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Crystal Structures of Dibenzo-14-crown-4 Alcohol and Diol Monohydrates

N. KENT DALLEY* and JIANG WEIMING
Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, U.S.A.

URIEL OLSHER* and FELIX FROLOW
Department of Chemical Services, Weizmann Institute of Science, Rehovot 76100, Israel

and

MICHAEL J. PUGIA, ZONG-YUAN YU and RICHARD A. BARTSCH*
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, U.S.A.

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Abstract. Monohydrate complexes **1**–**3** of *sym*-hydroxydibenzo-14-crown-4, *sym-cis*-dihydroxydibenzo-14-crown-4 and *sym-trans*-dihydroxydibenzo-14-crown-4, respectively, have been prepared and their solid state structures determined. For all three complexes the space group was $Cmc2_1$. The crystal data are: for **1**, a = 16.256(10), b = 12.076(5), c = 8.767(3) Å, V = 1721.0 Å^3 with Z = 4; for **2**, a = 16.437(3), b = 11.997(4), c = 8.640(3) Å, V = 1703.8 Å^3 with Z = 4; for **3**, a = 16.528(7), b = 12.306(3), c = 8.540(3) Å, V = 1737.0 Å^3 with Z = 4. The structures were refined to [R, R_w, unique data with $F < n\sigma(F)$]: for **1**, 0.066, 0.055, 828, 2.5; for **2**, 0.034, 0.035, 1090, 3.0; for **3**, 0.047, 0.036, 1038, 3.0. The three crystal structures have a high degree of isomophism and the dibenzo-14-crown-4 units in the three host–guest complexes are nearly identical. Intramolecular hydrogen bonds link an alcohol oxygen atom of the host to the oxygen atom of the guest water molecule and the oxygen atom of the guest water molecule to ether oxygen atoms of the host in **1**–**3**. In **2** and **3**, there is an intermolecular hydrogen bond between the hydrogen atom of an alcohol group of the host and the oxygen atom of a symmetry-related water molecule guest of another complex.

Key words: X-ray crystal structures, dibenzo-14-crown-4 alcohol and diols, neutral guest species.

1. Introduction

Crown ether alcohols and diols [1–12] resemble aliphatic alcohols and glycols in having one or more hydroxyl groups attached to a hydrophobic organic moiety. Therefore it might be anticipated that crown ether alcohols would form hydrates analogous to those observed for the aliphatic alcohols [13–16]. Such aliphatic alcohol hydrates may be separated into two distinct classes. The first group is the 'low' hydrates, in which the water molecules and the hydroxyl groups of the alcohol

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* Authors for correspondence.

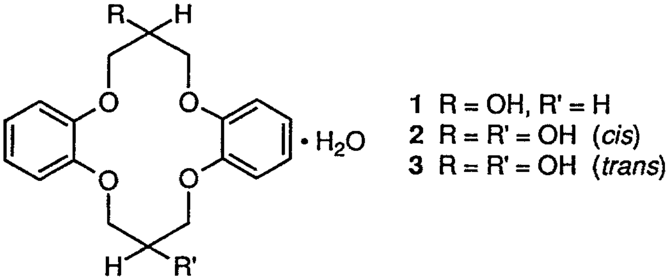

Fig. 1. A schematic drawing of complexes **1–3**.

are hydrogen-bonded in infinite or continuous chains or ribbons. The second class is the 'high' hydrates, in which the water molecules and the hydroxyl groups of the alcohol are linked by three-dimensional frameworks of hydrogen bonds. These frameworks contain voids which can accommodate the organic portion of the alcohol molecules. The 'high' hydrates are not true clathrates, as originally defined by Pauling and Powell [17] and exemplified by the gas hydrates [18]. The topological differences between the water structure in alcohol [14–16] and amine [19, 20] hydrates on the one hand and the gas hydrates on the other are so apparent that the former have been described as 'semiclathrates'.

A difference between crown ether alcohols and aliphatic alcohols is the presence of ethereal oxygens in the former. Such ethereal oxygens can form stable and well-oriented hydrogen bonds with acidic hydrogens, particularly with water molecules both in solution and in the solid state [10]. Such a hydrogen bond network may resemble those found for cyclodextrins and carbohydrates [21–24].

We have now prepared monohydrate complexes **1–3** of *sym*-hydroxydibenzo-14-crown-4, *sym-cis*-dihydroxydibenzo-14-crown-4 and *sym-trans*-dihydroxydibenzo-14-crown-4, respectively (see Figure 1), and determined their solid state structures by X-ray diffraction. In this paper, the crystal structures of **1–3** are reported and the hydrogen bonding patterns compared. In addition, the spatial relationships of the guest water molecules in monohydrates **1** and **3** are compared with those reported for the corresponding Li^+ complexes. In this way, potential differences in guest-host interactions for a neutral molecule guest versus a cationic guest are probed.

2. Experimental

The crown ether alcohol and diols utilized in the preparation of monohydrates **1–3** were synthesized by reported methods [10,11].

2.1. PREPARATION OF MONOHYDRATE COMPLEXES 1–3

Single crystals of *sym*-hydroxydibenzo-14-crown-4 monohydrate (**1**), *sym-cis*-dihydroxydibenzo-14-crown-4 monohydrate (**2**) and *sym-trans*-dihydroxydi-

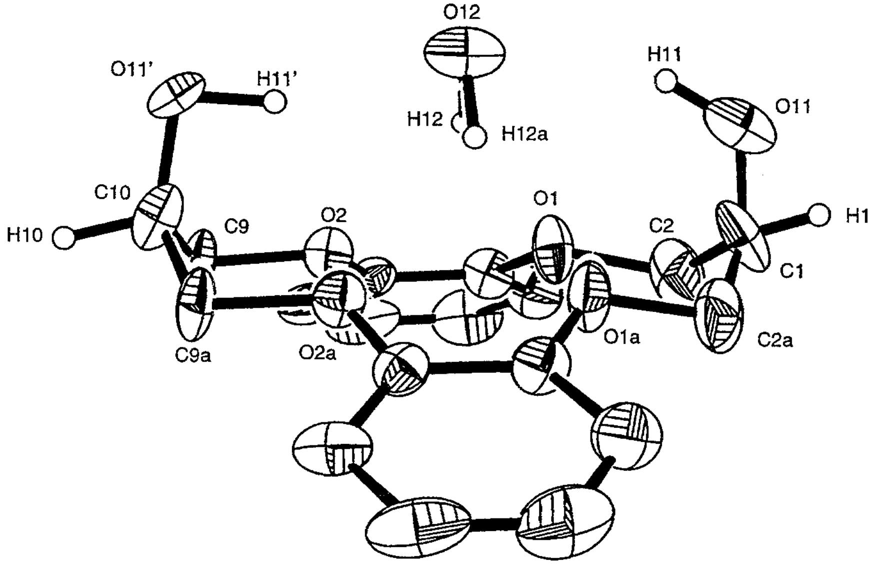

Fig. 2. Computer drawing of the crystal structure of *sym*-hydroxydibenzo-14-crown-4 monohydrate (**1**). Thermal ellipsoids are drawn at the 30% probability level.

benzo-14-crown-4 monohydrate (**3**) were prepared by dissolving the non-hydrated ligands in acetonitrile–water (9/1, v/v) and allowing the solvent to evaporate. Single crystals of monohydrate **3** could also be grown from methanol–water (19/1, v/v).

2.2. X-RAY CRYSTAL STRUCTURE DETERMINATIONS

All crystal and intensity data were obtained using a Siemens R3 automated diffractometer which utilized graphite crystal monochromated MoK_α radiation (λ = 0.71073 Å). The lattice parameters and orientation-matrix for each of the three crystals were calculated using a least-squares procedure which involved sets of carefully centered reflections. Single crystal intensity data for the three studies were collected with a θ–2θ variable speed scanning technique in which the scan speed was determined by the intensity of the individual reflections. Each of the three complexes crystallized in the orthorhombic crystal system. The similarity of the lattice parameters suggested that the structures had some degree of isomorphism. The systematic absences in the three data sets limited the possible space groups for the complexes to $Cmc2_1$ or $Cmcm$. The intensity statistics (the value of E^2-1 for each crystal was less than 0.80) indicated that the acentric space group $Cmc2_1$ was the proper choice and the successful solution of each structure in that space group supported that choice. Furthermore, attempts to solve the structures using the space group $Cmcm$ were unsuccessful. The crystal data and experimental details of the structure determinations are recorded in Table I.

TABLE I. Crystal data and some experimental details for the complexes **1**–**3**.

	1	**2**	**3**
Formula	$C_{18}H_{20}O_5{\cdot}H_2O$	$C_{18}H_{20}O_6{\cdot}H_2O$	$C_{18}H_{20}O_6{\cdot}H_2O$
Formula weight	334.4	350.4	350.4
F(000)	712	744	744
Crystal size, mm	0.15 × 0.30 × 0.40	0.30 × 0.40 × 0.40	0.15 × 0.20 × 0.40
μ, mm^{-1}	0.096	0.103	0.103
Space group	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$
Crystal system	Orthohombic	Orthohombic	Orthohombic
a (Å)	16.256(10)	16.437(3)	16.528(7)
b (Å)	12.075(5)	11.997(4)	12.306(3)
c (Å)	8.767(3)	8.640(3)	8.540(3)
V (Å^3)	1721.0	1703.8	1737.0
Z	4	4	4
ρ_x, mg/m^3	1.269	1.366	1.340
Scan range (2θ)°	4.0 to 50.0	4.0 to 55.0	4.0 to 50.0
Total data	869	1138	1781[a]
Unique data	828	1090	1584[a]
Observed data	515($F > 2.5\sigma(F)$)	930($F > 3.0\sigma(F)$)	1038[a]($F > 3.0\sigma(F)$)
R	0.066	0.034	0.047
R_w	0.055	0.035	0.036
Data : Parameter	4.3 : 1	6.7 : 1	7.6 : 1
Goodness of fit	1.53	1.60	1.29
Largest peak in Δ Map (eÅ^{-3})	0.19	0.13	0.26
Largest hole in Δ Map (eÅ^{-3})	−0.21	−0.13	−0.30
Index ranges	$0 \leq h \leq 19$ $0 \leq k \leq 13$ $0 \leq l \leq 10$	$0 \leq h \leq 21$ $0 \leq k \leq 15$ $0 \leq l \leq 11$	$0 \leq h \leq 18$ $0 \leq k \leq 14$ $-10 \leq l \leq 9$

[a] Includes unmerged data from two octants. The unmerged data set, which includes 557 unique observed reflections, was used in the refinement process. R_{int} is 2.07%.

The structures of the monohydrate complexes **1**, **2** and **3** were solved using direct methods. Each of the three structures contains a mirror plane which passes through the central carbon atoms of each three-carbon bridge. The structure of **1** is disordered and consists of two identical orientations which are related by a pseudo two-fold axis which lies in the mirror plane and is perpendicular to and bisects the line joining C(1) to C(10). In the resulting structure for **1**, the two dibenzo-14-crown-4 orientations are superimposed, which gives the appearance of **2**, except for the positions of the alcohol and water hydrogens (see Figures 2 and 3). Despite their similar appearances, **1** and **2** are distinctly different complexes since different crown ether compounds were used in their preparation. The structures also differ crystallographically, as the site occupancies of the alcohol groups in **1** are one-half those of the corresponding occupancies in **2**. Complex **2** is also disordered. As

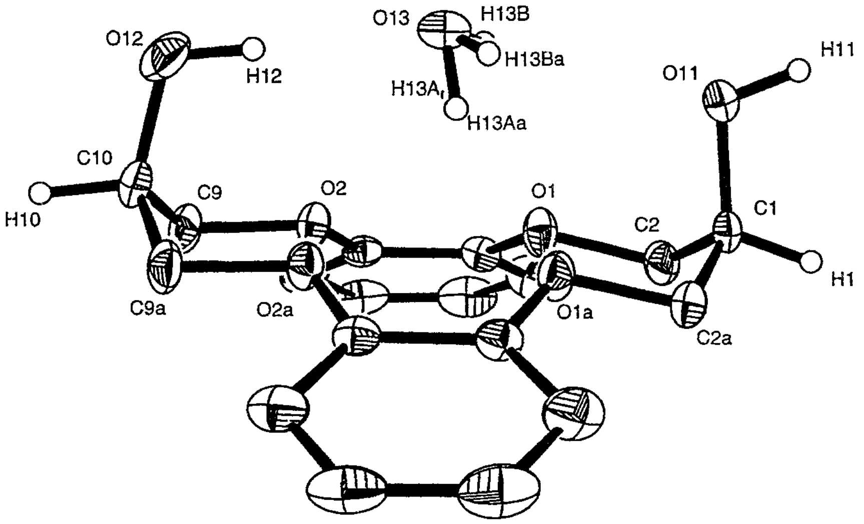

Fig. 3. Computer drawing of the crystal structure of *sym-cis*-dihydroxydibenzo-14-crown-4 monohydrate (**2**). Thermal ellipsoids are drawn at the 30% probability level.

shown in Figure 3, there are two separate sites for the water hydrogen atoms. One pair of hydrogen atoms, H(13A) and H(13Aa), have positions which are similar to those of the water hydrogen atoms in **1** and **3**, while the positions for H(13B) and H(13Ba) are clearly different from any found in **1** and **3** (see Tables II and IV). The site occupancies of the disordered hydrogen atoms were set equal to 0.50. During the anisotropic refinement process for **2**, it was observed that O(12), which was located on the mirror plane, had an unusually large thermal motion component perpendicular to the mirror plane. This suggested that O(12) and H(12) were located slightly off the mirror plane and were disordered. The x parameters of O(12) and H(12) were allowed to vary and O(12) refined to a position 0.0082 Å off the mirror plane while H(12), which was allowed to ride on O(12) during the refinement process, was 0.0279 Å from that plane. The positional coordinates of **3**, which were obtained by direct methods, were found to be similar to those of **2** except for the position of the isomer-differentiating alcohol oxygen, O(11). To illustrate the similarity of **2** and **3**, the structure of **3** was redetermined using as the starting point the positions of all of the non-hydrogen atoms of **2** except for that of O(11). The position of O(11) in **3** was obtained in the resulting difference map.

The non-hydrogen atoms of the three structures were refined anisotropically. In all three structures, the hydrogen atoms bonded to the water and alcohol oxygen atoms and to carbon atoms on the mirror plane were located in the respective difference maps. Positions for hydrogen atoms bonded to other carbon atoms were calculated based on known molecular geometry with the C–H bond distance fixed at 0.96 Å. All of the hydrogen atoms were allowed to ride on their neighboring atoms during the refinement. The isotropic thermal parameters of the hydrogen

TABLE II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients for non-hydrogen and isotropic displacement coefficients for hydrogen atoms ($\text{Å}^2 \times 10^3$) for complex **1**.

	x	y	z	U(eq)[a] or U
C(1)	0	3867(7)	10150	120(1)
C(2)	769(5)	3213(6)	10197(9)	117(1)
C(3)	1579(3)	1988(5)	8623(8)	72(1)
C(4)	2274(4)	2080(6)	9537(10)	104(1)
C(5)	2937(4)	1371(7)	9298(11)	126(1)
C(6)	2918(4)	632(7)	8183(9)	118(1)
C(7)	2219(3)	530(5)	7231(9)	83(1)
C(8)	1561(4)	1232(5)	7455(8)	66(1)
C(9)	763(4)	425(6)	5433(8)	92(1)
C(10)	0	657(8)	4552(11)	88(1)
O(1)	896(3)	2623(4)	8811(7)	91(1)
O(2)	856(2)	1236(3)	6615(6)	71(1)
O(11)[b]	0	4591(8)	9195(14)	128(1)
O(11′)[b]	0	1583(8)	3772(10)	80(1)
O(12)	0	3473(6)	6049(9)	118(1)
H(1)	0	4455	10700	140
H(2A)	726	2682	11017	141
H(2B)	1238	3704	10370	141
H(4)	2287	2626	10342	122
H(5)	3427	1417	9927	153
H(6)	3390	144	8022	142
H(7)	2212	-22	6433	99
H(9A)	1240	464	4771	107
H(9B)	727	-318	5865	107
H(10)	0	-9	3881	108
H(11)[b]	0	4455	8140	155
H(11′)[b]	0	2091	4701	97
H(12)	405	2995	6693	141

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[b] Disordered atom with an occupancy factor of 0.25.

atoms of **1** were set at 1.2 times the initial equivalent isotropic parameter of their neighboring atoms and were not refined. The isotropic thermal parameters of the hydrogens of **2** and **3** were refined. In the final stages of refinement of each structure, the data sets were weighted with weights based on counting statistics and an empirical extinction correction was applied to each data set. Scattering factors were obtained from Volume IV of *The International Tables for X-ray*

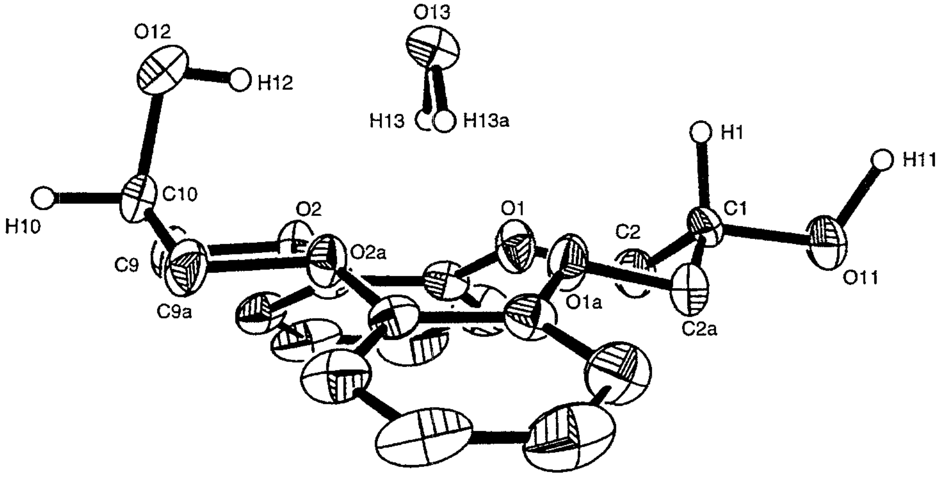

Fig. 4. Computer drawing of the crystal structure of *sym-trans*-dihydroxydibenzo-14-crown-4 monohydrate (**3**). Thermal ellipsoids are drawn at the 30% probability level.

Crystallography [25]. The solution and early refinements of the structures were conducted using the program package SHELXTL [26]. The final refinements and the drawings of the three structures were made using the programs contained in the SHELXTL-PLUS [27] program package.

3. Results

Structures of the three host–guest complexes **1**–**3** are shown in Figures 2–4, respectively. The positional and thermal parameters for the atoms of **1**, **2** and **3** are listed in Tables II, III and IV, respectively. The bond lengths and angles in the three host molecules are normal and are similar, except for those involving the disordered alcohol oxygen atoms of **1**. Average bond length and angle values calculated for the three structures are contained in Table V. The numbers in parentheses are the standard deviations from the average values which indicate the spread of the results for each value. Except for the results involving the disordered oxygen atoms in **1**, each relative standard deviation is less than 2%.

A pronounced degree of isomorphism of these structures is apparent from an examination of the crystal data for **1**–**3** (see Table I) and the positional parameters of the respective non-hydrogen atoms (see Tables II–IV). Because of the manner of selecting the origin for space group $Cmc2_1$ (the z parameter is arbitrarily established), the z parameter of the individual atoms is not critical in this comparison. However, because the initial z parameters of all the non-hydrogen atoms of **2** and **3**, except O(11), were identical (see the discussion of the redetermination of the structure of **3** in Section 2.2) and because z parameters of the atoms of **1** were similar to those of **2**, all positional parameters of the non-hydrogen atoms except those of O(11) are similar for the three structures.

TABLE III. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients for non-hydrogen and isotropic displacement coefficients for hydrogen atoms ($Å^2 \times 10^3$) for complex **2**.

	x	y	z	U(eq)[a] or U
C(1)	0	3901(2)	10295	53(1)
C(2)	783(2)	3240(2)	10283(3)	56(1)
C(3)	1562(1)	2024(2)	8685(3)	45(1)
C(4)	2248(1)	2108(2)	9617(3)	69(1)
C(5)	2910(1)	1408(2)	9351(3)	81(1)
C(6)	2885(1)	631(2)	8210(3)	74(1)
C(7)	2203(1)	542(2)	7269(3)	59(1)
C(8)	1546(1)	1246(2)	7492(3)	42(1)
C(9)	777(1)	402(2)	5458(3)	60(1)
C(10)	0	582(2)	4563(4)	60(1)
O(1)	874(1)	2647(1)	8862(2)	53(1)
O(2)	847(1)	1238(1)	6634(2)	47(1)
O(11)	0	4701(2)	9084(3)	59(1)
O(12)[b]	−5(5)	1599(2)	3761(3)	82(1)
O(13)	0	3545(2)	6008(3)	61(1)
H(1)	0	4224	11332	66(1)
H(2A)	770	2714	11121	72(1)
H(2B)	1237	3736	10416	73(1)
H(4)	2263	2644	10443	98(1)
H(5)	3388	1477	9983	89(1)
H(6)	3342	145	8052	83(1)
H(7)	2188	−11	6465	72(1)
H(9A)	1234	451	4769	77(1)
H(9B)	767	−323	5932	80(1)
H(10)	0	−66	3791	58(1)
H(11)	0	5367	9519	53(1)
H(12)[b]	−17	2182	4471	125(1)
H(13A)[b]	405	3067	6691	91(1)
H(13B)[b]	399	3591	6522 91(1)	

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[b] Disordered atom with an occupancy factor of 0.5.

The orientational disorder of **1** causes it to resemble **2**. The only significant difference between the structure of **3** and those of **1** and **2** is in the location of O(11). The similarities of some of the major structural features of the complexes are shown in Table VI. These features include the interatomic distances between the ether oxygen atoms, the average deviations of the non-hydrogen atoms from

TABLE IV. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients for non-hydrogen and isotropic displacement coefficients for hydrogen atoms ($\text{Å}^2 \times 10^3$) for complex **3**.

	x	y	z	$U(\text{eq})^a$ or U
C(1)	0	3890(3)	10295	71(1)
C(2)	767(2)	3251(2)	10374(4)	76(1)
C(3)	1567(2)	2016(2)	8859(4)	59(1)
C(4)	2248(2)	2123(3)	9772(5)	95(1)
C(5)	2906(2)	1447(3)	9563(5)	119(1)
C(6)	2882(2)	683(3)	8422(4)	102(1)
C(7)	2207(2)	552(3)	7494(4)	75(1)
C(8)	1555(2)	1232(2)	7701(4)	51(1)
C(9)	775(2)	346(2)	5715(4)	71(1)
C(10)	0	488(3)	4810(5)	73(1)
O(1)	887(1)	2646(2)	8987(3)	72(1)
O(2)	854(1)	1208(1)	6842(3)	58(1)
O(11)	0	4582(2)	11611(4)	117(1)
O(12)	0	1438(2)	3895(4)	91(1)
O(13)	0	3258(2)	6116(4)	61(1)
H(1)	0	4462	9366	14(1)
H(2A)	744	2762	11249	71(1)
H(2B)	1212	3744	10507	80(1)
H(4)	2264	2672	10570	167(1)
H(5)	3374	1522	10218	121(1)
H(6)	3345	226	8258	119(1)
H(7)	2195	−9	6713	67(1)
H(9A)	1227	359	5009	75(1)
H(9B)	763	−337	6257	130(1)
H(10)	0	−87	3971	44(1)
H(11)	0	5491	11372	108(1)
H(12)	0	1860	4659	84(1)
H(13)	363	2827	6777	186(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the two major planes in the structures and the dihedral angles between these planes (the hinge angles).

The hydrogen bonding arrangements found in the three structures are noteworthy. The hydrogen bond data are recorded in Table VII. In the three structures, there are host alcohol hydrogen–guest water oxygen and guest water hydrogen–host ether oxygen hydrogen bonds. Also, there is an intermolecular hydrogen bond between the hydrogen of the isomer-determining O(11) and a symmetry-related

TABLE V. Average bond lengths and angles in complexes **1–3**.

1	**2**	**3**	**1–2 Å**	**1–2–3 (°)**
C(2)	C(1)	O(11)	1.495(16)	110.2(3.8)
C(2)	C(1)	C(2A)		116.1(7)
O(11)	C(1)	C(2A)	1.348(118)	110.2(3.8)
C(1)	C(2)	O(1)		111.1(3)
C(4)	C(3)	C(8)	1.385(8)	119.5(6)
O(1)	C(3)	C(4)	1.364(5)	124.3(8)
C(8)	C(3)	O(1)	1.381(9)	116.2(4)
C(3)	C(4)	C(5)		120.1(8)
C(4)	C(5)	C(6)	1.389(7)	120.1(8)
C(5)	C(6)	C(7)	1.345(19)	120.7(6)
C(6)	C(7)	C(8)	1.394(20)	119.5(6)
C(3)	C(8)	C(7)		120.1(4)
O(2)	C(8)	C(3)	1.368(5)	114.5(4)
C(7)	C(8)	O(2)	1.380(4)	125.3(2)
O(2)	C(9)	C(10)	1.435(4)	109.5(1)
C(9)	C(10)	O(4)	1.500(12)	113.5(1.8)
C(9)	C(10)	C(9A)		115.1(1.8)
O(12)[a]	C(10)	C(9A)	1.373(54)	113.3(2.0)
C(2)	O(1)	C(3)	1.421(7)	118.7(1.5)
C(8)	O(2)	C(9)		117.5(9)

[a] O(11′) in **1**.

TABLE VI. Calculated hinge angles and ether oxygen planarities for complexes **1–3** and dibenzo-14-crown-4.

Compound	O—O interatomic distances (Å)			Average deviation (Å) of nonhydrogen atoms from the major planes[a]	Dihedral angle between two major planes (deg) (hinge angle)
	O(1)—O(2)	O(1)—O(1a)	O(2)—O(2a)		
1	2.552	2.912	2.783	0.075	136.4
2	2.561	2.896	2.782	0.076	139.9
3	2.548	2.932	2.824	0.070	138.5
Dibenzo-14-crown-4[b]				0.021	122.8

[a] Least-square plane which consists of all 12 non-hydrogen atoms of each 'side' including the central carbons which are in both planes.

[b] Reference 28.

TABLE VII. Hydrogen bond data for complexes **1–3**.

Cmpd.	D	H	A	H···A (Å)	D···A (Å)	D—H···A (°)	Symmetry Translation of A
1	O(11)	H(11)	O(12)	2.20	3.091	157	x, y, z
	O(11′)	H(11′)	O(12)	2.04	3.027	162	x, y, z
	O(12)	H(12)	O(1)	2.07	3.008	148	x, y, z
	O(12)	H(12)	O(2)	2.24	3.075	136	x, y, z
2	O(11)	H(11)	O(13a)	1.92	2.780	163	$x, 1-y, 0.5+z$
	O(12)	H(12)	O(13)	2.02	2.947	178	x, y, z
	O(13)	H(13A)	O(1)	2.09	3.013	152	x, y, z
	O(13)	H(13A)	O(2)	2.31	3.050	130	x, y, z
	O(13)	H(13B)	O(1)	2.44	3.013	128	x, y, z
3	O(11)	H(11)	O(13a)	1.54	2.691(4)	178	$x, 1-y, 0.5+z$
	O(12)	H(12)	O(13)	2.12	2.935(4)	164	x, y, z
	O(13)	H(13)	O(1)	2.09	2.955(4)	146	x, y, z
	O(13)	H(13)	O(2)	2.15	2.957(3)	138	x, y, z

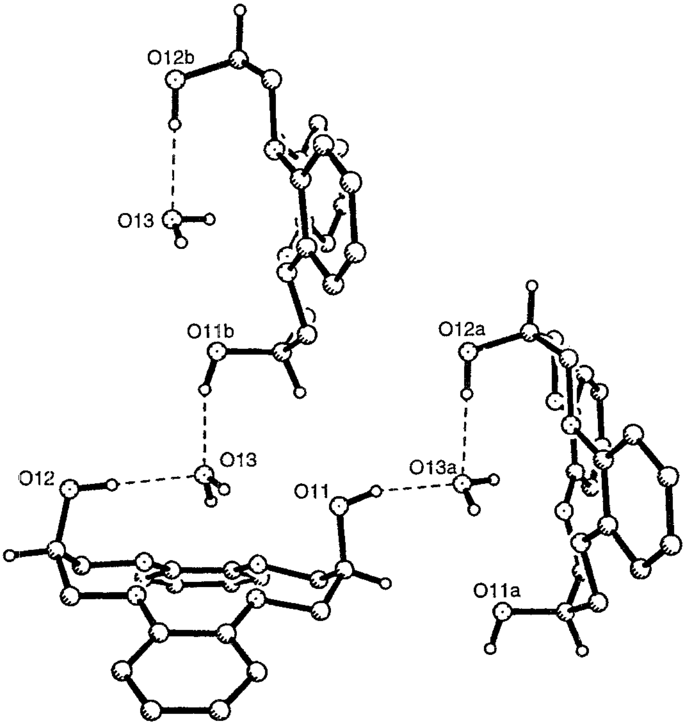

Fig. 5. Intercomplex hydrogen bonding in complex **2**.

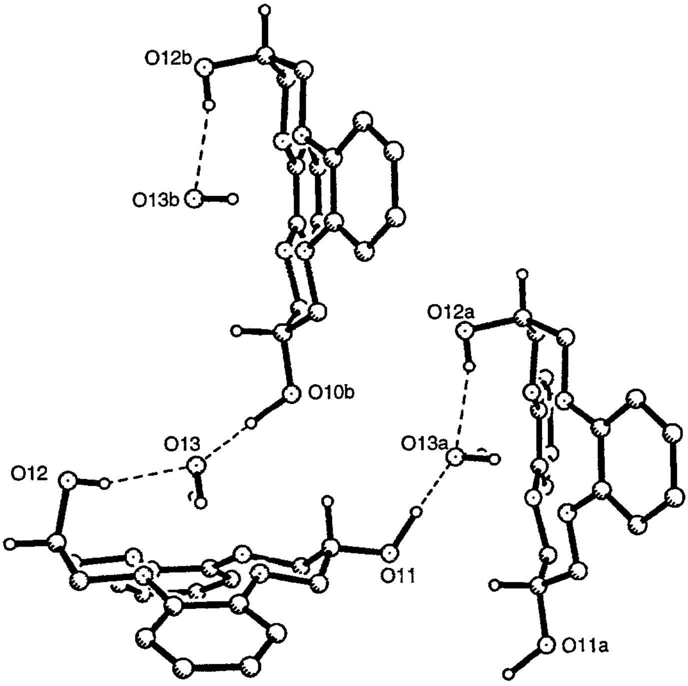

Fig. 6. Intercomplex hydrogen bonding in complex **3**.

water oxygen of another molecule of both **2** and **3** (see Figures 5 and 6, respectively).

4. Discussion

The degree of isomorphism displayed by the three structures which differ in composition (**1** differs from **2** and **3** by an OH group) and conformation (**2** is the *cis* isomer and **3** is the *trans* isomer) is in large measure due to the rigidity of the dibenzo-14-crown-4 unit. Examination of the drawings of the three structures (Figures 2–4) shows that the dibenzo-14-crown-4 units in the three host–guest complexes are nearly identical. This structural similarity is further verified by the data for corresponding structural features of the three complexes which appear in Table VI. The nearly planar rectangles formed by the ether oxygen atoms in monohydrate complexes **1**–**3** are very similar to each other. Each of the three host molecules contain a crystallographic mirror plane passing through C(1) and C(10). Each molecule has two major planes of atoms, one which includes atoms C(1) through C(10) and the other which contains C(1), C(10) and the mirrored atoms C(2a) through C(9a). The average deviations of an atom from these planes in the three molecules are about the same (see Table VI). The hinge angles (dihedral angles) between the major planes in each complex are also similar, ranging from 136.4° to 139.9°. Comparison of these hinge angles with data reported for uncomplexed dibenzo-14-crown-4 [28] reveals that the hinge angles for the alcohols are about 15° greater than that of the similar angle for the parent compound.

The disorder of **1** contributes to the structural similarity of **1** and **2**. In the case of the relationship between **2** and **3** and the similarity of the intermolecular hydrogen bonding, the packing of the molecules must be considered. Clearly the positions of the O(11)—H(11) alcohol groups are different in the respective structures, but there is sufficient space in each crystal lattice for an intermolecular hydrogen bond to exist involving the O(11) alcohol and the water oxygen atom of another complex which has the same symmetry translation in the two structures whether this alcohol group is pseudoaxial (in **2**) or pseudoequatorial (in **3**). This is illustrated in Figures 5 and 6.

In all three complexes, hydrogen atoms of the guest water molecule form weak hydrogen bonds with the ether oxygens of the crown ether host. In all cases, except in the case of H(13B) in **2** these hydrogen bonds are bifurcated, interacting with both O(1) and O(2) in the respective host molecules. The hydrogen bond involving H(13B) is weak (see Table VI). Distances from the oxygen atom of the guest water molecule to the plane of the four ether oxygen atoms of the hosts in **1**, **2**, and **3** are 2.36, 2.25 and 2.24 Å, respectively. It is interesting to compare these host–guest distances with those reported for the cationic guest Li^+ in 1 : 1 complexes of LiSCN with *sym*-hydroxydibenzo-14-crown-4 and *sym-trans*-dihydroxy-dibenzo-14-crown-4 [29]. In the two crystallographically non-equivalent complexes of the former with LiNCS, the distances from the Li^+ to the plane of the four ether oxygen atoms in the respective complexes are 0.68 and 0.71 Å and for the LiSCN complex with the latter the distance is 0.70 Å. Even accounting for the necessity of having the hydrogen atoms of the neutral guest molecule between the water oxygen atom and the polyether oxygen atoms in **1** and **3**, the cationic guest is significantly closer to the dibenzo-14-crown-4 unit of the host than is the neutral guest.

In previous work [10], we reported the crystal and molecular structure of a complex of *sym*-hydroxydibenzo-14-crown-4 with water and methanol molecules ($[C_{18}H_{20}O_5]\cdot 1.25[H_2O]\cdot 0.125[CH_3OH]$). In the crystals, which were grown from a CH_2Cl_2–CH_3OH–H_2O (10/9/1 v/v) solution, one water molecule forms a 1 : 1 monohydrate complex with the crown ether alcohol in which the water oxygen is hydrogen bonded to the crown ether hydroxyl group. Four monohydrate complexes are hydrogen bonded to a single central water molecule in a tetrahedral geometry which is required by the space group. In addition, each complex is hydrogen bonded to an apical methanol molecule. Unusual water–methanol channels were found in the structure. In contrast, when *sym*-hydoxydibenzo-14-crown-4 was crystallized from acetonitrile–water (9/1, v/v) in this study, only the 1 : 1 monohydrate complex **1** with no intercomplex interactions was noted. The intermolecular hydrogen bond present in **2** and **3** causes the formation of continuous zig-zag strings of molecules (see Figures 5 and 6) rather than a three-dimensional network of molecules.

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