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COMPLEXATION BY N-(3,6,9-TRIOXADECYL)MONOAZA-12-CROWN-4 LARIAT ETHER: A "CALABASH" COMPLEX OF A POTASSIUM CATION BY A SYNTHETIC MACROCYCLE CONTAINING A TOTAL OF ONLY SEVEN DONOR ATOMS[+]

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Abstract: Structural and cation binding data for the title compound demonstrate that the large value of K_s results from complete K^+ cation encapsulation by one nitrogen and six oxygen atoms despite the presence of a twelve-membered macroring.

In a previous study,[1] the myth of a hole-size relationship was dispelled, at least for the series of flexible mono-macrocycles 12-crown-4 through 24-crown-8 with the cations Na^+, K^+, NH_4^+, and Ca^{2+}. The prevailing view seems to be that a twelve-membered ring is "too small" to accommodate either a sodium or potassium cation. Were this so, 12-crown-4 should show selectivity for Li^+ over either Na^+ or K^+. Popov has reported that log K_s for Li^+ with 12-crown-4 in anhydrous MeOH solution is ca. 0.[2] This contrasts with 12-crown-4 to Na^+ and K^+ binding constants (log K_s, MeOH) of 1.7 for both cases.[1] N-(3,6,9-Trioxadecyl)monoaza-12-crown-4, **1** complexes Na^+ and K^+ with homogeneous stability constants (log K_s) of 3.97[3] and 3.84, respectively, in anhydrous MeOH. In marked contrast, the stability constants for Na^+ with 12-crown-4 or 15-crown-5 in MeOH are 1.7 and 3.24, respectively. Indeed, in the simple macrocycle series, only binding by 18-crown-6 (log K_s = 4.35) exceeds that for **1**. If a hole-size relationship of any sort operates, one might expect binding for the larger K^+ ion to be greatly diminished relative to that for the smaller Na^+ ion. We report here that not only is K^+ cation binding by **1** substantial and similar in magnitude to Na^+ binding, the cation is completely enveloped by the donor groups present in both ring and sidearm.

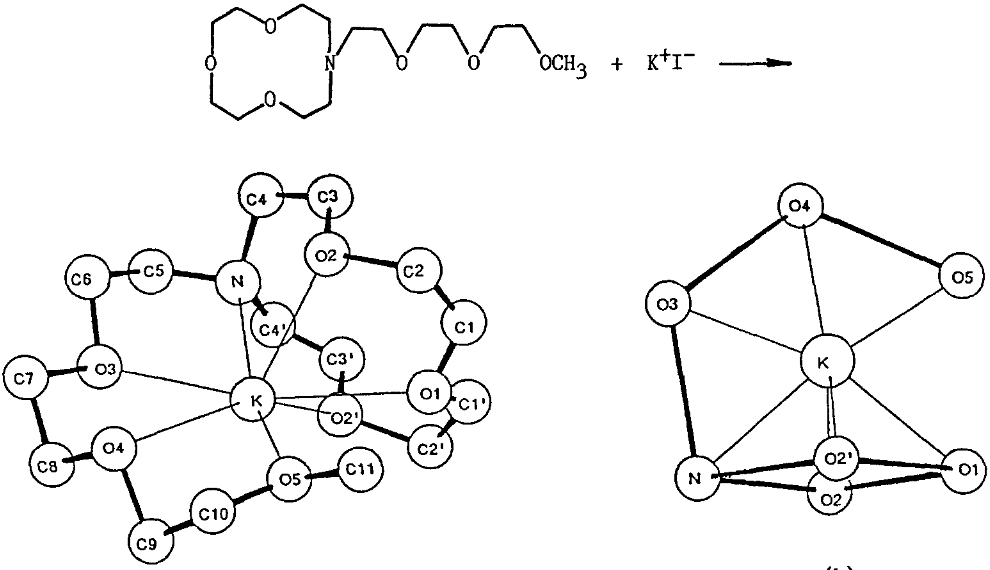
Compound **1** was prepared by alkylation of monoaza-12-crown-4 and the structure was ultimately confirmed by X-ray analysis.[4] Monoaza-12-crown-4 was obtained by hydrogenolysis[5] of N-benzylmonoaza-12-crown-4 which was, in turn, prepared as reported by Dale and Calverley from benzylamine and 1,11-diiodo-3,6,9-trioxaundecane (tetraethylene glycol diiodide).[6] Monoaza-12-crown-4 (1.0g, 0.006 mol) was dissolved in MeCN (25 mL) containing Na_2CO_3 (anhydrous, 0.7g, 0.007 mol) and heated to reflux under N_2. A solution of 1-tosyloxy-3,6,9-trioxadecane (1.9g, 0.006 mol) in MeCN (10 mL) was then added dropwise and reflux continued for 20h. The residue obtained after evaporation of MeCN was dissolved in CH_2Cl_2 (30 mL), and washed successively with 30 mL portions of H_2O and brine before drying over $MgSO_4$. Concentration, chromatography over Al_2O_3 (50% EtOAc/hexane), and molecular distillation afforded **1** as a colorless oil (52%, bp 155-160 °C/0.03 torr). IR (film): 2900, 1460, 1360, 1300, 1290, 1250, 1200, 1120, 1030, 920, cm^{-1}. ^1H-NMR ($CDCl_3$): 2.73 (t, 6H), 3.33 (s, 3H), 3.67 (m, 26H) ppm. Analysis: calculated for $C_{15}H_{31}NO_6$: C, 56.04; H, 9.74; N, 4.36. Found: C, 56.24; H, 9.89; N, 4.21. The complex was obtained as follows: KI (1.05 equiv and **1** were stirred in $ClCH_2CH_2Cl$ at ambient temperature for 1 h. Evaporation of the solvent afforded a crude solid which was recrystallized from THF. The complex, **1**•KI, was obtained as a white powder, mp 128-129 °C. Crystals suitable for structure determination were obtained by slow crystallization from THF.

The structure of **1**•KI is shown in the figure along with a skeletal drawing of the donor atoms and metal ion. The four donor atoms of the macroring are in the same plane. The skeletal drawing depicts a "basket" arrangement of donor atoms about the cation. Atoms O2, O2', and O3 lie closest to the metal atom. The macroring (the bowl of the basket) is rhombic rather than square, having the interdonor angles given in figure 1b. The complex also has two (pseudo) mirror planes, one of which contains O1, O3, N, and K; the other contains O2, O2', O4, and K. The former is a crystallographic mirror which bisects the macroring, and across which the sidechain is disordered. We call this arrangement a "calabash" complex. The name derives from the similarity in shape between complex **1**•KI and the Ugandan ladle known as a "calabash ladle."[7] The donor atoms approximate the point group C_{2v}. Note that the iodide anion is not within the cation's coordination sphere (K-I distance = 6.703 Angstroms).

In the 12-crown-4 to 24-crown-8 series of macrocycles, peak cation binding for Na^+, K^+, NH_4^+, or Ca^{2+} is always observed for 18-crown-6.[1] The special stability of 18-crown-6 complexes is attributed, at least in part, to favorable conformations of this ring system. When complexation occurs between K^+ and 18-crown-6, the macroring contributes solvation only in the equatorial plane. The voids above and below the plane in monocyclic crown complexes are usually filled by anions or water molecules. This is not the case for lariat ethers.

N-(2-Methoxyethyl)monoaza-18-crown-6 forms a complex with KI in which the bottom of the hexagonal bipyramid is filled by I^- and the top is filled by the sidearm oxygen donor.[8] The N,N'-bis-hydroxyethyl-4,13-diaza-18-crown-6 complex of NaI has only N or O atoms in the coordination sphere of Na^+ and the I^- ion is remote.[8] This cation-directed organization of binding sites about the metal ion, is also apparent in the KI•**1** complex. In fact, there is no void below the cation since this area is filled by the monoaza-12-crown-4 ring. Again, iodide is not in the cation's coordination sphere and the complex has the structure anticipated for the unknown [3.1.1]-cryptand.

The structural information presented here suggests that cation binding by the unknown [3.1.1]-cryptand should be as strong as for [2.2.2]-cryptand, a prediction which we are currently attempting to corroborate.



(a) (b)

Figure. (a) Perspective drawing of "calabash" complex. (b) Skeletal drawing. K-donor distances (in Angstroms): O1, 2.84(1); O2, 2.715(4); O3, 2.72(1); O4, 2.927(8); O5, 2.90(1); N, 2.85(1). Dimensions of macroring donors (distances in Angstroms: O1-O2, 2.85(2); O2-N, 2.88(2). Angles (°): O2-O1-O2', 85(1); O1-O2-N, 96(1); O2-N-O2', 84(1).

Coordinates for the $1{\cdot}K^+I^-$ Complex

Atom	X	Y	Z	Atom	X	Y	Z
I	0.25	0.15452(4)	0	C3	0.019(2)	0.3056(5)	0.088(2)
K	0.25	0.4224(1)	1.0009(9)	C4	0.064(2)	0.3192(6)	0.215(2)
O1	0.25	0.3497(4)	0.779(2)	C5	0.25	0.3736(7)	1.360(2)
O2	0.0219(9)	0.3473(2)	0.996(2)	C6*	0.144(3)	0.4280(9)	1.363(3)
O3	0.25	0.4608(5)	1.263(2)	C7*	0.163(3)	0.5166(10)	1.285(3)
O4*	0.1506(17)	0.5312(5)	1.040(1)	C8	0.25	0.5452(7)	1.163(2)
O5*	0.1470(21)	0.4841(6)	0.766(2)	C9	0.25	0.5539(7)	0.910(2)
N	0.25	0.3468(5)	1.218(1)	C10*	0.121(3)	0.5377(9)	0.799(3)
C1	0.137(2)	0.3147(6)	0.780(1)	C11*	0.068(4)	0.4692(11)	0.645(3)
C2	-0.001(3)	0.3292(6)	0.835(2)	* = population 1/2			

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Notes and References

+Portions of this work were conducted at the University of Maryland, College Park, MD 20742.

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4. Crystal Data: $C_{15}H_{31}NO_6 \cdot KI$, FW = 487.4, orthorhombic space group Ama2, a = 8.416(2), b=25.544(4), c = 9.684(3) Å, Z = 4, d_c = 1.555 gcm^{-3}, MoK_α radiation (μ = 0.71073 Å), λ = 17.5 cm^{-1}. R = 0.057 for 899 reflections with I > 0 (of 1036 unique data) measured by an Enraf-Nonius CAD4 by ω-2θ scans, $1^\circ = \theta = 25^\circ$.

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