mation on the influence of solid-state lattice forces on its structure.

Experimental Section

Materials. $Me_2Sn(acac)_2$ was recrystallized from benzene as reported in the paper describing its X-ray structure.[10] Small, colorless hexagonal plates of $Me_2Sn(S_2CNEt_2)_2$[16] (orthorhombic modification) were obtained by slow, room temperature evaporation of a chloroform–ethanol solution of the compound. Mixed crops of monoclinic and triclinic crystals in addition to the orthorhombic form were sometimes obtained; though we have varied recrystallization solvents, temperature, and the rate of crystallization, we have been unable to find a procedure for obtaining these other forms pure.

NMR Spectroscopy. Solid-state ^{13}C NMR spectra were obtained on ca. 0.4 g of polycrystalline dimethyltin(IV) compounds at 15.08 MHz with 60-MHz high-power proton decoupling. Magic-angle spinning at 2300 Hz in an Andrew-type rotor and spin-locking cross-polarization with the ^1H and ^{13}C fields matched at 57 kHz for 2 ms were used to obtain high-resolution solid-state spectra. Dwell times of 50 μs and repetition rates of 3 s were possible for the tin dithiocarbamate, while $Me_2Sn(acac)_2$ required repetition rates of 10 s; <1K scans were sufficient for chemical shift determination while 3–20K were required to obtain $|^1J|$. Chemical shifts (+/− 0.3 ppm) are relative to the internal secondary standard, delrin (89.1 ppm). Solution ^{13}C NMR spectra run at 100 MHz on a Bruker WM-400 spectrometer were ca. 5% by weight methyltin(IV). Line widths at half-height were <5 Hz and chemical shifts, referenced to Me_4Si (0 ppm), are +/− 0.1 ppm.

Structure Determination and Refinement. Crystal and data collection parameters for the orthorhombic modification of $Me_2Sn(S_2CNEt_2)_2$ are given in Table VII. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma^2_{\text{counting}} + (0.040F_o)^2)/4F_o^2$. Also 2086 reflections with $F_o^2 > 2\sigma(F_o^2)$ were used to refine 277 variables [x, y, z, 6 β's for non-hydrogen atoms; x, y, z for hydrogen atoms, and an isotropic extinction parameter ($g = 4.99 \times 10^{-8}$)]. The final agreement factors were $R = 0.020$, $R_w = 0.029$, and $S = 1.05$. The final difference Fourier synthesis showed no residuals greater than 0.5 e/A^3. Atomic scattering factors, including f' and f'', were taken from the *International Tables for X-ray Crystallography*, Vol. 4. Tables of anisotropic thermal parameters and F_o and F_c (×10) values are available as supplemental material.

Acknowledgment. The work of J.J.Z. is supported by the Office of Naval Research.

Registry No. $Me_2Sn(acac)_2$, 19631-04-0; $Me_2Sn(S_2CNEt_2)_2$, 27399-43-5.

Supplementary Material Available: Tables of anisotropic thermal factors and F_o and F_c (×10) values (8 pages). See any current masthead page for ordering information.

Solid-State Structural Chemistry of Lariat Ether and BiBLE Cation Complexes: Metal Ion Identity and Coordination Number Determine Cavity Size[†1]

Richard D. Gandour,*[‡] Frank R. Fronczek,[‡] Vincent J. Gatto, Carlo Minganti, Rose Ann Schultz, Banita D. White, Kristin A. Arnold, D. Mazzocchi, Steven R. Miller, and George W. Gokel*[§]

Contribution from the Departments of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, and the University of Miami, Coral Gables, Florida 33124.

Received November 18, 1985

Abstract: X-ray crystal structure data are presented for K^+ complexes of *N*-allylmonoaza-18-crown-6 (**1**) monohydrate $[K^+\subset\text{5-allyl}\cdot H_2O\ I^-]$, *N,N'*-bis(3-oxabutyl)diaza-18-crown-6 (**2**) $[K^+\subset\text{1-22-1}\ I^-]$, *N*-(3-oxabutyl)monoaza-15-crown-5 (**3**) $[K^+\subset\text{4-1}\ I^-]$, *N*-(3,6-dioxaheptyl)monoaza-15-crown-5 (**4**) $[K^+\subset\text{4-2}\ I^-]$, and *N,N'*-bis(2-hydroxyethyl)diaza-18-crown-6 (**5**) $[K^+\subset\text{H1-22-1H}\ I^-]$ along with the related complexes reported in preliminary form: $[Na^+\subset\text{H1-22-1H}\ I^-]$ and the K^+ complex of *N*-(3-oxabutyl)monoaza-18-crown-6 (**6**) $[K^+\subset\text{5-1}\ I^-]$ (*J. Am. Chem. Soc.* **1983**, *105*, 6717–6718) as well as the Na^+ complex of *N*-(ethoxycarbonylmethyl)monoaza-15-crown-5 (**7**) $[Na^+\subset\text{4-1E}\ Br^-]$ (*J. Am. Chem. Soc.* **1984**, *106*, 7244–7245). The crystals of $K^+\subset\text{5-allyl}\cdot H_2O\ I^-$ are monoclinic, space group $C2/m$ with four molecules in the unit cell dimensions $a = 13.254$ (3) Å, $b = 19.673$ (3) Å, $c = 9.111$ (1) Å, and $\beta = 112.72$ (2)°. $R = 0.052$ for 1416 observed reflections. The crystals of $K^+\subset\text{1-22-1}\ I^-$ are monoclinic, space group $C2/c$ with four molecules in the unit cell dimensions $a = 15.823$ (4) Å, $b = 9.076$ (4) Å, $c = 17.132$ (3) Å, and $\beta = 92.90$ (2)°. $R = 0.027$ for 2614 observed reflections. The crystals of $K^+\subset\text{4-1}\ I^-$ are monoclinic, space group $P2_1/n$ with four molecules in the unit cell dimensions $a = 8.813$ (2) Å, $b = 13.283$ (2) Å, $c = 16.604$ (2) Å, and $\beta = 102.59$ (2)°. $R = 0.033$ for 2398 observed reflections. The crystals of $K^+\subset\text{4-2}\ I^-$ are monoclinic, space group $P2_1/n$ with four molecules in the unit cell dimensions $a = 11.199$ (2) Å, $b = 16.297$ (2) Å, $c = 12.047$ (2) Å, and $\beta = 104.48$ (2)°. $R = 0.025$ for 2899 observed reflections. The crystals of $K^+\subset\text{H1-22-1H}\ I^-$ are monoclinic, space group $C2/c$ with four molecules in the unit cell dimensions $a = 13.696$ (2) Å, $b = 16.441$ (2) Å, $c = 11.739$ (2) Å, and $\beta = 117.02$ (1)°. $R = 0.029$ for 2352 observed reflections. The crystals of $Na^+\subset\text{H1-22-1H}\ I^-$ are monoclinic, space $P2_1$ with two molecules in the unit cell dimensions $a = 8.027$ (5) Å, $b = 15.618$ (4) Å, $c = 9.228$ (4) Å, and $\beta = 107.61$ (4)°. $R = 0.028$ for 1820 observed reflections. The crystals of $K^+\subset\text{5-1}\ I^-$ are orthorhombic, space group $P2_12_12_1$ with four molecules in the unit cell dimensions $a = 10.733$ (1) Å, $b = 12.806$ (2) Å, and $c = 15.762$ (3) Å. $R = 0.020$ for 1530 observed reflections. The crystals of $Na^+\subset\text{4-1E}\ Br^-$ are monoclinic, space group $P2_1/c$ with four molecules in the unit cell dimensions $a = 12.868$ (2) Å, $b = 9.037$ (1) Å, $c = 16.513$ (3) Å, and $\beta = 102.89$ (1)°. $R = 0.045$ for 1757 observed reflections. Comparisons made with these structures and complexes of chorands and cryptands show that neither "hole-size" nor "cavity-size" concepts provide satisfactory explanations for the data. Instead, experimentally determined metal-ion-to-donor distances coincide with the effective ionic radius defined by Shannon for various ions of differing coordination numbers. For these flexible ligands, the guest cation organizes the host's donor group array.

The rational design of alkali metal cation ionophores requires an appreciation of both the molecular-architecture-chemical-function relationship and synthetic execution. Lehn[2] has provided the blueprints for compounds having supramolecular topography,

---

[†] Portions of this work were performed at the University of Maryland.

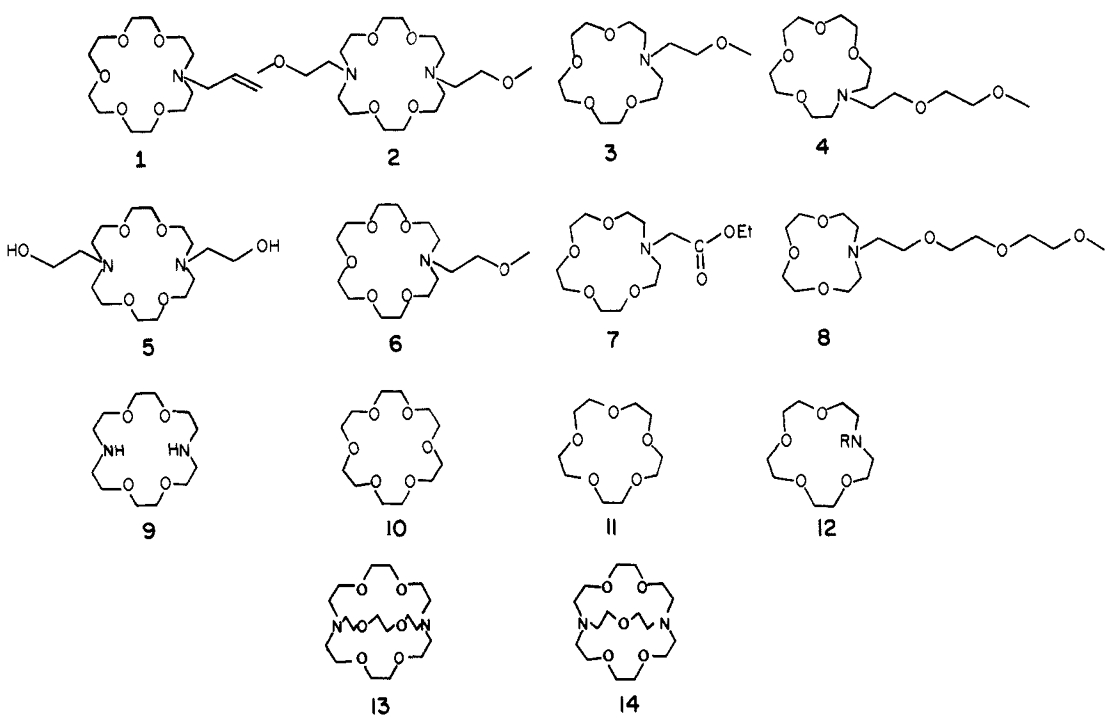
[‡] Louisiana State University.

[§] University of Miami.

[1] Presented in part at the 40th Southwest Regional ACS Meeting, Abstract 287.

0002-7863/86/1508-4078$01.50/0

Chart I



1 2 3 4 5 6 7 8 9 10 11 12 13 14

Table I. Effective Radii (Å) of Sodium and Potassium Cation as a Function of the Number of Donors[7]

no. of donors	Na^+	K^+	no. of donors	Na^+	K^+
4	0.99	1.37	8	1.18	1.51
5	1.00		9	1.24	1.55
6	1.02	1.38	10		1.59
7	1.12	1.46	12	1.39	1.64

emphasizing hole size for chorands (two-dimensional structures) and spherical cavity size for cryptands (three-dimensional structures). Although these concepts have been valuable and have stimulated much research, they serve only as a first approximation for fully comprehending the molecular architecture required for optimal ionophoric function.

We[3] and others[4] have shown from binding studies with cations that the hole-size relationship fails to explain cation selectivity in flexible macrocycles and lariat ethers. Instead, the key factor is the number of oxygen donors. In this paper, we demonstrate that the "cavity-size" hypothesis is as misleading as the "hole-size" relationship and that the number of donors and their topographical arrangement about the metal ion's coordination sphere are the critical factors in determining the optimum molecular architecture.

Two ideas that prove useful for understanding the structure and the binding properties of lariat ethers[5] and BiBLEs[6] (bibrachial lariat ethers) are effective ionic radii[7] and the molecular topography of complexes of high (>7) coordination number.[8] Effective ionic radii increase with increasing coordination number. Table I illustrates this for sodium and potassium cations. As the coordination number increases, so do the number of discrete coordination polyhedra. The polyhedra optimal for given numbers and types of donors varies.[8]

The solid-state structures and solution binding constants of macrocycles **1**–**14** are compared in Chart I. In describing the complexes, a shorthand (analogous to that used for cryptates[2]) has been adopted. For example, compound **6** is an 18-membered macrocycle containing five oxygen and one nitrogen donor atoms with an additional oxygen on the sidearm. Thus this compound is referred to as "5-1". Similarly, **4** is a "4-2" and **8** is a "3-3" system. Each compound has a total of six oxygen atoms and seven donor atoms. We have designated BiBLEs **2** and **5** as 1-22-1 and H1-22-1H, respectively, where H1 refers to a hydroxyl oxygen rather than an ether. Each of these compounds contains six oxygens and a total of eight donor atoms.

By comparing crystal structures of complexes of lariat ethers and chorands as well as those of BiBLEs and cryptands we demonstrate that the effective-ionic-radius relationship[7] applies to their binding of alkali metal cations. Moreover, an examination of both structural and binding data suggests that there is an optimal topography for any given number of donor atoms and that the guest cation organizes the donor atoms on these flexible ligands for binding.

Results

Tables II and III present the atomic positional parameters for the new complexes of lariat ethers and BiBLEs, **1**–**5**, as well as complexes of the armed macrocycles, **5**–**7**, previously reported[9,10] in preliminary form. Figure 1 gives the structural drawings for these new complexes while Figures 2, 3, 4, and 5 present skeletal drawings of donor atoms and metal ions for all of the complexes.

$K^+\subset$5-allyl·H_2O I^-. Figure 1a presents the structure of KI·**1**, *N*-allylmonoaza-18-crown-6 monohydrate ($K^+\subset$5-allyl·H_2O I^-), and Figure 2a shows a skeletal drawing of its donor atoms and the metal ion. The skeletal drawing reveals that the donor atoms are arranged in a chair conformation. The metal ion is heptacoordinated and resides slightly above the plane of the ring coordinated to a water molecule. The complex resides on a mirror plane containing K, O1, O3, and O4W. Rather than being directly involved with the metal ion, the iodide ion is hydrogen bonded

---

(2) Lehn, J.-M. *Struct. Bonding (Berlin)* **1973**, *16*, 1–69. Lehn, J.-M. *Science* **1985**, *227*, 849–856.

(3) (a) Schultz, R. A.; Dishong, D. M.; Gokel, G. W. *J. Am. Chem. Soc.* **1982**, *104*, 625–626. (b) Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786–6788. (c) Schultz, R. A.; White, B. D.; Dishong, D. M.; Arnold, K. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6659–6668.

(4) Michaux, G.; Reisse, J. *J. Am. Chem. Soc.* **1982**, *104*, 6895–6899.

(5) Schultz, R. A.; Dishong, D. M.; Gokel, G. W. *Tetrahedron Lett.* **1981**, *22*, 2623–2626.

(6) Gatto, V. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 8240–8244.

(7) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

(8) Muetterties, E. L.; Wright, C. M. *Quart. Rev.* **1967**, *67*, 109–194.

(9) Fronczek, F. R.; Gatto, V. J.; Schultz, R. A.; Jungk, S. J.; Colucci, W. J.; Gandour, R. D.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 6717–6718.

(10) Fronczek, F. R.; Gatto, V. J.; Minganti, C.; Schultz, R. A.; Gandour, R. D.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 7244–7245.

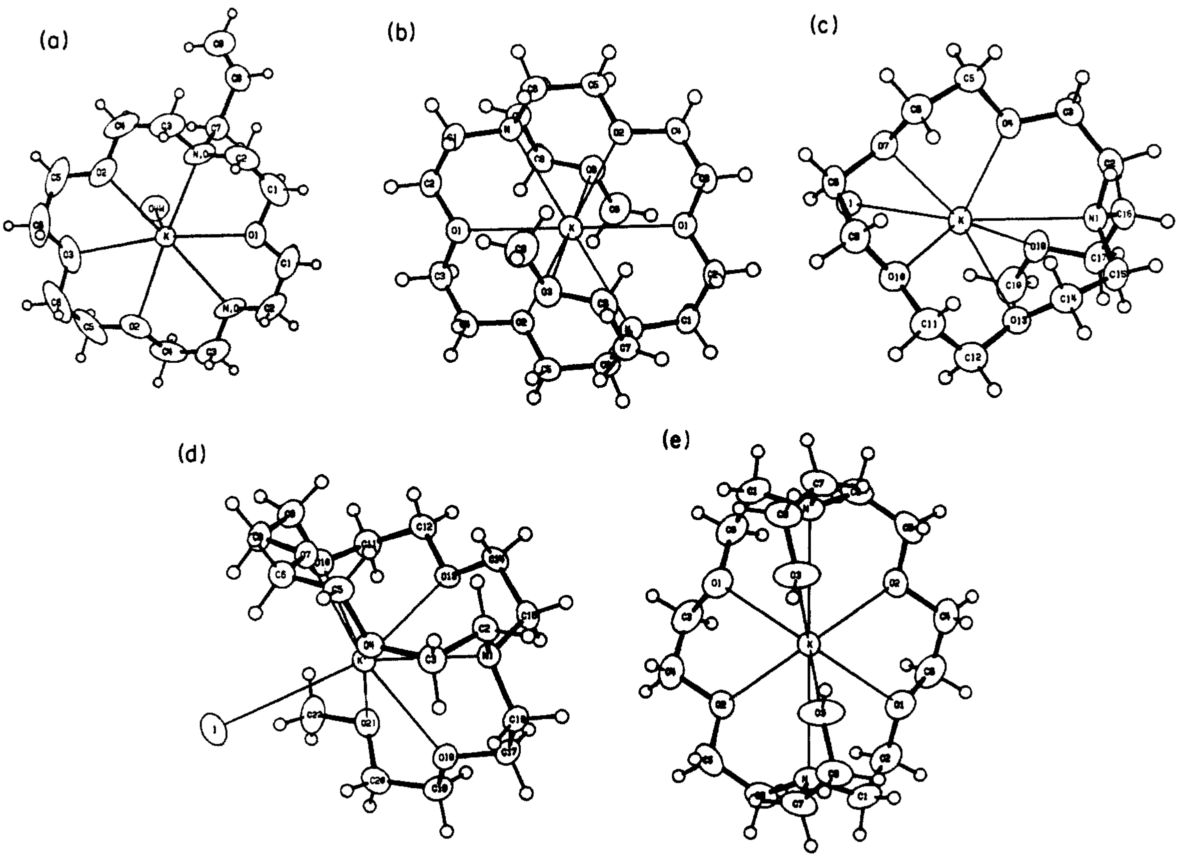


Figure 1. Ortep drawings of (a) $K^+\subset$5-allyl·$H_2O\,I^-$; (b) $K^+\subset$1-22-1 I^-; (c) $K^+\subset$4-1 I^-; (d) $K^+\subset$4-2 I^-; and (e) $K^+\subset$H1-22-1H I^-.

to the water. As expected, the allyl sidearm does not participate in binding the metal ion but instead projects axially from the macroring on the same side as the ligating water molecule and is disordered into two half-populated positions across the mirror plane.

$K^+\subset$1-22-1 I^-. Figure 1b presents the structure of KI·**2**, *N*,*N'*-bis(3-oxabutyl)-1,10-diaza-18-crown-6 ($K^+\subset$1-22-1 I^-), and Figure 2e shows a skeletal drawing of its donor atoms and the metal ion. The skeletal drawing reveals that the donor atoms of the macroring donor atoms adopt a chair conformation. The complex lies on a center of symmetry, and thus the oxygen atoms of the two sidearms are located above and below the plane of the chair. The arrangement of all the donor atoms is reminiscent of a macrotricyclic complex. Because the iodide ion is not coordinated to the metal ion, K^+ is octacoordinated. As a result of the C_i symmetry of the complex, the potassium ion lies on the line connecting the two nitrogens.

$K^+\subset$4-1 I^-. Figure 1c presents the structure of KI·**3**, *N*-(3-oxabutyl)monoaza-15-crown-5 ($K^+\subset$4-1 I^-), and Figure 3a shows a skeletal drawing of its donor atoms and the metal ion. The skeletal drawing reveals that the five donor atoms are arranged in a half-chair conformation (nearly an envelope) with a pseudo-C_2 axis passing through O13 and the midpoint between O4 and O7. The sidearm donor, O18, resides in the plane of O7, O10, and K and thus completes a distorted trigonal arrangement (O7-K-O10 angle = 62.0°; O7-K-O18 angle = 155.8°; O10-K-O18 angle = 142.2°). The donors occupy one hemisphere of the coordination sphere about the metal while an iodide ion occupies the other. The metal ion is heptacoordinated in this complex.

$K^+\subset$4-2 I^-. Figure 1d presents the structure of KI·**4**, *N*-(3,6-dioxaheptyl)monoaza-15-crown-5 ($K^+\subset$4-2 I^-), and Figure 3b shows the skeletal drawing of its donor atoms and metal ion. The skeletal drawing reveals that the five donor atoms of the macroring are arranged in a half-chair conformation with pseudo-C_2 symmetry with N1 on the axis. The two donor atoms, O18 and O21, on the sidearm bind so that the arrangement of the donor atoms resembles a half-closed cryptate structure. Atom O21 is 0.1 Å farther from the metal than O18. The iodide ion also serves as a donor, making K^+ octacoordinated.

$K^+\subset$H1-22-1H I^-. Figure 1e presents the structure of KI·**5**, *N*,*N'*-bis(2-hydroxyethyl)-1,10-diaza-18-crown-6 ($K^+\subset$H1-22-1H I^-), and Figure 4e shows a skeletal drawing of its donor atoms and the metal ion. The skeletal drawing reveals that the donor atoms of the macroring are arranged in a (slightly twisted) boat conformation of crystallographic C_2 symmetry; the potassium ion lies nearly on the line between the two nitrogens, and the oxygen atom in each sidearm occupies a "flagpole" position. The arrangement of the donor atoms is reminiscent of a 222 cryptate complex. Because the iodide ion is not coordinated to the metal ion, K^+ is octacoordinated.

Discussion

Four comparisons are made: (i) potassium complexes of 18-membered chorands and lariat ethers, (ii) 15-membered chorand and lariat ether complexes of potassium and sodium cations, (iii) sodium and potassium cation complexes of cryptands and the BiBLE, **5**, and (iv) potassium complexes of three lariat ethers, two BiBLEs, 18-crown-6, and 222 cryptand. (All of these complexes contain six oxygen atoms but their structures vary.)

A figure of skeletal drawings of the complexes as well as a table of structural and binding data are presented for each comparison. Donor atom connectivities in these skeletal drawings are indicated by solid lines to emphasize the coordination geometry of donor atoms about the cation. In addition to metal–donor distances and binding constants, a complex's mean cavity radius, *R*, as defined by Mathieu et al.,[11] is given in each of the tables. This value is calculated by averaging for the ligand's donors the differences between metal–donor distance and the donor's covalent radius, 1.4 Å (O) or 1.5 Å (N). These *R* values can be compared with the effective ionic radii calculated and tabulated by Shannon[7] (see Table I).

Potassium Complexes of 18-Membered Macrocycles. Figure 2 presents skeletal drawings of the potassium cation complexes

---

(11) Mathieu, F.; Metz, B.; Moras, D.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4412–1146.

Table II. Atomic Positional Parameters for Complexes of **1–4**[a]

$K^+{\subset}5\text{-allyl}\cdot H_2O\,I^-$							
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
I	0	0.15398 (5)	0	C2	0.2451 (9)	0.1175 (5)	0.483 (1)
K	0.2639 (2)	0	0.8058 (3)	C3	0.2881 (8)	0.1789 (5)	0.714 (1)
O1	0.2522 (7)	0	0.4865 (9)	C4	0.2893 (8)	0.1806 (5)	0.876 (1)
O2	0.3494 (4)	0.1222 (3)	0.9618 (7)	C5	0.3670 (9)	0.1195 (7)	1.125 (1)
O3	0.3762 (7)	0	1.1372 (10)	C6	0.4344 (8)	0.0609 (8)	1.205 (1)
O4W	0.0837 (6)	0	0.8673 (10)	C7[a]	0.0963 (13)	0.1308 (9)	0.576 (2)
N,O	0.2338 (6)	0.1222 (3)	0.6319 (8)	C8[a]	0.0384 (13)	0.1937 (10)	0.480 (2)
C1	0.1993 (9)	0.0575 (6)	0.401 (1)	C9[a]	0.0029 (38)	0.2398 (9)	0.529 (4)

$K^+{\subset}1\text{-}22\text{-}1\,I^-$							
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
I	0	0.19809 (3)	0.25	C3	0.4047 (1)	0.1365 (3)	0.1569 (1)
K	0.25	0.25	0	C4	0.3968 (1)	0.0066 (2)	0.1040 (1)
O1	0.32659 (9)	0.2139 (2)	0.15286 (8)	C5	0.3839 (1)	−0.0692 (2)	−0.0262 (1)
O2	0.38575 (8)	0.0543 (2)	0.02471 (7)	C6	0.3598 (1)	−0.0235 (2)	−0.1082 (1)
O3	0.32322 (9)	0.5348 (2)	−0.02011 (8)	C7	0.2894 (1)	0.5961 (2)	0.1097 (1)
N	0.22844 (9)	0.4759 (2)	0.12040 (9)	C8	0.3589 (1)	0.5547 (3)	0.0566 (1)
C1	0.2407 (1)	0.4077 (3)	0.1976(1)	C9	0.3850 (2)	0.4979 (4)	−0.0747 (2)
C2	0.3239 (1)	0.3295 (2)	0.2090 (1)				

$K^+{\subset}4\text{-}2\,I^-$							
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
I	0.35382 (2)	0.13489 (2)	0.19133 (2)	C6	0.0231 (3)	0.2498 (2)	0.0023 (2)
K	0.04793 (5)	0.11690 (4)	0.23793 (5)	C8	0.0810 (3)	0.3257 (2)	0.1755 (3)
O4	−0.0531 (2)	0.1140 (1)	0.0000 (2)	C9	0.0399 (3)	0.3427 (2)	0.2829 (3)
O7	−0.0002 (2)	0.2670 (1)	0.1114 (1)	C11	−0.0158 (3)	0.2677 (2)	0.4319 (3)
O10	0.0601 (2)	0.2709 (1)	0.3527 (2)	C12	−0.1457 (3)	0.2444 (2)	0.3756 (3)
O13	−0.1503 (2)	0.1642 (1)	0.3299 (2)	C14	−0.2675 (3)	0.1464 (2)	0.2571 (3)
O18	0.0247 (2)	−0.0491 (1)	0.2922 (2)	C15	−0.2741 (3)	0.0572 (2)	0.2243 (3)
O21	0.1801 (2)	0.0524 (1)	0.4603 (2)	C16	−0.1710 (3)	−0.0555 (2)	0.1566 (3)
N1	−0.1906 (2)	0.0340 (1)	0.1519 (2)	C17	−0.0931 (3)	−0.0860 (2)	0.2687 (3)
C2	−0.2431 (2)	0.0597 (2)	0.0331 (2)	C19	0.1023 (3)	−0.0789 (2)	0.3957 (3)
C3	−0.1506 (3)	0.0569 (2)	−0.0394 (2)	C20	0.2144 (3)	−0.0256 (2)	0.4290 (3)
C5	−0.0731 (3)	0.1909 (2)	−0.0583 (2)	C22	0.2826 (3)	0.1037 (3)	0.5045 (3)

$K^+{\subset}4\text{-}1\,I^-$							
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
I	0.63922 (3)	0.39675 (3)	0.83081 (2)	C6	0.0886 (6)	0.3096 (4)	0.9228 (3)
K	0.2417 (1)	0.39025 (8)	0.74980 (5)	C8	0.2425 (6)	0.4577 (4)	0.9532 (3)
O4	0.0630 (5)	0.2420 (3)	0.7911 (2)	C9	0.1266 (7)	0.5352 (4)	0.9146 (3)
O7	0.2221 (3)	0.3624 (3)	0.9133 (2)	C11	0.0131 (8)	0.6094 (4)	0.7863 (4)
O10	0.1404 (4)	0.5510 (3)	0.8315 (2)	C12	0.0207 (8)	0.6152 (5)	0.7008 (4)
O13	0.0189 (4)	0.5208 (3)	0.6597 (2)	C14	−0.1255 (6)	0.4714 (4)	0.6429 (3)
O18	0.3029 (4)	0.3356 (3)	0.5999 (2)	C15	−0.1173 (6)	0.3874 (4)	0.5821 (3)
N1	−0.0157 (4)	0.3052 (3)	0.6200 (2)	C16	0.0559 (6)	0.2534 (4)	0.5590 (3)
C2	−0.1037 (6)	0.2330 (5)	0.6594 (3)	C17	0.1789 (6)	0.3155 (4)	0.5320 (3)
C3	−0.0149 (7)	0.1795 (4)	0.7300 (3)	C19	0.4194 (6)	0.3948 (5)	0.5791 (3)
C5	0.0717 (7)	0.2171 (4)	0.8732 (3)				

[a] Atoms C7, C8, and C9 are half-populated.

of **1**, **2**, **6**, **9** (1,10-diaza-18-crown-6),[12] and **10** (18-crown-6).[13] The macroring's donor atoms in all these complexes are arranged in the "chair" conformation. For 18-crown-6, this arrangement is usually referred to as the D_{3d} conformation. For complexes of the two chorands, **9** and **10**, and the BiBLE, **2**, the metal is nestled in the macroring. In complexes of the two lariats, **1** and **6**, the metal is slightly out of the best plane of the macroring. In complexes of the two chorands, the counterion occupies nearly exact apical positions above and below the macroring. In $K^+{\subset}1\text{-}22\text{-}1\,I^-$ and $K^+{\subset}5\text{-}1\,I^-$ the sidearms' donor atoms occupy positions above and below the macroring, skewed from true apical. In $K^+{\subset}5\text{-allyl}\cdot H_2O\,I^-$, there is a donor in an apical position on only one side.

Structural and homogeneous stability constant data for potassium complexes of **1**, **2**, **6**, **9**, and **10** are summarized in Table IV. Potassium–oxygen bond distances for all of these complexes range from 2.77 to 2.91 Å. This is true whether the oxygen donors are in the macroring or sidearm. The K–N distances are slightly longer than the K–O distances, and none of the individual values is surprising. *R* values fall into two distinct groups: 1.400–1.406 Å for complexes of **1**, **9**, and **10**; 1.438 and 1.451 Å for complexes of **2** and **6**, respectively. The compounds in the former group do not have sidearms participating in the binding; but in the latter group they do.

Homogeneous stability constants (log K_s's) for potassium cation binding by compounds **1**, **9**, and **10** in methanol are recorded in Table IV. Potassium cation binding should not be enhanced relative to 18-crown-6 by the presence of an allyl sidearm. In addition, potassium cation binding should be disfavored by macroring nitrogen. As expected, the log K_s's for **1**, **9**, and **10** respectively are 5.02, 1.80, and 6.08. The value for **9** has previously been reported[15] as 2.04, but in acetonitrile,[16] log K_s for **9** is 4.32. In any event, the binding affinity of **9** for potassium cation is expected to be low because less electronegative nitrogen atoms substitute for oxygen atoms in the macroring[15] and because both intramolecular hydrogen bonding and hydrogen bonding to solvent[16] stabilize the uncomplexed ligand. These latter conclusions are supported by the fact that the log K_s in methanol[17] is 5.3 for *N*,*N'*-dimethyl-1,10-diaza-18-crown-6, a ligand in which intramolecular hydrogen bonding is not possible.

As anticipated, incorporation of a donor group in the sidearm enhances binding. log K_s for **6** is 5.77 but that for **1** is 5.02. The two-sidearmed ligand, **2**, binds better than its counterparts as well. log K_s for **2** is 5.46 while that for the dimethyl analogue mentioned above is 5.3, but the dibenzyl analogue[6] is only 3.38.

Complexes of 15-Membered Macrocycles. Skeletal drawings of potassium cation complexes of **3** and **4** as well as sodium cation complexes of **7**, **11** (15-crown-5),[18] and **12** (R = Ph) (*N*-phenylmonoaza-15-crown-5)[19] are shown in Figure 3. The donor atoms of the macroring in all five complexes are in the half-chair arrangement, and the metal resides significantly out of the best plane. In the lariats, the coordination sphere of each cation contains a donor group from the sidearm. The first oxygen atom (O18) in the NCH_2CH_2O– unit of $K^+{\subset}4\text{-}1\,I^-$ and $K^+{\subset}4\text{-}2\,I^-$ is at nearly a 90° angle to the ring plane. In contrast, in the sodium complex of **7**, the carbonyl oxygen forms a more acute angle, due to the metal's smaller size. Although the sidearms of **3** and **4** are ethyleneoxy units and the sidearm of **7** is a glycine residue, each sidearm comprises an N–C–C–O unit.

Binding and structural data for three, monoaza-15-crown-5 lariat ether complexes as well as two chorand complexes are summarized in Table V. The sidearms are **3** ($CH_2CH_2OCH_3$),

---

(12) Moras, D.; Metz, B.; Herceg, M.; Weiss, R. *Bull. Soc. Chim. Fr.* **1972**, 551–555.

(13) Seiler, P.; Dobler, M.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2744–2745.

(14) Gokel, G. W., unpublished.

(15) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600–606.

(16) Kulstad, S.; Malmsten, L. Å. *J. Inorg. Nucl. Chem.* **1980**, *42*, 573–578.

(17) Lehn, J. M.; Sauvage, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6700–6707.

(18) Groth, P. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 721–724.

(19) Weber, G.; Sheldrick, G. M.; Dix, J. P.; Vögtle, F. *Cryst. Struct. Commun.* **1980**, *9*, 1157–1162.

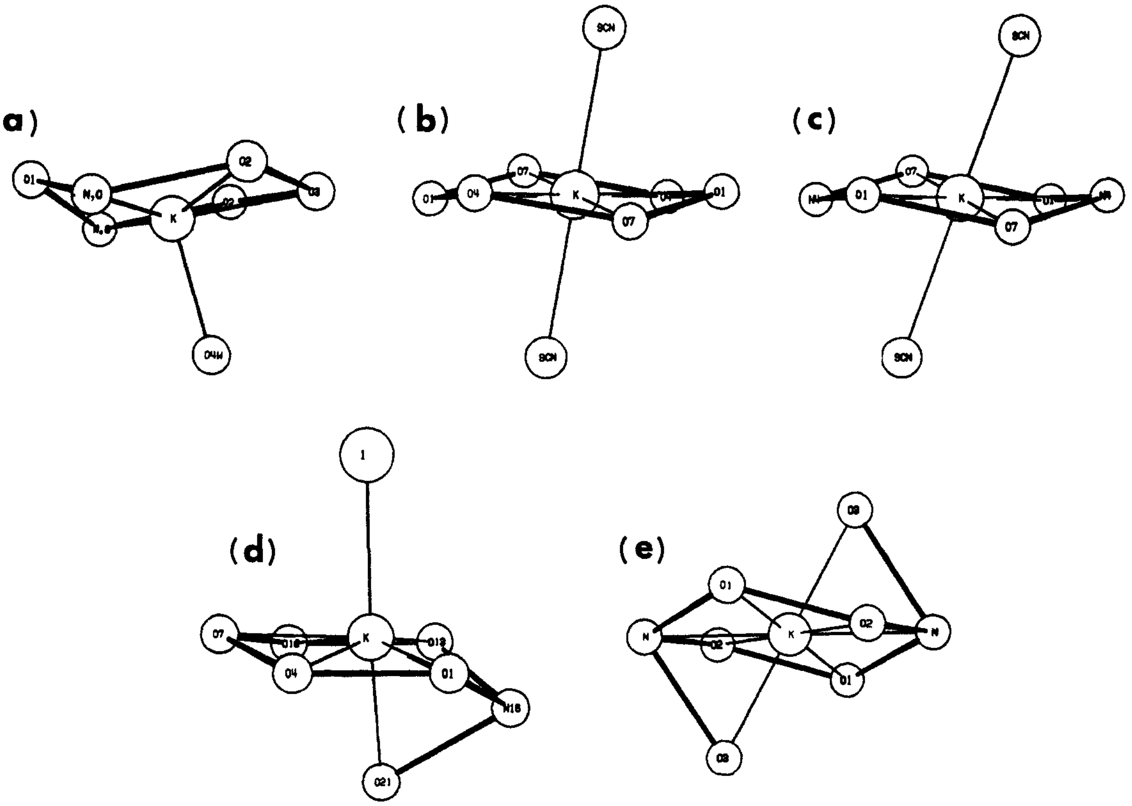


Figure 2. Skeletal drawings of potassium cation complexes of 18-membered macrocyclic chorands and lariat ethers: (a) $K^+\subset$5-allyl·H_2O I^-; (b) $K^+\subset$18-crown-6 SCN^-; (c) $K^+\subset$1,10-diaza-18-crown-6 SCN^-; (d) $K^+\subset$5-1 I^-; and (e) $K^+\subset$1-22-1 I^-.

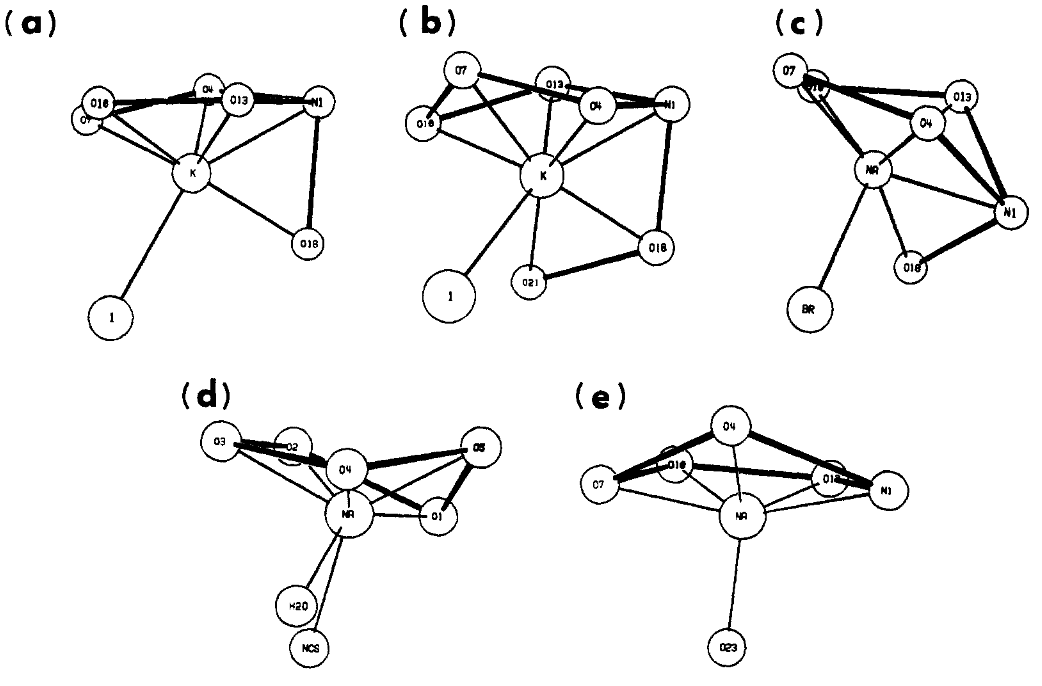


Figure 3. Skeletal drawings of sodium and potassium cation complexes of 15-membered macrocyclic chorands and lariat ethers: (a) $K^+\subset$4-1 I^-; (b) $K^+\subset$4-2 I^-; (c) $Na^+\subset$4-1E Br^-; (d) $Na^+\subset$15-crown-5 SCN^- H_2O; and (e) $Na^+\subset$N-phenylmonoaza-15-crown-5 ClO_4^-.

4 ($CH_2CH_2OCH_2CH_2OCH_3$), and 7 (CH_2–CO–OCH_2CH_3). The complexes of 3 and 4 contain K^+ and 7 contains Na^+. Further, the donor oxygens in 3 and 4 are sp^3-hybridized ether oxygens, whereas the sidearm donor group in 7 is an sp^2-hybridized (ester) carbonyl oxygen.

Not all of the M–O distances and *R* values for the complexes can be compared directly because different donor atoms and different cations are involved, although some comparison can be made. The shorter K–O distances in the potassium complex of 3 than in 4 are reflected in their respective *R* values of 1.38 and 1.44 Å. They are expected to differ since the corresponding coordination numbers about K^+ are seven and eight. These *R* values are smaller than expected for the coordination number, according to Shannon's[7] tabulations (see Table I). Among the sodium complexes, the lariat ether has the largest *R*. This is also true for the 18-membered macrocycles, of which lariat ether complexes have larger *R* values than their chorand counterparts. Sodium cation, in its complex with 7, is heptacoordinated and the *R* value is 1.11 Å. The Shannon radius for heptacoordinated Na^+ is 1.12 Å.

Both sodium and potassium cations are complexed more strongly by 4 than by 3 (see log K_s values in Table V). This is

Table III. Atomic Positional Parameters for Complexes of 5–7

K^{+}⊂H1-22-1H I^{-}

atom	x	y	z
I	0	0.02640 (1)	1/4
K	0	0.30016 (4)	3/4
O1	0.1930 (2)	0.3746 (1)	0.7678 (2)
O2	0.1425 (2)	0.3842 (1)	0.9775 (2)
O3	0.0446 (2)	0.1636 (1)	0.6512 (2)
N	0.0470 (2)	0.3062 (1)	0.5131 (2)
C1	0.1579 (2)	0.3377 (2)	0.5564 (3)
C2	0.1873 (2)	0.4056 (2)	0.6519 (3)
C3	0.2420 (2)	0.4297 (2)	0.8709 (4)
C4	0.2495 (3)	0.3923 (3)	0.9885 (4)
C5	0.1448 (3)	0.3541 (2)	1.0922 (3)
C6	0.0342 (3)	0.3600 (2)	1.0842 (3)
C7	0.0379 (3)	0.2228 (2)	0.4635 (3)
C8	0.0891 (3)	0.1597 (2)	0.5658 (3)

Na^{+}⊂H1-22-1H I^{-}

atom	x	y	z	atom	x	y	z
I	–0.46837 (4)	0	–0.43340 (4)	C4	0.2817 (6)	–0.2677 (5)	–0.8717 (7)
Na	–0.1197 (2)	–0.3028 (1)	–0.8317 (2)	C5	0.2851 (7)	–0.2330 (5)	–0.6228 (7)
O1	0.0079 (4)	–0.3151 (2)	–1.0597 (3)	C6	0.1756 (8)	–0.2392 (5)	–0.5160 (6)
O2	0.1861 (4)	–0.2602 (3)	–0.7679 (4)	C7	–0.0181 (7)	–0.1188 (4)	–0.6218 (6)
O3	–0.1913 (4)	–0.1414 (2)	–0.8762 (4)	C8	–0.1845 (7)	–0.0981 (4)	–0.7397 (6)
O4	–0.3918 (4)	0.2698 (2)	–1.0556 (3)	C9	–0.3492 (6)	–0.1235 (3)	–0.9947 (6)
O5	0.0270 (5)	–0.4441 (3)	–0.7115 (5)	C10	–0.3731 (7)	–0.1890 (3)	–1.1174 (6)
O6	–0.2903 (5)	–0.3308 (3)	–0.6601 (4)	C11	–0.4336 (7)	–0.3355 (4)	–1.1692 (6)
N1	–0.2254 (4)	–0.4374 (2)	–1.0066 (4)	C12	–0.4101 (6)	–0.4211 (3)	–1.0907 (5)
N2	–0.0042 (5)	–0.2103 (3)	–0.5823 (4)	C13	–0.2153 (6)	–0.5079 (3)	–0.8995 (5)
C1	–0.1197 (6)	–0.4533 (3)	–1.1099 (5)	C14	–0.0314 (8)	–0.5211 (3)	–0.7922 (6)
C2	0.0492 (7)	–0.4022 (4)	–1.0634 (6)	C15	–0.1115 (8)	–0.2325 (4)	–0.4835 (5)
C3	0.1563 (7)	–0.2592 (5)	–1.0289 (6)	C16	–0.1778 (7)	–0.3215 (4)	–0.5058 (5)

Na^{+}⊂4-1E Br^{-}

atom	x	y	z	atom	x	y	z
Br	0.28553 (5)	0.00299 (7)	0.13761 (4)	C6	0.4339 (4)	0.4673 (6)	0.2115 (3)
Na	0.2482 (1)	0.3167 (2)	0.0580 (1)	C8	0.2704 (5)	0.5948 (6)	0.1981 (3)
O4	0.4500 (2)	0.3375 (4)	0.0913 (2)	C9	0.1551 (5)	0.5713 (7)	0.1659 (4)
O7	0.3210 (3)	0.4585 (4)	0.1895 (2)	C11	0.1213 (5)	0.6423 (7)	0.0225 (4)
O10	0.1291 (3)	0.5252 (4)	0.0811 (2)	C12	0.2019 (7)	0.6340 (9)	–0.0237 (5)
O13	0.2241 (4)	0.5103 (4)	–0.0513 (2)	C14	0.2936 (5)	0.4970 (7)	–0.1061 (4)
O18	0.1225 (2)	0.1759 (4)	–0.0474 (2)	C15	0.2909 (4)	0.3400 (7)	–0.1338 (3)
O19	0.1196 (3)	–0.0245 (4)	–0.1280 (2)	C16	0.2856 (4)	0.0900 (6)	–0.0824 (3)
N1	0.3302 (3)	0.2377 (5)	–0.0642 (2)	C17	0.1665 (4)	0.0897 (6)	–0.0829 (3)
C2	0.4475 (4)	0.2330 (6)	–0.0390 (3)	C20	0.0063 (4)	–0.0427 (7)	–0.1302 (4)
C3	0.4862 (4)	0.2141 (6)	0.0524 (3)	C21	–0.0342 (5)	–0.1666 (9)	–0.1874 (4)
C5	0.4789 (4)	0.3322 (6)	0.1800 (3)				

K^{+}⊂5-1 I^{-}

atom	x	y	z	atom	x	y	z
I	–0.28020 (3)	–0.04407 (2)	–0.60377 (2)	C6	–0.6136 (4)	–0.3125 (4)	–0.6855 (4)
K	–0.27260 (9)	–0.27310 (7)	–0.71694 (6)	C8	–0.5797 (5)	–0.2352 (4)	–0.8210 (4)
O1	–0.1859 (3)	–0.3892 (3)	–0.5796 (2)	C9	–0.4949 (6)	–0.1621 (4)	–0.8639 (4)
O4	–0.4459 (3)	–0.3724 (3)	–0.6003 (2)	C11	–0.2917 (6)	–0.1409 (5)	–0.9129 (3)
O7	–0.5334 (3)	–0.2517 (3)	–0.7369 (2)	C12	–0.1747 (6)	–0.1994 (5)	–0.9312 (4)
O10	–0.3778 (3)	–0.2103 (3)	–0.8752 (2)	C14	–0.0075 (5)	–0.2901 (5)	–0.8660 (4)
O13	–0.1133 (3)	–0.2254 (3)	–0.8535 (2)	C15	0.0479 (4)	–0.3197 (5)	–0.7828 (4)
O21	–0.2491 (3)	–0.4580 (2)	–0.8230 (2)	C17	0.0142 (5)	–0.3893 (5)	–0.6433 (4)
N16	–0.0324 (3)	–0.3852 (3)	–0.7290 (3)	C18	–0.0704 (6)	–0.4421 (5)	–0.5812 (3)
C2	–0.2751 (6)	–0.4373 (6)	–0.5254 (3)	C19	–0.0483 (5)	–0.4906 (4)	–0.7655 (4)
C3	–0.3895 (6)	–0.3741 (6)	–0.5205 (3)	C20	–0.1818 (5)	–0.5224 (4)	–0.7710 (4)
C5	–0.5610 (5)	–0.3152 (5)	–0.5992 (4)	C22	–0.3789 (5)	–0.4833 (4)	–0.8244 (4)

Table IV. Comparison of Selected Structural and Binding Parameters in 18-Membered Macrocyclic Complexes with Potassium Cation

	compound						compound				
interaction	**1**	**2**	**6**	**9**[a]	**10**[b]	interaction	**1**	**2**	**6**	**9**[a]	**10**[b]
K–O, Å	2.853	2.848	2.853	2.836	2.770	K–N, Å	2.821	2.941	2.957	2.856	na
ring	2.800	2.848	2.830	2.836	2.770			2.941	2.957		
	2.800	2.803	2.816	2.825	2.811	R, Å	1.400	1.438	1.451	1.406	1.405
	2.804	2.803	2.786	2.825	2.811	coordn no.	7	8	8	8	8
	2.821		2.908		2.833	log K_s, K$^+$	5.02[c]	5.46[d]	5.77[c]	1.8[d]	6.08[e]
					2.833						
sidearm		2.860	2.909								
		2.860									

[a] Reference 12. [b] Reference 13. [c] Reference 14. [d] Reference 6. [e] Reference 3b.

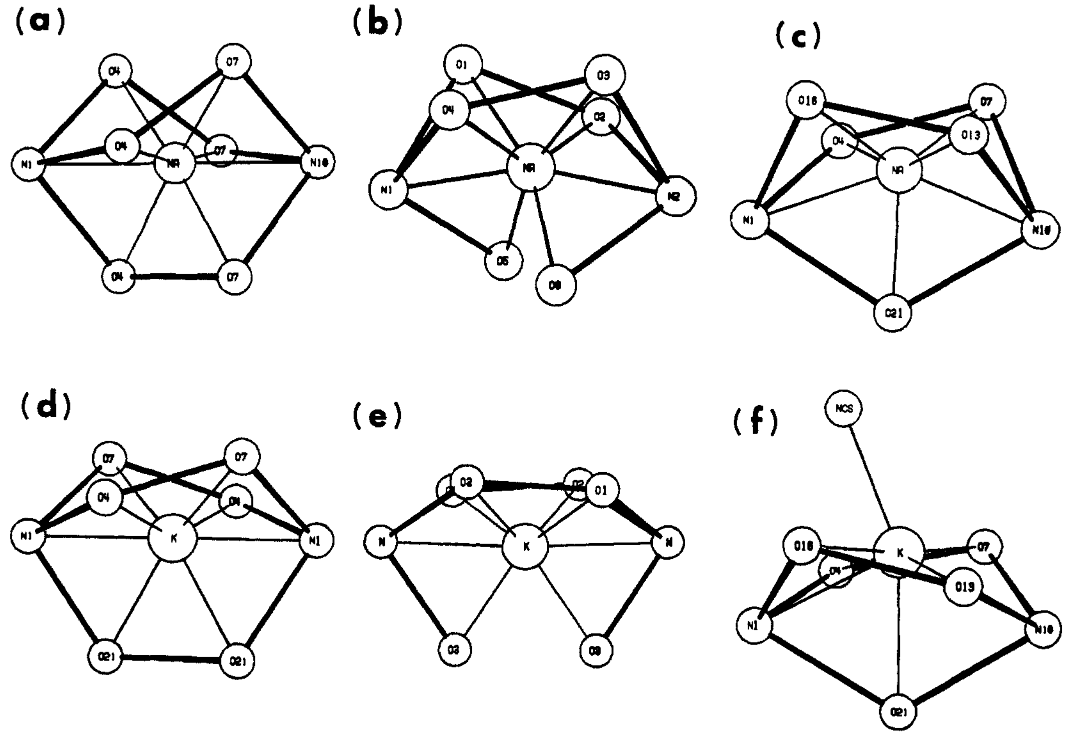


Figure 4. Skeletal drawings of sodium and potassium cation complexes of cryptands and 5: (a) $Na^+ \subset 222\,I^-$; (b) $Na^+ \subset H1\text{-}22\text{-}1H\,I^-$; (c) $Na^+ \subset 221\,SCN^-$; (d) $K^+ \subset 222\,I^-$; (e) $K^+ \subset H1\text{-}22\text{-}1H\,I^-$; and (f) $K^+ \subset 221\,SCN^-$.

Table V. Comparison of Selected Structural and Binding Parameters for Alkali Metal Complexes of 15-Membered Macrocycles

	compound				
interaction	3	4	7	11[a]	12[b]
M–O, Å	2.702	2.806	2.515	2.330	2.330
ring	2.783	2.862	2.511	2.509	2.485
	2.779	2.852	2.483	2.424	2.443
	2.797	2.825	2.616	2.486	2.344
				2.430	
sidearm	2.757	2.811	2.451		
		2.913			
M–N, Å	2.989	2.942	2.578	na	2.658
R, Å	1.38	1.44	1.11	1.036	1.08
coordn no.	7	8	7	7	6
log K_s, Na^+	3.88[c]	4.54[c]	4.10[d]	3.24[e]	1.70[f]
log K_s, K^+	3.95[g]	4.68[g]	4.03[g]	3.43[e]	1.60[h]

[a] Reference 18. [b] R = phenyl, ref 17. [c] Reference 3a. [d] Reference 10. [e] Reference 3b. [f] R = H, ref 3c. [g] Reference 14. [h] R = H, ref 14.

expected because complexes of **4** have more oxygen donor atoms[3a] than complexes of **3**. In other words, the cation is more encapsulated and, consequently, more stabilized. The reason for the increase in stability constants for complexes of **7** compared to **3** is that the ester residue has a higher dipole moment and is consequently a stronger donor group.[10] The lariat ethers are better complexing agents than the chorands for both sodium and potassium cations because of two factors: (a) there are more donor atoms in the lariat ethers and (b) the 15-membered macrocycle does not adopt a conformation suitable for encapsulating the sodium or the potassium cation.

Bibracchial Lariat Ether Complexes, BiBLEs. When two sidearms are attached to a macroring, complexation may be augmented by ligation from the same or opposite sides of the macroring. When complexation occurs from the same side, the complexes are expected to resemble cryptate complexes. The donor group arrangements in the sodium and potassium cation complexes of **5**, **13** (222 cryptand),[20,21] and **14** (221 cryptand)[11] are shown in Figure 4. The sidearms may also interact with a ring-bound cation from opposite sides as seen before in the potassium cation complex of **2**. Comparison of the potassium cation complexes of **2** and **5** is presented later.

Table VI. Comparison of Selected Structural and Binding Parameters of Sodium and Potassium Complexes of 5 with Sodium and Potassium Cryptates

	sodium complex with			potassium complex with		
interaction	13[a]	5	14[b]	13[c]	5	14[b]
M–O, Å	2.582	2.611	2.491	2.776	2.834	2.871
ring	2.582	2.437	2.499	2.776	2.834	2.759
	2.582	2.590	2.451	2.789	2.848	2.818
	2.566	2.564	2.519	2.789	2.848	2.702
	2.566		2.446	2.790		2.850
	2.566			2.790		
sidearm		2.426			2.721	
		2.588			2.721	
M–N, Å	2.782	2.630	2.703	2.874	3.128	2.916
	2.722	2.637	2.591	2.874	3.128	2.897
R, Å	1.19	1.14	1.10	1.38	1.46	1.40
N–M–N, deg	180	159.5	138.1	180	176.4	124.4
N–N, Å	5.504	5.183	4.944	5.748	6.253	5.143
coordn no.	8	8	7	8	8	8
log K_s	7.98[d]	4.87[e]	9.65[d]	10.41[d]	5.08[e]	8.54[d]

[a] Reference 20. [b] Reference 11. [c] Reference 21. [d] Reference 22. [e] Reference 6.

Binding and structural data for Na^+ and K^+ complexes of **5** are presented in Table VI along with comparable data for cryptate complexes. The structural parameters (N–N distances, N–M–N angles, and R value) for $Na^+ \subset H1\text{-}22\text{-}1H\,I^-$ fall between those previously observed for the Na^+ complexes of 222 and 221 cryptands. The K^+ complex of **5** has a larger R value and a longer N–N distance than observed in either of the cryptate complexes. Indeed, the large N–K distance (3.128 Å) in $K^+ \subset H1\text{-}22\text{-}1H\,I^-$ suggests that nitrogen may not be involved as a donor at all. Qualitatively, this is confirmed by the macroring conformations. Both cryptate complexes of sodium cation and the sodium cation

---

(20) Moras, D.; Weiss, R. *Acta Crystallogr., Sect. B* **1973**, *B29*, 396–399.

(21) Moras, D.; Metz, B.; Weiss, R. *Acta Crystallogr., Sect B* **1973**, *B29*, 383–388.

(22) Cox, B. G.; Schneider, H.; Stroka, J. *J. Am. Chem. Soc.* **1978**, *100*, 4746–4749.

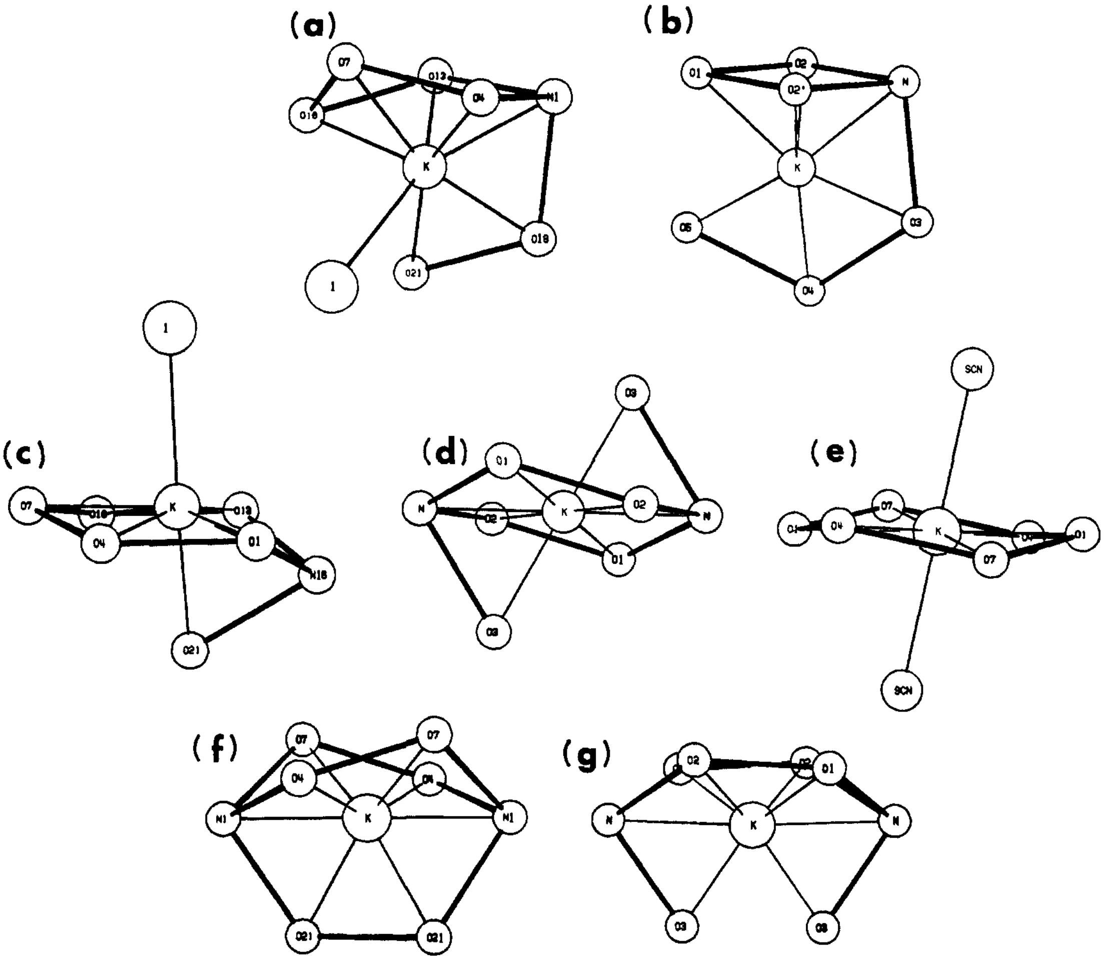


Figure 5. Skeletal drawings of potassium cation complexes of macrocycles containing six oxygen atoms: (a) K$^+$⊂4-2 I$^-$; (b) K$^+$⊂3-3 I$^-$; (c) K$^+$⊂5-1 I$^-$; (d) K$^+$⊂1-22-1 I$^-$; (e) K$^+$⊂18-crown-6 SCN$^-$; (f) K$^+$⊂222 I$^-$; and (g) K$^+$⊂H1-22-1H I$^-$.

complex of **5** have macroring donors which adopt the twist-boat conformation. A similar conformation is observed for the potassium cation cryptate complexes, but in the potassium cation complex of **5**, the macroring donors adopt a boat conformation with almost no twist.

The effective ionic radii[7] for sodium cation are 1.12 Å when heptacoordinated and 1.18 Å when octacoordinated. These values correspond nicely to the *R* values for the two cryptate complexes of sodium cation, but the BiBLE complex has an intermediate value.

The *R* values for the cryptate cavities in the potassium complexes correspond well to the *R* values observed in the chorand and lariat ether complexes. However, the coordination number (eight) observed in these cryptate complexes is greater than the coordination number (six) predicted from Shannon's table (see Table I). In contrast, the BiBLE complex also has a coordination number of eight but shows an *R* value equal to the Shannon value for a heptacoordinated potassium cation. A peculiarity in K$^+$⊂221 SCN$^-$ is that the thiocyanate anion is in the cation's coordination sphere.

Comparison of the binding data for sodium by the three ligands reveals that the order of binding is 221 > 222 > H1-22-1H. This has been rationalized[11] by the better fit of Na$^+$ to the 221 cavity. Indeed, *R* for 221 is 1.10 Å and the effective ionic radius of Na$^+$(VII) is 1.12 Å. However, the 222 cavity (*R* = 1.19 Å) also corresponds to the effective ionic radius of Na$^+$(VIII) (1.18 Å). The notion that the tighter the fit the better the binding appears to be borne out by the data. The BiBLE, which is less restricted than the cryptands in adjusting its cavity size, has a smaller *R* value (1.14 Å) than anticipated for an octacoordinated complex. The poorer binding by **5** compared to both cryptands can be ascribed to conformational factors. The uncomplexed BiBLE probably exists in a conformation with sidearms on opposite sides of the macroring whose donor atoms are in a chair conformation in terms of a skeletal picture. Changing to the cryptand conformation, i.e., a boat skeleton, results in an energy cost that probably reduces the cation binding strength of the BiBLE.

Comparison of the binding data for potassium cation by these complexing agents reveals that 222 > 221 > H1-22-1H. Binding efficiency of the cryptands has traditionally been ascribed to differences in cavity size. In the case of 222, the metal ion resides in the center of the ligand, while for 221, the metal is displaced off the center toward the largest ring. The cavity size is similar for both, although in 221 the anion complexes to the metal. The BiBLE binds potassium cation strongly, log K_s = 5.08, comparable to a chorand analogue such as *N,N'*-dimethyl-1,10-diaza-18-crown-6, log K_s = 5.3,[17] but poorly compared to the cryptands. The structural data suggest that the BiBLE does not encapsulate the metal as well as the cryptands. The binding profile of each can be explained in the same way as for the sodium cation complexes.

Six-Oxygen, Lariat Ether Complexes. Skeletal drawings of potassium cation complexes of **2**, **4**, **5**, **6**, **8**, **10**, and **13** are shown in Figure 5. This figure illustrates the variety of topographies suitable for binding potassium cation. The six donor atoms in 18-membered macroring ligands may adopt either a chair or a boat conformation. The macroring of K$^+$⊂4-2 I$^-$ is in the half-chair conformation and the macroring of K$^+$⊂3-3 I$^-$ is rhombic.

The coordination number of potassium ion is eight in all the complexes except K$^+$⊂3-3 I$^-$. This complex is heptacoordinate and has the usual "calabash" structure previously reported.[23] In this complex, the iodide ion is remote from the solvation shell although clearly present in the unit cell. In the crystal structure

---

(23) White, B. D.; Arnold, K. A.; Fronczek, F. R.; Gandour, R. D.; Gokel, G. W. *Tetrahedron Lett.* **1985**, *26*, 4035–4038.

Table VII. Comparison of Cavity Sizes in Six-Oxygen Macrocyclic Complexes with Potassium Cation and of Binding Constants for Sodium and Potassium Cations

	compound						
interaction	**6**	**4**	**8**[a]	**10**[b]	**2**	**5**	**13**[c]
R, Å	1.451	1.444	1.396	1.405	1.438	1.46	1.38
coordn no.	8	8	7	8	8	8	8
log K_s, Na^+	4.58[d]	4.54[d]	3.97[a]	4.35[f]	4.75[e]	4.87[e]	7.98[g]
log K_s, K^+	5.77[c]	4.68[c]	3.84[a]	6.08[f]	5.46[e]	5.08[e]	10.41[g]

[a] Reference 23. [b] Reference 13. [c] Reference 21. [d] Reference 3a. [e] Reference 6. [f] Reference 3b. [g] Reference 22.

of 18-crown-6 complexes with KSCN, the thiocyanate ion bridges two ring-bound potassium cations. Thiocyanate may be thought of as a seventh donor in each 1:1 complex. The crystal packing is such that either N or S from SCN^- is coordinated above and below each ring-bound cation. Formally, potassium cation is octacoordinated.

Structural and homogeneous stability constant data for these complexes are summarized in Table VII. For this series of complexes, the mean cavity radii fall into two distinct groups. *R* values for **2**, **4**, **5**, and **6** fall between 1.438 and 1.46 Å while the *R* values for **8**, **10**, and **13** range from 1.38 to 1.405 Å. Except for $K^+\subset$3-3 I^-, lariat ethers and BiBLEs have larger *R* values than chorands and cryptands. The exception occurs because in $K^+\subset$3-3 I^-, potassium cation is heptacoordinated and is expected to have an *R* value smaller than lariat ethers with eight donor atoms. For $K^+\subset$H1-22-1H I^-, the *R* value is 1.46 Å, but if the K–N distances, which are substantially longer than in any other complex, are excluded, *R* is 1.40 Å. Excluding the two N atoms makes K^+ formally hexacoordinated.

The homogeneous stability constants show several expected trends. The lariat ethers and BiBLEs described here do not bind potassium cations as well as either 222-cryptand (**13**) or 18-crown-6 (**10**). Binding strengths for the cryptands always exceed those for chorands and, among the chorands, the potassium cation–**10** interaction is especially favorable.[3b,4] Potassium cation binding decreases in the series, 5-1 (**6**) > 4-2 (**4**) > 3-3 (**8**). The variation in log K_s values, i.e., 5.46, 4.68, and 3.84, respectively, might be accounted for in terms of the so-called "hole-size" concept that says that the larger cations are bound more effectively by larger macrorings than are smaller cations. Such a concept is inappropriate to the present discussion since the cations are not generally nestled in the macroring (hole). Of course, the hole-size concept has been discredited[3b] for simple, all-oxygen chorands having no sidearms. Potassium cation's binding by **8** is more favorable than expected due to the formation of the calabash complex. The calabash complex of **8** approximates the symmetry expected for the unknown 311-cryptand. Considered in this way, the largest ring in the ligand contains six donor atoms. The calculated cavity size of $K^+\subset$3-3 I^- is virtually identical with those calculated for complexes of **10** and **13**. BiBLE **2** binds potassium cation more strongly than **5**. Two factors that contribute to the improved binding are better donicity of ether oxygen than hydroxyl oxygen and less conformational strain in the ligand of $K^+\subset$1-22-1 I^- than $K^+\subset$H1-22-1H I^-.

The arguments presented above are reinforced by the sodium cation binding data for **6**, **4**, and **8**. If hole size affects binding, then the order should be **6** > **4** > **8**. log K_s values (Table VII) for **6** and **4** are, within experimental error, identical. Both **6** and **4** have the same number of donor atoms, sodium cation is probably octacoordinated in both, and the sodium cation binding affinities are the same.

Conclusions

The key finding of this study is that the cavity sizes for a variety of ligands in potassium cation complexes fall into two discrete, nonoverlapping ranges. These ranges, indicated by the *R* values, are 1.380–1.406 and 1.438–1.460 Å. The compounds upon which this finding is based include chorands, lariat ethers, bibracchial lariat ethers, and cryptands. In general, lariat ethers and BiBLEs fall into the larger range and chorands and cryptands into the smaller. The single exception is $K^+\subset$3-3 I^- in which the potassium cation is heptacoordinated rather than octacoordinated.

These discrete ranges of *R* values coincide nicely with Shannon's effective ionic radii of potassium cation for six (1.38 Å) and seven (1.46 Å) donors. These donor numbers are invariably one lower than the coordination number observed in complexes of lariat ethers and BiBLEs and two lower for chorands and cryptands. Shannon's computations are based on oxides and fluorides. These macrocycles with neutral donor atoms would differ because for a given distance more of these softer donors are required to neutralize the charge.

Cram and Trueblood's hypothesis[24] that the guest organizes the host clearly applies to lariat ethers and BiBLEs. In flexible lariat ethers and bibracchial lariat ethers, the carbon framework primarily maintains the connectivity relationships among the donors rather than imposing a rigid conformational or steric bias on the system. The structural flexibility of a chorand and its tendency to adopt different conformations appropriate to its environment has been recognized ever since the first structures appeared.[25] Ligand flexibility is also a major factor in complexation by cryptands.[11] Complexation by these flexible ligands largely depends on neutralizing the charge on the metal, which requires an appropriate number of donors in an appropriate topography. Recent calculations[26] support these ideas. Pattern recognition analyses of Monte Carlo calculations by Marchese and Beveridge[26a] suggest the optimal topography for solvation of alkali cations by neutral oxygen. A molecular mechanics study by Wipff, Weiner, and Kollman[26b] has shown that structural flexibility and electrostatic attraction are the key factors in binding of alkali cations by 18-crown-6.

Alkali metal cations have a lower affinity for nitrogen than for oxygen donor atoms. The large K–N distances in $K^+\subset$H1-22-1H I^- suggest that nitrogen atoms are poorer donor atoms and are not as effectively involved in binding the cations as are the oxygen atoms. The poor donor properties of nitrogen relative to oxygen toward alkali metal cations have been established by Day et al.[27] and by Shamsipur and Popov[28] using NMR technqiues as well as by previous binding studies[3a] and the binding constant data discussed here. For example, **11**, **12** (R = Bu), and **3** have homogeneous stability constants, log K_s for sodium cation in methanol, of 3.24, 3.02, and 3.88, respectively. Exchanging an oxygen atom for an NR group reduces the cation affinity by a factor of 2. Providing an additional donor group in the sidearm (**12** (R = Bu) vs. **3**) raises the binding by nearly a power of ten.

The fact that the binding constants differ so much among classes suggests that donor number and topography rather than hole size and cavity size are the primary factors that influence binding strength. The finding that the *R* values for macrocycles are quantized is important, especially to those who design new ligands. The ideal ligand would have high binding affinity and cation selectivity as well as fast on–off rates.

Experimental Section

Preparation of Lariat Ether–Cation Complexes. All of the *N*-pivot lariat ethers[3c] and BiBLEs[6] were prepared as previously described. All of the complexes, except **5**·NaI, were prepared by adding excess alkali

---

(24) Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43–106.

(25) Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizackerley, R. P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2733–2738.

(26) (a) Marchese, F. T.; Beveridge, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 3713–3720. (b) Wipff, G.; Weiner, P.; Kollman, P. *J. Am. Chem. Soc.* **1982**, *104*, 3249–3758.

(27) Day, M. C.; Medley, J. H.; Ahmad, N. *Can. J. Chem.* **1983**, *61*, 1719–1721.

(28) Shamispur, M.; Popov, A. I. *Inorg. Chim. Acta* **1980**, *43*, 243–247.

Table VIII. Crystal Data and Data Collection Parameters for Complexes of **1–4**

compound	$K^+\subset$5-allyl-$H_2O\ I^-$	$K^+\subset$1-22-1 I^-	$K^+\subset$4-1 I^-	$K^+\subset$4-2 I^-
formula	$C_{15}H_{29}NO_5 \cdot KI \cdot H_2O$	$C_{18}H_{38}N_2O_6 \cdot KI$	$C_{13}H_{27}NO_5 \cdot KI$	$C_{15}H_{31}NO_6 \cdot KI$
fw	487.4	544.5	443.4	487.4
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/m$	$C2/c$	$P2_1/n$	$P2_1/n$
a, Å	13.254 (3)	15.823 (4)	8.813 (2)	11.199 (2)
b, Å	19.673 (3)	9.076	13.283 (2)	16.297 (4)
c, Å	9.111 (1)	17.132 (3)	16.604 (2)	12.047 (2)
β, deg	112.72 (2)	92.90 (2)	102.59 (2)	104.48 (2)
V, Å^3	2191 (1)	2457 (2)	1897 (1)	2129 (1)
Z	4	4	4	4
D, g cm^{-3}	1.477	1.472	1.552	1.521
T, °C	25	30	27	23
μ, cm^{-1}	16.6	14.9	19.1	17.1
$F(000)$	992	1120	896	992
cryst size, mm	0.20 × 0.26 × 0.32	0.14 × 0.32 × 0.40	0.36 × 0.40 × 0.56	0.40 × 0.40 × 0.48
min. rel trans. %	84.61	78.19	91.74	93.72
θ limits, deg	1–27	1–32	1–25	1–25
scan rates, deg min^{-1}	0.49–10.0	0.35–4.0	0.53–5.0	0.53–4.0
precision, $I/\sigma(I)$	50	50	25	50
max. scan time, s	120	180	120	120
decay, %	7.8			
unique data	2610	4260	3552	3748
observed data	1416	2614	2398	2899
variables	129	205	191	217
B for H atoms, Å^2	10.0	refined	7.0	5.0
extinction			2.1 (3) × 10^{-7}	
R	0.052	0.027	0.033	0.025
R_w	0.052	0.031	0.045	0.043
GOF	2.86	1.55	1.28	1.20
max residual, e Å^{-3}	1.51	0.73	0.61	0.74
notes	disordered allyl		in capillary	in capillary

Table IX. Crystal Data and Data Collection Parameters for Complexes of **5–7**

compound	$K^+\subset$H1-22-1H I^-	$Na^+\subset$H1-22-1H I^-	$K^+\subset$5-1 I^-	$Na^+\subset$4-1E Br^-
formula	$C_{16}H_{34}N_2O_6 \cdot KI$	$C_{16}H_{34}N_2O_6 \cdot NaI$	$C_{15}H_{27}NO_6 \cdot KI$	$C_{14}H_{27}NO_6 \cdot NaBr$
fw	516.5	500.4	483.4	408.3
cryst system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$P2_1$	$P2_12_12_1$	$P2_1/c$
a, Å	13.696 (2)	8.027 (5)	10.733 (1)	12.868 (2)
b, Å	16.441 (2)	15.618 (4)	12.806 (2)	9.037 (1)
c, Å	11.739 (2)	9.228 (4)	15.762 (3)	16.513 (3)
β, deg	117.02 (1)	107.61 (4)		102.89 (1)
V, Å^3	2355 (1)	1103 (2)	2166 (1)	1872 (1)
Z	4	2	4	4
D, g cm^{-3}	1.457	1.507	1.482	1.449
T, °C	27	23	25	27
μ, cm^{-1}	15.5	14.8	16.8	22.2
$F(000)$	1056	512	976	848
cryst size, mm	0.28 × 0.36 × 0.44	0.36 × 0.52 × 0.64	0.24 × 0.24 × 0.44	0.40 × 0.44 × 0.60
min. rel trans, %	84.44	75.47	94.90	80.04
θ limits, deg	1–30	1–25	1–25	1–25
scan rates, deg min^{-1}	0.37–5.0	0.63–5.0	0.49–20.0	0.45–5.0
precision, $I/\sigma(I)$	50	50	50	50
max. scan time, s	180	120	120	120
decay, %	7.1			3.0
unique data	3431	2016	2176	3292
observed data	2352	1820	1530	1757
variables	119	235	218	209
B for H atoms, Å^2	7.0	5.0	5.0	6.0
extinction		1.2 (1) × 10^{-6}	1.8 (3) × 10^{-7}	1.38 (6) × 10^{-6}
R	0.029	0.028	0.020	0.045
R_w	0.039	0.038	0.028	0.058
GOF	1.14	1.175	0.948	1.738
max residual, e Å^{-3}	0.46	0.48	0.46	0.74
notes		absolute conf	absolute conf	capillary

metal halide to a methylene chloride solution of the ligand. After being stirred at room temperature for approximately 1 h, the solution was filtered and concentrated in vacuo. Recrystallization from the appropriate solvent provided the desired complexes.

***N*-Allylmonoaza-18-crown-6-KI·H$_2$O (1·KI·H$_2$O).** Recrystallization (THF) gave pure **1**·KI·H$_2$O (52%) as a white crystalline solid (mp 91–92 °C). Anal. Calcd for $C_{15}H_{29}NO_5KI \cdot H_2O$: C, 36.96; H, 6.42; N, 2.87. Found: C, 36.95; H, 6.44; N, 2.86.

***N,N'*-Bis(3-oxabutyl)-1,10-diaza-18-crown-6-KI (2·KI).** Recrystallization (THF) gave pure **2**·KI (84%) as a white crystalline solid (mp 144–145 °C). Anal. Calcd for $C_{16}H_{34}N_2O_6KI$: C, 39.70; H, 7.05; N, 5.15. Found: C, 39.82; H, 7.30; N, 5.04.

***N*-(3-Oxabutyl)monoaza-15-crown-5·KI (3·KI).** Recrystallization (THF) gave pure **3**·KI (97%) as a white crystalline solid (mp 129.5–131 °C). Anal. Calcd for $C_{13}H_{27}NO_5KI$: C, 35.21; H, 6.15; N, 3.16. Found: C, 35.29; H, 6.33; N, 3.17.

***N*-(3,6-Dioxaheptyl)monoaza-15-crown-5-KI (4·KI).** Recrystallization (THF) gave pure **4**·KI (97%) as a white crystalline solid (mp 138–139 °C). Anal. Calcd for $C_{15}H_{31}NO_6KI$: C, 36.96; H, 6.42; N, 2.87. Found: C, 36.98; H, 6.60; N, 2.74%.

***N,N'*-Bis(2-hydroxyethyl)-1,10-diaza-18-crown-6·KI (5·KI).** Recrystallization (THF) gave pure 5·KI (56%) as a white crystalline solid (mp 187–188° C). Anal. Calcd for $C_{18}H_{38}N_2O_6KI$: C, 37.20; H, 6.65; N, 5.42. Found: C, 37.58; H, 6.68; N, 5.42.

***N,N'*-Bis(2-hydroxyethyl)-1,10-diaza-18-crown-6·NaI (5·NaI).** This complex was prepared as previously described.[6]

***N*-(3-Oxabutyl)monoaza-18-crown-6·KI (6·KI).** Recrystallization (THF) gave pure 6·KI (94%) as a white crystalline solid (mp 125–126.5 °C). Anal. Calcd for $C_{15}H_{27}NO_6KI$: C, 36.96; H, 6.42; N, 2.87. Found: C, 37.00; H, 6.55; N, 2.79.

***N*-(Ethoxycarbonylmethyl)monoaza-15-crown-5·NaBr (7·NaBr).** Recrystallization (acetone) gave pure 7·NaBr (53%) as a white crystalline solid (mp 125–126.5 °C). Anal. Calcd for $C_{14}H_{27}NO_6NaBr$: C, 41.19; H, 6.84; N, 3.22; Br, 21.10. Found: C, 41.02; H, 6.84; N, 3.22; Br, 21.10.

X-ray Experimental. Intensity data were collected by ω–2θ scans of variable rate designed to yield measurements of equal relative precision for all significant reflections, using an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. A maximum was placed on the scan time spent on any reflection. One quadrant of data was collected for each crystal within the specified angular limits, one octant for the orthorhombic $K^+\subset$5-1 I^-. Crystal data and specifics of data collection are given in Tables VIII and IX. Data reduction included corrections for background, Lorentz, polarization, absorption, and in two cases decay. The absorption corrections were based on ψ scans of reflections near χ = 90°. Equivalent data were merged, and all reflections having $I > 3\sigma(I)$ were used in the refinements. All structures were solved by the heavy atom method and refined by full-matrix least squares based on F with weights $w = \sigma^{-2}(F_0)$, using the Enraf-Nonius SDP programs. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in difference maps but placed in calculated positions where possible. In the case of $K^+\subset$1-22-1 I^-, refinement of H atoms was possible.

R factors and residuals in final difference maps are given in the tables.

Acknowledgment. G.W.G. warmly thanks the National Institutes of Health (Grants CM-29150, GM-31864, and GM-36262) and W.R. Grace and Co. for partial support of this work.

Registry No. K^+C5-allyl·H_2O I^-, 102422-62-8; K^+C1-22-1 I^-, 102422-63-9; K^+C4-1 I^-, 102422-64-0; K^+C4-2 I^-, 102422-65-1; K^+-CH1-22-1H I^-, 102422-66-2; Na^+CH1-22-1H I^-, 87249-10-3; K^+C5-1 I^-, 102422-67-3; Na^+C4-1E Br^-, 102434-64-0.

Supplementary Material Available: Tables of distances, angles, and selected torsion angles, coordinates for hydrogen atoms, anisotropic thermal parameters, and structure factors (88 pages). Ordering information is given on any current masthead page.

Vanadium Phenolates as Models for Vanadium in Biological Systems. 1. Synthesis, Spectroscopy, and Electrochemistry of Vanadium Complexes of Ethylenebis[(*o*-hydroxyphenyl)glycine] and Its Derivatives

Joseph A. Bonadies and Carl J. Carrano*

Contribution from the Department of Chemistry, University of Vermont,
Burlington, Vermont 05405. *Received November 8, 1985*

Abstract: The ligand ethylenebis[(*o*-hydroxyphenyl)glycine] (EHPG) and its derivatives have been studied as models for vanadium binding sites in biomolecules. A series of vanadium complexes are presented which elucidate the behavior of oxovanadium–phenolate coordination. Vanadium–phenolate chemistry is shown to be quite diverse with stable complexes involving the VO^{2+}, VO^{3+}, $VOOH^{2+}$, and VO_2^+ moieties being isolated and characterized by NMR, UV–visible, EPR, and infrared spectroscopy. Several of these forms of vanadium are seldom observed in chelate chemistry. The electrochemical behavior of these species is also described. In the pentavalent state, vanadium is seen to promote an unusual, stepwise, metal-assisted, oxidative decarboxylation of the EHPG ligand to yield oxovanadium(IV) complexes of *N*-[2-(*o*-salicylideneamino)ethyl](*o*-hydroxyphenyl)glycine (EHGS) and *N,N'*-disalicylideneethylenediamine (SALEN). This reaction has been investigated and a mechanism is proposed. The results of this work should be of value in elucidating the coordination chemistry of vanadium in a variety of biological systems.

In contrast to many other of the biologically important transition metals (Fe, Cu, Mo, etc.), the biochemistry of vanadium has remained for the most part obscure. Vanadium is normally found only in trace amounts in living systems, but certain organisms have been found which concentrate this element, for unknown purposes, to an extraordinary degree.[1,2]

In order to better understand the biological role of vanadium, the coordination chemistry of this element in its three accessible oxidation states (+III, +IV, and +V) with relevant ligands needs to be explored. In light of the reported binding of vanadium to the metal–tyrosinate protein transferrin[3] and its interaction with the recently characterized polyphenol, tunichrome, in the vanadocytes of the tunicates,[4] vanadium–phenolate chemistry seemed an appropriate starting point. To this end we report here the extensive coordination and redox chemistry of vanadium with the ligand, *N,N'*-ethylenebis[(o-hydroxyphenyl)glycine] (EHPG) (Table I) and its derivatives. This ligand has already proved useful in providing insights into the structure and chemistry of a number of iron–phenolate proteins.[5,6] Some of the data reported here have already appeared in communication form.[7]

Experimental Section

Materials. EHPG was purchased from Sigma and purified by extensive soxhlet extraction with acetone. As obtained commercially, EHPG consists of a 50:50 mixture of two isomers, the racemic *R,R/S,S* pair and a meso *R,S* form. No attempt was made to separate these isomers. Sodium vanadate and 8-hydroxyquinoline purchased from Fisher Scientific and vanadyl sulfate from Aldrich were used without

---

* Author to whom correspondence should be addressed.

(1) Chasteen, N. D. *Struct. Bonding* **1983**, *107*, 53.
(2) Boyd, D. W.; Kustin, K. *Adv. Inorg. Biochem.* **1985**, *6* (9), 311.
(3) Harris, W. R.; Carrano, C. J. *J. Inorg. Biochem.* **1984**, *22*, 201.
(4) Bruening, R. C.; Oltz, E. M.; Furukawa, J.; Nakanishi, K.; Kustin, K. *J. Am. Chem. Soc.* **1985**, *107*, 5298.
(5) Patch, M. G.; Simolo, K. P.; Carrano, C. J. *Inorg. Chem.* **1983**, *22*, 2630.
(6) Carrano, C. J.; Spartalian, K.; Appa Rao, G. V. N.; Pecoraro, V. L.; Sundaralingam, M. *J. Am. Chem. Soc.* **1985**, *107*, 1651.
(7) Pecoraro, V.; Bonadies, J. A.; Marrese, C. A.; Carrano, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 3360.