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Crystal structure of the 1:1 molecular complex between water and 18,19-benz-1,16-diaza-4,7,10,13-tetraoxacycloeicosa-17,20-dione

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The twenty-membered macrocycle, 18,19-benz-1,16-diaza-4,7,10,13-tetraoxacycloeicosa-17,20-dione (1) and water form a stoichiometric 1:1 inclusion compound. The crystal structure of [1.H_2O] has been determined by X-ray crystallography. Crystals of [1.H_2O] are orthorhombic, space group Pca2_1, a = 8.654(2), b = 10.947(2), c = 21.486(4) Å and Z = 4. The final R-value is 0.046 for 1795 reflections with $I > 2\sigma(I)$. The structure reveals host-guest hydrogen bonding with the mixed set of ligand sites (O,N). Between the molecular complexes there are NH ... O = C contacts joining these entities in chains along the x axis. Besides these, intramolecular C = O ... C = O dipole-dipole interactions have been found in (1).

INTRODUCTION

A distinctive property of crown ethers, is the binding of cations and uncharged molecules. Unlike H-bonded crystalline complexes between crown ethers and NH- or CH-uncharged organic molecules, similar complexes involving water or OH-acidic organic molecules are rather rare. A water molecule may fulfill three main functions in these compounds: serving as a guest in the macrocyclic cavity, acting as a bridge between crown ether and a second guest entity, and filling the intermolecular emptinesses in the crystal. Direct contact between water and crown ethers was revealed in numerous complexes with the aqua-containing coordination compounds; the uranyl complex [18C6.UO_2 $(NO_3)_2$.$2H_2O$][1] is a classic one. A similar situation is realized in a number of nitrate complexes of the rare metals, e.g. [$Tm(NO_3)_3(H_2O)_3$].DCH-6A.CH_3CN[2] etc. The other series of complexes with the direct interaction is the species obtained in an acidic medium, where water is transformed into the hydroxonium ion[3–4]. The bridge water function was found in the compounds where it interacts both with the crown ether and a second guest molecule[5–6]. A very small number of structures which exhibit an exclusive inclusion of neutral water molecules within a crown ether macrocycle are known. The first example involves a 1:1 water adduct of 3,3'-(1,1'-bi-2-naphthol)-21-crown-5[7]. The water molecule appears to be too small to fit into the ligand cavity and occupies only a part of it. In the modified crown ethers, NH or OH macrocycle H-donor groups are principally used for complexation. In this case, the crown ether acts not only as an acceptor but also its donor function in the H-bonds is revealed as well. The cavity sizes are important for the number of water molecules bound with the host. A systematic approach to the water binding by pyridino crowns has been done reported[8]. The specific feature of these macrocycles is the pyridinium nitrogen protonation and its participation in the water binding. In the complexes with 2,6-pyridino-18-crown-6, one water molecule is bound to the 18-membered macrocycle and is located above the mean plane of the ring heteroatoms forming a pyramidal arrangement of H-bonds (O ... N =

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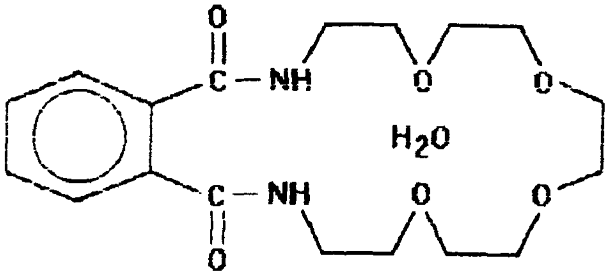
2.70–2.74Å, O ... O = 2.84–2.95Å). The larger 2,6-pyridino-21-crown-7 ligand forms an aqua complex where the water molecule is encapsulated almost at the centre of the cavity, the three H-bonds (2OH ... O and 1NH ... O) being nearly coplanar. The larger 2,6-pyridino-24-crown-8 ligand is large enough to accommodate a pair of water molecules (O ... O = 2.90Å), each of them being surrounded by an 18-membered-like environment, consisting its six heteroatoms in an almost planar arrangement. Host species containing >C = O binding sites were found to be suitable to interact with proton donating H_2O or CH_2Cl_2 guest entities as well[9]. The crystal structure of the 1:1 complex formed between a 20-membered diamide crown and water has been determine in which a mixed set of ligand sites (NH, O) is used for hydrogen bonding with the included water.[10] Neither the pyridino nitrogens nor the carbonyl oxygens are involved in H bridges. Although the host is likely to accommodate more than one guest, e.g., from both sides of the macroring, only a single water molecule per crown ligand is complexed.

The easily available 1:1 complex formed between phthalic acid diamide crown (1) (Scheme 1) and water was synthesized and its structure was determined by X-ray crystallography to further understand water complexation by modified crown ethers. The macrocycle conformation peculiarities are of independent interest because there have been few structural determinations of the smaller macrocyclic analogs.[11]

EXPERIMENTAL

Preparation of complex

A single crystal of [1.H_2O] suitable for the crystallographic study was obtained by recrystallization of (1)[12] from a 1:1 acetone/hexane mixture. Colorless, transparent crystals, soluble in methanol, ethanol, unsoluble in hexane, m.p. 129–130°C. IR: ν, cm^{-1}: 3295 (NH), 1640 (CO), 1110 (COC). NMR ($CDCl_3$), σ, 3.93 br.s. (2OH, CH_2O, CH_2N), 7.67s. (2H, NH), 7.83m (4H, Ph).



Scheme 1 Schematic representation of the complex [1.H_2O]

X-ray data

A colorless transparent prismatic crystal was used for the X-ray analysis. Its dimensions and the main crystallographic data are given in Table 1. X-ray data collection was made on a Siemens AED diffractometer. Lattice parameters were obtained with a routine which repeatedly improves the angular values to reach the maximum of the peaks until the angles change by not more than 0.001°, using 28 reflections in θ range 15.2–46.8°. The intensity data were collected at room temperature by the ω-2θ scan technique in the range $3 < \theta < 70°$. One standard reflection for every hundred was monitored for the compound every 60 minutes without significant variations in their intensity (less then 1%). Intensity data were corrected for Lp factors but not for absorption. The structure was solved by direct methods using the SHELXS-86 package[13]. All calculations were performed using an IBM PS2/80 persònal computer. Scattering factors were those of SHELX. The structure was refined by the full-matrix technique using SHELX76[14]. H-atoms were located from a difference Fourier map and refined isotropically. The final difference Fourier map did not show any residual peaks having significant intensity. The final agreement factor was R = 0.046 for 1795 independent reflections. Final positional parameters are collected in Table 2, bond distances and angles are in Table 3. The figures have been produced using the CRYSRULER[15] and ORTEP[16] packages. The atomic numbering scheme in the molecules forming [1.H_2O] is given in Fig. 1.

TABLE 1 Crystal data and summary of intensity data collection and structure refinement for complex [1.H_2O].

Formula	$C_{18}H_{28}N_2O_7$
Crystal system	orthorhombic
Space group	$Pca2_1$
Cell parameters	
a(Å)	8.654(2)
b(Å)	10.947(2)
c(Å)	21.486(4)
$V(Å)^3$	2035.5(6)
Z	4
$D_x(Mgm^{-3})$	1.254(1)
Crystal form	prism.
Crystal sizes (mm)	0.2 × 0.4 × 0.6
Diffractometer	Siemens AED
Radiation	$CuK_a(\lambda = 1.54178)$
μ (mm^{-1})	0.05
T(K)	293
Number of reflections	
collected	2262
observed	1816
independent	1795
Condition for obs.	$I(hkl) > 2\sigma$ (I)
No of variables	355
$(\Delta/\sigma)_{max}$	0.514
$\Delta\rho_{min}$ $(eÅ^{-3})$	−0.19
$\Delta\rho_{max}$ $(eÅ^{-3})$	0.61
R(hkl)	0.046
$R_w(hkl)$	0.051
$w = 1.5001/(\sigma^2(F) + 0.01042F^2)$	

TABLE 2 Atomic coordinates and mean temperature factors for non-hydrogen atoms of [1.H2O].

Atom	x/a	y/b	z/c	Beq
N(1)	0.2693(4)	1.3718(2)	0.3611(2)	4.52(6)
C(2)	0.3915(5)	1.4435(4)	0.3332(3)	5.6(1)
C(3)	0.3410(6)	1.5141(3)	0.2776(2)	5.68(9)
O(4)	0.3132(4)	1.4333(2)	0.2282(2)	6.16(8)
C(5)	0.2583(8)	1.4933(5)	0.1753(3)	7.0(1)
C(6)	0.2396(9)	1.4046(6)	0.1238(3)	7.9(2)
O(7)	0.1278(4)	1.3155(3)	0.1408(2)	6.60(9)
C(8)	0.0867(7)	1.2422(6)	0.0896(2)	6.9(1)
C(9)	−0.0256(6)	1.1477(5)	0.1106(3)	6.4(1)
O(10)	0.0507(3)	1.0559(3)	0.1447(2)	5.33(6)
C(11)	−0.0520(4)	0.9698(5)	0.1708(2)	5.8(1)
C(12)	0.0361(4)	0.8757(4)	0.2055(2)	5.52(9)
O(13)	0.1188(3)	0.9324(2)	0.2548(2)	4.44(5)
C(14)	0.1978(4)	0.8460(3)	0.2922(2)	4.74(7)
C(15)	0.2963(3)	0.9118(3)	0.3394(2)	4.43(7)
N(16)	0.2017(3)	0.9858(2)	0.3801(2)	3.87(5)
C(17)	0.2545(3)	1.0868(2)	0.4068(2)	3.57(5)
C(18)	0.1384(3)	1.1536(2)	0.4464(1)	3.59(5)
C(19)	0.1377(4)	1.2812(3)	0.4501(2)	4.32(7)
C(20)	0.2592(5)	1.3616(3)	0.4222(2)	5.05(8)
C(21)	0.0326(4)	1.0873(3)	0.4812(2)	4.43(7)
C(22)	−0.0778(5)	1.1446(4)	0.5172(2)	5.63(9)
C(23)	−0.0844(6)	1.2700(5)	0.5181(3)	6.7(1)
C(24)	0.0239(6)	1.3375(4)	0.4857(2)	5.8(1)
O(25)	0.3874(2)	1.1245(2)	0.4003(2)	4.67(6)
O(26)	0.3364(7)	1.4229(4)	0.4578(2)	9.7(1)
O(1W)	0.1201(4)	1.2055(3)	0.2694(2)	5.92(7)

TABLE 3 Bond distances and angles for [1.H2O].

Atom 1-Atom 2	Distance (Å)	Atom 1-Atom 2-Atom 3	Angle (deg)
N(1)–C(2)	1.447(6)	C(20)–N(1)–C(2)	120.4(4)
C(2)–C(3)	1.488(7)	N(1)–C(2)–C(3)	113.6(4)
C(3)–O(4)	1.402(5)	C(2)–C(3)–O(4)	109.3(3)
O(4)–C(5)	1.396(7)	C(3)–O(4)–C(5)	112.2(3)
C(5)–C(6)	1.481(9)	O(4)–C(5)–C(6)	109.7(5)
C(6)–O(7)	1.422(8)	C(5)–C(6)–O(7)	109.4(5)
O(7)–C(8)	1.407(7)	C(6)–O(7)–C(8)	111.3(4)
C(8)–C(9)	1.489(8)	O(7)–C(8)–C(9)	108.9(4)
C(9)–O(18)	1.408(7)	C(8)–C(9)–O(10)	110.3(4)
O(10)–C(11)	1.412(6)	C(9)–O(10)–C(11)	112.8(3)
C(11)–C(12)	1.483(6)	O(10)–C(11)–C(12)	109.9(3)
C(12)–O(13)	1.421(6)	C(11)–C(12)–O(13)	109.3(3)
O(13)–C(14)	1.417(5)	C(12)–O(13)–C(14)	111.9(3)
C(14)–C(15)	1.508(5)	O(13)–C(14)–C(15)	109.6(3)
C(15)–N(16)	1.446(5)	C(14)–C(15)–N(16)	110.8(3)
N(16)–C(17)	1.327(4)	C(15)–N(16)–C(17)	122.2(3)
C(17)–O(25)	1.230(3)	N(16)–C(17)–C(18)	114.8(2)
C(18)–C(21)	1.387(4)	N(16)–C(17)–O(25)	123.6(3)
C(18)–C(19)	1.399(4)	C(18)–C(17)–O(25)	121.7(2)
C(18)–C(17)	1.506(4)	C(17)–C(18)–C(21)	119.4(2)
C(19)–C(20)	1.497(5)	C(19)–C(18)–C(17)	121.3(2)
C(20)–O(26)	1.217(6)	C(19)–C(18)–C(21)	119.3(2)
C(20)–N(1)	1.320(6)	C(18)–C(19)–C(24)	118.5(3)
C(21)–C(22)	1.380(6)	C(24)–C(19)–C(20)	117.2(3)
C(22)–C(23)	1.374(7)	C(18)–C(19)–C(20)	124.2(3)
C(23)–C(24)	1.382(7)	C(19)–C(20)–N(1)	119.6(4)
C(24)–C(19)	1.391(6)	C(19)–C(20)–O(26)	117.3(4)
		N(1)–C(20)–O(26)	122.8(4)
		C(18)–C(21)–C(22)	121.4(3)
		C(21)–C(22)–C(23)	119.4(4)
		C(22)–C(23)–C(24)	119.9(5)
		C(23)–C(24)–C(19)	121.4(4)

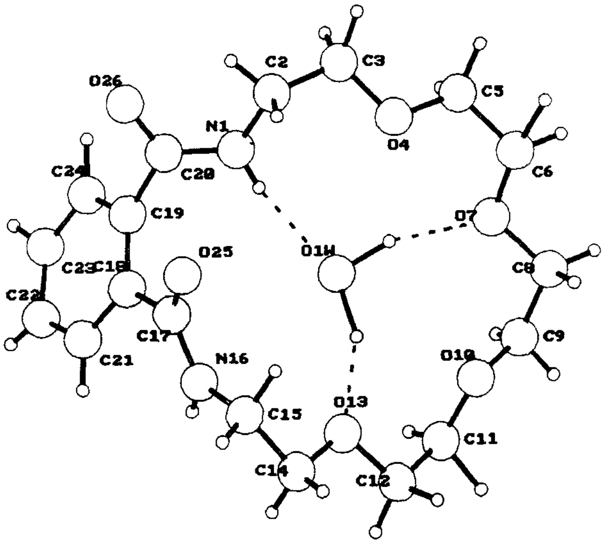


Figure 1 Structure of the complex $[1.H_2O]$ with the atomic numbering scheme and H-bonds shown as the dotted lines.

RESULTS AND DISCUSSION

Hydrogen bonding mode

The molecular structure of the complex $[1.H_2O]$ is shown in Fig. 1. 18-Crown-6 can be considered as the nearest "all-oxygens" analog of (1). In order to transform 18-crown-6 into (1) one can substitute one oxydiethylene fragment by the phthalic acid diamide residue. In the final molecule two amide nitrogen atoms (see Scheme 1 and Fig. 1) appeared as macrocyclic heteroatoms together with the oxygen ones. The water molecule is in the perching mode with the oxygen atom 0.64Å above the plane of the six (4O and 2N) macrocycle heteroatoms. The water forms two H-bonds with O-atoms of the host: O1W ... 07 = 3.015(6), O1W ... O13 = 3.006(4)Å, in the range with literature values[17]. The geometric parameters are given in Table 4. As usual, acceptor macrocycle O-atoms are separated by the oxyethylene moiety. In turn, a water lone pair is engaged in an H-bond with the N1-atom, O1W ... N1 = 2.977(5)Å. The remaining two O1W ... O_{crown} contacts are O1W ... 04=3.130(5) and O1W ... O10=3.197(6)Å. Unlike complexes with the pyridino crowns, the water molecule is not in an 18-membered environment, due to N16 out of the range of possible N ... O contacts, N16 ... O1W 3.456(5)Å. This *atom is engaged in* NH ... O = C *intermolecular* H-bonds, N16 ... O25 = 3.007(6), H(N16) ... O25 = 2.15(1)Å, between the complexes connected by the symmetry operation (−*x*, *2* − *y*, *1/2* + *z*). By this H-bond the complexes are united in zigzag-like chains directed along the crystal *x* axis. Between the chains only van der Waals interactions occur.

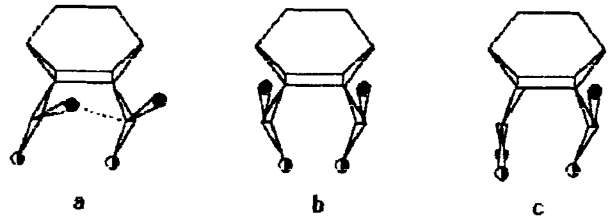
TABLE 4 Geometric parameters of H-bonds in [1.H2O].

N-H (A)	N...O (A)	H...O (A)	NH...O (deg)
N(1) -H(1N1)	N(1)....O(1W)	H(1N1)...O(1W)	N(1) -H(1N1)...O(1W)
0.81(1)	2.977(5)	2.19(1)	165(6)
O(1W) -H(1W)	O(1W)....O(7)	H(1W)...O(7)	O(1W) -H(1W)...O(7)
1.12(1)	3.015(6)	1.93(1)	161(5)
O(1W) -H(2W)	O(1W)....O(13)	H(2W)...O(13)	O(1W) -H(2W)...O(13)
1.27(1)	3.006(4)	1.81(1)	154(9)

Host conformation and geometry

The macrocyclic host (1) consists of a 20-membered heterocyclic cavity fused with the aromatic moiety (Scheme 1). Previously, the crystal structures of 11- and 14-membered macrocyclic phthalic acid diamides, 9,10-benz- 1,7-diaza-4-oxacycloundecane-8,11-dione (2) and 12,13-benz-1,10-diaza-4,7-dioxacycloundecane-11,14-dione (3), were defined by X-ray diffraction techniques[11]. Three possible conformations of the phthalic amide moiety, including in the macrocyclic framework, were defined (Scheme 2). In (1), as in (3), the conformation is of the *a* type. Both carbonyl groups are on the same side of the macrocyclic cavity and displace in a such a way that O25 approaches C20. The shortened >C=O ... C contact is 2.862(4)Å between O25 and C20 (for comparison, in (3) this distance is 2.881Å). Perhaps due to these contacts the bond distance C17—O25=1.230(3)Å is a little longer than C20—O26=1.217(6)Å, which is expected. As the analysis of the Corey-Pauling-Koltun (CPK) model shows, due to the smaller size of the macrocycle (2), the similar conformation is forbidden because of the steric contacts arising when the nitrogen H-atom enters the cavity. Thus, for (2) the more suitable is the *c* type conformation. Therefore, the macrocycle stabilization is fulfilled by the N(O)H ... O H-bonds and >C=O ... C dipole-dipole interactions.

The cycle conformation is described by the following set of torsion angles: *ag* − *aag* + *aag* − *aag* + *aag* + *aassg* + *a* (their meanings are given in Table 5). C—C bonds excepting C17—C18 (35°) and C18—C19(−7°) are in the *gauche* configuration with the torsion angles in the range 61–72°; C—O and C—N torsion angles correspond to the *anti*-configuration with the range 170–180° for the first and 142–179° for the second. The heteroatoms of the macrocyclic cavity deviate from the plane defined by all six of them as follows: N(1), 0.373Å; O(4), −0.502Å; O(7), 0.219Å; O(10), 0.143Å; O(13), −0.180Å; O(16), −0.053Å. The flat aromatic moiety forms a dihedral angle with this plane of 66.9° (Fig. 2). Both diamide fragments are in *cis* configuration with the torsion angles *C—N—C—O* equal to O26—C20—N1—C2 = 10° and O25—C17—N16—C15 = 1°, respectively.



Scheme 2 The possible configurations of the phthalic acid diamide fragment in the macrocyclic molecule (reproduced from ref.11)

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TABLE 5 Selected torsion angles in the heterocyclic framework in [1.H2O].

Atom 1-	Atom 2-	Atom 3-	Atom 4	Angle (deg)
C(20)	-N(1)	-C(2)	-C(3)	−141.7(4)
N(1)	-C(2)	-C(3)	-O(4)	−70.7(5)
C(2)	-C(3)	-O(4)	-C(5)	177.2(4)
C(3)	-O(4)	-C(5)	-C(6)	176.8(5)
O(4)	-C(5)	-C(6)	-O(7)	62.3(7)
C(5)	-C(6)	-O(7)	-C(8)	169.8(5)
C(6)	-O(7)	-C(8)	-C(9)	177.8(5)
O(7)	-C(8)	-C(9)	-O(10)	−74.9(6)
C(8)	-C(9)	-O(10)	-C(11)	174.4(4)
C(9)	-O(10)	-C(11)	-C(12)	179.6(4)
O(10)	-C(11)	-C(12)	-O(13)	61.4(4)
C(11)	-C(12)	-O(13)	-C(14)	176.3(3)
C(12)	-O(13)	-C(14)	-C(15)	174.2(3)
O(13)	-C(14)	-C(15)	-N(16)	61.3(4)
C(14)	-C(15)	-N(16)	-C(17)	−151.4(3)
C(15)	-N(16)	-C(17)	-C(18)	178.6(3)
N(16)	-C(17)	-C(18)	-C(19)	−145.2(3)
C(17)	-C(18)	-C(19)	-C(20)	−7.3(5)
C(18)	-C(19)	-C(20)	-N(1)	69.7(5)

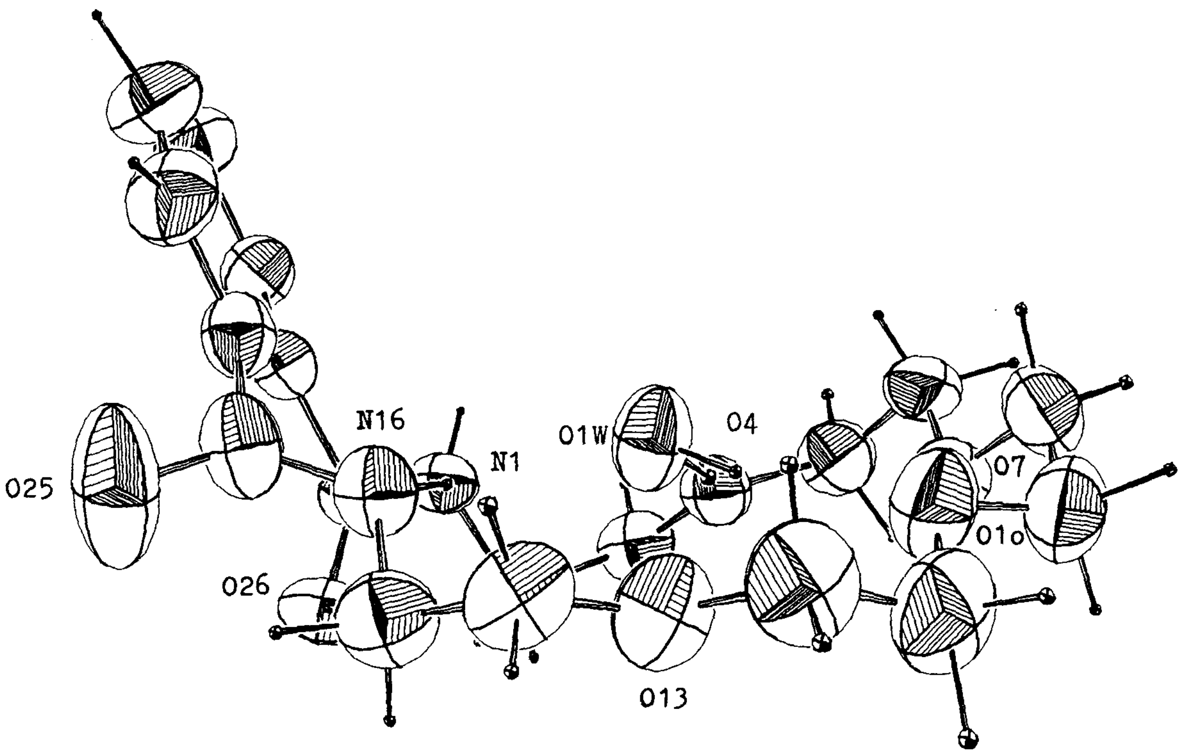

Figure 2 ORTEP plot of the molecular structure of the complex [$1.H_2O$].

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