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

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Key indicators

Single-crystal X-ray study
T = 160 K
Mean *σ*(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.062
Data-to-parameter ratio = 14.2

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

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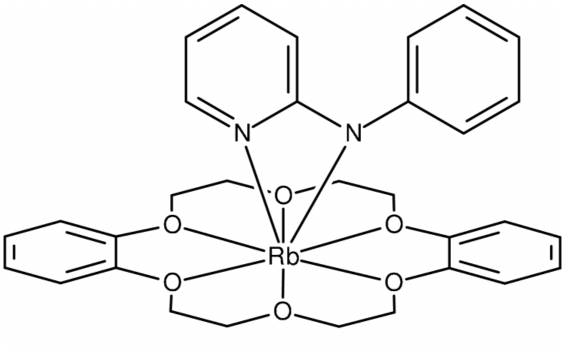
The title complex, [Rb($C_{11}H_9N_2$)($C_{20}H_{24}O_6$)], has rubidium in an irregular eightfold coordination, with a hexadentate crown ether ligand and a chelating bidentate amidopyridine ligand, each occupying one hemisphere of the coordination. The chelate RbNCN ring is essentially planar, but the two rings of the amidopyridine ligand are not coplanar, because of steric interaction of H atoms on the rings. The Rb—N(amido) bond is shorter than the Rb—N(pyridine) bond.

Comment

We have recently reported the synthesis and structural characterization of a range of complexes of alkali metals (Li—Cs) with the 2-phenylamidopyridine ligand (L^-) and the crown ethers 12-crown-4, 15-crown-5 and 18-crown-6 (Liddle & Clegg, 2003; Liddle *et al.*, 2004). This included the complex (18-crown-6)Rb(L). We have also prepared the related complex with dibenzo-18-crown-6, and report its structure here.



(I)

Like the analogous complex (18-crown-6)Rb(L), the title complex (dibenzo-18-crown-6)Rb(L), (I), consists of discrete neutral molecules with no special intermolecular interactions. The crown ligand is hexadentate and occupies one coordination hemisphere, with the bidentate amide ligand occupying the other, giving irregular eightfold coordination for the rubidium ion. The complex may be described as a contact ion-pair, in contrast to several of the crown-ligated complexes of alkali metals with the amide L^-, which exist in the solid state as separated ion pairs (Liddle *et al.*, 2004).

The molecular structure of (I) (Fig. 1 and Table 1) is very similar to that of the (18-crown-6) complex, which has already been described and compared with related complexes (Liddle *et al.*, 2004). The main differences are probably due predominantly to the greater rigidity of dibenzo-18-crown-6 compared with 18-crown-6. The range of Rb—O bond lengths is somewhat smaller, and the two Rb—N bonds are both

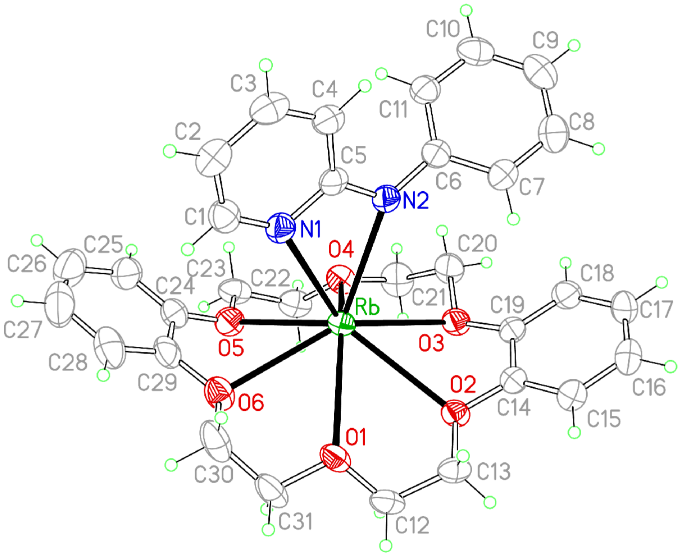


Figure 1
The molecular structure of (I), showing the atom labels and 50% probability displacement ellipsoids for non-H atoms.

shorter in (I), by about 0.05–0.08 Å, with the shorter bond to the amide N atom in both complexes. The Rb^+ ion lies 1.0945 (6) Å out of the mean plane of the six O atoms of the crown (r.m.s. deviation 0.111 Å), displaced towards the amide ligand, and the two benzene rings of the crown are folded out of the oxygen mean plane towards the amide ligand by 22.93 (7) and 25.94 (7)°, presumably as a result of intermolecular packing interactions in the absence of an obvious electronic factor. As expected, the crown ether ring displays a sequence of *anti* (or *trans*) conformations about C—C—O—C and *gauche* conformations about O—C—C—O linkages, except for the near-zero torsion angles for O—C—C—O at the constrained benzo fusions (Table 1).

Chelation by the amide ligand forces a *syn* arrangement for the two N atoms. The two rings are not coplanar, however, because of steric interaction of the H atoms bonded to C4 and C11; the dihedral angle between the rings is 58.10 (5)°. The four-membered chelate ring (RbNCN) is essentially planar, the dihedral angle between the RbN_2 and CN_2 planes being only 0.3 (3)°.

Experimental

n-Butyllithium (0.4 ml of a 2.5 *M* solution in hexanes, 1.0 mmol) was added dropwise 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), followed by rubidium 2-ethylhexoxide (0.22 g, 1.0 mmol) in THF (10 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 0.31 g, 51%). Chemical analysis results were satisfactory, and the ^1H and $^{13}C\{^1H\}$ NMR signals could be assigned on the basis of the crystal structure (Liddle, 2000).

Crystal data

$[Rb(C_{11}H_9N_2)(C_{20}H_{24}O_6)]$
$M_r = 615.06$
Monoclinic, $P2_1/n$
$a = 8.1464$ (5) Å
$b = 23.5768$ (14) Å
$c = 15.2385$ (9) Å
$\beta = 96.626$ (2)°
$V = 2907.2$ (3) Å^3
$Z = 4$

$D_x = 1.405$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14292 reflections
$\theta = 2.7$–28.3°
$\mu = 1.75$ mm^{-1}
$T = 160$ (2) K
Plate, yellow
0.88 × 0.62 × 0.10 mm

Data collection

Bruker SMART 1K CCD diffractometer
Thin-slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.308$, $T_{\max} = 0.845$
20580 measured reflections

5112 independent reflections
3890 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 25.0$°
$h = -9 \rightarrow 9$
$k = -28 \rightarrow 28$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.062$
$S = 0.92$
5112 reflections
361 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rb—N1	2.9441 (18)	Rb—O5	2.9593 (14)
Rb—N2	2.9025 (17)	Rb—O6	2.8829 (15)
Rb—O1	2.9640 (14)	N1—C1	1.331 (3)
Rb—O2	2.9700 (14)	N1—C5	1.378 (3)
Rb—O3	2.9536 (15)	N2—C5	1.332 (3)
Rb—O4	2.9508 (14)	N2—C6	1.385 (3)
N1—Rb—N2	46.13 (5)	Rb—N1—C1	143.59 (15)
O1—Rb—O2	57.05 (4)	Rb—N1—C5	97.67 (13)
O1—Rb—O6	57.59 (4)	C1—N1—C5	118.6 (2)
O2—Rb—O3	51.74 (4)	Rb—N2—C5	100.80 (13)
O3—Rb—O4	58.15 (4)	Rb—N2—C6	136.58 (14)
O4—Rb—O5	56.03 (4)	C5—N2—C6	121.37 (18)
O5—Rb—O6	51.94 (4)	N1—C5—N2	115.39 (19)
C6—N2—C5—N1	169.51 (18)	C22—O4—C21—C20	−166.07 (18)
C6—N2—C5—C4	−14.6 (3)	O3—C20—C21—O4	68.4 (2)
C5—N2—C6—C7	136.0 (2)	C21—O4—C22—C23	−168.59 (17)
C5—N2—C6—C11	−50.3 (3)	C24—O5—C23—C22	176.63 (18)
C31—O1—C12—C13	−174.83 (17)	O4—C22—C23—O5	−61.3 (2)
C14—O2—C13—C12	−176.31 (17)	C23—O5—C24—C29	173.54 (18)
O1—C12—C13—O2	−64.4 (2)	C30—O6—C29—C24	−176.59 (19)
C13—O2—C14—C19	178.36 (17)	O5—C24—C29—O6	−0.9 (3)
C20—O3—C19—C14	169.43 (19)	C29—O6—C30—C31	167.46 (19)
O2—C14—C19—O3	−1.4 (3)	C12—O1—C31—C30	−173.43 (18)
C19—O3—C20—C21	164.94 (19)	O6—C30—C31—O1	65.1 (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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References

Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Liddle, S. T. (2000). PhD thesis, University of Newcastle upon Tyne, England.

Liddle, S. T. & Clegg, W. (2003). *Polyhedron*, **22**, 3507–3513.

Liddle, S. T., Clegg, W. & Morrison, C. A. (2004). *Dalton Trans.* pp. 2514–2525.

Sheldrick, G. M. (2001). *SHELXTL*. Version 5. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2002). *SADABS*. University of Göttingen, Germany.