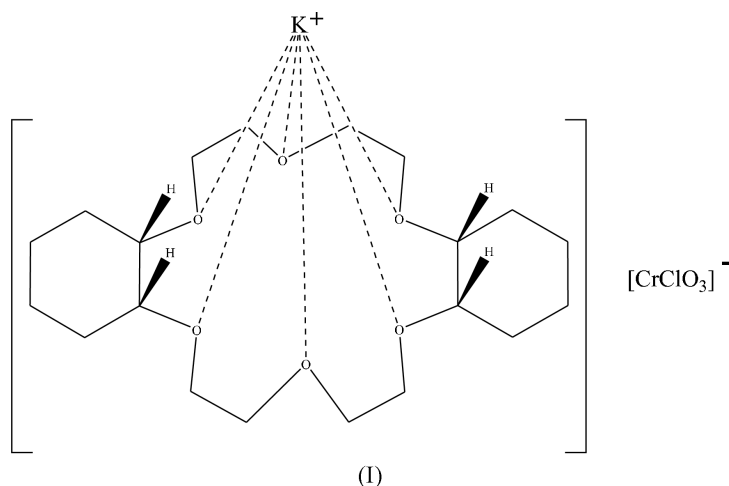


**(*cis-syn-cis*-Dicyclohexano-18-crown-6)-
potassium chlorochromate**Sergey A. Kotlyar,^a Roman I. Zubatyuk,^{b*} Marina V. Zhigalko,^b Oleg V. Shishkin,^b Gennady N. Chuprin,^a Andrey V. Kiriya^a and Gerbert L. Kamalov^a^aA. V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, Odessa 65080, Ukraine, and ^bInstitute for Scintillation Materials, STC 'Institute for Single Crystals', National Academy of Sciences of Ukraine, 60 Lenina ave., Kharkiv 61001, UkraineCorrespondence e-mail:
roman@xray.isc.kharkov.com**Key indicators**Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C)$ = 0.009 Å
R factor = 0.038
wR factor = 0.091
Data-to-parameter ratio = 8.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

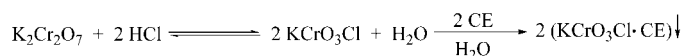
The title compound, (*cis-syn-cis*-icosahydrodibenzo-*[b,k]*[1,4,7,10,13,16]hexaoxacyclooctadecin)potassium chlorochromate, $[K(C_{20}H_{36}O_6)][CrClO_3]$, is the complex of a potassium cation with one crown ether molecule and a chlorochromate anion. The cation is situated in the macrocyclic cavity and bonded to the ether O atoms with K–O distances in the range 2.749 (4)–2.991 (3) Å. It also forms two bonds with O atoms of the anion [2.789 (5) and 3.315 (7) Å].

Comment

There are five known stereoisomers for dicyclohexano-18-crown-6, which is widely used in host–guest chemistry (Hiraoka, 1982). Earlier, for the first time, we obtained individual *cis-syn-cis* (isomer A) and *cis-anti-cis* (isomer B) isomers of dicyclohexano-18-crown-6 from a mixture of dibenzo-18-crown-6 hydrogenation products using neutral organic guest molecules (Ganin *et al.*, 1988). We have synthesized the corresponding stable crystalline complexes of those isomers with potassium chlorochromate and noticed the differences in their reactivity in complex formation. Isomer A easily forms a complex with this salt in the equilibrium acid aqueous solution, similar to previously reported complexes of *cis*-cyclohexano-12-crown-4 (Kotlyar *et al.*, 2004a) and *cis*-cyclohexano-18-crown-6 with $KCrO_3Cl$ (Kotlyar *et al.*, 2004b), or crystallizes during mixing of ethyl acetate solutions of salt and crown ether (CE). In contrast, the pure complex of isomer B was obtained only by the latter method.



We now report the crystal structure of the title complex, (I), of *cis-syn-cis*-dicyclohexano-18-crown-6 with potassium chlorochromate obtained in a 1:1 ratio according to the reaction scheme below.



The macrocycle of (I) adopts a considerably flattened crown-like conformation (Fig. 1). The r.m.s. deviation of the ether O atoms from their mean plane is only 0.13 Å. The potassium cation is displaced from this plane by 0.591 (2) Å towards the anion. The bond lengths between cation and the O atoms of CE are in the wide range 2.75–3.00 Å (Table 1). By comparison, the K–O bond lengths in *cis*-cyclohexano-18-crown-6·KCrO₃Cl (Kotlyar *et al.*, 2004b) are in the range 2.78–2.89 Å. The shorter bonds in (I) are formed with atoms O4, O5 and O6 and the longer bonds with atoms O1, O2 and O3. We can assume that the variation of the K–O_{ether} distances is probably caused by the asymmetry of electrostatic field around the cation in the crystal structure. Thus, the potassium cation forms two non-equivalent bonds with the O atoms of the anion: a normal K1–O8 bond and a weak K1–O7 bond. The latter can be classified as an extra-coordination bond.

Experimental

To a stirred saturated solution of potassium dichromate (2.18 g, 7.5 mmol) in distilled water and 13 M hydrochloric acid (5 ml) at room temperature was added *cis-syn-cis*-dicyclohexano-18-crown-6 (2.79 g, 7.5 mmol) and an orange precipitate was obtained over a period of 2–3 min. This was filtered off, washed with cold water (2 ml) and diethyl ether (5 ml), dried at reduced pressure and heated at 323 K to constant weight (yield 86%, 3.36 g). Transparent pale-orange crystals suitable for X-ray investigation [m.p. 381–385 K (decomposition)] were obtained by evaporation of a methylene chloride solution. Analysis calculated for C₂₀H₃₆ClCrKO₉: C 43.91, H 6.63; Cl 6.48; Cr 9.50%; found: C 43.99, H 6.58; Cl 6.57; Cr 9.64%. The crystals are soluble in methylene chloride, dimethyl sulfoxide and dimethylformamide, weakly soluble in chloroform, acetone, and slightly soluble in ethyl acetate.

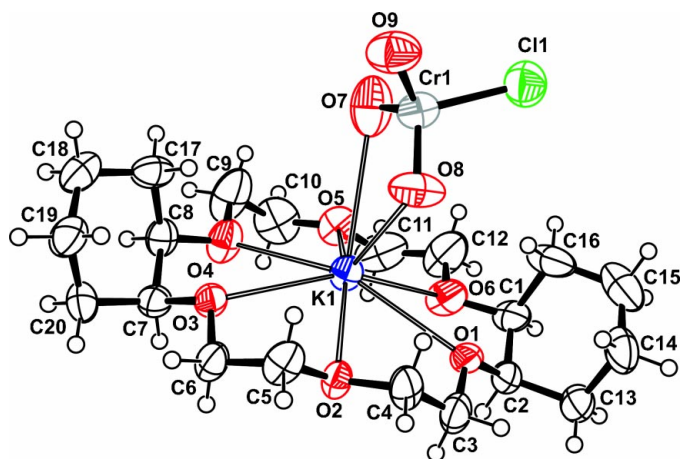


Figure 1
View of (I), with 50% probability displacement ellipsoids.

Crystal data

[K(C₂₀H₃₆O₆)] [CrClO₃]
M_r = 547.04
 Monoclinic, *P*2₁
a = 8.8828 (17) Å
b = 10.271 (2) Å
c = 14.408 (3) Å
 β = 104.306 (17)°
V = 1273.8 (4) Å³
Z = 2

D_x = 1.426 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 12–15°
 μ = 0.76 mm⁻¹
T = 293 (2) K
 Block, pale orange
 0.20 × 0.20 × 0.10 mm

Data collection

Siemens *P3/PC* diffractometer
 θ –2 θ scans
 Absorption correction: none
 2518 measured reflections
 2367 independent reflections
 1729 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.046

θ_{max} = 25.1°
h = 0 → 10
k = 0 → 12
l = –17 → 16
 2 standard reflections
 every 98 reflections
 intensity decay: 5%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.038
wR(*F*²) = 0.091
S = 0.93
 2367 reflections
 289 parameters

H-atom parameters constrained
w = 1/[$\sigma^2(F_o^2) + (0.0528P)^2$]
 where *P* = (*F_o*² + 2*F_c*²)/3
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-----------|---------------|-----------|
| K1–O1 | 2.922 (3) | K1–O5 | 2.808 (4) |
| K1–O2 | 2.814 (3) | K1–O6 | 2.806 (4) |
| K1–O3 | 2.991 (3) | K1–O7 | 3.315 (7) |
| K1–O4 | 2.749 (4) | K1–O8 | 2.789 (5) |
| O1–C3–C4–O2 | 70.8 (7) | O3–C7–C8–O4 | 60.7 (5) |
| O6–C1–C2–O1 | –60.5 (6) | O4–C9–C10–O5 | –63.2 (9) |
| O2–C5–C6–O3 | –71.5 (6) | O5–C11–C12–O6 | 64.3 (8) |

All H atoms were placed in calculated positions and included in the refinement in the riding-model approximation; C–H = 0.97–0.98 Å and *U*_{iso}(H) = 1.2*U*_{eq}(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*.

References

- Ganin, E., Makarov, V., Lukyanenko, N. & Kotlyar, S. (1988). *Russ. J. Gen. Chem. (Engl. Transl.)*, **58**, 1309–1313.
- Hiraoka, M. (1982). *Crown Compounds: Their Characteristics and Application*, p. 46. Tokyo: Kodansha Ltd.
- Kotlyar, S., Zubatyuk, R., Shishkin, O., Chuprin, G., Kiriya, A. & Kamalov, G. (2004a). *Acta Cryst. E60*, m907–m909.
- Kotlyar, S., Zubatyuk, R., Shishkin, O., Chuprin, G., Kiriya, A. & Kamalov, G. (2004b). *Acta Cryst. E60*, m1015–m1016.
- Sheldrick, G. M. (1990). *Acta Cryst. A46*, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1989). *P3*. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.
- Siemens (1991). *XDISK* and *XP*. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.