



Crown Inclusion Compounds with 3,4-Diamino-1,2,5-Oxadiazole. X-ray Structures of Its 1:1 Inclusion Complexes with 15-Crown-5 and Benzo-15-crown-5*

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Abstract

The X-ray crystal structures of two closely related molecular complexes of 15-crown-5 and benzo-15-crown-5 with 3,4-diamino-1,2,5-oxadiazole are reported (**I** and **II**). Both complexes are of 1:1 stoichiometry with the host–guest alternation in the infinite chains formed due to the unsymmetrical H-bonding patterns between the components. Crystals of **I** are monoclinic, $P2_1/c$, $a = 7.856(3)$, $b = 12.994(1)$, $c = 16.033(1)$ Å, $\beta = 94.79(2)^\circ$, $Z = 4$, final R-factor is 0.0488. Crystals of **II** are orthorhombic, $P2_12_12_1$, $a = 8.260(4)$, $b = 15.692(5)$, $c = 13.955(7)$ Å, $Z = 4$, final R-factor is 0.0522.

Introduction

Many complexes that incorporate 15-crown-5 and benzo-15-crown-5 ligands cover a wide range of over 30 metal cations as a search of the Cambridge Structural Database (version 5.19) [1] reveals. Both crowns form 1:1 complexes with Na^+ [2] and 2:1 complexes with K^+ , Ba^{2+} [3–4], Ag^+ [5] etc. For the transition elements two main types of complexes, with direct metal to crown interactions and those with the crown ether oxygens bound to the metal *via* a bridging water and $\text{OH} \cdots \text{O}$ hydrogen bonds [6] (second sphere coordination) have been reported. These two types have been also found in one structure [7], where each Li^+ ion from the $[\text{Li}_2(\text{H}_2\text{O})_2(\text{benzo-15-crown-5})_3]^{2+}$ cation is coordinated to one benzo-15-crown-5 and one water molecule, and, in their turn, each of the two water molecules is H-bonded to the third crown molecule. The area of host–guest complexes between 15-membered crown ethers and neutral H-donor molecules is not extensively studied due to the components being sterically or symmetry mismatched, resulting in subtle, unsymmetrical hydrogen bonding patterns. In the 1:1 complexes of 15-crown-5 and benzo-15-crown-5 with aminosulfuric acid the guest molecule exists in the zwitterionic form $\text{NH}_3^+\text{SO}_3^-$ with well separated positively

(NH_3^+) and negatively (SO_3^-) charged centers. In contrast to the 18-membered crown ether complexes [8], the cavity dimension of the 15-membered crown ring is not sufficient to accommodate the NH_3^+ group. That is why only two of the NH_3^+ hydrogens participate in $\text{NH} \cdots \text{O}$ host–guest contacts of the H-bond type in the same way as in the complexes $[(\text{NH}_4)(15\text{-crown-5})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{CH}_3\text{CN}$ and $[(\text{NH}_4)(\text{benzo-15-crown-5})_2]_2[\text{UO}_2\text{Cl}_4] \cdot \text{CH}_3\text{CN}$, [9] where the ammonium ion forms two hydrogen bonds with each crown entity.

No host–guest complex between a neutral organic molecule and 15-crown-5 has been described yet, while for benzo-15-crown-5 two complexes with dithioamide and thioacetamide as the guest have been reported. There the host–guest interactions are similar to those described for 18-crown-6 and the crystals of the 1:1 complex with the bifunctional thioamide consist of infinite chains of alternating guest–host molecules [10]. In the 1:2 complex with thioacetamide the host forms a distinct molecular entity with two molecules of the guest. In both structures the crown host is approached from both sides by two coordinating guest molecules, its oxygens being involved in one bifurcated and one simple hydrogen-bonding interaction on each face. In the ternary 1:1:1 complex between benzo-15-crown-5, 3,4-dinitrobenzoic acid and water [11], the water molecule is involved as a H-donor in the hydrogen bonding to three O atoms of the most flexible part of the crown (one single and

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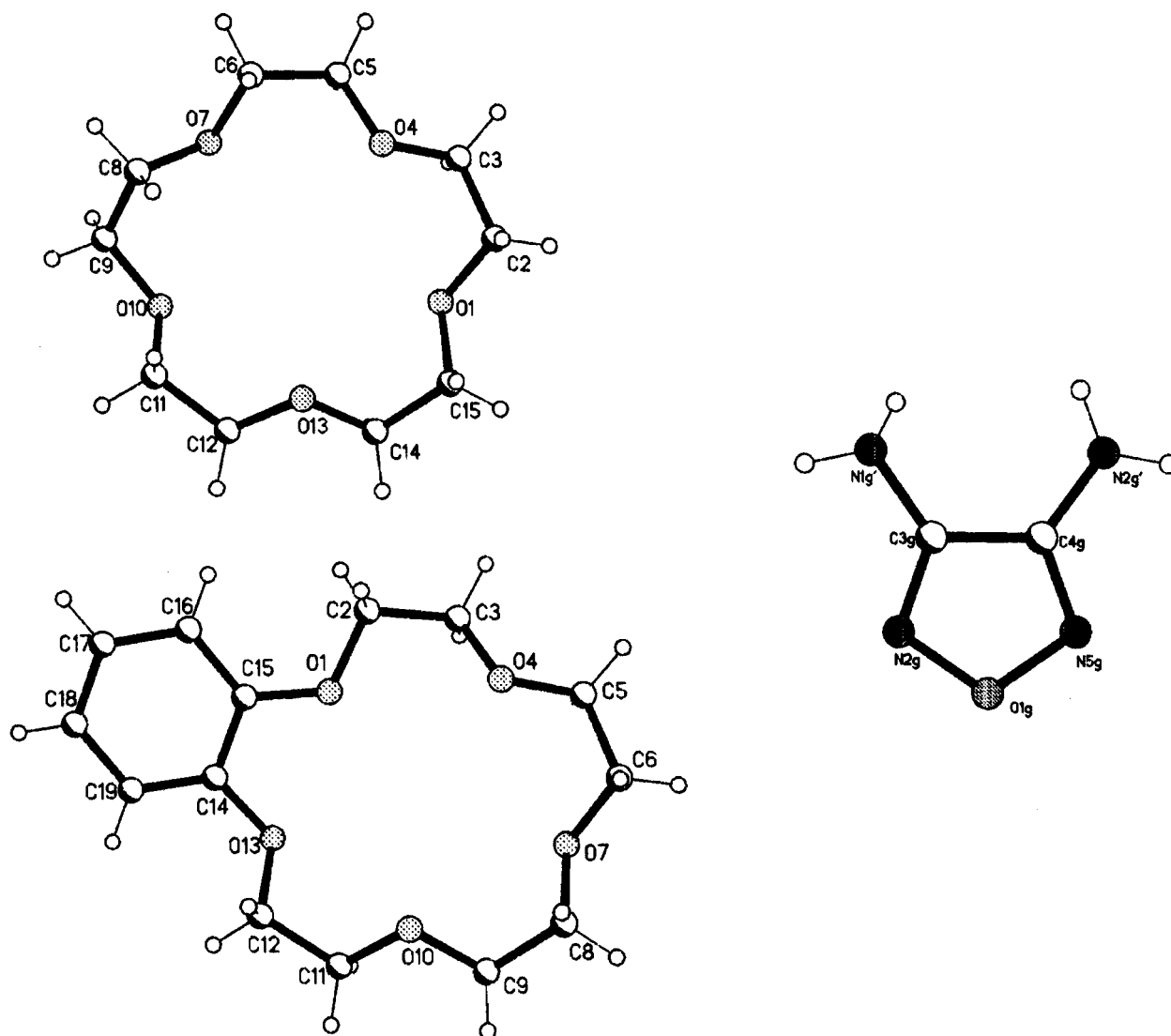


Figure 1. Numbering scheme of the two host molecules (complexes **I** and **II**) and the guest molecule present in both complexes.

one bifurcated bond) and as an acceptor in a hydrogen bond with the carboxylic group of 3,4-dinitrobenzoic acid.

In earlier work [12] we have described the crystal structures of one ternary and one binary complex between the bifunctional diamine, 3,4-diamino-1,2,5-oxadiazole and 18-crown-6 and *cis-anti-cis*-dicyclohexano-18-crown-6. In the former complex the water molecule is inserted as ambifunctional hydrogen-bonding links (complementary mediator) between the NH-donor and the hexaoxa ring. In the latter binary complex both amine groups offer all of their protons for direct host-guest interactions.

The present contribution is confined to the structures of two new host-guest inclusion complexes of 15-crown-5 and benzo-15-crown-5 with the same guest, 3,4-diamino-1,2,5-oxadiazole, (complexes **I** and **II**). For 15-crown-5 it is the first example of a host-guest complex with a neutral organic molecule. Features of these complexes of interest to us include the number of crown oxygen atoms that participate in hydrogen bonding and the extent this hydrogen bonding influences the crown ether conformation.

Synthesis

Both complexes were prepared in a similar way. 1 mmol of the respective crown ether and 1 mmol of 3,4-diamino-1,2,5-oxadiazole were dissolved simultaneously in 10 mL of methanol at 65 °C. The crystals precipitated on cooling to 20 °C were separated and air-dried. Crystals suitable for X-ray crystallography were obtained by recrystallization from a 1:1 benzene:methanol mixture.

Complex I

Colorless, transparent crystals, soluble in methanol, ethanol, acetone, m.p. 86–87 °C. *Anal. Calc. (%)*: C = 44.99, H = 7.55, N = 17.49 for the composition $C_{12}H_{24}N_4O_6$. *Found*: C = 44.59, H = 7.60, N = 17.90.

Complex II

Colorless, transparent crystals, soluble in methanol, ethanol, acetone, m.p. 107–108 °C. *Anal. Calc. (%)*: C = 52.17, H =

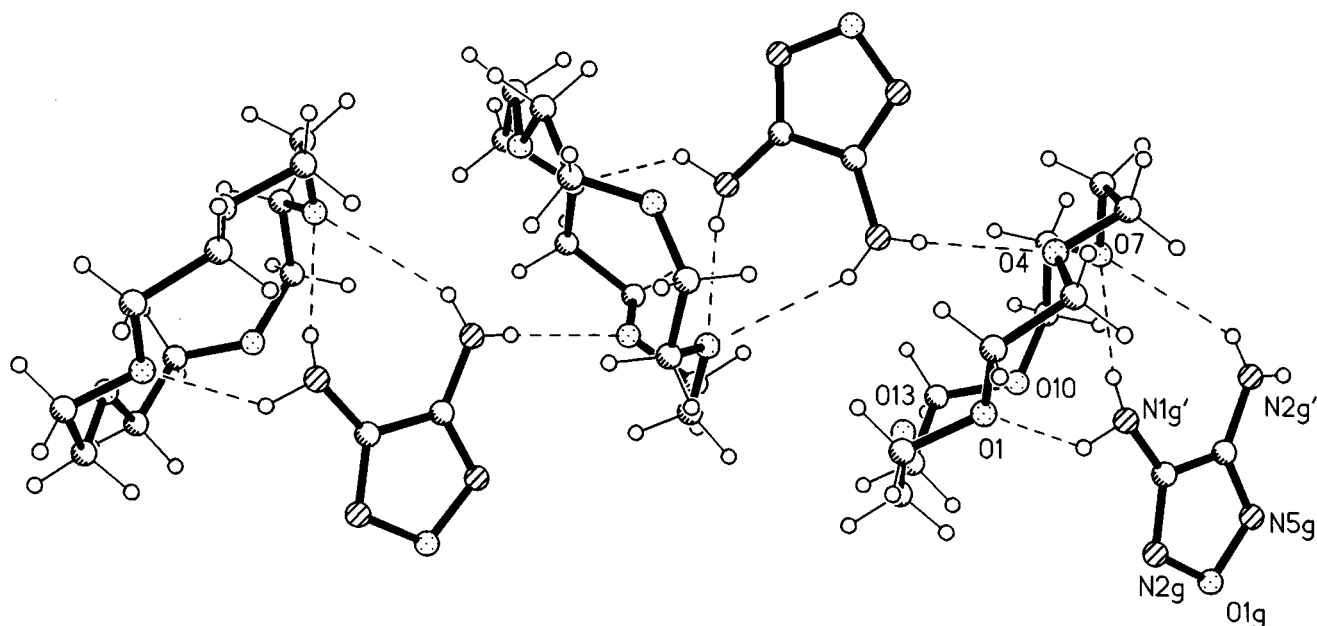


Figure 2. Fragment of the infinite chain in I.

Table 1. Crystal data and structure refinement for I and II.

Complex	I	II
CCDC deposit no.	146586	146587
Color/shape	Colorless/prismatic	Colorless/parallelepiped
Empirical formula	C ₁₂ H ₂₄ N ₄ O ₆	C ₁₆ H ₂₄ N ₄ O ₆
Formula weight	320.35	368.39
Radiation/Å	0.71080	0.71080
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions		
<i>a</i> /Å	7.856(3)	8.260(4)
<i>b</i> /Å	12.994(1)	15.692(5)
<i>c</i> /Å	16.033(1)	13.955(7)
α /degree	90	90
β /degree	94.79(2)	90
γ /degree	90	90
Volume/Å ³	1630.9(6)	1808.8(14)
<i>Z</i>	4	4
<i>D</i> _{calc} /g cm ⁻³	1.305	1.353
η /mm ⁻¹	0.105	0.104
<i>F</i> (000)	688	784
Crystal size/mm	0.2 × 0.35 × 0.35	0.25 × 0.3 × 0.3
θ range for data collection/°	2.02–28.00	2.60–29.00
Index ranges	0 < <i>h</i> < 10, 0 < <i>k</i> < 17, –21 < <i>l</i> < 21	0 < <i>h</i> < 11, 0 < <i>k</i> < 21, –19 < <i>l</i> < 0
Reflections collected/unique	4204/3928 [R(int) = 0.034]	2700/2700 [R(int) = 0.000]
Refinement method	Full-matrix least squares on <i>F</i> ²	
Data/restraints/parameters	3928/4/211	2700/4/247
Goodness-of-fit on <i>F</i> ²	0.997	1.064
Final R indices [<i>I</i> > 2(<i>I</i>)]	<i>R</i> ₁ = 0.0487, <i>wR</i> ² = 0.1283	<i>R</i> ₁ = 0.0522, <i>wR</i> ² = 0.1038
R indices (all data)	<i>R</i> ₁ = 0.1742, <i>R</i> ₁ = 0.1309, <i>wR</i> ² = 0.1736	<i>wR</i> ² = 0.1567
Weighting scheme: a, b ^a	0.0745, 0.15	0.0722, 1.24
Largest diff. peak/hole/e Å ⁻³	0.399/–0.222	0.349/–0.333

^a*w* = 1/[$\sigma^2(F_0^2) + (aP)^2 + bP$] where *p* = (Max(*F*₀², 0) + 2*F*_c²)/3.

6.75, N = 15.21 for the composition C₁₆H₂₄N₄O₆. Found: C = 52.30, H = 6.45, N = 15.55.

X-ray diffraction measurements

X-ray data were collected on a KM4 (Kuma Diffraction) four-circle diffractometer, using graphite monochromated MoK α radiation, $\lambda = 0.7108$ Å. The intensities of three standard reflections were measured periodically during data collection and gave no indication of crystal decay or sample movement. Lorentz-polarization but no absorption corrections were made. The structures were solved by direct methods and refined by a full-matrix least-squares procedure (SHELX97) [13]. The hydrogen atoms associated with the crown ether molecules were idealized and included as fixed contributions using a riding model with the isotropic temperature factors set at 1.2 times the corresponding value of the isotropic temperature factor of the adjacent carbon atom. The hydrogen atoms in the amine groups were found from the ΔF map and were refined with restraints to keep the tetrahedral geometry. Full crystallographic data are given in Table 1. Figure 1 shows the numbering scheme of the guest and two host molecules. Table 2 contains selected bond lengths and angles for **I** and **II**, respectively.

Discussion

Crystal structure of **I**

The fragment of the 1:1 infinite chain in **I** propagated along the *b* direction in the unit cell is portrayed in Figure 2. The guest bridges two adjacent crown molecules by both of its NH₂ functional groups via traditional N—H \cdots O hydrogen bonds. The shortest NH \cdots O contacts range from 2.993(3) (O1) to 3.273(3) Å (O7). The amine group defined by the N(1g') atom participates in two NH \cdots O H-bonds: N(1g') \cdots O(1) = 2.993(3), N(1g') \cdots O(7) = 3.029(3) Å (angles subtended at the H atoms are 142 and 172°); the crown oxygen atoms are separated as usual by the —(CH₂)₂—O—(CH₂)₂— moiety (Figure 3a). The NH₂ group defined by the N(2g') atom, has one short N \cdots O contact with the O(7) oxygen at the same face of the macrocyclic cavity, N(2g') \cdots O(7) = 3.273(3) Å. Furthermore, N(2g') donates its other H-atom to the O-atom of a neighboring crown molecule related to the former by a 2₁ screw axis. The corresponding N(2g') \cdots O(4)(-x + 1, y - 1/2, -z + 1/2) separation is 3.069(3) Å (the angle at the H-atom is 172°) (Figure 3b). Two NH₂-groups in the guest molecule share their hydrogens with crown oxygens in such a fashion that the crown molecule behaves as the different-faced ligand with one of its sides participating in three and the other in only one H-bond. Two nitrogen atoms are at 2.151(3) for N(1g') and 3.167(3) Å for N(2g') above the mean plane defined by the five crown oxygens, and the distance between N(2g') and the same plane of the neighboring host molecule equals 2.727(3) Å. The angle between the N(1g')—C(2g') bond and the normal to the latter plane is equal to 42.9(1)°.

Table 2. Selected bond lengths [Å] and angles [deg] for **I** and **II**.

	I	II
O(1)—C(15)	1.413(4)	1.369(5)
O(1)—C(2)	1.419(4)	1.436(5)
C(2)—C(3)	1.488(5)	1.503(6)
C(3)—O(4)	1.412(3)	1.414(5)
O(4)—C(5)	1.428(3)	1.426(5)
C(5)—C(6)	1.476(4)	1.506(5)
C(6)—O(7)	1.426(3)	1.431(5)
O(7)—C(8)	1.415(3)	1.436(5)
C(8)—C(9)	1.447(5)	1.501(6)
C(9)—O(10)	1.439(4)	1.422(4)
O(10)—C(11)	1.405(4)	1.428(5)
C(11)—C(12)	1.500(5)	1.508(6)
C(12)—O(13)	1.413(4)	1.439(4)
O(13)—C(14)	1.412(4)	1.377(4)
C(14)—C(15)	1.490(5)	1.385(5)
C(15)—O(1)—C(2)	116.0(3)	118.1(3)
O(1)—C(2)—C(3)	108.1(2)	107.6(3)
C(2)—C(3)—O(4)	107.6(2)	110.1(3)
C(3)—O(4)—C(5)	113.7(2)	112.1(3)
O(4)—C(5)—C(6)	107.5(2)	108.8(3)
C(5)—C(6)—O(7)	109.6(2)	108.7(3)
C(6)—O(7)—C(8)	112.1(2)	114.3(3)
O(7)—C(8)—C(9)	108.6(3)	109.2(3)
C(8)—C(9)—O(10)	113.2(3)	109.5(3)
C(9)—O(10)—C(11)	117.0(3)	111.2(3)
O(10)—C(11)—C(12)	108.7(3)	109.7(4)
C(11)—C(12)—O(13)	109.6(3)	107.4(3)
C(12)—O(13)—C(14)	115.2(3)	115.8(3)
O(13)—C(14)—C(15)	108.7(3)	116.8(3)
O(1)—C(15)—C(14)	108.0(3)	114.4(3)
O(1)—C(2)—C(3)—O(4)	66.7(3)	-60.8(5)
C(2)—C(3)—O(4)—C(5)	-173.4(2)	173.4(3)
C(3)—O(4)—C(5)—C(6)	169.8(2)	-165.0(4)
O(4)—C(5)—C(6)—O(7)	-73.3(3)	67.9(4)
C(5)—C(6)—O(7)—C(8)	154.2(3)	-152.0(3)
C(6)—O(7)—C(8)—C(9)	-177.6(3)	159.4(3)
O(7)—C(8)—C(9)—O(10)	61.9(4)	-69.1(4)
C(8)—C(9)—O(10)—C(11)	91.9(4)	172.7(4)
C(9)—O(10)—C(11)—C(12)	-169.8(3)	-175.2(3)
O(10)—C(11)—C(12)—O(13)	77.9(3)	68.6(5)
C(11)—C(12)—O(13)—C(14)	-165.0(3)	-168.1(4)
C(12)—O(13)—C(14)—C(15)	171.7(3)	129.7(4)
O(13)—C(14)—C(15)—O(1)	-66.8(3)	0.3(5)
C(14)—C(15)—O(1)—C(2)	164.6(2)	-176.2(3)
C(15)—O(1)—C(2)—C(3)	-162.6(2)	-169.9(3)
O(1g)—N(5g)	1.395(3)	1.408(5)
O(1g)—N(2g)	1.401(3)	1.410(4)
N(2g)—C(3g)	1.292(3)	1.299(5)
C(3g)—N(1g')	1.363(3)	1.345(5)
C(3g)—C(4g)	1.426(4)	1.455(5)
C(4g)—N(5g)	1.300(3)	1.297(5)
C(4g)—N(2g')	1.359(4)	1.360(5)
N(5g)—O(1g)—N(2g)	110.6(2)	110.1(3)
C(3g)—N(2g)—O(1g)	105.5(2)	105.7(3)
N(2g)—C(3g)—N(1g')	125.6(3)	125.2(4)
N(2g)—C(3g)—C(4g)	109.2(2)	109.1(3)
N(1g')—C(3g)—C(4g)	125.0(2)	125.5(3)
N(5g)—C(4g)—N(2g')	123.9(3)	125.3(4)
N(5g)—C(4g)—C(3g)	110.1(2)	109.3(3)
N(2g')—C(4g)—C(3g)	125.9(2)	125.3(3)
C(4g)—N(5g)—O(1g)	104.7(2)	105.7(3)

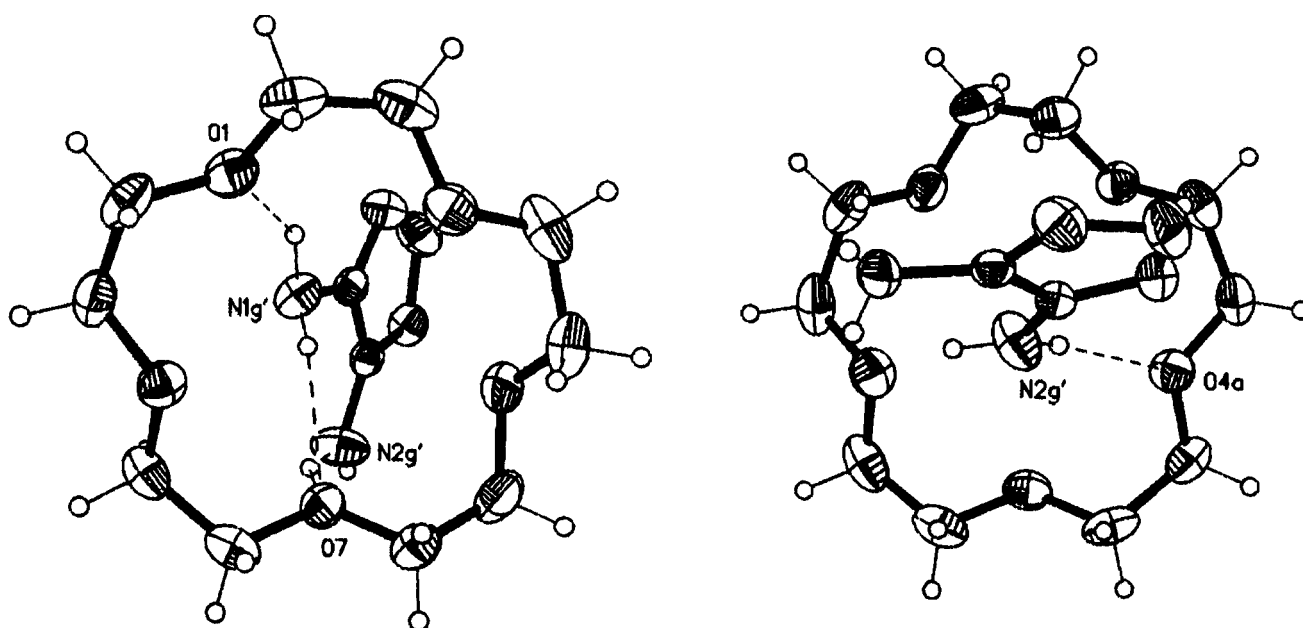


Figure 3. Hydrogen bonding patterns in **I**.

For $N(2g')\text{---}C(4g)$ the corresponding angle has a value of $33.1(1)^\circ$. The dihedral angle between the average planes through the guest heterocyclic ring and host O-atoms is $52.53(8)^\circ$. The full geometry of hydrogen bonds in **I** and **II** is given in Table 3.

Crystal structure of **II**

The chain fragment for **II** running along the c direction in the unit cell is shown in Figure 4. In **II** the host–guest bonding pattern is practically the same as in **I**. $N\cdots O$ separations fall in the range $2.955(5)\text{--}3.208(5)$ Å. Similar to **I**, $N(1g')$ donates both of its H-atoms to form two single H-bonds: $N(1g')\cdots O(13) = 2.953(5)$, $N(1g')\cdots O(7) = 2.896(5)$ Å (angles subtended at the H atoms are 147 and 165°); (Figure 5a). These H-bonds are with the more basic alkyl O-atoms separated by the oxyethylene moiety. The $N(2g')$ amino group gives one of its protons for H-bonding with the same $O(7)$ atom being already involved in H-bonds, the $N(2g')\cdots O(7)$ distance being $3.186(5)$ Å, while the second hydrogen atom is bound with the $O(1)$ atom of the neighboring crown molecule, related to the basic one by the 2_1 screw axis, the $N(2g')\cdots O(1)(-x+3/2, -y+2, z+1/2)$ separation being $3.208(5)$ Å (Figure 5b). The deviations of $N(1g')$ and $N(2g')$ from the mean plane defined by the five macrocycle oxygens are $2.056(4)$ and $3.616(4)$ Å respectively, while the distance between $N(2g')$ and the mean plane of the O atoms of the neighboring host molecule equals $2.736(4)$ Å. The $N(1g')\text{---}C(3g)$ bond forms with the normal to the respective host plane an angle of $11.3(2)^\circ$. The $N(2g')\text{---}C(4g)$ bond forms an angle of $52.0(2)^\circ$ with the same plane of the symmetry related host.

The crystal structures of **I** and **II** clearly indicate their close similarity and the negligible influence of the aryl substituent on the supramolecular architecture. Both structures represent infinite chains $\cdots\text{---}H=G\text{---}H=G\text{---}H=G\text{---}$

\cdots where host (H) and guest (G) occupy the alternating positions.

Crown ether conformations

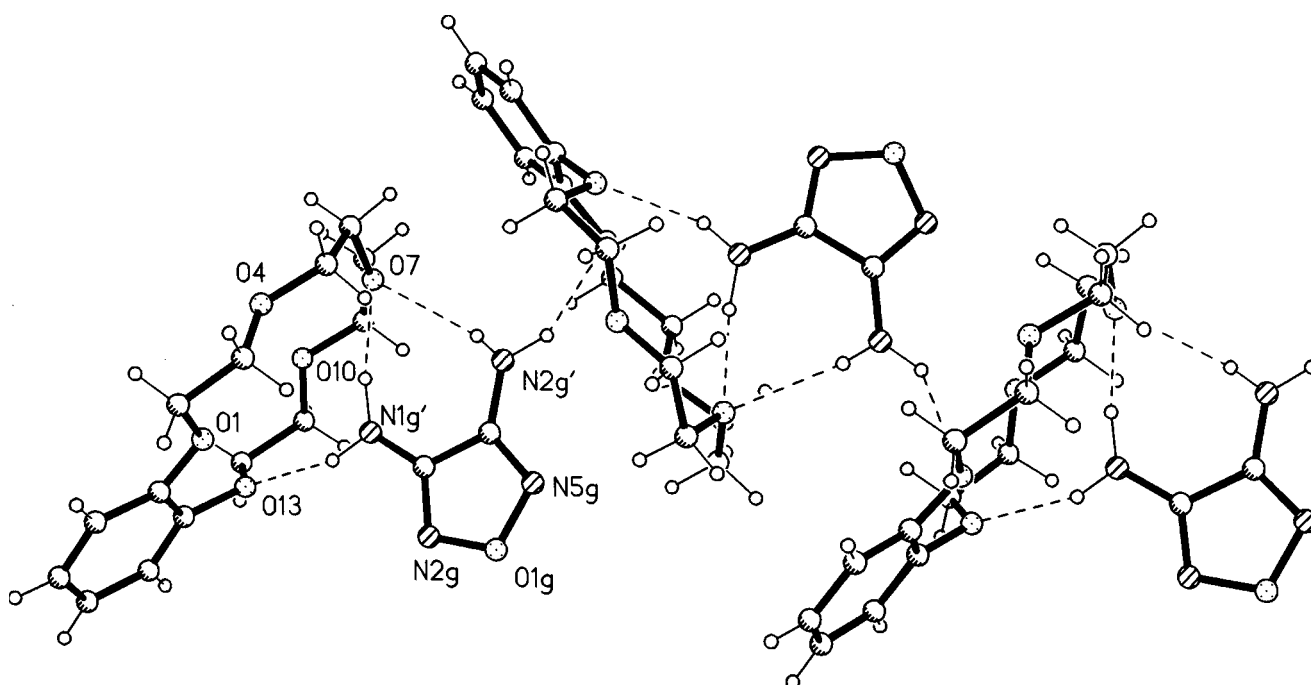
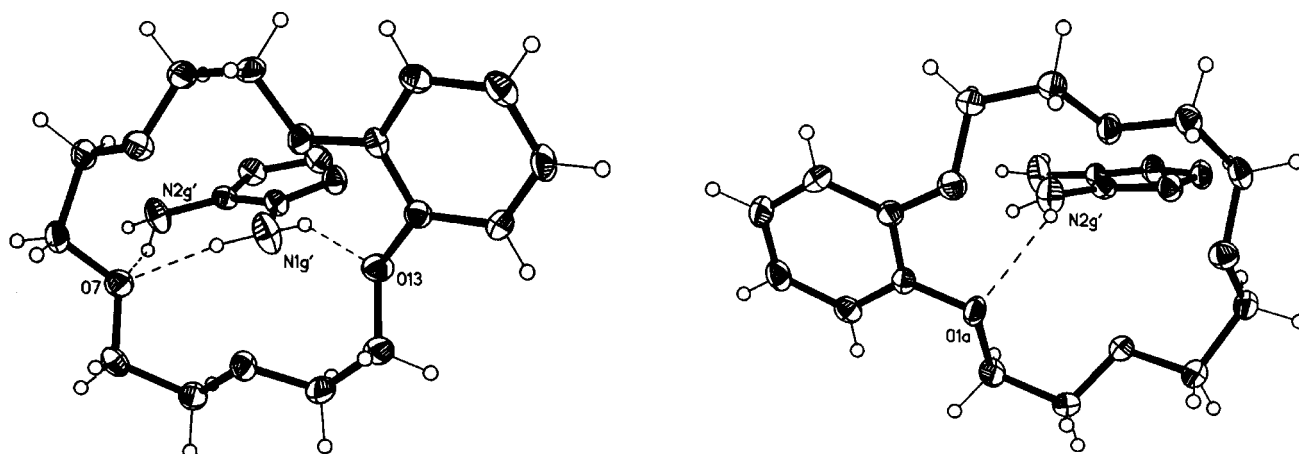
15-Crown-5

In the 15-crown-5 molecule three O-atoms, $O(1)$, $O(7)$ and $O(10)$ are at one side from their least-squares plane, being at distances of $-0.498(1)$, $-0.028(1)$ and $-0.258(1)$ Å, respectively, while $O(4)$ and $O(13)$ are on the other side with deviations of $0.308(1)$ and $0.475(1)$ Å, and all but $O(10)$ pointing toward the corresponding amine group involved in the H-bonds. The $O\cdots O$ distances between the neighboring O atoms are in the range of $2.784\text{--}2.949$ Å. The macrocyclic strand of the molecule displays the $ag + a$, $ag - a$, $ag + g+$, $ag + a$, $ag - a$ set of torsion angles. All of the C—C bonds have *gauche*-conformations (angles in the range $61.6(3)\text{--}77.8(3)^\circ$) and all of the C—O bonds are close to the *anti*-conformation ($154.3(2)\text{--}177.4(2)^\circ$ range), with the exception of $C(8)\text{---}C(9)\text{---}O(10)\text{---}C(11)$ that is also *gauche*- ($92.1(3)^\circ$). The given conformation is essentially identical to that found in the [15-crown-5·NaI] [2a] and [15-crown-5·NaClO₄] [2c] complexes and is the most common for this macrocyclic ether [14]. A further three different crown conformations are found in the well-known example, $[UO_2(H_2O)_5][ClO_4]_2\cdot 3(15\text{-crown-5})\cdot CH_3CN\cdot H_2O$ [6a] where two crown molecules differ in the signs of the *gauche*-angles and the C—C bonds are defined by $g+$, $g+$, $g-$, $g+$, $g-$ and $g-$, $g-$, $g+$, $g+$, $g-$, sequences, all C—O bonds being in the *anti*-conformation (the same conformations were found in $CuBr_2(H_2O)_2(15\text{-crown-5})$ [15] and in $[Ba(15\text{-crown-5})_2]Br_2\cdot 2H_2O$ [16]). The third 15-crown-5 molecule adopts the so-called three-angular conformation, where three $g+$, $g+$ pairs (O—C—C—O, C—O—C—C) are observed. A similar type of conformation with one $g-$, $g-$ and two $g+$, $g+$ torsion angles sequence was found in the 15-crown-5 host–guest complex with NH_3SO_3 [8].

Table 3. Hydrogen bonds in **I** and **II**.

D—H···A	d(D—H), Å	d(H···A), Å	d(D···A), Å	∠(DHA), degree
Complex I				
N(1g')—H(11N)···O(7)	0.86(1)	2.18(1)	3.029(3)	172(3)
N(1g')—H(12N)···O(1)	0.86(1)	2.27(2)	2.993(3)	142(3)
N(2g')—H(21N)···O(4) ^a	0.85(1)	2.23(1)	3.069(3)	172(3)
N(2g')—H(22N)···O(7)	0.86(1)	2.59(3)	3.273(3)	137(3)
Complex II				
N(1g')—H(11N)···O(13)	0.86(1)	2.20(3)	2.955(5)	147(5)
N(1g')—H(12N)···O(7)	0.86(1)	2.06(2)	2.903(5)	165(5)
N(2g')—H(21N)···O(7)	0.86(1)	2.41(3)	3.186(5)	150(4)
N(2g')—H(22N)···O(1) ^b	0.86(1)	2.50(3)	3.208(5)	140(5)

Symmetry transformations used to generate equivalent atoms: ^a $-x + 1, y - 1/2, -z + 1/2$; ^b $-x + 3/2, -y + 2, z + 1/2$.

Figure 4. Fragment of the infinite chain in **II**.Figure 5. Hydrogen bonding patterns in **II**.

Benzo-15-crown-5

In the crown molecule three O atoms, O(1), O(4) and O(10) are on one side of the least-squares plane with the deviations $-0.006(2)$, $-0.253(2)$ and $-0.494(2)$ Å, respectively, whilst O(4) and O(13) are on the other side at $0.448(2)$ and $0.305(2)$ Å. The average deviation of O-atom positions is 0.36 Å, a value quite the same as in complex **I**. The angle which the aromatic ring plane makes with the plane of the macrocycle O-atoms is $15.6(2)^\circ$. The crown C—C bonds adopt the conformations $g-, g+, g-, g+$ (the exception is one *syn*-angle corresponding to the aromatic ring), C—C *gauche*-angles are in the range of $60.9(4)$ – $68.9(4)^\circ$, C—O *anti*-torsion angles are in the range of $129.7(4)$ – $176.2(3)^\circ$, giving a conformation similar to that found in the [dithiooxamide-benzo-15-crown-5] complex [10]. Besides, both in the uncomplexed state [17] and in its complexes [8] benzo-15-crown-5 adopts two angular conformations with two neighboring C—O and C—C bonds both being *gauche*- and the sequence of angles along the macrocyclic strand is $a, g-, a, g-, g-, a, a, g+, g+, a, g+, a, a, s, a$.

The geometry of the host molecules in **I** and **II** is quite common (Table 2), the phenyl ring in the benzo-15-crown-5 molecule has a geometry of a rather regular hexagon, with the average C—C distance of $1.391(6)$ and average C—C—C angle of $120.0(4)^\circ$. The geometry of the guest molecules in **I** and **II** is also ordinal and similar to that found in the related 18-membered complexes [12].

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