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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.048
wR factor = 0.114
Data-to-parameter ratio = 13.3

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

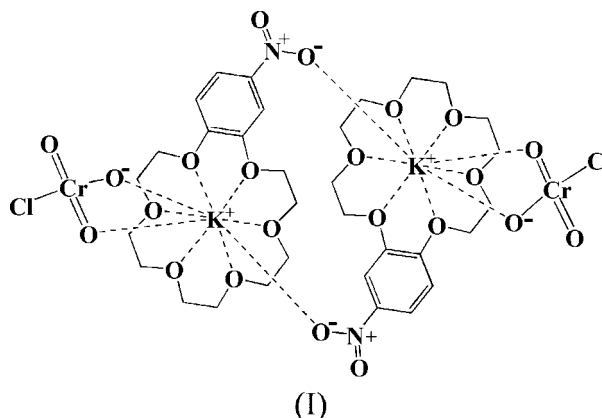
Bis(μ -18-nitro-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine)-bis[(chlorochromato)potassium]

In the title dimeric structure, $[\text{K}_2(\text{C}_{16}\text{H}_{23}\text{NO}_8)_2\{\text{CrClO}_3\}_2]$, the two macrocyclic ligands are oriented head-to-head with the stacked nitrobenzene groups.

Received 27 June 2006
Accepted 7 July 2006

Comment

Recent investigation of the structure of the complex of 4-bromobenzo-18-crown-6 with KCrClO_3 (Kotlyar *et al.*, 2006) demonstrated that the K^+ cation is coordinated by the O atoms of the macrocycle and two neighbouring anions. In the crystal structure, such coordination results in the formation of one-dimensional polymeric chains along [001]. The crystal structure of the title compound, (I), a complex of 4-nitrobenzo-18-crown-6 with KCrClO_3 (asymmetric unit shown in Fig. 1), reveals that replacing the Br substituent by a nitro group results in significant changes to the crystal structure.



The dimeric structure of (I), which is generated by a crystallographic centre of symmetry, is shown in Fig. 2. Two macrocyclic ligands are oriented head-to-head with two stacked nitrobenzene fragments (perpendicular distance between rings = 3.47 Å). The nitro group is slightly twisted out of the plane of the C1–C6 ring, with a torsion angle O7–N1–C4–C3 = 2.2 (5)°. The K^+ ion is coordinated equatorially by six O atoms of the macrocycle, and in the axial positions by atoms O9 and O11 of the anion on one side of the crown ether and by atom O7ⁱ [symmetry code: (i) 1 – x, 1 – y, 2 – z] of a nitro group on the other side of the macrocycle. The aliphatic macrocycle has the expected crown-like conformation, with the O–C–C–O sequence of atoms having alternating +sc and –sc conformations (Table 1).

The aromatic ring deviates from the macrocycle plane toward the K^+ ion of the inversion-related cation. Unlike in the structure of the 4-bromobenzo derivative (Kotlyar *et al.*, 2006), each chlorochromate anion in (I) coordinates to only

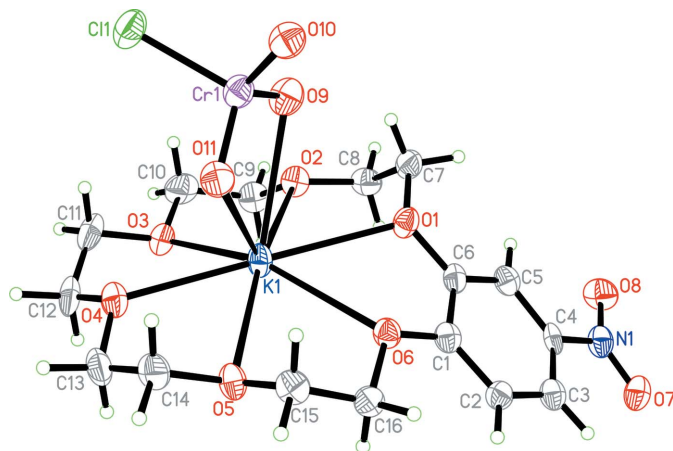


Figure 1
A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level.

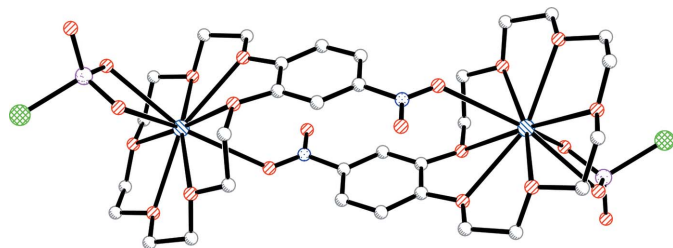


Figure 2
A view of the dimeric structure of (I). H atoms have been omitted for clarity.

one K^+ ion. The macrocycle O atoms and the K^+ ion are coplanar to within 0.24 Å. The range of K—O distances (Table 1) is typical for this type of compound. Repulsion between the aromatic ring and the atoms of the macrocycle is reflected in some short intramolecular non-bonded distances, e.g. $H2 \cdots C16 = 2.52$ Å (sum of the van der Waals radii = 2.87 Å; Zefirov & Zorky, 1995), $H2 \cdots H16B = 2.25$ Å (2.34 Å), $H16B \cdots C2 = 2.75$ Å, $H16A \cdots C2 = 2.77$ Å, $H5 \cdots C7 = 2.60$ Å, $H5 \cdots H7B = 2.03$ Å and $H7B \cdots C5 = 2.53$ Å.

Some short intermolecular distances are also observed, e.g. $H3 \cdots H8A(1-x, 1-y, 2-z) = 2.28$ Å (sum of van der Waals radii is 2.34 Å), $H7B \cdots O10(2-x, 2-y, 2-z) = 2.33$ Å (2.46 Å), $C11 \cdots C11(2-x, 2-y, 1-z) = 3.49$ Å (3.61 Å), $C11 \cdots C13(1-x, 2-y, 1-z) = 3.54$ Å, $C11 \cdots H11A(2-x, 2-y, 1-z) = 2.89$ Å (3.06 Å) and $C11 \cdots H13A(1-x, 2-y, 1-z) = 2.99$ Å.

Experimental

Complex (I) was prepared according to the previously described procedure of Kotlyar *et al.* (2000) by mixing ethyl acetate solutions (10 ml) of 4-nitrobenzo-18-crown-6 (2.0 g, 5.6 mmol) and potassium chlorochromate (0.98 g, 5.6 mmol) at room temperature (yield 83%, 2.47 g). Transparent yellow crystals of (I) suitable for X-ray investigation were obtained by evaporation from dichloromethane solution [m.p. 442–445 K (decomposition)]. Analysis, calculated for $C_{16}H_{23}NClCrKO_{11}$: C 36.13, H 4.36, Cl 6.67, Cr 9.78, N 2.63%; found:

C 36.20, H 4.28, Cl 6.64, Cr 9.71, N 2.65%. The crystals are soluble in dichloromethane, chloroform, dimethyl sulfoxide, dimethylformamide and acetone, sparingly soluble in ethyl acetate, and practically insoluble in benzene and toluene.

Crystal data

$[K_2Cr_2Cl_2O_6(C_{16}H_{23}NO_8)_2]$
 $M_r = 1063.82$
Triclinic, $P\bar{1}$
 $a = 8.778$ (1) Å
 $b = 9.531$ (1) Å
 $c = 13.678$ (1) Å
 $\alpha = 100.959$ (9)°
 $\beta = 98.728$ (9)°
 $\gamma = 98.782$ (9)°

$V = 1090.8$ (2) Å³
 $Z = 1$
 $D_x = 1.619$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.90$ mm⁻¹
 $T = 100$ (2) K
Block, yellow
0.20 × 0.20 × 0.10 mm

Data collection

Oxford Xcalibur3 diffractometer
 ω scans
Absorption correction: none
8636 measured reflections

3715 independent reflections
2363 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.039$
 $\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.114$
 $S = 0.89$
3715 reflections
280 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0655P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.66$ e Å⁻³
 $\Delta\rho_{min} = -0.29$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

K1—O4	2.725 (3)	K1—O6	2.858 (3)
K1—O2	2.768 (3)	K1—O11	2.914 (3)
K1—O3	2.769 (3)	K1—O7 ⁱ	3.001 (3)
K1—O5	2.773 (3)	K1—O9	3.029 (3)
K1—O1	2.784 (3)		
O6—C1—C6—O1	4.9 (5)	O3—C11—C12—O4	63.0 (4)
O1—C7—C8—O2	68.5 (4)	O4—C13—C14—O5	−67.5 (4)
O2—C9—C10—O3	−66.6 (5)	O5—C15—C16—O6	67.7 (4)

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

All H atoms were located in difference Fourier maps but were subsequently placed in calculated positions, with C—H distances in the range 0.95–0.99 Å, and included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *XP* (Siemens, 1998); software used to prepare material for publication: *SHELXTL/PC*.

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