screw diad and forms a molecular complex having the open-type helical structure around the screw diad.

The authors wish to express their thanks to Drs Y. Takagi, O. Kawashima, T. Tsuchiya, H. Sano and Professor S. Umezawa of the Institute of Bioorganic Chemistry, for supplying a sample of the complex and for valuable advice. They are also grateful to Professor Hamao Umezawa, Director of the Institute of Microbial Chemistry, for his interest in this study and his encouragement.

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A Host–Guest-Type Water Adduct of 3,3'-(1,1'-Bi-2-naphthol)-21-crown-5*

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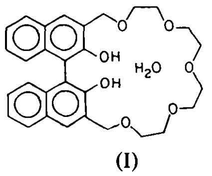
Abstract. $C_{30}H_{32}O_7.H_2O$, M_r = 522·6, monoclinic, $P2_1/c$, a = 12·334 (3), b = 10·638 (2), c = 21·704 (4) Å, β = 110·81 (2)°, V = 2662·0 Å^3, Z = 4, D_x = 1·304 g cm^{-3}. The structure was solved by direct and Fourier methods, and refined by block-diagonal least squares with 2640 observations to R = 0·065. The component species in the crystal associate *via* hydrogen-bonding interactions; the H_2O molecule, too small to fit into the macrocyclic cavity, is preferentially coordinated to some of the O atom sites of the ligand. That part of the ring which is not involved in specific interactions with the guest molecule exhibits an irregular conformation and is probably disordered.

Introduction. In a recent communication Koenig, Helgeson & Cram (1976) report the synthesis and binding characteristics of macrocyclic polyethers containing phenolic ether groups. They also indicate that incorporation of phenolic substituents into crown ether rings may have a potential influence on the ligand-binding capability. As part of our systematic investigation of ligand–substrate interactions within inclusion compounds, it was of interest to study the nature of the association between ligand (I) and water, and to describe the conformational features of the complexed host molecule. Coordination of H_2O molecules to cyclic polyethers has been previously observed by other workers but not described in sufficient detail (Cradwick & Poonia, 1977; Hughes & Wingfield, 1977).



(I)

Crystals of the title compound were kindly supplied by Professor Cram of the University of California at Los Angeles.

Intensity data were collected on a four-circle diffractometer (Syntex $P\bar{1}$) with graphite-crystal-monochromatized Cu $K\alpha$ radiation (λ_{mean} = 1·5418 Å). 3159 unique reflections within $0 < 2\theta \leq 113°$ ($\sin\theta/\lambda \leq 0·54$ Å^{-1}) were measured by the θ–2θ scan technique at a constant scan rate (2° min^{-1}). Each of the three standard reflections $12\bar{6}$, 212 and 031 that were recorded after every fiftieth measurement suffered, however, about 30% loss of intensity (in total) during data collection. The data processing was carried out in the usual manner, and included renormalization of the intensities to account for the marked deterioration of the crystal. The structure was solved by a combination of direct methods (*MULTAN*) and Fourier techniques, and refined by least-squares analysis. The H atoms were introduced in calculated positions except for those of the phenolic groups and the H_2O molecule which were located from a difference Fourier synthesis. The H atom parameters, including isotropic U = 0·05 Å^2, were held constant during refinement. The atomic scattering factors for C and O were those of Hanson, Herman, Lea & Skillman (1964) and for H those given by Stewart, Davidson & Simpson (1965).

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* Structure and Binding in Molecular Complexes of Cyclic Polyethers. V.

Table 1. *Atomic fractional coordinates*

	x	*y*	*z*
O(1)	.0871(2)	.1499(3)	.9808(1)
C(2)	.1522(3)	.1788(3)	.9432(2)
C(3)	.2498(3)	.2551(3)	.9652(1)
C(4)	.3088(3)	.2845(3)	.9211(2)
C(5)	.4056(3)	.3668(4)	.9392(2)
C(6)	.4578(3)	.3971(4)	.8951(2)
C(7)	.4189(4)	.3454(5)	.8314(2)
C(8)	.3278(3)	.2637(4)	.8130(2)
C(9)	.2702(3)	.2312(3)	.8568(2)
C(10)	.1751(3)	.1471(4)	.8387(2)
C(11)	.1158(3)	.1213(3)	.8800(2)
C(12)	.0132(4)	.0337(4)	.8593(2)
O(13)	-.0882(2)	.1068(3)	.8271(1)
C(14)	-.1925(4)	.0364(5)	.8019(3)
C(15)	-.2470(5)	.0032(6)	.8512(3)
O(16)	-.2847(3)	.1117(4)	.8756(2)
C(17)	-.2163(6)	.1295(6)	.9414(3)
C(18)	-.2851(5)	.2061(7)	.9722(3)
O(19)	-.2118(3)	.2411(3)	1.0364(2)
C(20)	-.2754(4)	.3254(5)	1.0607(3)
C(21)	-.1983(4)	.3787(5)	1.1249(2)
O(22)	-.1147(2)	.4598(3)	1.1139(1)
C(23)	-.0443(4)	.5197(5)	1.1729(2)
C(24)	.0567(4)	.5821(4)	1.1629(2)
O(25)	.1345(2)	.4863(2)	1.1579(1)
C(26)	.2331(4)	.5398(4)	1.1466(2)
C(27)	.2933(3)	.4358(4)	1.1245(2)
C(28)	.3895(3)	.3760(4)	1.1672(2)
C(29)	.4443(3)	.2767(4)	1.1468(2)
C(30)	.5448(3)	.2153(5)	1.1907(2)
C(31)	.5937(4)	.1162(5)	1.1700(2)
C(32)	.5444(4)	.0720(5)	1.1051(2)
C(33)	.4491(3)	.1308(4)	1.0611(2)
C(34)	.3963(3)	.2350(4)	1.0799(2)
C(35)	.2975(3)	.2980(3)	1.0351(2)
C(36)	.2494(3)	.3971(3)	1.0569(2)
O(37)	.1562(2)	.4645(2)	1.0172(1)
O(38)	.0453(3)	.2566(3)	1.0823(2)
H(1)	.1010	.2176	1.0148
H(37)	.1410	.4630	.9687
H(38A)	.0672	.3313	1.1085
H(38B)	-.0354	.2516	1.0715

Several aspects of the least-squares refinement, such as slow convergence and appearance of peaks whose heights ranged from 0·3 to 0·5 e Å^{-3} on difference Fourier maps, indicated that the molecular structure is partly disordered. Moreover, the refined thermal parameters of C(15), O(16), C(17) and C(18) had rather large values and corresponded to equivalent isotropic vibrations of nearly 0·10 Å^2. In order to avoid unreliable distortion of the molecular geometry caused by the assumedly artificial effect of thermal motion, the bond lengths C(14)—C(15) and C(17)—C(18) were constrained to 1·494 ± 0·003 Å (the average length of the other three C—C ring bonds) in the final computations. With these constraints, the final refinement of the non-hydrogen atom coordinates and anisotropic temperature factors converged at $R = 0{\cdot}065$. The value of $[\sum w(\Delta F)^2/(n-m)]^{1/2}$ was 1·37 for $m = 343$ and $n = 2640$ observations above threshold $[F^2 \geq 3\sigma(F^2)]$. Table 1 lists the coordinates of all C and O atoms; several H atoms whose positions are relevant to the following discussion are also included.*

Discussion. The present structure provides an excellent example of the most common features of molecular conformation occurring in macrocyclic polyether species. The water molecule is too small to fit into the ligand cavity and occupies only a part of it (Fig. 1). Within this part, the component moieties of the structure are held together by an extensive array of hydrogen bonds, the geometrical parameters of which are: O(38)···O(19) 2·97, H(38*b*)···O(19) 2·0 Å and O(38)—H(38*b*)···O(19) 173°; O(38)···O(25) 2·93, H(38*a*)···O(25) 2·0 Å and O(38)—H(38*a*)···O(25) 171°; O(1)···O(38) 2·69, H(1)···O(38) 1·9 Å and O(1)—H(1)···O(38) 136°. Less important is the direct O(38)···O(22) interaction of 3·18 Å. As a result, the interacting fragment of the aliphatic ring, O(19) through C(26), has an energetically favorable conformation that corresponds to synclinal torsion angles

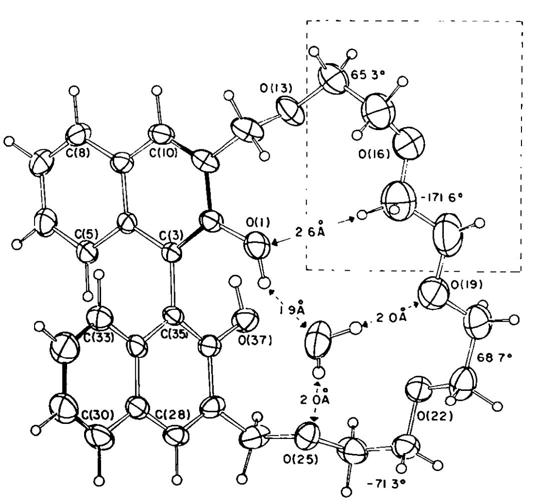

Fig. 1. View of the molecular structure showing 40% probability thermal ellipsoids and the intracomplex hydrogen bonding. The marked frame encloses the conformationally disordered part of the molecule.

Table 2. *Torsion angles* (°)

C(2)—C(11)—C(12)—O(13)	90·5 (4)
C(11)—C(12)—O(13)—C(14)	177·4 (4)
C(12)—O(13)—C(14)—C(15)	81·6 (5)
O(13)—C(14)—C(15)—O(16)	64·9 (5)
C(14)—C(15)—O(16)—C(17)	−111·2 (5)
C(15)—O(16)—C(17)—C(18)	−156·7 (6)
O(16)—C(17)—C(18)—O(19)	−171·6 (5)
C(17)—C(18)—O(19)—C(20)	173·0 (5)
C(18)—O(19)—C(20)—C(21)	−172·9 (5)
O(19)—C(20)—C(21)—O(22)	68·9 (5)
C(20)—C(21)—O(22)—C(23)	176·0 (4)
C(21)—O(22)—C(23)—C(24)	168·3 (4)
O(22)—C(23)—C(24)—O(25)	−71·5 (4)
C(23)—C(24)—O(25)—C(26)	178·6 (3)
C(24)—O(25)—C(26)—C(27)	−165·4 (3)
O(25)—C(26)—C(27)—C(36)	81·5 (4)

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* Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33643 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å)

O(1) - C(2)	1.368(5)	C(21) - O(22)	1.429(6)
C(2) - C(3)	1.388(4)	O(22) - C(23)	1.418(5)
C(2) - C(11)	1.421(5)	C(23) - C(24)	1.494(7)
C(3) - C(35)	1.491(4)	C(24) - O(25)	1.431(6)
C(3) - C(4)	1.426(5)	O(25) - C(26)	1.441(6)
C(4) - C(5)	1.420(5)	C(26) - C(27)	1.502(6)
C(4) - C(9)	1.422(5)	C(27) - C(28)	1.375(5)
C(5) - C(6)	1.368(6)	C(27) - C(36)	1.432(5)
C(6) - C(7)	1.406(6)	C(28) - C(29)	1.407(6)
C(7) - C(8)	1.364(6)	C(29) - C(30)	1.426(5)
C(8) - C(9)	1.416(6)	C(29) - C(34)	1.430(5)
C(9) - C(10)	1.415(5)	C(30) - C(31)	1.367(7)
C(10) - C(11)	1.372(6)	C(31) - C(32)	1.402(6)
C(11) - C(12)	1.506(5)	C(32) - C(33)	1.374(5)
C(12) - O(13)	1.427(5)	C(33) - C(34)	1.418(6)
O(13) - C(14)	1.419(6)	C(34) - C(35)	1.428(4)
C(14) - C(15)	1.493	C(35) - C(36)	1.373(5)
C(15) - O(16)	1.416(8)	C(36) - O(37)	1.369(4)
O(16) - C(17)	1.389(7)	O(1) - H(1)	1.00
C(17) - C(18)	1.495	O(37) - H(37)	1.00
C(18) - O(19)	1.416(7)	O(38) - H(38A)	.96
O(19) - C(20)	1.410(7)	O(38) - H(38B)	.94
C(20) - C(21)	1.492(6)		

Table 4. *Bond angles* (°)

O(1)-C(2)-C(3)	123.3(3)	C(20)-C(21)-O(22)	109.4(4)
O(1)-C(2)-C(11)	115.3(3)	C(21)-O(22)-C(23)	111.5(3)
C(3)-C(2)-C(11)	121.4(4)	O(22)-C(23)-C(24)	110.0(4)
C(2)-C(3)-C(4)	119.0(3)	C(23)-C(24)-O(25)	108.1(4)
C(2)-C(3)-C(35)	120.6(3)	C(24)-O(25)-C(26)	111.2(3)
C(35)-C(3)-C(4)	120.3(3)	O(25)-C(26)-C(27)	107.8(3)
C(3)-C(4)-C(9)	119.8(3)	C(26)-C(27)-C(36)	119.2(3)
C(5)-C(4)-C(9)	118.2(3)	C(28)-C(27)-C(36)	118.6(4)
C(4)-C(5)-C(6)	120.7(3)	C(27)-C(28)-C(29)	122.1(3)
C(5)-C(6)-C(7)	121.0(4)	C(28)-C(29)-C(34)	118.7(3)
C(6)-C(7)-C(8)	119.6(4)	C(30)-C(29)-C(34)	119.0(4)
C(7)-C(8)-C(9)	121.2(4)	C(29)-C(30)-C(31)	120.9(3)
C(8)-C(9)-C(4)	119.2(3)	C(30)-C(31)-C(32)	120.3(4)
C(4)-C(9)-C(10)	118.7(4)	C(31)-C(32)-C(33)	120.4(5)
C(9)-C(10)-C(11)	121.8(3)	C(32)-C(33)-C(34)	121.5(4)
C(10)-C(11)-C(2)	119.0(3)	C(33)-C(34)-C(29)	117.9(3)
C(2)-C(11)-C(12)	119.9(4)	C(29)-C(34)-C(35)	119.4(3)
C(11)-C(12)-O(13)	107.8(3)	C(34)-C(35)-C(36)	119.6(3)
C(12)-O(13)-C(14)	114.7(3)	C(34)-C(35)-C(3)	118.8(3)
O(13)-C(14)-C(15)	115.3(4)	C(3)-C(35)-C(36)	121.5(3)
C(14)-C(15)-O(16)	111.5(5)	C(35)-C(36)-C(27)	121.4(3)
C(15)-O(16)-C(17)	109.6(4)	C(35)-C(36)-O(37)	123.6(3)
O(16)-C(17)-C(18)	107.5(5)	C(27)-C(36)-O(37)	114.9(3)
C(17)-C(18)-O(19)	108.6(5)	H(1)-O(1)-C(2)	107
C(18)-O(19)-C(20)	106.8(4)	H(37)-O(37)-C(36)	117
O(19)-C(20)-C(21)	109.6(4)	H(38A)-O(38)-H(38B)	104

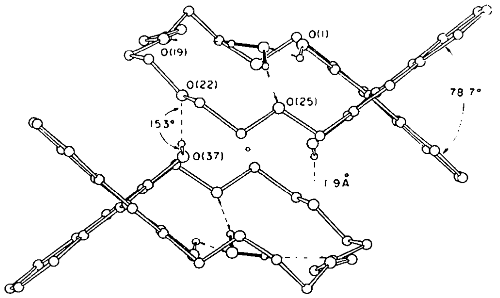

Fig. 2. Illustration of the pairing interaction between two adduct units located across the $0,\frac{1}{2},0$ or $0,0,\frac{1}{2}$ centers of inversion.

about the C—C bonds (the observed values are 69 and 71°) and antiplanar torsion angles about the C—O bonds (the observed values range from 166 to 179°; Table 2). Similar regular geometries have been found in the crystal structures of various complexed crown ethers (*e.g.* Dunitz, Dobler, Seiler & Phizackerley, 1974; Goldberg, 1977).

The empty part of the ligand exhibits a markedly distorted conformation. This is reflected mainly in an antiplanar arrangement of the O—C(17)—C(18)—O group (torsion angle 172°) associated with the formation of a relatively short transannular C(17)—H··· O(1) contact (Fig. 1); comparable features of the molecular structure are also characteristic of uncomplexed 18-crown-6 (Dunitz & Seiler, 1974) and tetramethyldibenzo-18-crown-6 (Mallinson, 1975): crystalline compounds which seem to be stabilized by intramolecular C—H···O dipolar attractions. Furthermore, the irregular pattern of the ligand conformation with C—O—C—C torsion angles having magnitudes in the range 82–157°, intermediate between *gauche* and *trans* geometries, is confined (expectedly) to the disordered fragment of the molecule (Fig. 1).

The overall shape of the aromatic substituent is almost identical to that found in the structure of the binaphthylbis(18-crown-6) ligand (Goldberg, 1977), the dihedral angles between the two planar rings of the respective 2,2′,3,3′-substituted 1,1′-binaphthyl units being 78·7 and 77·6°. The covalent-bond parameters of the two compounds are very similar, and they are also in good agreement with the average values of the corresponding parameters in previously reported polyether-containing structures. The bond lengths and angles along with their estimated standard deviations are given in Tables 3 and 4.

The crystal structure is composed of centrosymmetrically related dimeric units of the complex. The pairing interaction involves hydrogen bonding between the O(37) hydroxyl group and O(22) of the macro-ring (Fig. 2). In spite of the fact that all O—H electrophilic groups participate in hydrogen bonds, the lack of specific inter- or intramolecular forces acting on the O(13) and O(16) nucleophilic sites is probably the cause of the conformational disorder in this structure.

The author wishes to thank Professor D. J. Cram for providing the crystals, Dr J. Bernstein for making his diffractometer available to him and Mrs I. Bar for her assistance.

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Structures of Substituted Oxadiazoles: 3-(*p*-Aminophenyl)-5-phenyl-1,2,4-oxadiazole

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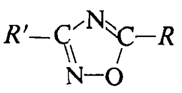
Abstract. $C_{14}H_{11}N_3O$, M_r = 238·27, monoclinic, $P2_1/c$, Z = 4, a = 7·348 (2), b = 12·687 (3), c = 13·383 (3) Å, β = 105·56 (6)° (from a least-squares refinement of 2θ values of 20 reflections), V = 1201·89 Å^3, D_x = 1·32, D_m = 1·31 (3) g cm^{-3}. The two phenyl rings are slightly twisted out of the plane of the oxadiazole ring in opposite directions.

Introduction. Recently, a systematic mass spectrometric study of a series of 3,5-diaryl-1,2,4-oxadiazoles (I) (Selva, Traldi, Zerilli, Cavalleri & Gallo, 1974; Selva, Traldi, Zerilli & Gallo, 1978) has been carried out to elucidate the effect of substitution on the mechanism of fragmentation of these compounds. For example, for 3,5-diphenyl-1,2,4-oxadiazole (II) a stepwise *retro* 1,3-dipolar cycloaddition has been proposed (Selva, Traldi, Zerilli & Gallo, 1976) on the basis of kinetics arguments and CNDO/2 calculations (Selva, Traldi & Fantucci, 1976). In order to test the possible extension of these arguments to other substituted oxadiazoles their detailed geometries have to be known; therefore, as part of a systematic study, we have determined the molecular structure of the title compound (III).



$R = R' = C_6H_5$ (II)

$R = C_6H_5$; $R' = C_6H_4NH_2$ (III)

(I)

A crystal of approximate dimensions 0·25 × 0·20 × 0·15 mm was obtained by slow evaporation from a methanol/*n*-hexane mixture.

The intensities of 2801 reflections were collected up to 2θ = 50° (graphite-monochromated Mo $K\alpha$ radiation) with a Philips automated four-circle diffractometer using an $\omega/2\theta$ scan technique (scan speed 0·04° s^{-1}, scan range 1·1°). For each reflection, two background counts (11 s at each side of the peak) were averaged; three standard reflections, every 60,

Table 1. *Final positional parameters* (×10^4, *for* H ×10^3)

The e.s.d.'s are given in parentheses and refer to the last significant figures.

	x	y	z	B_{iso} (Å^2)
C(1)	4141 (2)	8914 (1)	8517 (2)	
C(2)	4401 (2)	8657 (1)	9564 (1)	
C(3)	5244 (2)	7723 (1)	9956 (1)	
C(4)	5877 (2)	7014 (1)	9333 (1)	
C(5)	5638 (2)	7280 (1)	8292 (1)	
C(6)	4803 (2)	8214 (1)	7894 (1)	
C(7)	6754 (2)	6019 (1)	9772 (1)	
C(8)	7844 (2)	4850 (1)	10875 (1)	
C(9)	8525 (2)	4204 (1)	11809 (2)	
C(10)	8262 (3)	4568 (1)	12735 (1)	
C(11)	8905 (3)	3969 (2)	13631 (1)	
C(12)	9784 (3)	3016 (2)	13592 (2)	
C(13)	10046 (3)	2659 (2)	12676 (2)	
C(14)	9406 (2)	3249 (1)	11777 (1)	
N(1)	7080 (2)	5777 (1)	10811 (1)	
N(2)	7277 (2)	5285 (1)	9224 (1)	
N(3)	3290 (2)	9844 (1)	8118 (1)	
O	8020 (3)	4485 (1)	9968 (1)	
H(C2)	396 (3)	914 (1)	1001 (1)	6·2 (5)
H(C3)	534 (2)	757 (1)	1064 (1)	3·9 (3)
H(C5)	607 (2)	679 (1)	786 (1)	4·8 (4)
H(C6)	470 (2)	838 (1)	718 (1)	4·2 (4)
H(C10)	762 (2)	522 (1)	1275 (1)	5·6 (4)
H(C11)	878 (3)	426 (1)	1428 (1)	6·2 (5)
H(C12)	1031 (3)	260 (2)	1424 (2)	8·5 (6)
H(C13)	1065 (3)	198 (1)	1264 (2)	6·8 (5)
H(C14)	951 (2)	300 (1)	1109 (1)	5·8 (5)
H(N3)	300 (2)	994 (1)	742 (1)	5·7 (4)
H′(N3)	278 (3)	1025 (1)	851 (2)	6·5 (5)