Structure and Thermodynamic Aspects of Macrobicyclic Polyether–Metal Ion Interactions [#]

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Abstract. The crystals structure of a K^+-diptychand-15C5-18C6 iodide complex has been determined from X-ray data. The complexed bicyclic molecule crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.995(4)$ Å, $b = 10.097(4)$ Å, $c = 13.725(6)$ Å, $\alpha = 90.12(3)°$, $\beta = 93.62(4)°$, $\gamma = 97.56(3)°$. The structure was solved using heavy atom methods and refined to $R = 0.032$ for 3262 independent reflections. In the crystal structure, the K^+ lies between the two crown ether rings, and is coordinated by the nine donor atoms of the ligand molecule. The complexation properties of the ligand with K^+ and Na^+ were studied by titration calorimetry in 90% (v/v) $MeOH/H_2O$ solution. The studies indicate the formation of 1 : 1 ligand : metal ion complexes in both solid state and solution.

Key words. X-ray crystal structure, macrobicycle, diptychand, equilibrium constant, K^+ binding.

1. Introduction

Crown compounds, first popularized by Pedersen [1], have been shown to have a high degree of selectivity for certain metal cations, organic cations, and organic molecules. This selectivity is based primarily on the preorganization and size of the cavity and types of donor atoms. It has been found that the presence of one or two nitrogen atoms in the ring of a bicyclic macrocycle may be desirable for selective complexation of alkali metal ions [2, 3]. Also, nitrogen atoms are Brønsted–Lowry bases. Thus, complexation by the aza-crowns is pH dependent which allows the metal ion stripping process to take place by decreasing the pH of the solution. The monocyclic aza-crowns show low selectivities towards the alkali metal ions but cryptands, which contain two nitrogen atoms, have high selectivity for these ions. However, the cryptands are difficult and expensive to prepare and show slow kinetics towards releasing metal ions.

In order for a complexing agent to have practical use for separating metal ions, it must have high selectivity and labile kinetics, be inexpensive, and the complexed metal ions must be easily stripped at the end of the separation process. Macrocycles with pendant arms containing donor atoms (the lariat crown ethers) have many of these desired properties [4–7]. However, most of the lariat crowns have a low degree of preorganization and the stoichiometry of complexation is often uncertain. This paper reports a study of the structure and complexation properties of one of

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[#] This paper is dedicated to the memory of the late Dr C. J. Pedersen.
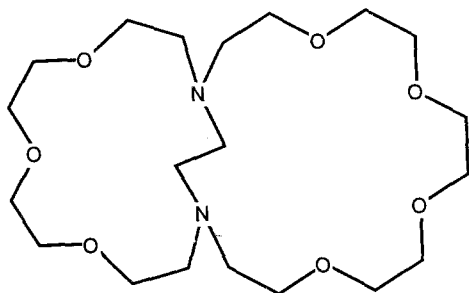* Author for correspondence.

Fig. 1. Structural formula of diptychand—15C5—18C6.

a series of macrobicyclic polyethers containing nitrogen atom bridgeheads [8] which appears to have several advantages over lariat crown ethers and the cryptands as complexing agents for alkali metal ions. These new compounds are more rigid and preorganized than the lariat crowns and have an optimum balance of high selectivity, labile kinetics, low cost, ease of synthesis, and pH stripping capability.

2. Experimental

The synthesis of the macrobicyclic polyether receptor, diptychand—15C5—18C6 (see Figure 1) has been reported [8]. Complexation between dipytchand—15C5—18C6 and K^+ or Na^+ has been studied by a calorimetric titration technique in a 90% methanol/10% H_2O (v/v) solvent at 25°C. The calorimetric experimental procedures have been described [9]. The computer program EQDH [10] was used to process the calorimetric data and calculate the $\log K$ and ΔH values.

Crystals of KI—diptychand—15C5—18C6 were prepared by dissolving equal molar quantities of the ligand and KI in a warm methanol solution and then allowing the solvent to evaporate. The material obtained was recrystallized from warm methylene chloride and, after slow evaporation of the solvent, single crystals of the title compound suitable for an X-ray study were obtained. A crystal was mounted on a Nicolet R3 diffractometer which utilized graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The lattice parameters and orientation matrix were obtained using a least-squares procedure involving 21 carefully centered reflections with $10.27 < 2\theta < 35.67°$. Crystal data and X-ray crystallographic experimental conditions are summarized in Table I. Single crystal data were collected to a $\sin\theta/\lambda$ limit of 0.59. The structure of the macrobicycle-K^+ complex was solved using the heavy-atom method. The position of the iodide ion was obtained from a Patterson map. Positions of the remaining atoms were then obtained from difference Fourier maps phased by the iodide ion. An extra peak located in the difference map was identified as an oxygen of a water of crystallisation. The positions of all hydrogen atoms were obtained from difference maps. The positional and isotropic thermal parameters of these atoms were included in the refinement. The C—H bonds range from 0.91(3) Å to 1.12(4) Å while the H—C—H angles range from 103(3)° to 120(3)°. The Ow—H distances were 0.75(3) Å and 1.06(11) Å and the H—Ow—H angle was 85(8)°. All non-hydrogen atoms were refined anisotropically. An empirical extinction correction was applied to the data but no absorption correction was

Table I. Details of the crystallographic analysis of K^+–diptychand–15C5–18C6.

Formula	$[K(C_{20}H_{40}N_2O_7)]I \cdot H_2O$
F.W.	604.55
Crystal size (mm)	$0.20 \times 0.35 \times 0.35$
Space group	$P\bar{1}$
$a(\text{Å})$	9.995(4)
$b(\text{Å})$	10.097(4)
$c(\text{Å})$	13.725(6)
$\alpha(°)$	90.12(3)
$\beta(°)$	93.62(4)
$\gamma(°)$	97.56(3)
$V(\text{Å}^3)$	1370.2(9)
Z	2
$D_x(\text{g cm}^{-3})$	1.465
Number of unique data collected	4000
Unique observed data $F > 3\sigma(F)$	3263
Scan rate (°/min)	3.9–29.3
2θ range (°)	4–45
R	0.032
R_s	0.031
Goodness of fit	1.36
Residuals in final ΔF map $(e/\text{Å}^3)$	general ± 0.35
	near I ± 0.58

made. Calculations were carried out using the SHELXTL program package [11]. Atomic scattering factors were obtained from The International Tables for X-ray Crystallography [12].

3. Results and Discussion

The bicyclic ligand coordinates the potassium cation with all nine donor atoms as shown in Figures 2 and 3. The positional and isotropic thermal parameters of the non-hydrogen atoms are given in Table II. The K^+—O distances range from 2.772(2) Å to 2.898(3) Å and K^+ − N distances are 2.910(3) Å and 2.926(3) Å.

The nine-fold coordination can best be described as follows. The K^+ is coordinated by four nearly planar atoms N(1), O(4), O(6), and O(9) with the largest deviation of a donor atom from the least-squares plane of these atoms being 0.13 Å. The K^+ is 0.21 Å above this plane. Three more donor atoms, O(5), O(7), and O(9), form a triangular plane above the K^+ and this plane forms a dihedral angle of 21° with the four donor atom plane. An additional two donor atoms complex the K^+ below the four atom plane. The line determined by these donor atoms, N(2) and O(3), is nearly parallel to the least-squares plane of the four atoms. Figure 3 shows the relationship of K^+ to the donor atoms when viewed in a direction nearly parallel to the four atom plane.

Donor atom—K^+ interatomic distances and donor atom—K^+—donor atom angles are listed in Table III. Torsion angles about C—C bonds in the ligand are given in Table IV. The K^+—I^- ($-x, -y, 1-z$) distance of 6.429(2) Å indicates that the I^- does not interact with the K^+. The water molecule in the crystal structure also does not interact with the K^+ as the Ow—K^+ ($1-x, 1-y, 1-z$)
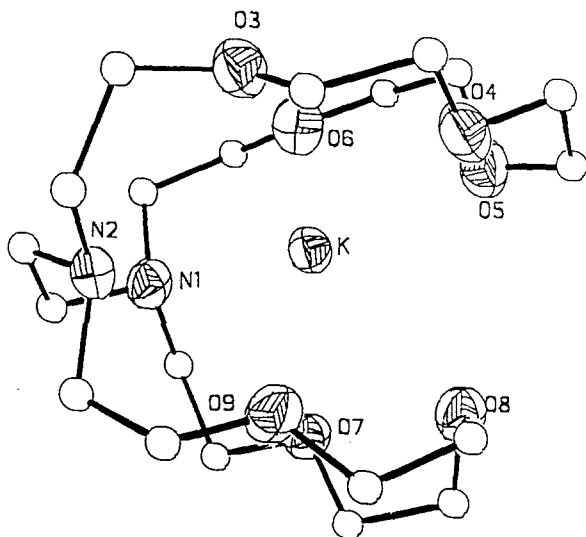
Fig. 2. Computer drawing of the K$^+$ complex showing the conformation of the two rings.

distance is 6.351(2) Å. However, it likely interacts with the I$^-$ as indicated by two fairly short Ow—I$^-$ interatomic distances. They are Ow—I$^-$ $(1 - x, 1 - y, 1 - z)$, 3.707(2) Å and Ow—I $(1 + x, y, z)$, 3.882(2) Å. The symmetry translation in parenthesis indicates the symmetry relationship of the second atom listed to the atom coordinates contained in Table II.

The conformation of the uncomplexed diptychand–15C5–18C6 determined by molecular mechanics (MM) calculations is similar to the conformation of the ligand in the K$^+$-complex as determined in this X-ray study. This fact suggests that the
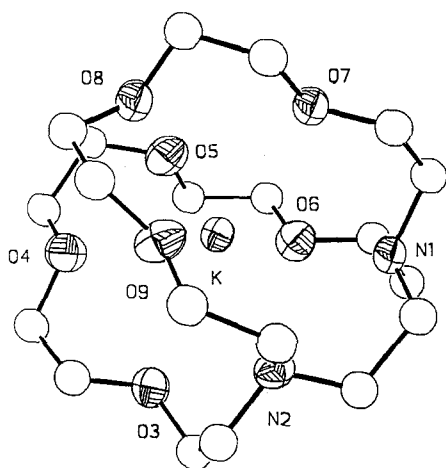

Fig. 3. A view of the K$^+$ complex viewed nearly parallel to the four donor atom plane consisting of N(1), O(4), O(6), and O(9).

Table II. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{Å}^2 \times 10^3$) for non-hydrogen atoms with e.s.d. values in parenthesis

atom	x/a	y/b	z/c	U^a
I	1201(1)	3300(1)	6760(1)	60(1)
K	3058(1)	1601(1)	1925(1)	35(1)
N(1)	3574(3)	−1057(2)	2527(2)	43(1)
N(2)	2416(3)	877(3)	3921(2)	41(1)
O(3)	384(2)	1937(2)	2506(2)	49(1)
O(4)	1676(2)	3664(3)	1159(2)	56(1)
O(5)	2853(3)	2039(3)	−104(2)	60(1)
O(6)	2066(3)	−513(2)	663(2)	55(1)
O(7)	5779(2)	1075(2)	2066(2)	44(1)
O(8)	5150(2)	3698(2)	1679(2)	47(1)
O(9)	4137(2)	3232(2)	3485(2)	51(1)
C(1)	3382(4)	−1257(4)	3573(3)	55(1)
C(2)	2248(4)	−596(4)	3966(3)	52(1)
C(3)	1165(4)	1381(4)	4176(3)	52(1)
C(4)	47(4)	1212(4)	3378(3)	55(1)
C(5)	541(4)	3351(4)	2620(3)	52(1)
C(6)	517(4)	3962(4)	1629(3)	55(1)
C(7)	1624(4)	3942(4)	145(3)	67(2)
C(8)	2795(5)	3418(4)	−294(3)	67(2)
C(9)	1726(5)	1154(5)	−509(3)	69(2)
C(10)	2030(5)	−234(4)	−365(3)	70(2)
C(11)	2488(4)	−1769(4)	878(3)	61(2)
C(12)	2580(4)	−1993(3)	1953(3)	57(1)
C(13)	4964(4)	−1233(4)	2310(3)	55(1)
C(14)	5991(4)	−65(4)	2636(3)	53(1)
C(15)	6692(3)	2220(3)	2381(3)	50(1)
C(16)	6500(4)	3382(3)	1731(3)	51(1)
C(17)	4893(4)	4769(3)	2276(3)	58(1)
C(18)	4931(4)	4491(4)	3346(3)	59(1)
C(19)	3959(4)	2943(4)	4482(3)	57(1)
C(20)	3558(4)	1451(4)	4582(3)	55(1)
Ow	8140(5)	4005(7)	5046(5)	174(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

ligand is preorganized in such a way that it contains 'preorganized convergent endodentate donor atoms' [13]. As shown in Table IV, the torsion angles of X—C—C—X (X = O or N) are about 60° which supports this idea. The C—X—C—C torsion angles also have low energy values. There are a total of 26 such torsion angles in the structure, 16 of which are within 20° of 180° (*trans*) and 10 are closer to 60° (*gauche*). Of the 10 near-*gauche* angles, two are in the 15-crown-5 ring both involving the same donor oxygen and two are in the 18-crown-6 ring involving two oxygens joined by a two carbon bridge. The remaining six *gauche* angles involve angles about C—N bonds. Since there are three carbons bonded to each nitrogen there are two torsion angles involving each C—C—N three atom group and only one of those can be *trans*. This accounts for the six other *gauche* C—C—N—C torsion angles.

Table III. K$^+$–Donor atom interatomic distances (Å) and donor atom K$^+$–donor atom angles (deg.).

1	2	3	1—2 (Å)	1—2—3 (deg)
N(1)	K	N(2)	2.910(3)	64.4(1)
N(2)	K	O(3)	2.926(3)	62.5(1)
O(3)	K	O(4)	2.898(3)	58.7(1)
O(4)	K	O(5)	2.817(3)	59.6(1)
O(5)	K	O(6)	2.820(2)	60.4(1)
O(6)	K	N(1)	2.784(2)	63.0(1)
O(7)	K	O(8)	2.834(2)	60.5(1)
O(8)	K	O(9)	2.810(2)	59.2(1)
O(9)	K	N(2)	2.772(2)	59.6(1)
O(7)	K	N(1)	—	62.3(1)

Table IV. Torsion angles about C—C bonds in the complex K$^+$–diptychand–15C5–18C6.

Atoms	Torsion Angle (deg.)
N(1)—C(1)—C(2)—N(2)	−63.2(4)
N(2)—C(3)—C(4)—O(3)	−62.5(4)
O(3)—C(5)—C(6)—O(4)	−65.3(3)
O(4)—C(7)—C(8)—O(5)	54.5(4)
O(5)—C(9)—C(10)—O(6)	67.5(4)
O(6)—C(11)—C(12)—N(1)	−62.9(4)
N(1)—C(13)—C(14)—O(7)	−67.4(4)
O(7)—C(15)—C(16)—O(8)	56.6(4)
O(8)—C(17)—C(18)—O(9)	−48.1(4)
O(9)—C(19)—C(20)—N(2)	−51.3(4)

Table V. Thermodynamic binding properties of diptychand–15C5–18C6 with K$^+$ and Na$^+$ ions in 90% MeOH/10% H$_2$O (v/v) solvent at 25°C.

Cation	Stoichiometry	Log K	ΔH(kJ/mol)	ΔS(J/mol K^{-1})
K$^+$	1 : 1	4.35(4)	−63.2(2)	−129
Na$^+$	1 : 1	3.56(3)	−35.4(3)	−51

As expected from the X-ray study, the thermodynamic values of complexation obtained from calorimetry experiments indicate the formation of stable 1 : 1 complexes of diptychand with either K$^+$ or Na$^+$ in solution. The calorimetric titrations also show a selectivity for K$^+$ over Na$^+$. The data given in Table V indicate that the complexation for both alkali metal ions is an enthalpy-driven process. The selectivity for K$^+$ over Na$^+$ can be explained by the fact that the larger of the two cations, K$^+$, can interact with more donor atoms than Na$^+$ without costing energy because of donor atom-donor atom repulsion. This is in agreement with the known trend [14] that there is a decreased coordination number with a decrease in metal

ion radius. The entropy changes for the interactions of the bicyclic ligand with K^+ and Na^+ are also consistent with the trends [15] of the entropy changes of the corresponding reactions with monocyclic crown ethers and bicyclic cryptands. The negative entropy changes for these interactions may result from the combination of (1) the increased molecular orderliness in solution, (2) the restricted conformational tumbling of the ligand molecule, and (3) the minor contribution from the desolvation of both ligand and metal ion during complexation. The Na^+–ligand interaction leads to a more favorable entropy change compared to that for the K^+–ligand interaction because of the difference in the metal ion desolvation processes [16]. It should be noted that, although the selectivity of K^+ over Na^+ observed in this study is not as high as in the case of 18-crown-6, the moderate metal ion selectivity coupled with a pH complexation dependency and the effortless syntheses make this ligand a possible candidate for practical use in metal separations chemistry.

Acknowledgement

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