The Crystal Structure of a Complex between 2,3,11,12-(Bis-1,2-acenaphtho)-18-crown-6 and Potassium Isothiocyanate

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'Benzo-crowns', *i.e.* macrocyclic oligoethers containing 1,2-phenylene entities, have long been known to form stable complexes with alkali and alkaline earth metal ions [1, 2]. The title ligand **L** [3] may be considered an acenaphthyleno analogue of dibenzo-18-crown-6. However, its coordination abilities turned out to be very poor; only an **L**·KNCS complex could be isolated [3] to study and compare its crystal structure with those of related compounds.

Experimental

The title complex could not be recrystallised without disintegration [3]; hence the crystal quality was rather poor.

Crystal Data

$C_{32}H_{28}O_6 \cdot KNCS$, M = 605.76, orthorhombic space group $Cmc2_1$, a = 22.814(9), b = 15.170(6), c = 8.282(4) Å, $D_{calc.}$ = 1.404 g cm^{-3} for Z = 4, μ(MoKα) = 0.30 mm^{-1}.

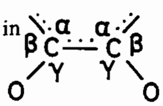
TABLE I. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3).

	x	y	z	U[a]
K	0	3625(1)	4426[b]	59(1)
S	0	783(3)	1714(13)	179(4)
C	0	1836(8)	1774(17)	69(4)
N	0	2581(8)	1745(15)	84(4)
O(1)	0	2075(4)	6044(10)	60(2)
C(2)	515(3)	1664(5)	6529(15)	79(3)
C(3)	1023(3)	2020(4)	5741(14)	78(3)
O(4)	1077(2)	2934(3)	6060(7)	62(2)
C(5)	1576(3)	3359(4)	5555(9)	44(2)
C(6)	1584(2)	4140(4)	4863(9)	51(2)
O(7)	1079(2)	4584(2)	4377(7)	55(1)
C(8)	1039(3)	5483(4)	4895(11)	63(3)
C(9)	512(3)	5877(4)	4169(14)	70(3)
O(10)	0	5466(4)	4729(11)	63(3)
C(11)	2190(3)	3049(4)	5798(8)	48(2)
C(12)	2470(3)	2332(5)	6421(11)	64(3)
C(13)	3092(3)	2318(6)	6428(11)	70(3)
C(14)	3424(3)	2965(5)	5797(10)	61(3)
C(15)	3149(3)	3723(4)	5129(10)	55(2)
C(16)	3423(3)	4469(5)	4424(10)	63(2)
C(17)	3093(3)	5143(6)	3801(11)	72(3)
C(18)	2465(3)	5139(6)	3841(10)	62(3)
C(19)	2189(2)	4437(4)	4545(10)	51(2)
C(20)	2538(3)	3735(4)	5149(10)	49(2)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b]Fixed to define the origin on the polar axis.

1832 observed [$F > 3\sigma(F)$] profile-fitted [4] diffractometer data up to 2θ = 47° were collected from a red prism *ca.* 0.3 × 0.5 × 0.6 mm with monochromated MoKα-radiation (λ = 0.71069 Å). The structure was solved by direct methods and subsequent Fourier syntheses [5], and refined anisotropically to a final R of 0.083 with H-atoms included in calculated positions [C–H = 0.96 Å, $U(H_i)$ = 1.2 $U_{eq}(C_i)$].

Atom parameters are listed in Table I; further crystallographic information is available from GW on request.

TABLE II. Mean Distances (Å) and Angles (°) in 

Units of Crown Ethers.

	C⋯C	α	β	γ	O⋅⋅O
L [3]	1.36	109	120, 126	125, 131	3.04
L·KNCS	1.32	110	126	124	2.87
DB-18-Cr-6 [6]	1.41	119	127	114	2.55
DB-18-Cr-6·KI [8]	1.39	121	124	116	2.56

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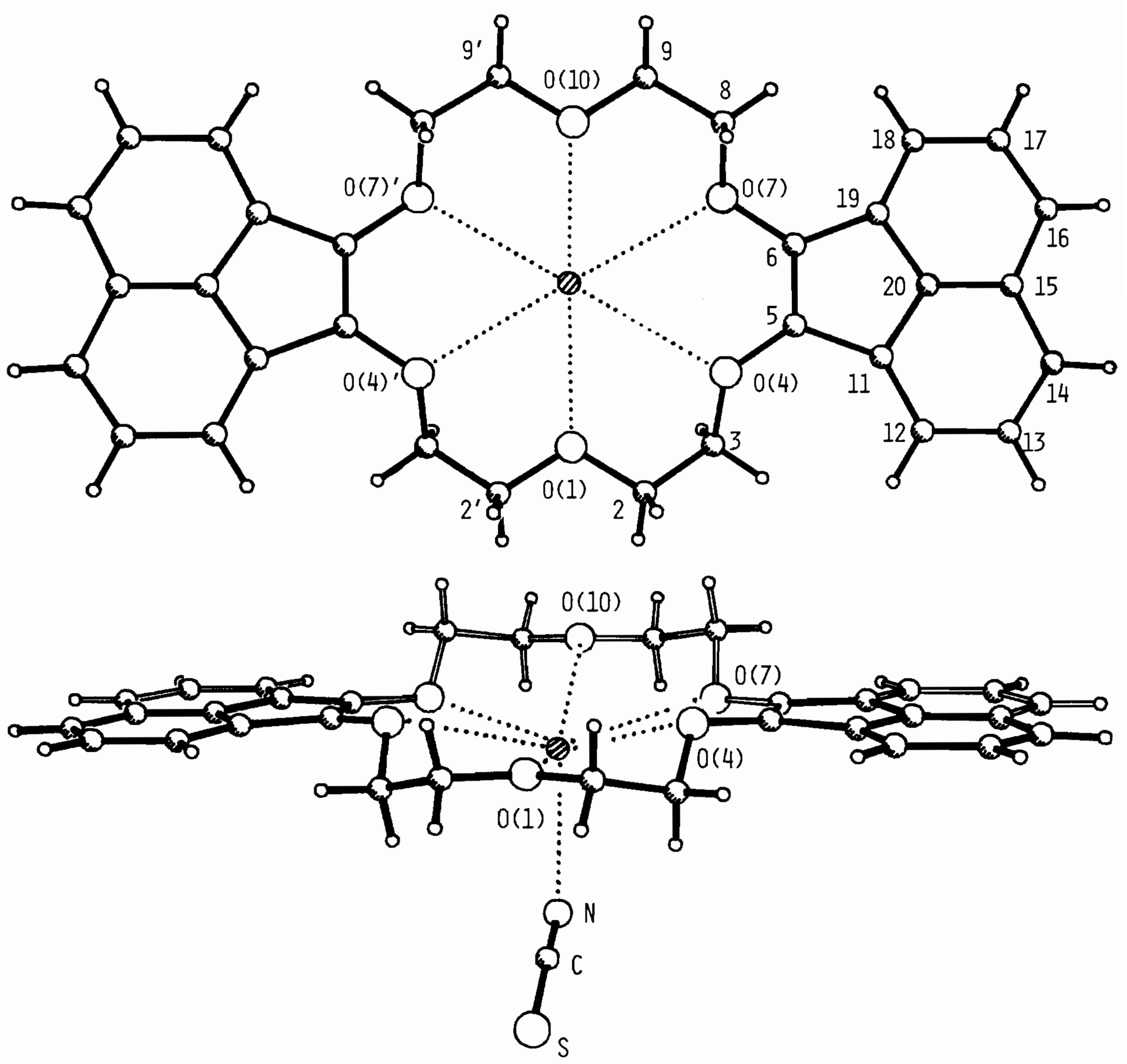

Fig. 1. Top and side views of the title complex including the numbering scheme. Primed atoms are related to the respective unprimed ones by a mirror running through O(1), O(10), K, N, C, and S. Radii are arbitrary; the anion in the top view is omitted for clarity. Coordination distances (Å) are to O(1): 2.706(6), to O(4): 2.994(8), to O(7): 2.860(7), to O(10): 2.804(6), to N: 2.727(9).

Results and Discussion

In the uncomplexed state, the title ligand **L** displays an elongated conformation [3] comparable to those found in uncomplexed dibenzo-18-crown-6 [6] or in 18-crown-6 itself [7]. However, when coordinating a 'fitting' spherical e^- acceptor like K^+, 18-membered crown ethers usually adopt a circular form (*e.g.* [8, 9]). This also holds for the present complex (Fig. 1) but torsion angles of 137.2(8)° [C(3)–O(4)–C(5)–C(6)] and 130.6(7)° [C(5)–C(6)–O(7)–C(8)] deviate considerably from the respective torsions (≈*anti*) in dibenzo-18-crown-6·KI [8] and thereby indicate the steric strain induced by the acenaphthylene nuclei.

The poor complexing ability of **L**, as compared to that of the analogous dibenzo-18-crown-6, was attributed mainly [3] to the unfavourable geometry at the O–C=C–O entity. The shortened C(5)–C(6) bond and widened exocyclic and narrowed endocyclic $O–C_{sp^2}–C_{sp^2}$ angles in **L**·KNCS all facilitate an O(4)··O(7) distance of 2.87(1) Å. This value is much more appropriate for vicinal oxygen atoms (when part of a hexagonal environment of K^+) than is the observed 3.04 Å in free **L**, but it is still larger than in dibenzo-18-crown-6 (see Table II).

The six O(ether) atoms (co-planar to within ±0.35 Å; *cf.* ±0.19 Å in 18-crown-6·KNCS [9] and ±0.13 Å in dibenzo-18-crown-6·KI [8]) are thus able to form the basal plane of the quite common (*e.g.* [8–11]) hexagonal coordination pyramid of potassium, with K^+ displaced by 0.73(2) Å towards the apical anion (*cf.* [8, 10]).

However, the gain of energy on complex formation may well be modest since $K^+\cdot\cdot O$ distances (mean 2.87 Å; *cf.* 2.76 Å in dibenzo-18-crown-6·KI [8, 11] and 2.80 Å in 18-crown-6·KNCS [9]) give rise to a $K^+\cdot\cdot O$ bond valence [12] of only 0.77 (*cf.* 1.04 in [8] and 0.90 in [9]). This might be taken as further evidence for the poorly-fitting geometry of **L** and is in agreement with the low stability of the title complex [3].

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