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(Dibenzo-18-crown-6)(2-phenylamidopyridine)-potassium(I)

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The title complex, [Rb($C_{11}H_9N_2$)($C_{20}H_{24}O_6$)], has potassium in an irregular eightfold coordination, with a hexadentate crown ether ligand and a chelating bidentate amidopyridine ligand, each occupying one hemisphere of the coordination. The chelate KNCN ring is slightly folded, and the two rings of the amidopyridine ligand are not coplanar, because of steric interaction of H atoms on the rings. The K—N(amido) bond is shorter than the K—N(pyridine) bond. The coordination of the crown ether to potassium is less symmetrical than that for the analogous rubidium complex, reflecting a poorer size match for K^+ in this coordination site.

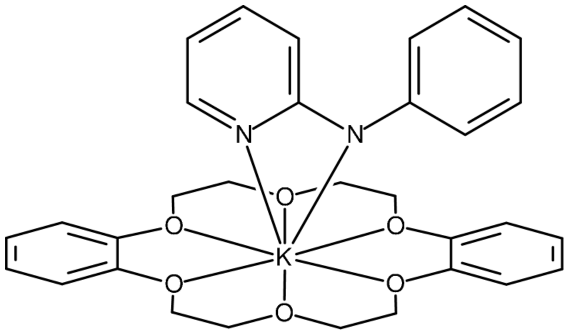
Key indicators

Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.110
Data-to-parameter ratio = 18.5

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

Comment

In the preceding paper (Liddle & Clegg, 2004), we described the structure of the complex (dibenzo-18-crown-6)Rb(L), where HL is 2-phenylaminopyridine. We present here the structure of the analogous potassium complex, (dibenzo-18-crown-6)K(L), (I). These complexes were prepared as part of a study of crown-ether-supported complexes of alkali metals with amide ligands, and were investigated specifically for comparison with the complexes with 18-crown-6 (Liddle *et al.*, 2004; Liddle & Clegg, 2003).



(I)

Although the Rb complexes with the two different crown ethers are structurally very similar, there is a marked difference for the K complexes. Reaction of equimolar amounts of 18-crown-6, potassium hydride and HL leads to the polymeric complex $[(18\text{-crown-}6)K(L)_2K]_\infty$, even though this product has a 1:2:2 stoichiometry (Liddle *et al.*, 2004). With dibenzo-18-crown-6 instead of 18-crown-6, the title complex (with a 1:1:1 stoichiometry) is obtained, exactly analogous to the Rb case.

The dibenzo-18-crown-6 complexes of Rb and K are structurally similar in gross terms; there are subtle but significant differences in detail. Fig. 1 shows the molecular structure of the title K complex, and selected geometric parameters are in Table 1. It consists of discrete neutral molecules with no special intermolecular interactions. The hexadentate crown ligand and the bidentate amide anion occupy the two coordination hemispheres of the potassium ion, giving irregular eightfold coordination, and the complex may be described as a contact ion pair.

The range of K—O distances and the difference between the two K—N distances are both somewhat greater than the corresponding values for the Rb complex, and this probably reflects the poorer fit of the smaller potassium ion in the coordination site; it is generally recognized that 18-crown-6 and its substituted derivatives provide an ideal fit for K^+ in the mean plane of the six O atoms rather than displaced from this plane. In the title complex, K lies 0.7830 (7) Å out of the oxygen mean plane (r.m.s. deviation 0.009 Å), compared with a deviation of 1.0945 (6) Å for Rb in the analogous complex. Although all four O—C—C—O aliphatic segments have a *gauche* conformation, as is expected for optimal chelation, the overall conformation of the crown in this complex differs from that in the Rb complex by conversion of one *anti* C—C—O—C linkage to *gauche*, the other eleven remaining *anti* (Table 1). The crown ligand is thus rather less symmetrical in the title complex than in the Rb complex. The two benzene rings are folded out of the oxygen mean plane, away from the amide ligand by 39.97 (6) and 8.52 (7)°, in contrast to the angles of 22.93 (7) and 25.94 (7)° towards the amide ligand in the Rb complex.

The two rings of the amide ligand have a dihedral angle of 49.91 (7)° because of steric interaction of H atoms bonded to C4 and C11. The four-membered chelate ring (KNCN) is approximately planar, the dihedral angle between the KN_2 and CN_2 planes being 7.3 (2)°, compared with only 0.3 (3)° in the Rb complex, once again displaying the effects of greater geometrical strain from the size mismatch of the metal ion and its ligand set.

Experimental

Potassium hydride (0.04 g, 1.0 mmol) was added to a solution of 2-phenylaminopyridine (0.17 g, 1.0 mmol) and dibenzo-18-crown-6 (0.36 g, 1.0 mmol) in tetrahydrofuran (THF, 40 ml), to give a pale yellow precipitate. Volatile components were removed *in vacuo* and the remaining solid was washed with petroleum ether (3 × 5 ml). Recrystallization from hot toluene containing a little hexamethylphosphoramide (HMPA) gave yellow crystals of (I) (yield 0.38 g, 67%). Chemical analysis results were satisfactory, and the ^{1}H and ^{13}C{^{1}H} NMR signals could be assigned on the basis of the crystal structure (Liddle, 2000).

Crystal data

$[K(C_{11}H_9N_2)(C_{20}H_{24}O_6)]$
$M_r = 568.69$
Monoclinic, $C2/c$
$a = 26.950$ (2) Å
$b = 10.3120$ (9) Å
$c = 22.8660$ (19) Å
$\beta = 117.607$ (2)°
$V = 5631.0$ (8) Å^3
$Z = 8$

$D_x = 1.342$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7626 reflections
$\theta = 2.5$–27.8°
$\mu = 0.24$ mm^{-1}
$T = 160$ (2) K
Needle, yellow
0.82 × 0.12 × 0.10 mm

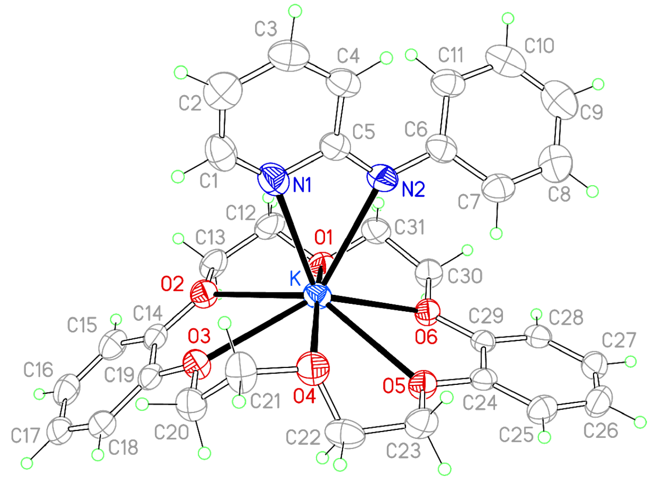


Figure 1
The molecular structure of (I), showing the atom labels and 50% probability displacement ellipsoids for non-H atoms.

Data collection

Bruker SMART 1K CCD diffractometer
Thin-slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min} = 0.830$, $T_{max} = 0.977$
21735 measured reflections

6673 independent reflections
4349 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 28.6°$
$h = -35 \rightarrow 35$
$k = -13 \rightarrow 12$
$l = -30 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.110$
$S = 1.04$
6673 reflections
361 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 1.0053P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

K—N1	2.8515 (18)	K—O5	2.8374 (12)
K—N2	2.7935 (16)	K—O6	2.8194 (12)
K—O1	2.8156 (13)	N1—C1	1.331 (3)
K—O2	2.8578 (12)	N1—C5	1.368 (2)
K—O3	2.8519 (12)	N2—C5	1.340 (2)
K—O4	2.7138 (13)	N2—C6	1.384 (2)
N1—K—N2	47.72 (5)	K—N1—C1	143.34 (14)
O1—K—O2	60.36 (4)	K—N1—C5	96.70 (12)
O1—K—O6	58.97 (3)	C1—N1—C5	118.40 (18)
O2—K—O3	54.13 (3)	K—N2—C5	100.10 (11)
O3—K—O4	61.85 (4)	K—N2—C6	136.59 (12)
O4—K—O5	60.48 (4)	C5—N2—C6	123.11 (16)
O5—K—O6	54.89 (3)	N1—C5—N2	115.03 (17)
C6—N2—C5—N1	168.74 (17)	C22—O4—C21—C20	−67.4 (2)
C6—N2—C5—C4	−16.0 (3)	O3—C20—C21—O4	−58.0 (2)
C5—N2—C6—C7	145.31 (18)	C21—O4—C22—C23	−170.92 (14)
C5—N2—C6—C11	−40.6 (3)	C24—O5—C23—C22	−171.65 (15)
C31—O1—C12—C13	−179.51 (15)	O4—C22—C23—O5	−62.1 (2)
C14—O2—C13—C12	−174.33 (15)	C23—O5—C24—C29	−175.53 (16)
O1—C12—C13—O2	68.2 (2)	C30—O6—C29—C24	175.55 (16)
C13—O2—C14—C19	170.87 (15)	O5—C24—C29—O6	3.8 (2)
C20—O3—C19—C14	175.63 (15)	C29—O6—C30—C31	−158.91 (15)
O2—C14—C19—O3	2.3 (2)	C12—O1—C31—C30	−179.30 (15)
C19—O3—C20—C21	−168.71 (16)	O6—C30—C31—O1	−59.1 (2)

H atoms were positioned geometrically, with C—H = 0.95 (aromatic) or 0.99 Å (aliphatic), and refined with a riding model, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2001); cell refinement: local programs; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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