109. Crystal Structures of the Lithium Cryptates of Two Macrobicyclic Ligands Containing Pyridine, Bipyridine, and Biisoquinoline Units

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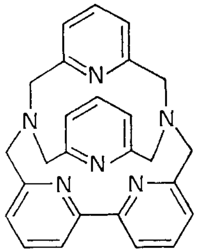
The crystal structures of the LiBr complexes of two macrobicyclic ligands, [py.py.bpy] **1** and [py.biqi.biqi] **2**, have been determined. They confirm the cryptate nature of these species. In **3**, the Li^+ cation is bound in the shallow cavity of a ligand of flattened shape, whereas in **4**, it is buried inside the macrobicycle and surrounded by its three bridges.

The synthesis of the LiBr and NaBr complexes of macrobicyclic ligands incorporating pyridine (py), 2,2′-bipyridine (bpy), and 2,2′-biisoquinoline (biqi) units has been described some time ago [1]. On the basis of their analytical and spectral properties and of earlier work on related complexes [2] [3], they were considered to be lithium and sodium cryptates, formed by inclusion of the Li^+ or Na^+ cation into the molecular cavity of the ligands.

We now describe the crystal structure of two such complexes, formed by LiBr with the ligands [py.py.bpy] **1** and [py.biqi.biqi] **2**, and confirm this assignment.

Structure of the Cryptate $[\mathrm{Li}^+ \subset \mathbf{1}]\mathrm{Br}^-$. – The crystal structure shows that the complex formed by LiBr with the macrobicyclic ligand **1** is of cryptate type, $[\mathrm{Li}^+ \subset \mathbf{1}]$, *i.e.* **3**, with the Li^+ cation contained in the molecular cavity of **1** (*Fig. 1*).



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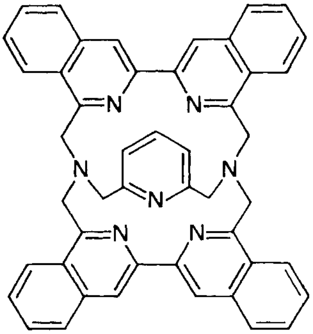

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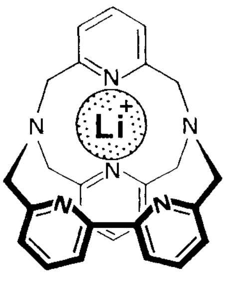

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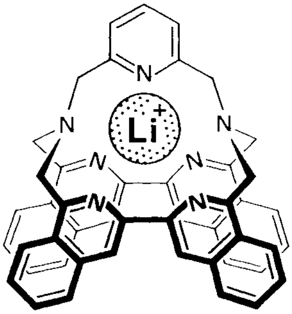

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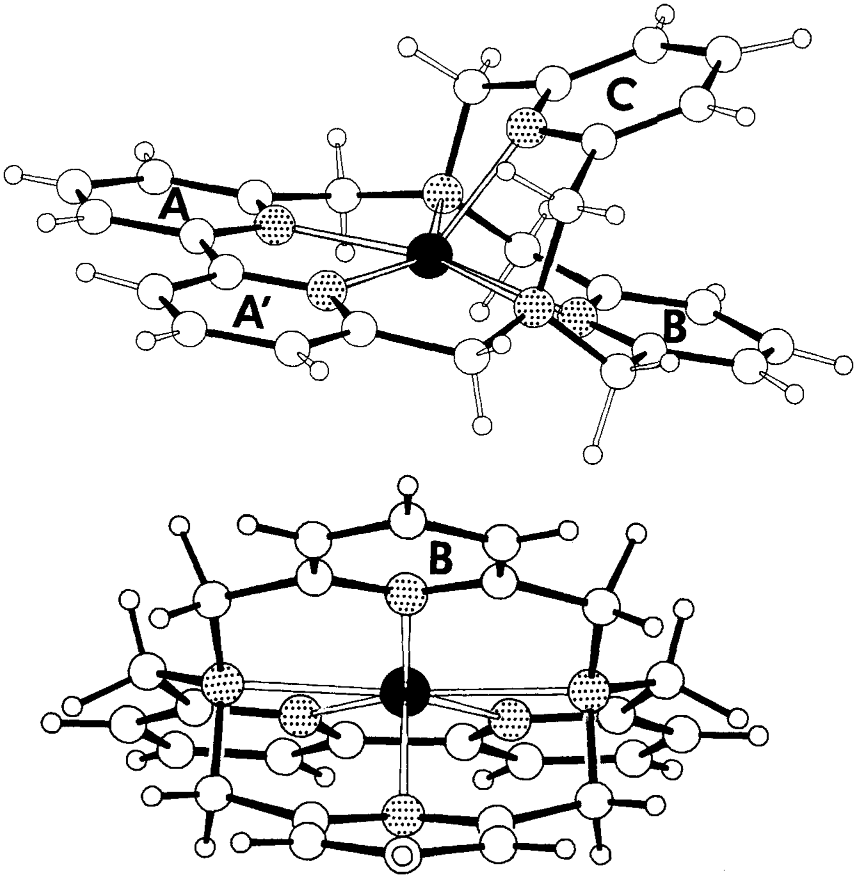

Fig. 1. *Two representations of the structure of the cryptate cation [Li$^+$ $\subset$ py.py.bpy]* **3**. N-Atoms, hatched circles; Li$^+$, black circle.

The *cryptate cation* possesses a mirror plane passing through the Li$^+$ ion and the N-atoms of the two pyridine groups. When it is viewed along the N,N′ bridgehead axis (*Fig. 2a*), one notes that the bridgehead N–C bonds are eclipsed (N–N′ distance, 4.58 Å), and the complex has a flattened shape. The bridges of the macrobicycle do not surround the cation regularly as in the [Na$^+$ $\subset$ phen.phen.phen] cryptate [3]. The Li$^+$ cation lies in the bpy plane (0.06 Å) which makes dihedral angles of 173 and of 155° with the two pyridine planes. The present cryptate cation thus presents two 'open' faces. A *CPK* representation (*Fig. 2b*) shows the Li$^+$ ion resting in the shallow cavity and being quite accessible from either side of the bpy plane.

The environment of the Li$^+$ cation in **3** contains six N-atoms. Li$^+$ lies roughly in the plane of three of them (the two bpy N-atoms N_A and $N_{A'}$ and the py(B) atom N_B) and is non-centered, being displaced from the N,N′ bridgehead axis. It forms a very distorted coordination tetrahedron with the four heterocyclic N-atoms, the N–N distances being N_A–$N_{A'}$ 2.62 Å, N_B–N_C 2.80 Å, $N_{A'}$–$N_{B'}$ 4.12 Å, and $N_{A'}$–N_C 3.66 Å. The corresponding

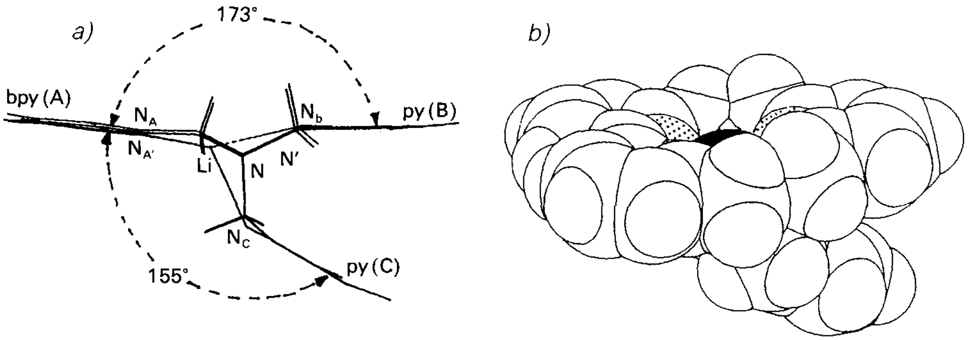

Fig. 2. a) *Profile view of the [$Li^+ \subset$ **1**] cryptate along the N,N' bridgehead axis;* b) *space-filling representation of [$Li^+ \subset$ **1**] viewed close to the N,N' axis*

angles are listed in *Table 1*. The N–Li distances lie between 2.126(7) and 2.244(7) Å (*Table 1*), which is somewhat shorter than the sum of the ionic radius of Li^+ and the *Van der Waals* radius of N, 0.78 + 1.5 = 2.28 Å [4]. The cavity of **1** is thus quite tight for Li^+. This coordination dissymmetry is also reflected in the absence of a second mirror plane, perpendicular to the first one and containing the bpy group. The two py units would then have been equivalent. The Li^+ coordination is completed by a weaker interaction with the two bridgehead N-atoms, the Li–N distances being 2.42 Å.

Table 1. *Selected Interatomic Distances and Angles for the Cryptate [$Li^+ \subset$ **1**]Br^-*

Distances [Å]		Distances [Å]		Angles [°]	
Li–N	2.424 (3)	N_A–$C(2)_A$	1.333 (4)	N_A–Li–$N_{A'}$	74.0 (3)
Li–N_A	2.175 (5)	N_A–$C(6)_A$	1.350 (4)	N–Li–N_A	71.9 (2)
Li–N_B	2.244 (7)	N_B–$C(2)_B$	1.343 (3)	N–Li–N_B	73.3 (2)
Li–N_C	2.126 (7)	N_B–$C(6)_B$	1.343 (3)	N–Li–N_C	78.2 (2)
N–C_A	1.462 (4)	N_C–$C(2)_C$	1.344 (3)	N_A–Li–N_B	137.2 (3)
N–C_B	1.459 (4)	N_C–$C(6)_C$	1.344 (3)	N_A–Li–N_C	116.4 (2)
N–C_C	1.480 (4)			N_B–Li–N_C	79.5 (2)
				Li–N–C_A	111.6 (2)
				Li–N–C_B	109.6 (2)
				Li–N–C_C	98.8 (2)

Structure of the Cryptate [$Li^+ \subset$ 2]$Br^- \cdot 2\ CH_2Cl_2$. – The crystal structure again shows that the complex formed by LiBr with the macrobicycle **2** is of cryptate type, [$Li^+ \subset$ **2**], as represented by **4**.

The *cryptate cation* **4** has a structure (*Fig. 3*) strikingly different from that of **3**. The ligand **2** possesses one more N-site and has a larger cavity than **1**, the faces of the macrobicyclic system being one 18-membered and two 15-membered rings. The Li^+ ion is buried inside the ligand and well protected from the environment by the three bridges which surround the included cation. The bridgehead N–C bonds are staggered, and the macrobicycle is twisted around the bridgehead axis as in the [$Na^+ \subset$ phen.phen.phen] cryptate [3] and in contrast to **3** (*Figs. 1* and *2*). The bridgehead N–N' distance (4.88 Å) is larger than in **3**, as expected. The two biisoquinoline units related by a dyad axis, are raised like wings and close the faces around the cation together with the py unit which is located 'vertically' in the middle along the binary axis. The angle of aperture between the two biqi groups on the 18-membered face is only 65° as compared to 155° or 173° in **3**.

The two moieties of each biqi group are not coplanar, the A and B isoquinoline parts making a torsion angle $N_A–C(3)_A–C(3)_B–N_B$ of 25.8°. The B-ring units are closer to each other than the A units; the dihedral angles are 65° for (B,B′), 96° for (A,A′), and 84.5° for (A,B′) (*Fig. 3*). The dihedral angles of A and B with the py ring are 76 and 51°, respectively. The py group is twisted around the dyad axis by 21° with respect to the N–Li–N′ plane; its thermal motion is highly anisotropic and perpendicular to the ring plane due to oscillation around the two $CH_2–C(py)$ bonds.

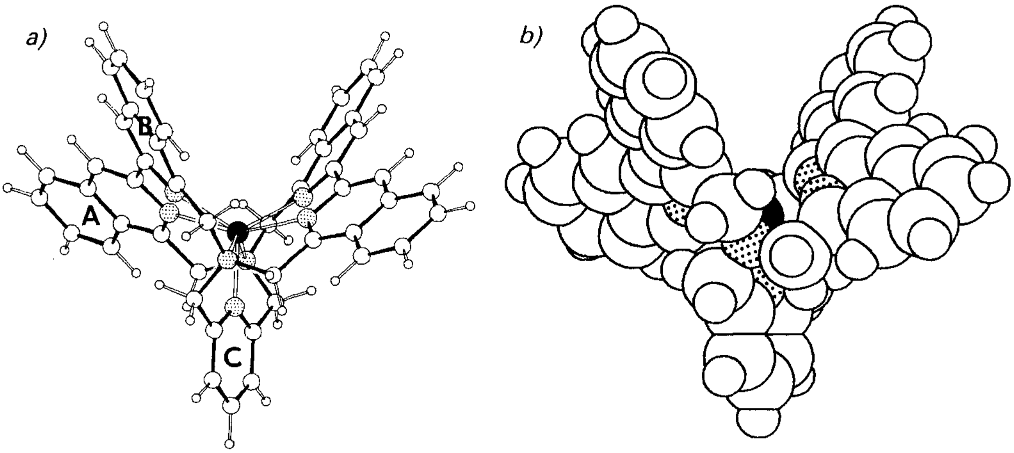

Fig. 3. *Structure of the cryptate cation [$Li^+ \subset$ py.biqi.biqi]* **4**. *a*) ORTEP representation along the N,N′ axis and slightly rotated for clarity; *b*) space-filling representation.

The environment of the Li^+ cation in **4** contains seven N-atoms and is more spherical than in **3**. All N-atoms (but N_B, $N_{B'}$) point toward the cation, the lone-pair axis of N_A ($N_{A'}$) and N_C of py making angles of 4 (4)° and 1°, respectively, with the N–Li direction; this angle is larger (6°) for the bridgehead N-atoms, and for $N_B(N_{B'})$, the angle is *ca.* 27°. The four biqi N-atoms are not coplanar and form a flattened tetrahedron. The coordination polyhedron is completed by the py and the two bridgehead N-atoms. The N–Li distances

Table 2. *Selected Interatomic Distances and Angles for the Cryptate [$Li^+ \subset$ **2**]$Br^- \cdot 2\,CH_2Cl_2$*

Distances [Å]		Distances [Å]		Angles [°]		Angles [°]	
Li–N	2.556 (9)	$C(1)_A–N_A$	1.309 (11)	N–Li–N′	145.5 (6)	$N_A–Li–N_B$	67.6 (4)
$Li–N_A$	2.449 (9)	$N_A–C(3)_A$	1.372 (12)	$N–Li–N_A$	64.0 (4)	$N_A–Li–N_C$	100.7 (6)
$Li–N_B$	2.331 (12)	$C(1)_B–N_B$	1.286 (11)	$N–Li–N_B$	131.5 (6)	$N_B–Li–N_C$	115.8 (6)
$Li–N_C$	2.070 (22)	$N_B–C(3)_B$	1.377 (12)	$N–Li–N_C$	72.8 (5)	$Li–N–C_A$	111.3 (6)
$N–C_A$	1.454 (11)	$N_C–C(2)_C$	1.341 (15)	$N'–Li–N_A$	123.2 (5)	$Li–N–C_B$	111.6 (6)
$N–C_B$	1.424 (12)	$N_C–C(6)_C$	1.341 (13)	$N'–Li–N_B$	66.1 (4)	$Li–N–C_C$	96.7 (5)
$N–C_C$	1.453 (11)			$N'–Li–N_C$	72.8 (5)		

are quite different. The shortest is to N_C (2.07 Å), while the other six are longer than in **3** being 2.33–2.45 Å to the four biqi N-atoms and even 2.5 Å to the bridgeheads (*Table 2*). These distances are longer than the N–Li contact (2.28 Å, see above) indicating than the cavity is too large for the Li^+ cation. Indeed, the earlier results on alkali-cation cryptates indicated that Li^+ was too small for the [2.2.1] macrobicycle which structurally corresponds to the present ligand **2** and which binds preferentially the Na^+ cation [4–6]. On the other hand, the cavity of **2** is probably somewhat tight for Na^+ which would require N–Na distances of *ca.* 0.98 + 1.5 = 2.48 Å [4].

The packing of the molecules in the crystal leaves channels, parallel to the *b* axis, in which the CH_2Cl_2 molecules are located.

Conclusions. – The present structural data confirm the cryptate nature of the alkali complexes formed by macrobicyclic ligands containing pyridine, bipyridine, and biisoquinoline units. They also provide detailed geometric information about the binding cavity and the coordination features. In particular, it appears that the introduction of these N-containing heterocycles into the parent cryptand structures leads, in addition to an expected marked increase in rigidity, to a decrease in cavity size due to the shorter bonds within the heterocyclic units.

Experimental Part

Synthesis of the Li-cryptates of Ligands **1** *and* **2**. See [1].

X-Ray Crystal Structures (*Table 3*). In both structures, the choice of the space group was not unambiguous: complex **3**·Br^- (with ligand **1**) could have crystallized in $P2_1$ and complex **4**·Br^-·2 CH_2Cl_2 (with ligand **2**) in *Pn*, the species **3**·Br^- and **4**·Br^-·2 CH_2Cl_2 being then without any symmetry element. The heavy-atom positions were given by the analysis of the *Patterson* function. Successive density maps revealed all the light atoms, including the H-atoms. Refinement with anisotropic parameters for non H-atoms was carried out using the large blocks least squares methods [7]. It was conducted in both structures in centric and acentric space groups: complex **3**·Br^-: in $P2_1$, final R = 5.6% and R_w = 5.6%; in *P*21/*n*, final R = 5.1% and R_w = 5.1%; complex **4**·Br^-·2 CH_2Cl_2: in *Pn*, final R = 7.5% and R_w = 7.8%; in *P*2/*n*, final R = 6.2% and R_w = 6.9%. These slight differences and the absence of significant deviation on atomic distances led us to give a mirror plane to cryptate **3**·Br^- and a binary axis to

Table 3. *Crystallographic Data*[a])

Complex **3**·Br^- (=[$Li^+ \subset$ **1**]Br^-)	Complex **4**·Br^-·2 CH_2Cl_2 (=[$Li^+ \subset$ **2**]Br^-·2 CH_2Cl_2)
Crystal size 0.4 × 0.3 × 0.2 mm	Crystal size 0.4 × 0.2 × 0.05 mm
$C_{26}H_{24}BrLiN_6$	$C_{47}H_{35}BrLiN_7 \cdot 2\,CH_2Cl_2$
Mol.wt. 507, monoclinic $P2_1/m$	Mol.wt. 950, monoclinic $P2/n$
a = 8.263 (4), b = 18.750 (8), c = 7.377 (4) Å	a = 15.632 (5), b = 9.504 (4), c = 14.829 (7) Å
β = 94.03 (2)°, V = 1140 Å^3, Z = 2	β = 93.03 (2)°, V = 2200 Å^3, Z = 2
D_x = 1.527, μ = 26.2 cm^{-1}	D_x = 1.474, μ = 51.2 cm^{-1}
$F(000)$ = 520, R = 5.1%, R_w = 5.1%	$F(000)$ = 976, R = 6.2%, R_w = 6.9%
$N > 3\sigma(I)$ = 2149	$N > 3\sigma(I)$ = 1424

[a]) Integrated intensities of the independent reflections in the range 3° < 2θ < 135° were measured in the $\omega/2\theta$ scan mode with a graphite-crystal monochromatized CuK_α radiation on an automated four-circle *PW1100 Philips* diffractometer. Corrections were applied for *Lorentz* and polarization effects. No absorption corrections were made. Only the N observations with $I > 3\sigma(I)$ were included in the calculations.

cryptate **4**$\cdot$Br$^-$$\cdot$2 CH_2Cl_2. Some structural data are listed in *Tables 1* and *2*. The final coordinates as well as a full list of bond lengths and angles are available⁴).

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⁴) The atomic parameters are available from the *Cambridge Crystallographic Data Center,* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. The list of observed and calculated structure factors is available from the authors at the Institut de Chimie des Substances Naturelles. Any request should be accompanied by the full literature citation.