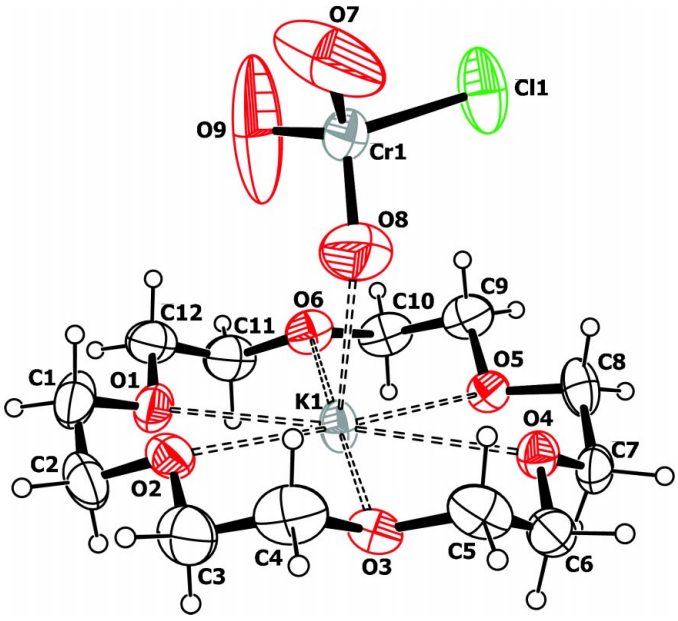


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

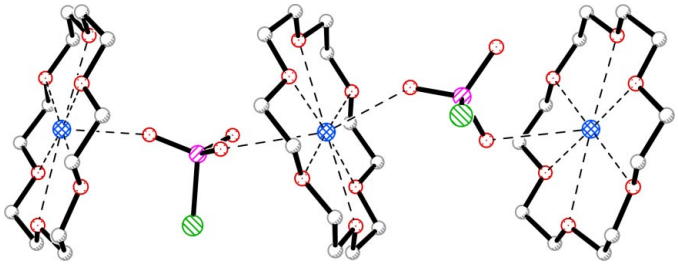


Figure 2
K^+–CrO_3^-–K^+ polymeric chains in the crystal structure of (I). H atoms have been omitted for clarity.

The macrocycle of (I) has a crown-like conformation. The O atoms are oriented toward the centre of the CE cavity and O—C—C—O fragments have alternate *+sc* and *−sc* conformations (Table 1). The cation is located approximately in the centre of this ring, lying within the mean plane of the ether O atoms [deviation only 0.004 (3) Å] and forming almost equivalent bonds to them (Table 1). Each cation is also bonded to the O atoms of two anions, leading to the formation of K^+–CrO_3^-–K^+ polymeric chains along the *a* axis of the crystal structure (Fig. 2). However, the K—O bonds to the anion are noticeably longer than those to the CE, especially for the anion at the symmetry position $(x-\frac{1}{2}, y, \frac{1}{2}-z)$, with lengths up to 3.52 (1) Å (Table 1). The weak bonding of the anion results in large-amplitude thermal motion of its O atoms (due to rotation around the Cr1—Cl1 bond) at room temperature (Fig. 1).

In the polymeric chains of (I), the mean planes of two neighbouring CE molecules form an angle of 47.44 (5)°. In the crystal structure, these chains form a herring-bone pattern (Fig. 3).

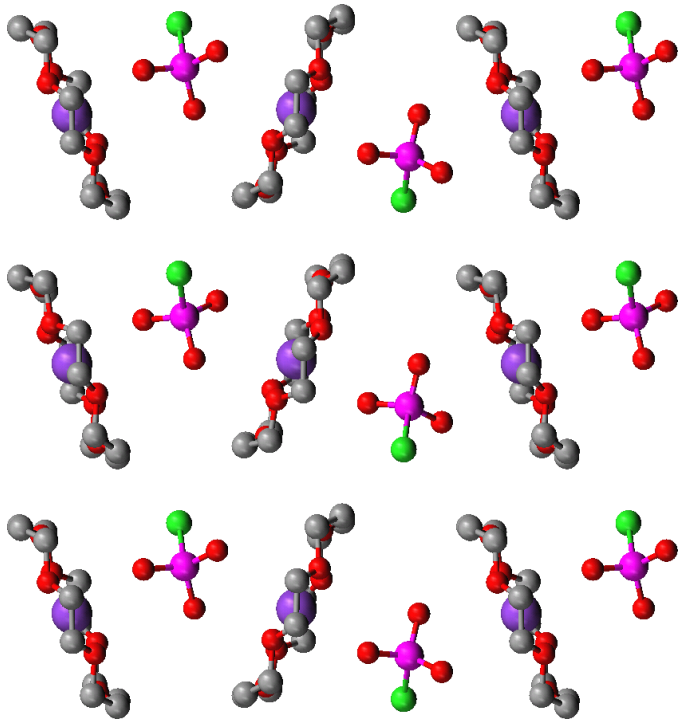


Figure 3
A packing diagram for (I), viewed along the *b* axis, showing the herring-bone pattern of crown ether molecules.

Experimental

The title complex, (I), was prepared according to the procedure of Kotlyar, Zubatyuk, Shishkin *et al.* (2004*a*), from a solution of potassium dichromate (4.41 g, 15 mmol) in distilled water, 13 *M* hydrochloric acid (10 ml) and 18-crown-6 (3.96 g, 15 mmol) (yield 93%, 6.12 g). Orange crystals of (I) suitable for X-ray investigation were obtained by evaporation of an acetone solution [m.p. 440–445 K (decomposed)]. Analysis calculated for $C_{12}H_{24}ClCrKO_9$: C 32.84, H 5.51, Cl 8.08, Cr 11.85%; found: C 32.99, H 5.39, Cl 8.19, Cr 11.77%. The crystals are soluble in dichloromethane, dimethyl sulfoxide, dimethylformamide and chloroform, weakly soluble in acetone, and slightly soluble in ethyl acetate, benzene and toluene.

Crystal data

$[K(C_{12}H_{24}O_6)][CrClO_3]$
M_r = 438.86
Orthorhombic, *Pbca*
a = 15.113 (2) Å
b = 15.692 (2) Å
c = 16.806 (2) Å
V = 3985.4 (9) Å^3
Z = 8
D_x = 1.463 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 24 reflections
θ = 12–14°
μ = 0.95 mm^{-1}
T = 293 (2) K
Block, pale orange
0.2 × 0.2 × 0.1 mm

Data collection

Siemens *P3*/PC diffractometer
$\theta/2\theta$ scans
3465 measured reflections
3416 independent reflections
1518 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 25.1°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 20$
2 standard reflections
every 98 reflections
intensity decay: 2%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.153P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.253$	$(\Delta/\sigma)_{max} < 0.0001$
$S = 0.91$	$\Delta\rho_{max} = 0.73$ e Å^{-3}
3416 reflections	$\Delta\rho_{min} = -0.38$ e Å^{-3}
217 parameters	

Table 1
Selected geometric parameters (Å, °).

K1—O1	2.804 (5)	K1—O6	2.836 (5)
K1—O2	2.785 (5)	K1—O8	2.983 (10)
K1—O3	2.800 (5)	K1—O7^{i}	3.522 (14)
K1—O4	2.811 (5)	K1—O9^{i}	3.474 (16)
K1—O5	2.815 (4)		
O1—C1—C2—O2	71.3 (8)	O4—C7—C8—O5	−71.0 (7)
O2—C3—C4—O3	−69.4 (9)	O5—C9—C10—O6	67.4 (8)
O3—C5—C6—O4	70.9 (8)	O6—C11—C12—O1	−68.7 (9)

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

All H atoms were placed in calculated positions and included in the refinement in the riding-model approximation, with C—H distance in the range 0.97–0.98 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The Cr—O distances were restrained to 1.620 (5) Å.

Data collection: *P*3 (Siemens, 1989); cell refinement: *P*3; 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: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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