The Crystal Structure of Dibenzo-14-Crown-4, A Preorganized Basis of Square Pyramid Coordination for Lithium Ions[#]

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Abstract. Dibenzo-14-crown-4 (DB14C4) has a high selectivity for Li^+. The rigidity of the molecule caused by the two benzene rings suggests that this is a preorganized ligand for metal ions and particularly for Li^+. A single crystal structure study of the molecule was performed. The crystal data are: space group $P2_1$, $a = 12.811(2)$, $b = 5.106(1)$, $c = 12.816(3)$Å, $\beta = 115.44(1)°$, $V = 757.0(2)$Å^3 with $Z = 2$. The structure was refined to $R = 0.049$ *and* $R_w = 0.058$ using 1804 unique data with $F < 4\sigma(F)$. The conformation of the free ligand was found to be similar to that of the complexed ligand and the conformational parameters of the free ligand and its derivatives are compared to Li^+ complexes of the ligand and its derivatives.

Key words. X-ray crystal structure, dibenzo-14-crown-4, preorganized ligand, Li^+ binding.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82126 (12 pages).

1. Introduction

Previously it was shown that small crown ethers with a ring size of 12–16 atoms containing four ether oxygens exhibit high selectivity toward Li^+ [1–8]. The fourteen membered ring crown-ethers dibenzo-14-crown-4 [3] and 14-crown-4 [4–6] exhibit the highest selectivity towards Li^+ among all the crown ethers which have been tested. Molecular structure studies of Li^+ complexes with crown ethers [9–19], linear related compounds [20], cryptands [21] and naturally occurring macromolecules [22, 23] reveal that Li^+ occurs in various coordinations (tetra, penta, hexa, hepta and octa), and the Li^+—ligand bond distances vary from 1.86 to 2.37Å [24]. In many cases the Li^+ is five coordinated and the most favorable coordination geometry is that of a square pyramid (SP) in which the macrocyclic ring provides the basis for a square pyramid, while the apical site is occupied by the anion [9, 10, 12–19, 24] or solvent molecule [11, 19, 22, 23, 24].
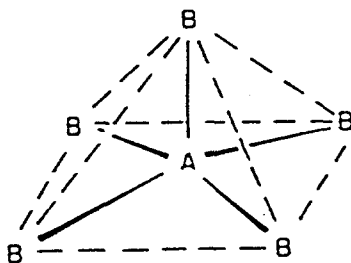
The most effective ion-dipole interactions in five-fold coordination geometry can be achieved in an arrangement of a square pyramid (SP) or a trigonal bipyramid (TBP) configuration of the dipoles around the Li^+ [25, 26] (see Figure 1). The

[#] This paper is dedicated to the memory of the late Dr C. J. Pedersen.
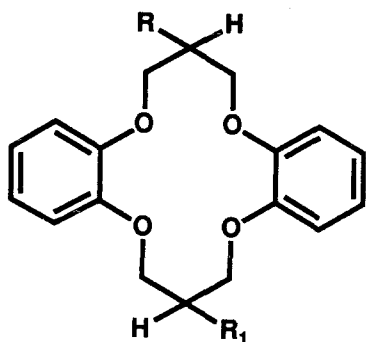*Author for correspondence
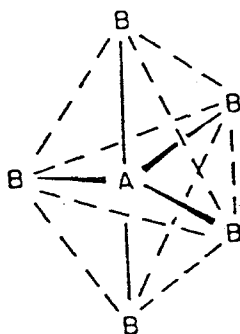
Trigonal bipyramid (TBP)   Square-pyramid (SP)

Fig. 1. Common types of five-fold coordination.

	R	R_1
1	H	H
2	OH	H
3	OH	OH (trans)
4	CH_2OH	H
5	OCH_2CO_2H	H

Fig. 2. A schematic drawing of compounds 1–5.

square pyramid conformation is dictated by the rigidity and the conformation of the macrocyclic ring.

   The dibenzo-14-crown-4 (DB14C4) (1) (see Figure 2) molecule provides an 'ideal base' of square-pyramidal coordination in LiNCS [9], LiPicrate, LiClO$_4$ and LiI [19, 24] complexes. The goal of this research is to find out whether DB14C4 is a preorganized basis of square pyramid coordination for lithium ions or whether conformational changes take place in DB14C4 upon complexation.

2. Experimental

The synthesis of DB14C4 has been described by Pedersen [27]. Single crystals of DB14C4 were grown from a 1:1 (volume) solution of CH_2Cl_2 and methanol. Crystal and intensity data were obtained using a Nicolet R3 automated diffractometer which utilized graphite monochromated MoK_α radiation ($\lambda = 0.71073$Å). The lattice parameters and orientation matrix were obtained using a least-squares procedure

Table I. Crystal data and experimental conditions.

Formula	$C_{18}H_{20}O_4$
Formula Weight	300.3
F(000)	320
Crystal Size (mm)	$0.25 \times 0.30 \times 0.40$
$\mu\,(cm^{-1})$	0.86
Space group	$P2_1$
$a(\text{Å})$	12.811(2)
$b(\text{Å})$	5.106(1)
$c(\text{Å})$	12.816(3)
$\beta(\deg)$	115.44(1)
$V(\text{Å}^3)$	757.0
Z	2
$D_x(g/cc)$	1.32
Max $\sin\theta/\lambda$	0.70
Observed unique data	1804
Unobserved data$(F < 4\sigma(F))$	524
R	0.049
R_w	0.058
G (in weights)	7.8×10^{-4}
GOOF	1.33
largest peaks in difference maps $(e\text{Å}^{-3})$	0.21, −0.18

involving 25 carefully centered data ($11.0° < 2\theta < 27.7°$). A cell reduction calculation yields the result that the unit cell could be described as C-centered orthorhombic but the diffraction symmetry ruled out that possibility. Intensity data were collected using a variable scan rate (4 to 60 deg/min) $\theta-2\theta$ scanning mode. Crystal data and experimental information are summarized in Table I.

The trial structure was obtained using direct methods. All non-hydrogen atoms were refined anisotropically. Positions for hydrogen atoms were obtained from difference maps. The hydrogen atoms were allowed to ride on the carbon to which they are bonded with a C—H distance of 0.96Å during the refinement procedure and only their isotropic thermal parameters were refined. The R values were $R = 0.049$ and $R_w = 0.058$. Weights were based on counting statistics and were of the form $w = 1/\sigma^2(F) + GF^2$ with G being refined to bring the goodness of fit value to approximately 1.0. Atomic scattering factors were obtained from the *International Tables for X-Ray Crystallography* Vol. 4. [28] All programs used in the solution and characterization of the structure are contained in the program package SHELXTL [29].

3. Results and Discussion

The conformation of DB14C4 and the atom labels are shown in the SHELXTL drawing of the molecule, Figure 3. Figure 4 shows a view of the molecule in which the angle between the planes, the hinge angle, is emphasized. Atomic parameters are listed in Table II. The atom groups C(2), C(3)—C(10), C(11) and C(11), C(12)—C(1), C(2) (see Figure 3) are essentially planar with the dihedral angle
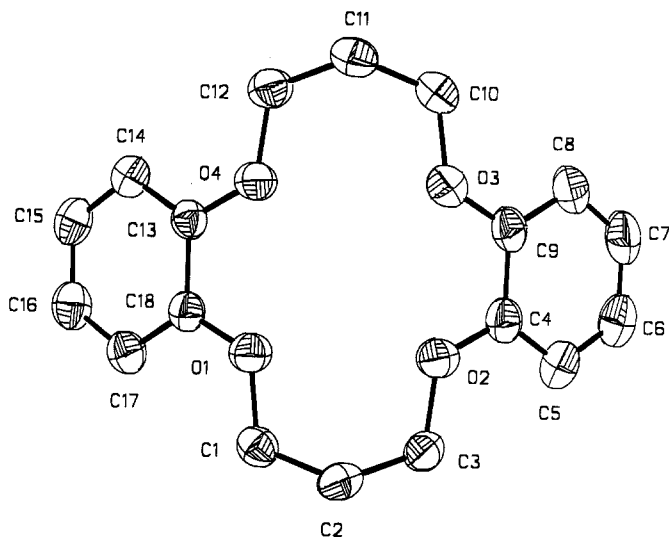
Fig. 3. A SHELXTL drawing of dibenzo-14-crown-4 with atom labels. Thermal ellipsoids are drawn at the 50% probability level.
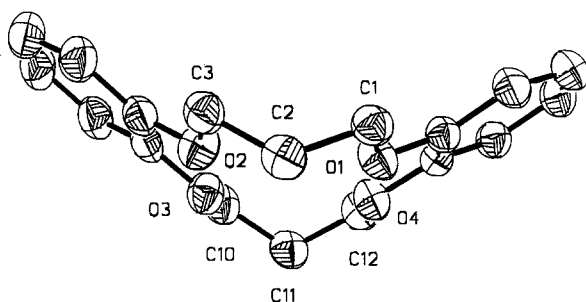

Fig. 4. A view of the dibenzo-14-crown-4 molecule which emphasizes the hinge angle between the two major planes of the molecule.

between these least squares planes being 122.8°. The four oxygen atoms form a plane, with the largest deviation of any oxygen from their least-squares plane being 0.02Å. The oxygens form a distorted rectangle, with dimensions O(1)—O(2) 2.860Å, O(2)—O(3) 2.575Å, O(3)–O(4) 2.916Å and O(4)–O(1) 2.563Å. The O—O—O angles range from 88.6° to 91.1°. The diagonal O—O distances are O(1)–O(3) 3.886Å and O(2)–O(4), 3.843Å. The bond lengths and angles in the ether portion of the molecule are typical of crown molecules with the average aliphatic C—C distance, 1.509(4) Å and C—O distance 1.429(5) Å being slightly shorter than those found in non-crown ethers. The $C_{benzene}$—O distances are not included in the C—O average. All bond lengths and angles are contained in Table III. The average C—O—C—C torsion angle is 176(2)° (*trans*) and the average O—C—C—C torsion angle is 73(1)° (*gauche*). These values indicate little strain in the ring.

Table II. Positional ($\times 10^4$) and thermal ($\mathring{A}^2 \times 10^3$) parameters for the atoms with e.s.d. values in parenthesis.

Atoms	x/a	y/b	z/c	U
O(1)	5373(1)	9060	2493(1)	45(1)[a]
C(1)	4968(2)	7297(6)	1542(2)	41(1)[a]
H(1)C(1)	4431	6059	1595	40(7)
H(2)C(1)	4579	8419	863	50(8)
C(2)	5988(2)	5833(6)	1547(2)	42(1)[a]
H(1)C(2)	5751	4533	981	56(8)
H(2)C(2)	6386	4766	2250	50(8)
C(3)	6791(2)	7412(7)	1206(2)	42(1)[a]
H(1)C(3)	7286	6093	1026	72(9)
H(2)C(3)	6339	8653	505	57(8)
O(2)	7429(2)	9153(5)	2137(2)	48(1)[a]
C(4)	8182(2)	10852(7)	1999(2)	44(1)[a]
C(5)	8443(2)	10899(8)	1051(3)	54(1)[a]
HC(5)	8199	9389	480	70(9)
C(6)	9224(3)	12761(8)	1008(3)	61(1)[a]
HC(6)	9436	13043	345	54(8)
C(7)	9733(2)	14500(8)	1889(3)	62(1)[a]
HC(7)	10172	15823	1823	59(8)
C(8)	9480(2)	14484(8)	2838(3)	53(1)[a]
HC(8)	9690	16038	3405	91(9)
C(9)	8698(2)	12677(7)	2898(2)	44(1)[a]
O(3)	8371(1)	12496(5)	3783(2)	48(1)[a]
C(10)	8657(2)	14651(7)	4576(2)	52(1)[a]
H(1)C(10)	9445	14820	4799	78(10)
H(2)C(10)	8271	16799	4109	123(14)
C(11)	8087(2)	14169(8)	5377(2)	51(1)[a]
H(1)C(11)	8302	12458	5762	47(7)
H(2)C(11)	8431	15663	5951	68(9)
C(12)	6798(2)	14616(7)	4866(2)	47(1)[a]
H(1)C(12)	6509	14564	5375	60(8)
H(2)C(12)	6627	16153	4586	57(9)
O(4)	6244(1)	12503(5)	4092(1)	45(1)[a]
C(13)	5069(2)	12594(6)	3493(2)	37(1)[a]
C(14)	4346(2)	14358(7)	3680(2)	45(1)[a]
HC(14)	4769	16011	4274	74(9)
C(15)	3158(2)	14263(7)	2991(2)	52(1)[a]
HC(15)	2653	15437	3148	59(8)
C(16)	2700(2)	12446(8)	2128(2)	52(1)[a]
HC(16)	1855	12111	1662	55(8)
C(17)	3409(2)	10659(7)	1930(2)	46(1)[a]
HC(17)	3070	9210	1275	49(7)
C(18)	4593(2)	10714(6)	2608(2)	38(1)[a]

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

A comparison of the conformational features of 1 and LiNCS–1 (see Table IV) shows that there are only small differences between the complexed and un-complexed ligand. The dihedral angles between the two major planes in the free and complexed ligand differ by only about 2°. The ether oxygens are essentially planar in both compounds and the diagonal oxygen interatomic distances in the

Table III. Bond lengths (Å) and angles (deg) in **1** with e.s.d. values in parentheses.

1	2	3	1—2(Å)	1—2—3(deg)
C(1)	O(1)	C(18)	1.422(3)	118.0(2)
O(1)	C(1)	C(2)		108.3(2)
C(1)	C(2)	C(3)	1.503(4)	115.6(3)
C(2)	C(3)	O(2)	1.511(4)	107.8(2)
C(3)	O(2)	C(4)	1.429(3)	118.0(2)
O(2)	C(4)	C(5)	1.365(4)	124.9(3)
O(2)	C(4)	C(9)		115.1(3)
C(5)	C(4)	C(9)	1.391(5)	120.0(3)
C(4)	C(5)	C(6)		119.4(3)
C(5)	C(6)	C(7)	1.398(5)	120.4(4)
C(6)	C(7)	C(8)	1.362(5)	120.9(4)
C(7)	C(8)	C(9)	1.388(5)	119.9(3)
C(4)	C(9)	C(8)	1.406(4)	119.4(3)
C(4)	C(9)	O(3)		115.5(3)
C(8)	C(9)	O(3)	1.388(5)	125.1(3)
C(9)	O(3)	C(10)	1.371(4)	117.3(3)
O(3)	C(10)	C(11)	1.435(4)	107.8(3)
C(10)	C(11)	C(12)	1.513(5)	116.0(2)
C(11)	C(12)	O(4)	1.510(4)	108.1(3)
C(12)	O(4)	C(13)	1.431(4)	117.5(2)
O(4)	C(13)	C(14)	1.366(3)	125.7(2)
O(4)	C(13)	C(18)		114.9(3)
C(14)	C(13)	C(18)	1.385(4)	119.5(2)
C(13)	C(14)	C(15)		119.8(3)
C(14)	C(15)	C(16)	1.395(3)	120.5(3)
C(15)	C(16)	C(17)	1.368(5)	120.5(2)
C(16)	C(17)	C(18)	1.385(5)	119.9(3)
O(1)	C(18)	C(13)	1.364(3)	115.1(2)
C(17)	C(18)	O(1)	1.387(3)	125.1(2)
C(13)	C(18)	C(17)	1.409(4)	119.8(3)

two molecules are similar. The fact that the conformation of the ligand in the solution and solid states are similar suggests that the ligand is preorganized in such a way that it will selectively complex a lithium ion.

Table IV also gives conformational features of derivatives of 1 and Li$^+$ complexes of those derivatives. A schematic drawing of compounds 1–5 is presented in Figure 2. The similarity of the values in the Table indicates a rigidity of the basic unit of the molecule. The values also suggest some trends in conformational differences in the various derivatives. For example, substitutents on the hinge carbons (C(2) and C(11) in the title compound) affect the hinge angle; the angle increases as OH groups are added (see compounds 2 and 3). Molecule 4 in which a CH$_2$—OH group is substituted on a hinge carbon has a larger angle between the major planes than either 2 or 3. Finally the hinge angle is always several degrees smaller in the complex than in the uncomplexed ligand except for the unsubstituted ligand where it is less than 2° smaller. The fact that the hinge angle in complexes of 4 is greater when the anion is NO$_3^-$ instead of SCN$^-$ may be significant but more data are required before it can be suggested that there is an anion effect.

Table IV. Comparison of complexed and uncomplexed DB14C4 and derivatives of that ligand.

Ligand	Dihedral angle between two major planes (deg) (hinge angle)	O(1)—O(3)(Å)	O(2)—O(4)(Å)	Average deviation of ether oxygen from planarity (Å)	Average Li—O distance (Å)	Ref.
1 uncomplexed	122.8	3.886	3.843	0.021		this study
LiNCS—1 complex	121	3.77	3.77	0.000[a]	2.043	9, 24
2 uncomplexed	129.7	3.813	3.813	0.000[a]		30
LiNCS—2 A molecule	125.8	3.679	3.852	0.087	2.003	31
B molecule	126.1	3.779	3.760	0.012	2.015	31
3 uncomplexed	132.5	3.787	3.808	0.012		30
LiNCS—3	124.4	3.792	3.802	0.017	2.029	31
4 uncomplexed	135.2	3.793	3.805	0.011		30
LiNCS—4	122.3	3.788	3.736	0.009	2.021	31
LiNO$_3$—4	126.3	3.699	3.824	0.056	2.038	31
Li—5[b]	118.6	3.70	3.83	0.046	2.047	11

[a] Required by the symmetry of the molecule.
[b] Ligand also is the anion.

The similarity of the conformations of 1 and its derivatives to the conformations of the respective ligands when complexing Li^+, is further evidence for the preorganization of the DB14C4 structural unit for the complexation of Li^+.

Acknowledgement

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