The H atoms of the OH groups were found in the difference syntheses and all their parameters were refined. However, the H atoms of the CH groups were located in suitable geometric positions calculated using *SHELXL*93 (Sheldrick, 1993), and were refined using a riding model with $U_{\rm iso}$ fixed at 0.08 Å^2.

During the refinement, two peaks with large residual electron density were found near the C6 and O5 sites, which were then further refined as split atom sites C6*a*/C6*b* and O5*a*/O5*b*, respectively. The occupancies of the C6*a* and C6*b* sites were then constrained to a sum of 1.0, while the occupancies of the O5*a* and O5*b* sites were constrained to be the same as those of the C6*a* and C6*b* sites, respectively. The displacement parameters of the above-mentioned atom sites were all left unconstrained however. Attempts to refine the structure with a single strongly anisotropic C6 site were unsuccessful and resulted in very odd displacements. Indeed, the present split sites have more realistic geometric positions; the bond distances C5—C6*a* 1.53 (2), C5—C6*b* 1.42 (1), C6*a*—O5*a* 1.42 (2) and C6*b*—O5*b* 1.41 (1) Å, and the bond angles N—C5—C6*a* 114.9 (6), N—C5—C6*b* 116.0 (5), C5—C6*a*—O5*a* 119.2 (12) and C5—C6*b*—O5*b* 107.8 (7)° are more comparable with those of similar compounds (Sun *et al.*, 1997, 1998). It seems that this kind of disorder, which originates from the one-dimensional zigzag chiral chain, is incompatible with the crystallographic 2_1 symmetry along the *b* axis or the thermal motion of the hydroxyethyl group in the ligand.

Full-matrix least-squares refinement using anomalous dispersion factors for all non-H atoms resulted in an *R* factor of 0.039 for the present absolute structure and 0.05 for the other enantiomorph. Consequently, the absolute configuration of the compound has been assigned as *R*. The Flack parameter (Flack, 1983) also confirmed this assignment.

In the final cycles of refinement, seven reflections were omitted because of their large $(F_o^2 - F_c^2)$/s.u. ratios. In the final electron-density difference map, the minimum of -1.012 e Å^{-3} and maximum of 0.54 e Å^{-3} were near the Mn atom at distances of 1.0 and 0.80 Å, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1217). Services for accessing these data are described at the back of the journal.

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5-(8,8-Dicyanoheptafulven-3-yl)-2-hydroxy-1,3-xylyl-18-crown-5 potassium salt monohydrate†

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Abstract

The title compound, $[K(C_{26}H_{27}N_2O_6)]\cdot H_2O$, is a potassium salt of the crown ether dye composed of 8,8-dicyanoheptafulvene and a crown ether having a phen-

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† Systematic name: potassium 19-(8,8-dicyanoheptafulven-3-yl)bicyclo[15.3.1][3,6,9,12,15]pentaoxahenicosa-1(20),17(21),18-trien-21-olate monohydrate.

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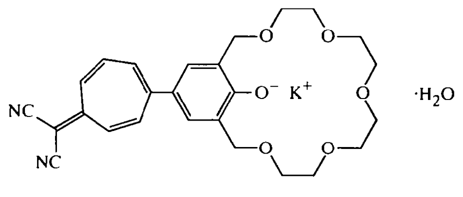
olic hydroxide in its cavity. Due to lone-pair repulsion of the inner O atoms of the crown ether ring and the phenoxide, the ether ring deviates significantly from the plane of the phenyl ring (by about 38.01°). On the other hand, the phenoxide anion (–O$^-$) remains in the plane of the phenyl ring and the potassium cation is included in the cavity of the crown ether ring. The phenyl ring is twisted out of the planar seven-membered ring by about 28.24°.

Comment

The title compound, (I), is a potassium salt of the crown ether dye 5-(8,8-dicyanoheptafulven-3-yl)-2-hydroxy-1,3-xylyl-18-crown-5, based on a novel 8,8-dicyanoheptafulvene chromophore. In the course of our studies on the metal-selective coloration of the crown ether dye in solution by means of a variety of alkali metal bases, we found that a significant color change occurs from red to blue, but quite irrespective of the cation species (Otani *et al.*, 1997; Yumura *et al.*, 1998). This result strongly suggests that the crown ether ring can deviate from the heptafulvene skeleton and the hydroxide group is consequently exposed. In fact, geometry optimization by molecular-orbital calculations supported this conformation. In order to confirm the present model experimentally, the structure analysis of (I) was undertaken.



(I)

The crown ether ring deviates significantly from the plane of the phenyl ring (by about 38.01°) due to lone-pair repulsion of the O atoms of the crown ether ring and the phenoxide. On the other hand, the phenoxide anion remains in the plane of the phenyl ring and the potassium cation is included in the cavity of the crown ether ring. The present result favors our expected model and is found to be very similar to that for a crowned *p*-nitrophenol derivative (Browne *et al.*, 1985).

Although some bond alteration is still recognized (Table 1) in the seven-membered ring, the ring is planar within experimental error. One water molecule, formed by a deprotonation reaction or from an aqueous solution of potassium hydroxide, is observed in the vicinity of the phenoxide, while the potassium cation is included in the cavity of the crown ether ring. Since the molecule possesses a large dipole moment of about 6.6 D (Yumura *et al.*, 1998), caused by the dicyanomethylidene group

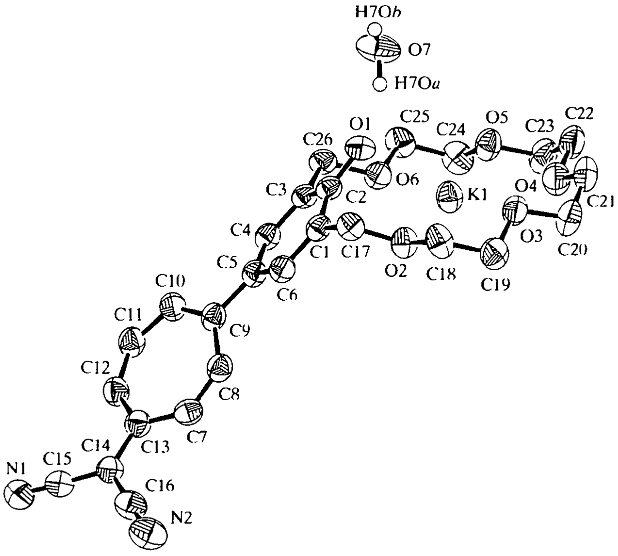


Fig. 1. The molecular conformation of (I) showing 50% probability displacement ellipsoids. H atoms, except those of water, have been omitted for clarity.

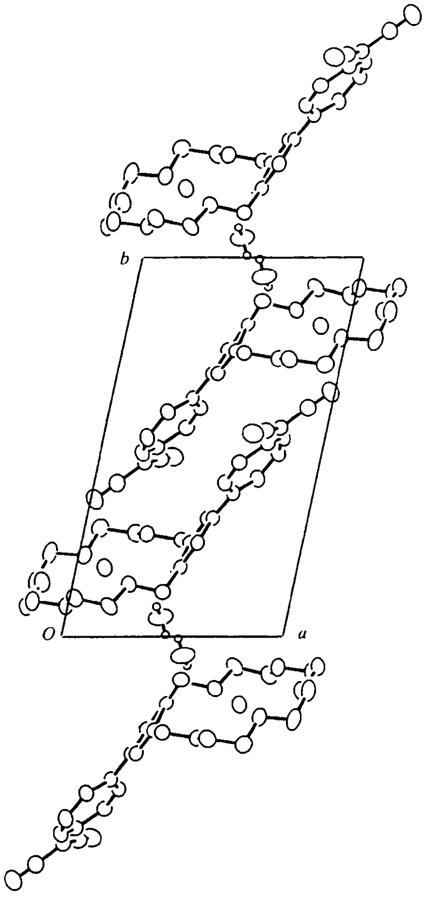


Fig. 2. Projection of the crystal structure onto the *ab* plane.

(electron acceptor) and the hydroxide group (electron donor), the molecules are likely to dimerize themselves so as to reduce the electrostatic energy, leading to the stabilization of the ground state of the total system. The molecules are therefore arranged alternately along the *a* axis, as well as along the *b* axis (Fig. 2).

Experimental

5-(8,8-Dicyanoheptafulven-3-yl)-2-hydroxy-1,3-xylyl-18-crown-5 was synthesized according to a method reported previously and the title compound was then prepared on 1:1 deprotonation with potassium hydroxide in acetonitrile (Yumura *et al.*, 1998). Single crystals were grown from the solution by solvent evaporation over several days.

Crystal data

$[K(C_{26}H_{27}N_2O_6)]\cdot H_2O$
$M_r = 520.62$
Triclinic
$P\bar{1}$
$a = 9.245\,(2)$ Å
$b = 16.226\,(2)$ Å
$c = 8.828\,(2)$ Å
$\alpha = 92.41\,(1)^\circ$
$\beta = 98.17\,(2)^\circ$
$\gamma = 78.08\,(1)^\circ$
$V = 1282.3\,(4)$ Å^3
$Z = 2$
$D_x = 1.348$ Mg m^{-3}
$D_m = 1.320$ Mg m^{-3}
D_m measured by flotation in C_6H_6/CCl_4

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 19 reflections
$\theta = 29.6$–30.0°
$\mu = 2.223$ mm^{-1}
$T = 296.2$ K
Platelet
0.25 × 0.25 × 0.01 mm
Brown

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.856$, $T_{\max} = 1.000$
4931 measured reflections
4618 independent reflections

3247 reflections with $I > \sigma(I)$
$R_{\text{int}} = 0.034$
$\theta_{\max} = 67.59^\circ$
$h = 0 \rightarrow 11$
$k = -19 \rightarrow 19$
$l = -10 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: 11.64%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.061$
$S = 1.312$
3247 reflections
326 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00068|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.016 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C2	1.293 (3)	C7—C8	1.345 (4)
N1—C15	1.141 (5)	C7—C13	1.436 (4)
N2—C16	1.141 (5)	C8—C9	1.441 (4)
C1—C2	1.431 (4)	C9—C10	1.372 (4)
C1—C6	1.380 (4)	C10—C11	1.411 (4)
C2—C3	1.433 (4)	C11—C12	1.354 (4)
C3—C4	1.371 (4)	C12—C13	1.429 (4)
C4—C5	1.405 (4)	C13—C14	1.395 (4)
C5—C6	1.405 (4)	C14—C15	1.422 (5)
C5—C9	1.474 (4)	C14—C16	1.423 (4)
C2—C1—C6	120.6 (3)	C5—C9—C10	119.1 (3)
O1—C2—C1	121.2 (3)	C8—C9—C10	122.9 (3)
O1—C2—C3	122.2 (2)	C9—C10—C11	129.2 (3)
C1—C2—C3	116.5 (3)	C10—C11—C12	131.3 (3)
C2—C3—C4	120.6 (3)	C11—C12—C13	129.3 (3)
C3—C4—C5	122.6 (3)	C7—C13—C12	121.9 (3)
C4—C5—C6	116.7 (3)	C7—C13—C14	118.9 (3)
C4—C5—C9	121.1 (3)	C12—C13—C14	119.0 (3)
C6—C5—C9	122.2 (3)	C13—C14—C15	121.2 (3)
C1—C6—C5	122.3 (3)	C13—C14—C16	121.8 (3)
C8—C7—C13	130.8 (3)	C15—C14—C16	116.9 (3)
C7—C8—C9	132.3 (3)	N1—C15—C14	178.7 (4)
C5—C9—C8	118.0 (3)	N2—C16—C14	178.9 (4)

The non-H atoms were refined anisotropically by full-matrix least-squares methods. The H atoms of water were localized, while the others were included but not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1064). Services for accessing these data are described at the back of the journal.

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