The Synthesis and Binding Properties of Bibracchial Lariat Ethers

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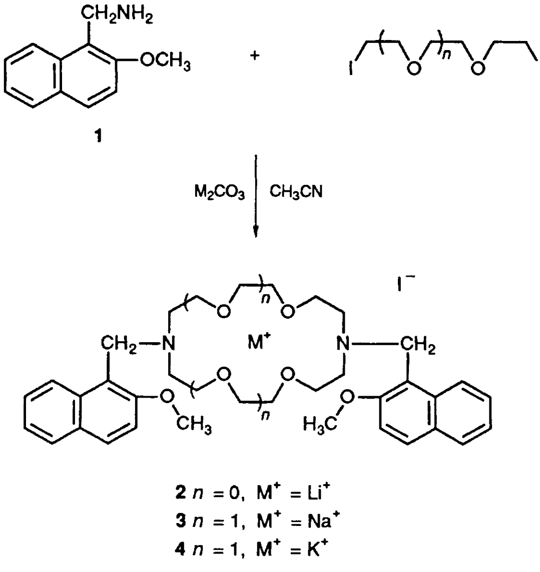
1-Aminomethyl-2-methoxynaphthalene was treated with polyethylene glycol diiodides in the presence of Li^+, Na^+ and K^+ ions as template to produce the corresponding bibracchial lariat ether (BIBLE) complexes; the crystal structures of its sodium and potassium complexes are reported.

In recent years, several methods for syntheses of BIBLEs and examination of their complexation properties with alkali and alkaline earth metal ions have been reported.[1–4] In the BIBLEs, the donor atoms of the macroring and sidearms cooperatively complex with cations to form a three dimensional intramolecular array of binding sites, as do cryptands. Consequently, their complexing capacity is greater than aza crown ethers. The dynamic properties of sidearms in BIBLEs for ionophores are of great importance.

The cyclization reaction of 1-aminomethyl-2-methoxynaphthalene **1** with 1,2-bis(2-iodoethoxy)ethane has been studied in the presence of metal carbonate and the effect of template ions on the cyclization reaction examined. Using the sodium or potassium template ions, the yield of new corresponding complexes of *N,N'*-bis(2-methoxy-1-naphthylmethyl)diaza crown ethers were 27.4 and 15% respectively. The reaction of **1** with 2,2'-diiodoethyl ether in acetonitrile was conducted in the presence of lithium carbonate, and the yield of the lithium iodide complex of *N,N'*-bis(2-methoxy-1-naphthylmethyl)-4,10-diaza-12-crown-4 was 41.2%. Under the same conditions, however, no product was identified using triethylene glycol ditosylate instead of the diiodo compound. The sodium iodide is highly soluble in acetonitrile, while the sodium tosylate formed as by-product is insoluble.[5] Hence the sodium ions cannot be utilized as template ions.

In order to determine how the two sidearms in the complexes of BIBLEs would contribute to the overall binding, **3** and **4** were dissolved in absolute ethanol, and the solvent was evaporated slowly. Single crystals of **3** and **4** were then obtained respectively. The structure of **3** *N,N'*-bis(2-methoxy-



2 $n = 0$, $M^+ = Li^+$
3 $n = 1$, $M^+ = Na^+$
4 $n = 1$, $M^+ = K^+$

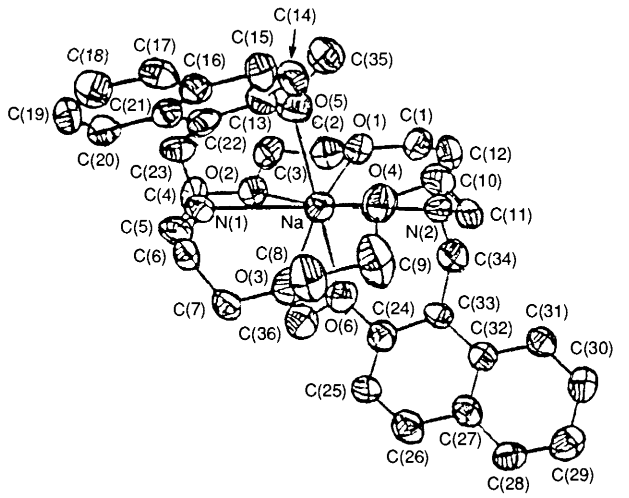


Fig. 1 The molecular structure of *N,N'*-bis(2-methoxy-1-naphthylmethyl)-4,13-diaza-18-crown-6 sodium iodide complex (BIBLE 3 complex)

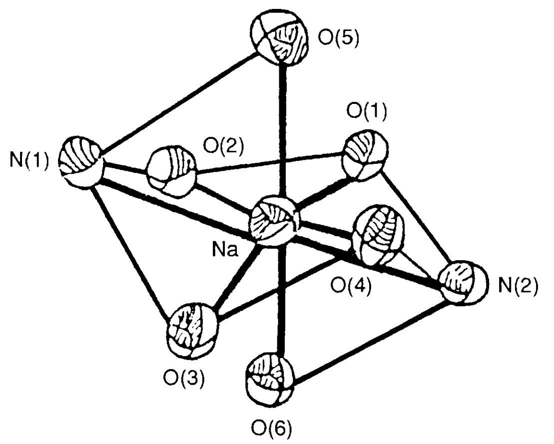


Fig. 2 Skeletal drawing of sodium cation complex of BIBLE 3

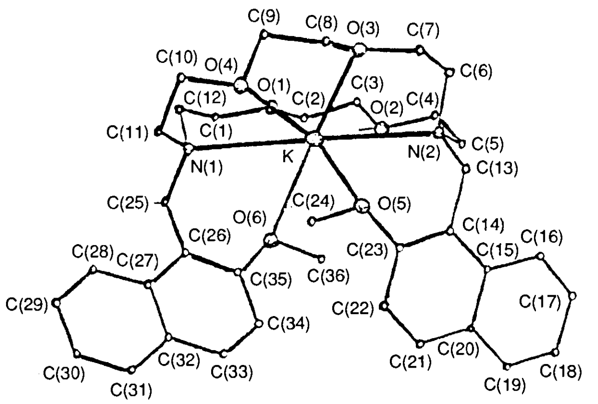


Fig. 3 The molecular structure of potassium complex of BIBLE 4

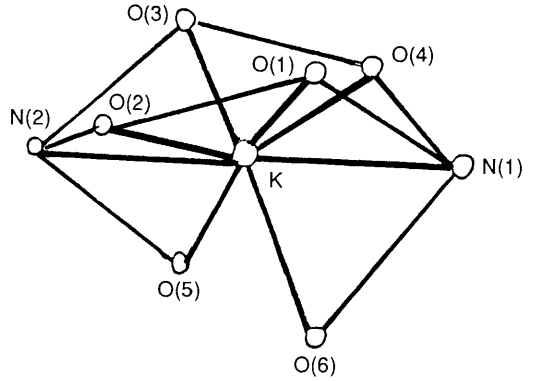


Fig. 4 Skeletal drawing of potassium cation complex of BIBLE 4

1-naphthylmethyl)-4,13-diaza-18-crown-6 Na^+ complex determined by X-ray diffraction, is depicted in Fig. 1† along with a skeletal drawing of donor atoms (containing the oxygen and nitrogen atoms in the macroring and the oxygen atoms in the side arms) and metal ion (Fig. 2). The skeletal drawing reveals that the donor atoms of the macroring are arranged in a chair conformation. The sodium ion lies almost in the cavity of the macroring and from Fig. 1 and 2, the oxygen atoms of the two arms O(5), O(6) are located above and below the plane of the chair to complex with the sodium ion, thus forming a distorted hexagonal bipyramidal coordination geometry. The iodide ion is not involved in the coordination, hence the sodium ion is octacoordinated. The molecular structure of **4** *N,N'*-bis(2-methoxy-1-naphthylmethyl)-4,13-diaza-18-crown-6 K^+ complex and its skeletal drawing are shown in Figs. 3 and 4.

The **4**–K^+ complex is quite different from the **3**–Na^+ complex. The donor atoms of the macroring are disposed in a twisted boat conformation. The potassium ion lies almost on the line between the two nitrogens. The oxygen atom in each sidearm [O(5), O(6)] occupies a 'flagpole' position. The arrangement of donor atoms are very similar to that for the K[2,2,2]I cryptate complex. The potassium ion is octacoordinated. The different conformation of Na^+ and K^+ complexes with the same BIBLEs appear to derive from different radii of Na^+ and K^+ and their electron charge density.

These complexes could be decoordinated by treatment with conc. HCl in a suitable solvent in which the inorganic salt could be separated from the BIBLEs as the hydrochloride. Conc. HCl was slowly added, with stirring to an acetone solution of complex **3** at ambient temp. for 2 h. The BIBLEs hydrochloride that precipitated was removed by filtration and suspended in $CHCl_3$. Tetramethylammonium hydroxide solution (25%) was then added until the solution became alkaline and the solid dissolved, the organic layer was separated and concentrated *in vacuo*. Recrystallization of the product from absolute ethanol yielded free *N,N'*-bis(2-methoxy-1-naphthylmethyl)-4,13-diaza-18-crown-6 (80% yield) as a white solid (m.p. 134–135 °C). The examination of its physical properties was in agreement with the presumed structure.

Complex **2** was decoordinated in $CHCl_3$ and the free *N,N'*-bis(2-methoxy-1-naphthylmethyl)-4,10-diaza-12-crown-

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† *Crystal data* for **3**: $C_{36}H_{46}N_2O_6{\cdot}NaI$, M_w 752, orthorhombic, space group $P2_12_12_1$ with $a = 10.421(2)$, $b = 10.439(3)$, $c = 32.243(9)$ Å, $V = 3507.53$ Å^3, $Z = 4$, $D_c = 1.424$ g cm^{-3}, $\mu = 9.58$ cm^{-1}, $F(000) = 1567.79$, $R = 0.0353$, $R_w = 0.0389$ for 2017 observable reflections in the range of $2° < 2\theta < 47°$.

For **4**: $C_{36}H_{46}N_2O_6{\cdot}KI{\cdot}2EtOH$, M_w 860.5, orthorhombic, space group *Pcab* with $a = 17.531(5)$, $b = 21.149(8)$, $c = 23.060(4)$ Å, $V = 8550.00$ Å^3, $Z = 8$, $D_c = 1.337$ g cm^{-3}, $\mu = 8.74$ cm^{-1}, $F(000) = 3167.64$. 2407 reflections with $I > 3\sigma(I)$ are considered observed and used in the refinements, $R = 0.0567$, $R_w = 0.0567$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

4 (91.7% yield) obtained was purified by column chromatography (silica, ethyl acetate : ethyl alcohol : triethylamine, 95 : 4 : 1) to give a pale yellow oil. Cooling gave a white solid, m.p. 62–63 °C. Examination of its physical properties was in agreement with the presumed structure.

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