J. Org. Chem. 1984, 49, 347-353

bulb-to-bulb distillation at 0.5 torr (30 °C) and then by column chromatography of the distillate on basic alumina. The first fraction eluted with ethyl acetate (10%) in hexane was **5** (7.2 g, 60%), with spectral data as in Table I.

Thermolysis of Oxadiazolines. For a small-scale run in solution, an oxadiazoline (ca. 25 mg) in C_6D_6 containing C_6H_6 as an internal standard was sealed into a medium-walled NMR tube after three cycles of freeze-pump-thaw degassing, and the ^1H NMR spectrum was recorded. The tube was then immersed in an oil bath at 80.0 ± 0.2 °C for 240 h (or more) with periodic monitoring for remaining substrate by ^1H NMR spectroscopy. When starting material could no longer be detected, the ^1H NMR spectrum (90 or 250 MHz) was measured again, for ultimate estimates of relative and absolute yields. The tube was then opened, volatile materials and solvent were distilled (bulb-to-bulb) on the vacuum line, and the residue was analyzed by GC/MS. Between 70% and 80% of the total ^1H NMR signal could be assigned to products of known structure.

Larger scale thermolyses carried out in solution or with neat oxadiazoline involved about 500 mg of oxadiazoline and heavy-walled Pyrex tubing instead of an NMR tube. The contents of such tubes were analyzed immediately after freezing, opening, and addition of solvent (neat samples) to minimize losses of the more volatile products. After distillation of the volatile materials, which except for propene were identified from their GC retention times and from the spectra of collected materials, the residual azines were separated by GC on an OV-17 column for the purpose of measuring their NMR spectra, mass spectra, and infrared spectra. Propene was identified by comparison of the ^1H NMR spectra of solutions of authentic propene in C_6D_6 and in CCl_4 with the spectra of total reaction mixtures.

Acknowledgment. This work was financed from a grant provided by the Natural Sciences and Engineering Research Council of Canada. We thank Dr. M. Bêkhazi, whose initial work with the oxadiazoline system indicated that neat samples led to a greater variety of products than did dilute samples.

Registry No. **1a**, 87937-99-3; **1b**, 87938-00-9; **1c**, 87938-01-0; **1d**, 87938-02-1; **1e**, 87938-03-2; **2a**, 87938-04-3; **2b**, 87938-05-4; **2c**, 87938-06-5; **2d**, 87938-07-6; **2e**, 87938-08-7; **2f**, 87938-09-8; **3a**, 87938-10-1; **3b**, 87938-11-2; **3c**, 87938-12-3; **3d**, 87938-13-4; **3e**, 87938-14-5; **5**, 87938-15-6; $[(CH_3)_2C{=}N-]_2$, 627-70-3; $(CH_3)_2C{=}NNHCOCH_3$, 3742-63-0; $(CH_3)_2C{=}NNHCOC_2H_5$, 3884-67-1; C_2H_5OH, 64-17-5; CH_3OH, 67-56-1; Cl_3CCH_2OH, 115-20-8; F_3CCH_2OH, 75-89-8; $CH_3CH_2OCH(CH_3)OC(CH_3){=}CH_2$, 87938-17-8; $CH_3CH{=}CH_2$, 115-07-1; ethyl acetate, 141-78-6; hydrazine, 302-01-2; γ-butyrolactone, 96-48-0; (4-hydroxybutanoyl)hydrazine, 3879-08-1; 1-(4-hydroxybutanoyl)-2-(1-methylethylidene)hydrazine, 87938-16-7; acetone, 67-64-1.

Host-Guest Complex Chemistry. Structures of 18-Crown-6 and Diaza-18-crown-6 with Neutral Molecules

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Single-crystal X-ray analyses of six stoichiometric complexes of neutral organic guest molecules (formamide, *N*-methylthiourea, dithiooxamide, 3-nitrophenol·$2H_2O$, 4-nitrobenzaldehyde oxime dihydrate, 2-guanidinobenzimidazole) with 18-crown-6 and diaza-18-crown-6 are described and discussed with respect to characteristic features of host/guest and receptor/substrate interactions and binding. In most cases the guest molecules approach from both sides of the plane of the crown ring, sterically fitting with XH_3, XH_2, and $XH{\cdots}H_2O-$ functional groups (X = C, N, O) and binding by multiple $NH_2{\cdots}O-$ and $OH{\cdots}O-$ hydrogen bonds. If the guest contains only one hydrogen suitable for hydrogen bonding, one water molecule per guest molecule is bound by the crown receptor. *N*-Methylthiourea as the guest is able to bind in a chain-type manner by using its amino as well as its CH_3 groups as links between neighboring crown ligands.

The study of well-defined complexes formed between uncharged molecules represents a relatively unexplored area although complexation of this type plays a fundamental role in many biochemical processes. The importance of such interactions in normal chemical reactions may also be an area which is not fully appreciated. Though much data on interactions involving hydrogen bonds has been gathered, it is still difficult to suggest specific hosts (receptors) for the complexation of neutral (uncharged) guest molecules. The importance of "acidic" methyl and methylene groups in stabilizing complexes between neutral molecules such as 18-crown-6 with dimethyl acetylenedicarboxylate,[1] dimethyl sulfone,[2] and malonodinitrile[3] has not generally been appreciated.[3b] Although the magnitudes of these hydrogen-oxygen interactions are probably not much greater than normal van der Waals forces, they are sufficient to lead to well-ordered crystalline solids. Such weak interactions may be of importance in orienting or directing substrate molecules at active sites. It is not known to what extent spatial fitting of CH_3 groups in the cavity of crown compounds helps host and guest to orient in the specific way observed. This question holds for the crystalline state as well as for host/guest interactions in solution. Stable complexes formed between crown ethers and many highly volatile toxic chemicals suggests this may be a convenient method of handling toxic reagents.[4] Substrates like the nitrophenylhydrazines, which exhibit low solubility in organic solvents, have been transferred into lipophilic phases by using this type of complexation.[5]

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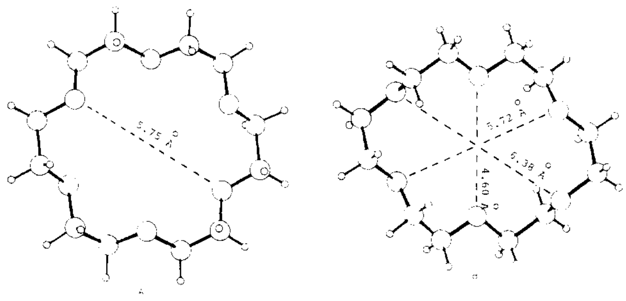

Figure 1. Two observed conformations for 18-crown-6 ligands and diaza-18-crown-6 in compounds 1–6. Conformation A exhibits an approximate D_{3d} symmetry.

More details of these interactions may be found in recent reviews[6] and papers.[7]

Discussion

The six complexes studied provide the opportunity to investigate bonding interactions of 18-crown-6 and diazo-18-crown-6 ligands with a variety of *neutral* substrates.[8] The neutral molecules have different binding requirements and geometrical constraints. The complexed 18-crown-6 ligand adopts principally a D_{3d} conformation (A in Figure 1) with C–O–C–C and O–C–C–O torsion angles near 180° and 70° (see Table III), which is the expected gauche conformation of the ethyleneoxy units.[9] The oxygen atoms are alternately about 0.25 Å above and below the mean plane through the molecule. Three oxygen atoms on each face are available for hydrogen bonding with an O···O separation of 4.90 Å (range 4.71–5.17 Å). Bifunctional groups such as NH_2 or H_2O efficiently form two hydrogen bonds with these oxygen atoms and stabilize the D_{3d} conformation. The oxygen atoms related by the center of symmetry are separated on the average by 5.67 Å (range 5.31-5.94 Å). Slight differences in binding requirements lead to deviations from the idealized geometry. The C–O and C–C bond distances average 1.41 (1) and 1.48 (1) Å while the O–C–C and C–O–C angles average 109.4 (9)° and 112.8 (6)°, respectively. These values are consistent with those reported for the majority of 18-crown-6 complexes which exhibit the D_{3d} conformation.[9] The complexed diaza-18-crown-6 ligand also exhibits this conformation.

The less common conformation of the complexed 18-crown-6 ligand (B) is also shown in Figure 1. This irregular conformation is more closely related to that of the *uncomplexed* ligand;[10a] however, there are significant differences.[10b] The center of symmetry is maintained, and one symmetry related oxygen pair is at 4.60 Å while the others are separated by 5.72 and 6.38 Å. The corresponding values for the *uncomplexed* ligand are 4.267, 6.832, and 6.972 Å. The 18-crown-6 ring is more flattened than in the D_{3d} conformation, and the short-distance oxygen pair lies almost in the mean plane. Unlike the D_{3d} conformation, adjacent oxygen atoms do not lie alternately above and below the mean plane. The oxygens lying close to the mean plane point toward the center of the ring while the two oxygen atoms lying on one side of this pair are up and those on the other side are down with respect to the mean plane. This conformation is suitable for forming single hydrogen bonds with several donor groups or two hydrogen bonds with a multiple donor. The latter involves one oxygen atom lying in the molecular plane and one out, O···O = 5.507 (7) and 4.441 (6) Å in compounds 2 and 3, respectively. Because of the differences in binding requirements, there are larger variations in the conformation. The C–O and C–C distances average 1.416 (7) and 1.476 (8) Å while the O–C–C and C–O–C angles average 111 (2)° and 112 (2)°. There is a greater angular distribution than in the D_{3d} conformation because of the less symmetric nature of the ring.

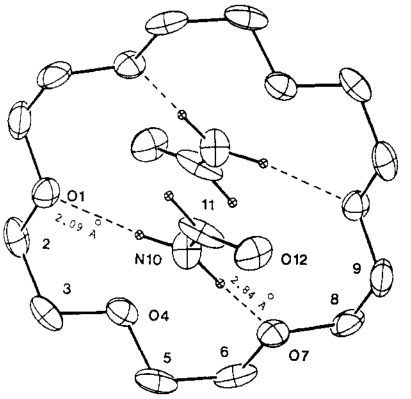

Figure 2. ORTEP drawing of the 2:1 complex of formamide and 18-crown-6 (1).

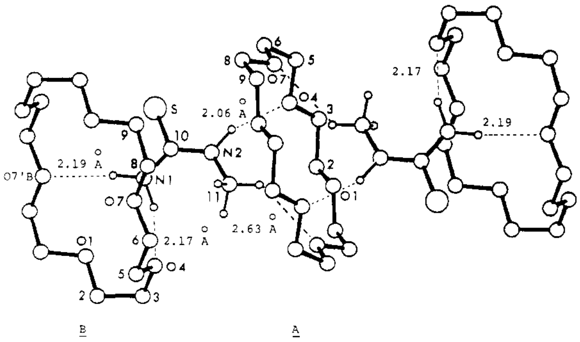

Figure 3. ORTEP drawing of 1:1 complex of *N*-methylthiourea and 18-crown-6 (2).

The important parameters for all potential hydrogen bonds are listed in Table IV. The bond lengths, valence angles, and torsion angles for all oxa and aza ligands are given in Tables I–III. Atomic parameters and other distances and angles are included in the supplementary material.

The 2:1 formamide–18-crown-6 complex[11] **(1)** exhibits the D_{3d} conformation (A), with the two centrosymmetrically related formamide molecules forming hydrogen bonds via O(1) or O(1′) and a much weaker interaction via O(7) or O(7′): H(10b)···O(1) = 2.09 Å, H(10a)···O(7) = 2.84 Å (see Figure 2). The NH_2 groups point directly into the cavity with the C–N bond almost perpendicular to the mean plane of the crown ether. The amide nitrogen lies

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Table I. Interatomic Distances (Å) for 18-Crown-6 and Diaza-18-crown-6 Ligands

	compd						
		2					
atoms	1	B	A	3	4	5	6[a]
O(1)-C(2)	1.440 (6)	1.381 (8)	1.397 (8)	1.433 (7)	1.413 (6)	1.421 (8)	1.425 (6)
O(1)-C(9′)	1.422 (7)	1.41 (1)	1.406 (5)	1.404 (4)	1.420 (5)	1.397 (9)	1.421 (6)
C(2)-C(3)	1.49 (1)	1.48 (1)	1.475 (6)	1.451 (7)	1.480 (7)	1.49 (1)	1.492 (8)
C(3)-O(4)	1.412 (8)	1.420 (7)	1.430 (8)	1.425 (7)	1.417 (5)	1.40 (1)	1.477 (6)
O(4)-C(5)	1.425 (8)	1.40 (1)	1.419 (7)	1.407 (5)	1.421 (5)	1.403 (9)	1.435 (7)
C(5)-C(6)	1.46 (1)	1.482 (8)	1.49 (1)	1.484 (7)	1.476 (8)	1.49 (1)	1.481 (8)
C(6)-O(7)	1.425 (6)	1.426 (7)	1.408 (7)	1.419 (6)	1.428 (6)	1.423 (7)	1.408 (6)
O(7)-C(8)	1.408 (9)	1.403 (7)	1.410 (9)	1.429 (5)	1.402 (6)	1.389 (9)	1.401 (6)
C(8)-C(9)	1.470 (9)	1.496 (8)	1.473 (9)	1.485 (7)	1.484 (7)	1.48 (1)	1.488 (7)
O(1)···O(4)	2.901 (5)	3.044 (6)	2.970 (6)	2.861 (4)	2.889 (4)	2.823 (8)	2.847 (5)
O(1)···O(7)	4.884 (5)	4.362 (6)	4.828 (6)	4.849 (4)	5.012 (4)	4.709 (8)	5.077 (5)
O(1)···O(1′)	5.616 (5)	5.614 (6)	5.471 (6)	6.292 (4)	5.557 (4)	5.566 (8)	5.795 (5)
O(1)···O(4′)	4.880 (5)	5.295 (6)	4.878 (6)	5.227 (4)	4.712 (4)	4.969 (8)	4.775 (5)
O(1)···O(7′)	2.856 (5)	2.899 (6)	2.945 (6)	1.783 (4)	2.823 (4)	2.892 (8)	2.758 (5)
O(4)···O(7)	2.836 (5)	2.723 (6)	2.819 (6)	2.816 (4)	2.879 (4)	2.840 (8)	2.891 (5)
O(4)···O(4′)	5.702 (5)	6.564 (6)	5.942 (6)	5.684 (4)	5.497 (4)	5.860 (8)	5.314 (5)
O(4)···O(7′)	4.945 (5)	5.078 (6)	5.169 (6)	4.441 (4)	4.947 (4)	4.914 (4)	4.730 (5)
O(7)···O(7′)	5.699 (5)	4.831 (6)	5.833 (6)	4.838 (4)	5.904 (4)	5.486 (8)	5.763 (5)

[a] O(4) is replaced by N(4).

Table II. Valence Angles (Degrees) for 18-Crown-6 and Diaza-18-crown-6 Ligands

	compd						
		2					
atoms	1	A	B	3	4	5	6
2-O(1)-9′	113.0 (5)	110.7 (5)	112.5 (5)	115.8 (3)	112.4 (3)	111.3 (5)	113.0 (3)
O(1)-2-3	109.4 (5)	110.8 (6)	110.1 (6)	114.6 (5)	110.2 (4)	107.6 (6)	108.6 (4)
2-3-O(4)	108.1 (5)	115.8 (5)	111.4 (6)	110.4 (4)	110.6 (4)	108.4 (6)	110.0 (4)
3-O(4)-5	113.4 (5)	113.0 (5)	112.5 (5)	109.2 (3)	112.9 (4)	112.1 (6)	113.4 (4)
O(4)-5-6	110.6 (5)	108.4 (6)	109.6 (6)	109.3 (3)	109.7 (4)	108.1 (6)	113.5 (5)
5-6-O(7)	108.6 (5)	109.4 (4)	108.6 (4)	109.4 (3)	109.2 (4)	108.8 (6)	110.0 (4)
6-O(7)-8	113.2 (5)	113.7 (4)	113.7 (3)	111.7 (3)	112.9 (4)	112.1 (6)	113.7 (4)
O(7)-8-9	108.2 (6)	111.3 (4)	109.9 (3)	109.2 (3)	109.2 (4)	110.4 (6)	108.9 (4)
8-9-O(1′)	109.3 (5)	108.9 (6)	110.1 (6)	109.5 (3)	108.4 (3)	109.5 (6)	109.1 (4)

Table III. Torsion Angles (Degrees) for 18-Crown-6 and Diaza-18-crown-6 Ligands[a]

	compd						
		2					
atoms	1	A	B[d]	3[b,d]	4	5	6[c]
9′-O(1)-2-3	−178.2 (6)	−174.6 (4)	−163.5 (5)	−176.4 (4)	−175.5 (4)	−179.1 (6)	−177.9 (4)
O(1)-2-3-O(4)	70.9 (7)	−71.2 (5)	59.8 (7)	59.3 (5)	−69.2 (5)	70.5 (6)	63.6 (5)
2-3-O(4)-5	−176.7 (6)	170.4 (4)	66.9 (6)	72.4 (5)	−178.1 (4)	−173.9 (5)	169.8 (4)
3-O(4)-5-6	−179.8 (7)	179.9 (3)	−178.5 (3)	176.4 (4)	178.7 (3)	177.1 (5)	−179.7 (4)
O(4)-5-6-O(7)	−70.3 (8)	70.6 (6)	62.2 (4)	61.4 (5)	70.5 (4)	−70.1 (7)	−63.5 (6)
5-6-O(7)-8	−178.6 (5)	−168.4 (6)	−177.0 (4)	165.2 (3)	−173.1 (3)	177.0 (6)	−174.9 (4)
6-O(7)-8-9	177.5 (5)	−177.6 (6)	170.8 (4)	173.4 (3)	174.1 (3)	176.1 (6)	−173.9 (4)
O(7)-8-9-O(1′)	65.9 (7)	−70.0 (7)	67.3 (6)	65.4 (4)	68.0 (5)	73.2 (7)	60.5 (5)
8-9-O(1′)-2′	−175.2 (6)	174.4 (4)	176.3 (5)	179.2 (4)	178.0 (4)	−178.8 (6)	177.4 (4)

[a] All exhibit the D_{3d} conformation except for **2B** and **3**. [b] Numbers interchanged to correspond to **2B**. [c] O(4) is replaced by N(4). [d] Conformation 3e of Bovill.[10b]

1.662(7) Å from the oxygen mean plane and 3.037 (7) and 3.133 (6) Å from 0(1) and 0(7). The two amide hydrogen atoms coordinate with two of the oxygen atoms lying on the same face, and there is no steric hindrance which would lead to significant conformational changes. The 2:1 formamide complex is an isolated cluster which interacts via van der Waals interactions with adjacent clusters.

The 1:1 *N*-methylthiourea–18-crown-6 complex[12] **(2)** is unique in that both ligand conformations A and B are found (Figure 3). A NH_2 group fits into the cavity of conformation B binding with the in-plane oxygen O(7′B) and with O(4B): H(1N1)···O(7′B) = 2.19 Å and H(2N1)···O(4B) = 2.17 Å. Conformation B is connected by four hydrogen bonds with two centrosymmetrically related NH_2 groups. A CH_3 group and an N–H fit into the cavity of conformation A. The ligand is centrosymmetrically hydrogen bonded via the hydrogen on N(2): H(2)···O(4) = 2.06 Å. The "acidic" methyl group, C(11), has one hydrogen oriented toward O(7′A) with a separation of 2.63 Å. Since such interactions have been observed with other "acidic" methyl groups,[1-3] this might be considered a weak hydrogen bond or at least an energetically favorable interaction. The N(1) nitrogen atom lies within 2.081 (6) Å of the oxygen mean plane in B while N(2) and C(11) lie

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(12) It is interesting to note that the complexes of 18-crown-6 with urea, thiourea and *N,N′*-dimethylthiourea exhibit 1:5, 1:4 (9) and 1:2 (8) host–guest stoichiometries, respectively. (a) The thiourea complex of 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (10) shows 1:4 stoichiometry. Weber, G. *Acta Crystallogr.*, in press.

Table IV. Parameters for Possible Hydrogen Bonds

compd	atoms	dist, Å	atoms	dist, Å	atoms	dist, Å	atoms	angle, deg
1	N(10)-H(10b)	0.97	H(10b)···O(1)	2.09	N(10)···O(1)	3.037 (7)	N-H···O	167.0
	N(10)-H(10a)	0.99	H(10a)···O(7)	2.84	N(10)···O(7)	3.133 (6)	N-H···O	97.9
2	N(2)-H	1.03	H···O(4A)	2.06	N(2)···O(4A)	3.037 (7)	N-H···O	156.7
	N(1)-H(1N1)	1.00	H···O(4B)	2.17	N(2)···O(4B)	3.115 (6)	N-H···O	157.8
	N(1)-H(2N1)	1.02	H···O(7′B)	2.19	N(1)···O(7′B)	3.177 (4)	N-H···O	162.6
3	N(10)-H(10b)	1.01	H(10b)···O(1)	1.85	N(10···O(1)	2.856 (4)	N-H···O	176.4
	N(14)-H(14a)[a]	1.01	H(14a)···O(4)	2.07	N(14)···O(4)	3.024 (4)	N-H···O	157.5
	N(14)-H(14b)[a]	1.01	H(14b)···O(7′)	2.61	N(14)···O(7′)	3.315 (4)	N-H···O	127.0
4	O(10)-H(10b)	1.01	H(10b)···O(1′)	1.86	O(10)···O(1′)	2.876 (4)	O-H···O	178.5
	O(10)-H(10a)	0.99	H(10a)···O(4)	1.92	O(10)···O(4)	2.914 (5)	O-H···O	175.0
	O(11)-H(11)	1.01	H(11)···O(10)	1.64	O(11)···O(10)	2.635 (5)	O-H···O	168.1
5	O(10)-H(10a)	1.01	H(10a)···O(1)	1.94	O(10)···O(1)	2.955 (7)	O-H···O	175.6
	O(10)-H(10b)	0.99	H(10b)···O(7)	1.99	O(10)···O(7)	2.980 (6)	O-H···O	176.1
	O(1)-H(11)	1.00	H(11)···O(10)	1.69	O(11)···O(10)	2.860 (6)	O-H···O	178.8
6					N(10)···O(1)	2.994 (6)		
					N(11)···O(7)	2.891 (6)		
					N(11)···N(4)	2.986 (6)		

[a] Generated by (x, $0.5 - y$, $0.5 + z$).

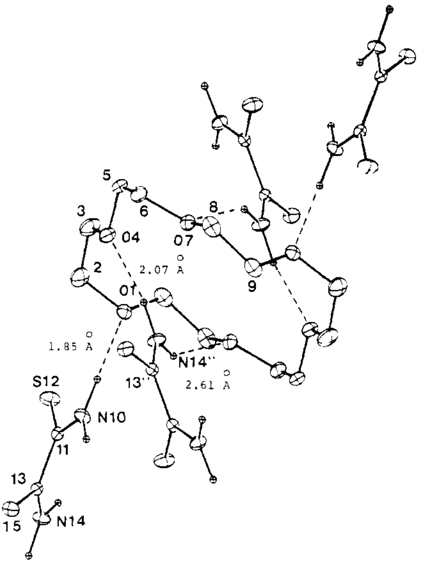

Figure 4. ORTEP drawing of the 2:1 complex of dithiooxamide and 18-crown-6 (**3**).

2.790 (6) and 2.365 (7) Å from plane A.

The five heavy atoms of the *N*-methylthiourea molecule are coplanar, and the C–S distance of 1.606 (5) Å is significantly shorter than the 1.716 (8) and 1.712 (8) Å values reported for thiourea.[13]

The 2:1 dithiooxamide–18-crown-6 complex[14] **(3)** also shows unique structural features. The 18-crown-6 ligand exists in the B conformation, but it is now hydrogen bonded to four different substrate molecules (Figure 4). One centrosymmetric pair is bonded via N(10) to O(1) and O(1′) [H(10)···O(1) = 1.85 Å], while the second centrosymmetric pair of substrate molecules (x, $0.5 - y$, $0.5 + z$) is bound via N(14″) to O(4) and O(7′): H(14a″)···O(4) = 2.07 and H(14b″)···O(7′) = 2.61 Å. The distances of N(10) and N(14) from the mean plane of the oxygen atoms are 2.354 (4) and 1.607 (4) Å, respectively. The four substrate molecules attached to each 18-crown-6 ligand serve as bridges to four additional ether ligands. All six oxygen atoms are involved in hydrogen bonding.

The dithioxamide molecule in the complex exists in the anti conformation; however, unlike uncomplexed oxamide[15] and dithiooxamide,[16] it is not planar. The two planar CCSN units form an interplanar angle of 39.1 (6)°. The molecule may adopt the twisted conformation in order to bridge the crown ether more efficiently. The SCN units form delocalized systems with S–C and C–N distances of 1.652 (3) and 1.310 (4) Å which agree reasonably well with the values for dithioxamide.[16] The S–C bond is shorter than that in thiourea[13] but longer than that observed in the *N*-methylthiourea moiety of complex **2**. The central C–C distance of 1.506 (5) Å is consistent with the single bond character.

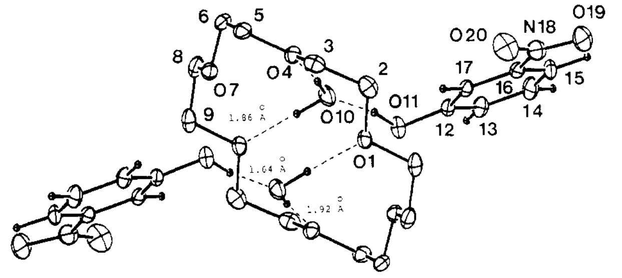

Figure 5. ORTEP drawing of the 2:1 diaquo complex of 3-nitrophenol and 18-crown-6 (**4**).

The 2:1 3-nitrophenol–18-crown-6 diaquo complex[14] **(4)** is better described as a complex between 3-nitrophenol and the hydrated 18-crown-6 ligand (Figure 5). The crown ligand adopts the D_{3d} conformation and is centrosymmetrically hydrogen bonded to two water molecules which sit with oxygen atoms 1.604 (5) Å from the mean plane. Both hydrogen atoms of the water molecule participate in hydrogen bonding: H(10a)···O(4) = 1.92 Å and H(10b)···O(1′) = 1.86 Å. The 3-nitrophenol is bound to the diaquo 18-crown-6 via a hydrogen bond between the water molecule and the phenol moiety, H(11)···O(10) = 1.64 Å. The interactions are similar to those in the 1:1 4,4′-dihydroxybiphenyl–18-crown-6 diaquo complex[17] except that the bifunctional 4,4′-dihydroxybiphenyl serves as a bridging ligand. Complex **4** is an independent cluster, which interacts with other clusters via van der Waals interactions.

The 3-nitrophenol molecule is planar and makes an angle of 62 (1)° with the plane of the 18-crown-6 molecule.

The 2:1 *p*-nitrobenzaldehyde oxime–18-crown-6 diaquo complex[14] **(5)** is structurally similar to that of complex **4** (Figure 6). The crown ether adopts the D_{3d}

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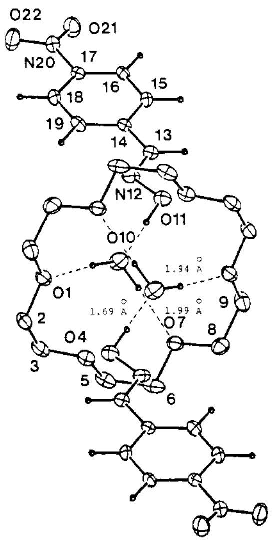

Figure 6. ORTEP drawing of the 2:1 diaquo complex of *p*-nitrobenzaldehyde oxime and 18-crown-6 (**5**).

conformation and is centrosymmetrically hydrogen bonded to both hydrogen atoms of the water molecules: H(10b)···O(1) = 1.94 Å and H(10a)···O(7) = 1.99 (1) Å. The oxygen atom of the water molecule sits 1.614 (7) Å from the mean plane. The *p*-nitrobenzaldehyde oxime is bonded via the oxime OH to the water molecule: H(11)···O(10) = 1.69 Å. Complex **5** is an independent cluster, which interacts with other clusters via van der Waals interactions.

The *p*-nitrobenzaldehyde oxime is planar, with the two oxygens of the nitro group twisted slightly out of the plane, 0.13 (1) Å. The planar molecule makes an angle of 75.3 (8)° with the mean plane of the crown ether.

The 2:1 2-guanidinobenzimidazole–diaza-18-crown-6 complex (6) is shown in Figure 7. The diaza-18-crown-6 (1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) ligand adopts the D_{3d} conformation. The oxygen and nitrogen atoms are alternately 0.18 (1) Å above and below the mean plane as compared to approximately 0.25 Å for the crown ether. The two nitrogen atoms in the diaza ligand possibly may act as either donors or acceptors. N(11) and N(4) are within 2.985 (6) Å, but hydrogen atom positions could not be located with any confidence. Each of the centrosymmetrically related 2-guanidinobenzimidazole molecules is oriented such that two additional hydrogen bonds are possible: N(11)···O(7) = 2.891 (6) Å and N(10)···O(1) = 2.994 (6) Å. N(11) and N(10) are situated 1.614 (6) and 2.847 (6) Å from the mean plane. The 2-guanidinobenzimidazole molecule is planar with maximum deviations from the mean plane of +0.13 (1) and −0.11 (1) Å by N(11) and N(15), respectively. The angle between the molecular plane and the mean plane of the crown either is 54 (1)°. The 2-guanidinobenzimidazole molecule exists in the tautomeric form with the double bonds primarily between C(12)–N(13) and C(14)–N(15).

Conclusions

The complexed 18-crown-6 ligands adopt conformations in which dipolar interactions are minimized by hydrogen bonding.[10b] Adjacent oxygen (or nitrogen) atoms are too close for the formation of two hydrogen bonds by the bifunctional donors NH_2 or H_2O. In the D_{3d} (A) conformation the oxygen atoms are alternately above and below the mean plane, and the separation between the acceptor atoms on each face is optimal for hydrogen bonding to bifunctional donors. Bifunctional donors stabilize the D_{3d} conformation. Conformation B has two symmetry related oxygens/nitrogens lying in the molecular plane. The other adjacent oxygen pairs lie either above or below the mean plane. Bifunctional donors can interact only with the in-plane oxygen and one of the out-of-plane oxygen atoms. Usually, this is sterically less favorable.

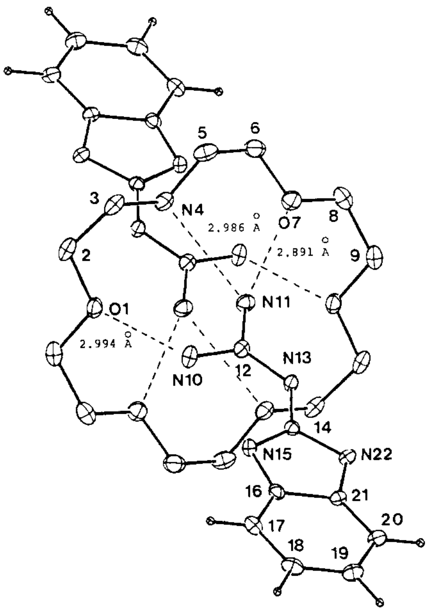

Figure 7. ORTEP drawing of the 2:1 complex of 2-guanidinobenzimidazole and diaza-18-crown-6 (**6**).

When the neutral organic molecule (guest) contains one bifunctional donor group such as in formamide, the crown ether (host) adopts the D_{3d} conformation, and symmetric, isolated complexes are formed. When the guest contains two or more well-separated donor groups, the guest molecule serves as a bridge between hosts. The nature of the bridging depends upon the separation and relative orientation of the donor groups. In *N*-methylurea a methyl hydrogen and the adjacent N–H interact with one crown ether while the NH_2 group acts as a bifunctional donor to a second host ligand. In the case of dithiooxamide there are two NH_2 groups, but steric constraints do not permit both to act as bifunctional donors. One NH_2 group forms two hydrogen bonds with a host molecule; however, only one hydrogen bond is formed by the other. Even this interaction requires a 39.1 (6)° twist from planarity of the guest. If coordination with the bridging multidonor guest leads to steric interactions between the hosts or inefficient packing, the donor capacity of the host molecule is reduced.

When the guest molecule contains only one donor atom capable of hydrogen bonding, water may be incorporated to form a ternary complex. The water molecule serves as a simple bifunctional donor complexing the ligand in the same manner as formamide. The guest molecule then uses its single donor site to form a hydrogen bond with the water molecule. Single donor site guests with unusual host to guest ratios are known; however, no structural work has yet been reported. Many of these may represent clathrate structures rather than normal host–guest complexes.

Large flexible crown ethers can realize a greater number of conformations. Close adjacent donor sites should lead to the host wrapping around the donor. Crown ethers with flexible clefts should let the host conform to the shape of the guest. When selected areas of rigidity are incorporated into the structure, a host can become shape and functionality specific. Such design closely approximates enzyme–substrate interactions, and the incorporation of reactivity sites would complete the analogy.[18]

Experimental Section

X-ray Structure Determination and Refinement. All data were collected on a Syntex P2_1 diffractometer system by the θ–2θ scanning technique using a variable scan speed and graphite-monochromatized radiation. Room-temperature lattice parameters were refined by a least-squares procedure using 15 reflections whose angles were measured by a centering routine associated with the diffractometer. Space groups were determined by systematic absences and statistics. Periodically monitored reference reflections showed no significant changes in intensity except where noted. Lorentz and polarization correlations were applied, but no absorption corrections were made.

The direct-methods program MULTAN[19] was used to calculate phases for the larger $|E|$ values. The phase set with the largest combined figure of merit revealed the molecular framework for all compounds. Hydrogen atom positions were either located in difference Fourier maps or were calculated and then checked by comparison with difference Fourier maps. The hydrogen atoms in several structures could not be located. Full-matrix least-squares refinements were terminated when the R value became stationary. R is defined as $\sum||F_o| - |F_c||/\sum|F_o|$. The function minimized in the refinement was $\sum w\,(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2\,(F_o)$ was determined by counting statistics. H atom thermal parameters were not refined.

Final difference maps were checked for residual electron density, and the shift/error for all parameters was examined. ORTEP[20] drawings were made of all structures and the XRAY76 program package[21] was used for all other computations. Tables of structure factors may be obtained from the authors (W.H.W.).

2:1 **Formamide–18-crown-6 complex (1)**: $C_{12}H_{24}O_6{\cdot}2CHONH_2$; fw = 354.5; $P\bar{1}$; a = 8.115 (5), b = 8.194 (2), c = 7.700 (6) Å; α = 90.89 (7)°, β = 111.22 (6)°, γ = 98.34 (6)°; V = 470.9 (6) Å^3; Z = 1; d_c = 1.25 Mg m^{-3}; $F(000)$ = 192; μ = 0.85 cm^{-1}; Mo K$_\alpha$ (λ = 0.71069 Å). The crystals are deliquescent and must be sealed in a capillary during data collection. A crystal of 0.33 × 0.25 × 0.5 mm was selected for all X-ray measurements. A total of 1482 unique reflections ($2\theta \le 48°$) were collected of which 970 had intensities greater than $3\sigma(I)$ and were used in the least-squares refinement. Refinement was terminated at R = 0.071 and R_w = 0.032. The average and maximum shift/error were 0.09 and 0.4, while the largest peak found in the final difference Fourier map was 0.5 e Å^{-3}. The structure of compound 1 is shown in Figure 2.

1:1 ***N*-Methylthiourea–18-crown-6 complex (2)**: $C_{12}H_{24}O_6{\cdot}C_2H_6N_2S$; fw = 354.5; $P\bar{1}$; a = 8.903 (2), b = 9.311 (2), c = 15.772 (3) Å; α = 120.69 (1)°, β = 94.62 (1)°, γ = 114.29 (1)°; V = 951.7 (3) Å^3; Z = 2, d_c = 1.24 Mg m^{-3}; $F(000)$ = 384; μ = 17.30 cm^{-1}; Cu Kα (λ = 1.54178 Å). A crystal of dimensions 0.40 × 0.30 × 0.25 mm was used for all X-ray measurements. A total of 2833 unique reflections ($2\theta \le 130°$) were collected of which 2527 had intensities greater than $3\sigma(I)$. Refinement was terminated at R = 0.068 and R_w = 0.063. The average and maximum shift/error were 0.07 and 0.5 while the largest peak found in the final difference Fourier map was 0.3 e Å^{-3}. The structure of complex 2 is shown in Figure 3.

2:1 **Dithiooxamide–18-crown-6 complex (3)**: $C_{12}H_{24}O_6{\cdot}2C_2H_4N_2S_2$; fw = 509.0; $P2_1/c$; a = 8.620 (2), b = 14.908 (5); c = 11.366 (6) Å; β = 121.02 (3)°; V = 1251.7 (8) Å^3; Z = 2, d_c = 1.348 Mg m^{-3}; $F(000)$ = 544; μ = 30.4 cm^{-1}; Mo K$_\alpha$. A crystal of dimensions 0.40 × 0.25 × 0.25 mm was used for all X-ray measurements. A total of 2041 unique reflections ($2\theta \le 49°$) were collected of which 1441 had intensities greater than $3\sigma(I)$. Refinement was terminated at R = 0.042 and R_w = 0.049. The average and maximum shift/error were 0.09 and 0.2 while the largest peak found in the final difference Fourier map was 0.43 e Å^{-3}. The structure of complex 3 is shown in Figure 4.

2:1 **3-Nitrophenol–18-crown-6 diaquo complex (4)**: $C_{12}H_{24}O_6{\cdot}2C_6H_5NO_3{\cdot}2H_2O$; fw = 578.6; $P2_1/c$; a = 12.47 (1), b = 7.520 (4), c = 15.90 (1) Å; β = 102.50 (8)°; V = 1456 (2) Å^3; Z = 2; d_c = 1.32 Mg m^{-3}; $F(000)$ = 616; μ = 1.02 cm^{-1}; Mo K$_\alpha$. A crystal of dimensions 0.40 × 0.50 × 0.67 mm was used for all X-ray measurements. A total of 2364 unique reflections ($2\theta \le 49°$) was collected of which 1170 had intensities greater than $3\sigma(I)$. Refinement was terminated at R = 0.050 and R_w = 0.052. The average and maximum shift/error were 0.05 and 0.5 while the largest peak found in the final difference Fourier map was 0.29 e Å^{-3}. The structure of complex 4 is shown in Figure 5.

2:1 ***p*-Nitrobenzaldehyde oxime–18-crown-6 diaquo complex (5)**: $C_{12}H_{24}O_6{\cdot}2C_7H_6N_2O_3{\cdot}2H_2O$; fw = 632.8; $P2_1/c$; a = 7.570 (5), b = 7.875 (3), c = 27.46 (2) Å; β = 101.19 (5)°; V = 1606 (1) Å^3; Z = 2; d_c = 1.308 Mg m^{-3}; $F(000)$ = 672; μ = 1.0 cm^{-1}; Mo Kα. A crystal of dimensions 0.67 × 0.67 × 0.33 mm was used for all X-ray measurements. A total of 2621 unique reflections ($2\theta \le 49°$) was collected of which 1498 had intensities greater than $3\sigma(I)$. Refinement was terminated at R = 0.072 and R_w = 0.10. The average and maximum shift/error were 0.03 and 0.5 while the largest peak found in the final difference Fourier map was 0.34 e Å^{-3}. The structure of complex 5 is shown in Figure 6.

2:1 **2-Guanidinobenzimidazole–diaza-18-crown-6 complex (6)**: $C_{12}H_{26}N_2O_4{\cdot}2C_8H_9N_5$; fw = 611.4; $C2/c$; a = 21.27 (1), b = 8.191 (3), c = 18.26 (1) Å; β = 93.10 (6)°; V = 3176 (3) Å^3; Z = 4; d_c = 1.280 Mg m^{-3}; $F(000)$ = 1312; μ = 0.92 cm^{-1}; Mo Kα. The crystals deteriorate upon exposure to air. A crystal of dimensions 0.67 × 0.60 × 0.33 mm was sealed in a capillary and was used for all X-ray measurements. A total of 2582 unique reflections ($2\theta \le 49°$) was collected, and 1805 had intensities greater than $3\sigma(I)$. Refinement was terminated at R = 0.069 and R_w = 0.087. The average and maximum shift/error were 0.03 and 0.7 while the largest peak found in the final difference Fourier map was 0.49 e Å^{-3}. The structure of complex 6 is shown in Figure 6.

Synthesis. The synthesis of 2:1 formamide–18-crown-6 (1), 2:1 dithiooxamide–18-crown-6 (3), 2:1 3-nitrophenol–18-crown-6 (4), and 2: *p*-nitrobenzaldehyde oxime–18-crown-6 (5) have been described in the literature.[11,14]

1:1 ***N*-Methylthiourea–18-Crown-6 Complex (2).** 18-Crown-6 (264 mg, 1.0 mmol) and *N*-methylthiourea (180 mg, 2.0 mmol) were refluxed for ca. 1 h in 7 mL of ethyl acetate. After hot filtration the complex crystallized at room temperature in long needles. Upon recrystallization from ethyl acetate the complex decomposes unstoichiometrically: yield 244 mg (68.8%); mp 85–95 °C. Anal. Calcd for $C_{14}H_{30}N_2O_6S$ (mol wt 354.5): C, 47.44; H, 8.53; N, 7.90. Found: C, 47.62; H, 8.68; N, 7.70.

2:1 **2-Guanidinobenzimidazole–1,7,10,16-Tetraoxa-4,13-diazacyclooctadecane Complex (6).** 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (262 mg, 1.0 mmol) and 2-guanidinobenzimidazole (350 mg, 2.0 mmol) were refluxed for 1.5 h in 10 mL of acetone, and after hot filtration the mixture was allowed to crystallize at room temperature: yield 217 mg (35.4%); mp 205–240 °C. Anal. Calcd for $C_{28}H_{44}N_{12}O_4$ (mol wt 612.7): C, 54.88; H, 7.24; N, 27.44. Found: C, 54.51; H, 7.03; N, 27.15.

2:1 **2-Guanidinobenzimidazole–18-Crown-6 Complex (7).** An analogous procedure as above was followed: yield 283 mg (46.0%); mp 180–182 °C. Anal. Calcd for $C_{28}H_{42}N_{10}O_6$ (mol wt 614.7): C, 54.71; H, 6.89; H, 22.79. Found: C, 54.48; H, 6.88; N, 23.02.

The following complexes of crown compounds with several uncharged organic guest molecules have not been investigated by single crystal X-ray analyses; nevertheless, their preparation is given below for the first time.

2:1 ***N,N'*-Dimethylthiourea–18-Crown-6 Complex (8).** 18-Crown-6 (132 mg, 0.5 mmol) and *N,N'*-dimethylthiourea (104 mg, 1.0 mmol) were refluxed for ca. 30 min in 5 mL of ethyl acetate. After filtration the solution was stored at room temperature, whereby the complex crystallized in thick needles. Recrystallization was from ethyl acetate: yield 158 mg (66.9%); mp 86–88 °C. Anal. Calcd for $C_{18}H_{40}N_4O_6S_2$ (mol wt 472.7): C, 45.74; H, 8.53; N, 11.86. Found: C, 45.97; H, 8.61; N, 12.02.

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4:1 Thiourea–18-Crown-6 Complex (9). 18-Crown-6 (264 mg, 1.0 mmol) and thiourea (304 mg, 4.0 mmol) were refluxed for 30 min in 5 mL of methanol and then evaporated to dryness. The crystalline residue was recrystallized from acetone or methanol/ethyl acetate (1:1): yield 186 mg (32.7%); mp 168–174 °C. Anal. Calcd for $C_{16}H_{40}N_8O_6S_4$ (mol wt 568.8): C, 33.78; H, 7.09; N, 19.70. Found: C, 33.88; H, 7.21; N, 19.86.

4:1 Thiourea–1,7,10,16-Tetraoxa-4,13-diazacyclooctadecane Complex (10). An analogous procedure to that above was followed: yield 259 mg (45.7%): mp 148–151 °C. Anal. Calcd for $C_{16}H_{42}N_{10}O_4S_4$ (mol wt 566.8): C, 33.90; H, 7.47; N, 24.71. Found: C, 33.60; H, 7.50; N, 24.74.

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Registry No. 1, 73961-14-5; 2, 87843-32-1; 3, 80027-36-7; 4, 87843-33-2; 5, 87843-34-3; 6, 87843-35-4; 7, 87843-36-5; 8, 86797-40-2; 9, 87843-37-6; 10, 83654-18-6.

Supplementary Material Available: Tables of atomic parameters and other distances for 18-crown-6 complexes (24 pages). Ordering information is given on any current masthead page.

Enantiomeric Recognition of Organic Ammonium Salts by Chiral Crown Ethers Based on the Pyridino-18-crown-6 Structure[1,2]

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Enantiomeric recognition by several chiral dimethyl-substituted macrocycles of the pyridino-18-crown-6 type for chiral organic ammonium salts has been studied by titration calorimetry in CH_3OH, temperature-dependent ^1H NMR spectroscopy in CD_2Cl_2, and selective crystallization. Results from the three procedures are consistent in demonstrating either host-guest recognition or nonrecognition in the systems investigated. Furthermore, enantiomeric recognition by one chiral host for a pair of chiral guests is correlated with X-ray crystallographic data for the same system. The chiral dimethyl-substituted ligands used in the study include three dimethyl diester pyridino-18-crown-6 ligands (1–3), dimethyl thiono diester pyridino-18-crown-6 (4), and dimethylpyridino-18-crown-6 (5). All of these ligands exhibited chiral recognition. Dimethylpyridino-18-crown-6 (5) in complexation with (*R*)- and (*S*)-[α-(1-naphthyl)ethyl]ammonium perchlorate exhibited the largest ratio of $\Delta G_c^{\ddagger}$ yet observed by the ^1H NMR technique. A diphenyl-substituted diester pyridino-18-crown-6 (6) where the phenyl substituents are in a less rigid portion of the macrocycle failed to show chiral recognition.

Introduction

There has been considerable interest in the design and synthesis of host chiral macrocyclic ligands that are able to distinguish between guest organic ammonium enantiomers.[3–6] A variety of chiral host macrocycles and chiral guests have been studied by using a number of different techniques. Cram and his co-workers have prepared chiral crown ethers containing the 1,1-binaphthyl moiety and have studied chiral recognition by these compounds using ^1H NMR spectroscopy,[7] solvent extraction,[8] transport through a liquid membrane,[9] and enantiomeric separation on either silica gel or polystyrene containing a chiral crown molecule.[10] A high degree of chiral recognition was observed in these studies. Lehn and his co-workers have prepared a large number of chiral macrocylic ligands of the 18-crown-6 variety from tartaric acid derivatives.[11] Although they did not study chiral recognition per se, they did observe interesting differences in reactivity between chiral host and chiral guest molecules.[5,11–13] Certain carbohydrate molecules have been incorporated into synthetic macrocyclic ligands by Stoddard and his co-workers. Little chiral recognition was observed by a ^1H NMR technique when these chiral host molecules were complexed with chiral alkylammonium salts.[14] Sutherland and his co-workers used the same ^1H NMR technique to show

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(1) Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, April 1982.

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