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Binding Neutral Guests to Concave Surfaces of Molecular Hosts. Directional Association of Water and Methylene Chloride with Hosts Containing Only Cyclic Urea Binding Sites

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Abstract. This paper is concerned with studies of weak intermolecular interactions in molecular inclusion type systems involving uncharged host and guest entities. Three new complexes of synthetic organic ligands with water and methylene chloride have been characterized by single-crystal X-ray diffraction. The hosts are composed of three cyclic urea units whose carbonyl groups are held in convergent positions by bonding their attached nitrogens to one another through two (noncyclic ligand) or three (macrocyclic ligand) rigid spacer units. Conformational organization is further enforced by an aliphatic bridge between two of the phenylene spacers in the macrocyclic hosts and an additional dimerization of the open-chain ligand. The host species were found to be particularly suitable to interact with proton donating H_2O and CH_2Cl_2 guest moieties, as their molecular surface contains appropriately sized polar cavities lined with the carbonyl functions. Association between the interacting components in these complexes is stabilized by O—H···O and C—H···O hydrogen bonds. In the corresponding crystal structures additional molecules of the solvent are located between units of the complex. The significance of preorganization of the host structure to an efficient guest binding is emphasized by an observation that no stable complexes of a similar but unbridged macrocyclic ligand could be crystallized from the same solvent. The structural features of the inclusion compounds are described in detail, and the host–guest interaction scheme is compared to that observed in complexes of 18-crown-6 with neutral guests.

Key words: Molecular inclusion of uncharged guests, weak interactions in host–guest complexes, hosts with cyclic urea binding sites.

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1. Introduction

During recent years host–guest chemistry has provided a large number of useful synthetic molecular models for the study of recognition and separation processes that occur in nature. Most extensively investigated were macro(poly)cyclic hosts of the crown/cryptate type (along with their open chain analogues) which turned out to be excellent and often selective

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complexors of metal ions and amino acid derivatives [1–4]. The presence of O and/or N heteroatoms in these macrocycles made them also suitable for an effective complexation through hydrogen bonding with uncharged guest molecules containing proton donating sites such as acidic CH, NH or OH [5, 6]. Least studied systematically were systems which involve encapsulation of apolar guests within apolar host molecules. Such complexes are more difficult to form in solution since only van der Waals interactions, usually too weak to compensate for desolvation, can contribute to their stability.

In a previous publication a rigid structural model for complexation between two lipophilic entities characterized by complementary surfaces has been described [7]. This model is based on ligands containing preorganized (during synthesis) cavities which do not collapse in solution but rather admit suitable solvent/guest species [8]. In this article we present some structural results of complexation studies between uncharged but polar species. While complexes of similar type with the crown-ether ligands are already known [5, 6], the

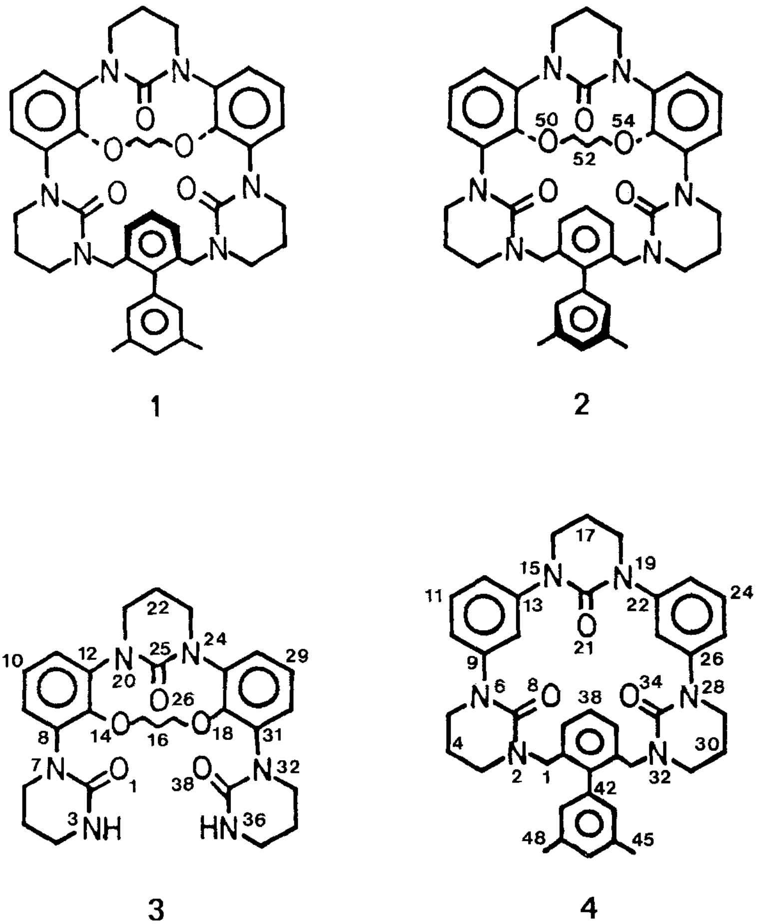

Fig. 1. Molecular formulae of the ligands **1–4**, showing the atom numbering. Atom numbering in the molecular framework of ligands **1** and **2** is the same as that of ligand **4**. In compound **I**, atoms in the second ligand of the asymmetric unit are denoted by an asterisks. Ligand **3** forms a dimer, and atoms in the second half of the dimer are numbered in the same sequence from 39 to 76.

compounds studied here involve a series of new hosts **1–4** which contain only cyclic urea binding sites (Figure 1). These hosts were designed by Prof. D. J. Cram and coworkers as part of an extensive research program on host–guest complexation; their syntheses will be reported elsewhere [9].

The cyclic urea unit has been used effectively as ring components in the syntheses of a variety of hemispherands and spherands, exhibiting a dominant contribution to the binding ability of these hosts toward metal and ammonium ions [10, 11]. In a typical structure three cyclic urea units are bound to one another in a triangular arrangement through phenylene spacer units. The carbonyl groups are held in convergent positions with their unshared electron pairs directed towards the centered guest moiety. The complexes formed are thus stabilized mainly either by pole-dipole interactions with the metal cations, or by tripod hydrogen bonding with alkylammonium ions.

Evidently, host–guest type complexes with uncharged guests can also be formed in spite of the fact that much weaker forces determine their structures. The two bridged macrocycles **1** and **2** are isomers with preorganized configurations as opposed to their unbridged analog **4** (Figure 1). The terminal rings in the noncyclic ligand **3** provide additional sites for H-bonding. At the first stage methylene chloride and water molecules from the solvent mixture served as potential guest species. These guests contain only two slightly acidic protons; their geometrically optimized association with either one of the hosts requires, therefore, a cavity lined with at least two carbonyl acceptors. In the current investigation we were able to obtain the following crystalline compounds, and analyze their detailed structures:

I. $C_{43}H_{46}N_6O_5$ (**1**) + $2H_2O$; **II.** $C_{43}H_{46}N_6O_5$ (**2**) + CH_2Cl_2 + H_2O;
III. $2[C_{27}H_{32}N_6O_5$ (**3**)$]$ + $2CH_2Cl_2$ + $1.6H_2O$; **IV.** $C_{40}H_{42}N_6O_3$ (**4**).

The geometry of interaction between H_2O and CH_2Cl_2 guests and the corresponding hosts **1–3** is described; the structural results are compared with those available for related systems. The nonbridged and conformationally more flexible ligand **4** crystallized as an uncomplexed species.

2. Experimental

Single crystals suitable for the crystallographic study were obtained from CH_2Cl_2/Et_2O and CH_2Cl_2/Et_2O/THF wet solution mixtures.

Diffraction data were measured at low temperature on an upgraded Picker (**I–III**) and Syntex $P\bar{1}$ (**IV**) diffractometers equipped with a graphite monochromator, employing either Mo$K\alpha$ or Cu$K\alpha$ radiation and an $\omega-2\theta$ scan technique. The cell constants and pertinent details of the experimental conditions are summarized in Table I. Measurements at low-temperatures were needed mainly to minimize the effects of thermal disorder (see below). Possible deterioration of the analyzed crystals was tested by detecting frequently the intensities of standard reflections, and was found negligible during the measurements. The data sets were not corrected for absorption and secondary extinction effects. Final refinements were based only on those observations that satisfied the condition $F_o^2 > 3\sigma(F_o^2)$.

The structures were solved by a combination of direct methods and Fourier techniques (MULTAN80, [12]). Their refinements were carried out by large block (**II–IV**) and block-diagonal (**I**) least-squares, including the positional and anisotropic thermal parameters of all the nonhydrogen atoms [13]. Most hydrogens were introduced into the structure-factor computations in calculated positions; those involved in hydrogen bonds were located directly

Table I. Summary of Crystal Data and Experimental Parameters

Compound	I	II	III	IV
Mol wt	762.9	829.8	1239.9	654.8
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/c$
Z	4	8	4	4
a, Å	13.070(3)	32.214(5)	17.560(3)	13.562(4)
b, Å	14.956(4)	11.276(2)	16.687(3)	13.573(3)
c, Å	20.803(3)	25.406(4)	20.499(3)	19.853(6)
α, deg	71.15(2)	90.0	90.0	90.0
β, deg	80.95(3)	115.70(1)	93.73(4)	114.80(2)
γ, deg	88.99(4)	90.0	90.0	90.0
V, Å^3	3798.1	8315.7	5994.0	3317.5
d_c, g·cm^{-3}	1.334	1.326	1.374	1.311
λ, Å	0.7107	0.7107	0.7107	1.5418
μ, cm^{-1}	0.86	2.08	2.65	6.35
Crystal size, mm	0.4 × 0.2 × 0.1	0.5 × 0.4 × 0.2	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.2
Temperature, K	128	128	128	115
2θ limits, deg	50	50	50	150
No. of unique data	6990	5795	8226	5000
Data with $I > 3\sigma_I$	4750	3624	5361	4559
$F(000)$, e	1624	3504	2608	1392
R	0.066	0.070	0.090	0.062
R_w	0.076	0.073	0.090	0.081
GOF, e	2.03	1.19	4.00	1.30

in difference-Fourier maps. One H of $H_2O(4)$ in **I**, and hydrogens of the disordered CH_2Cl_2 and fractional H_2O in **III** could not be located. Least-squares calculations were based on the experimental weights [$w = 1/\sigma^2(F_o)$] in **I**, **II** and **IV**, and on unit weights in **III**, the quantity minimized being $w(\Delta F)^2$.

Structures **I** and **IV** turned out to be perfectly ordered. In complex **II** the CH_2Cl_2 molecule which is not bound directly to the host exhibits a slight disorder; it is well reflected in the relatively large parameters of thermal motion characterizing the individual atoms. Most problematic was the refinement of compound **III**, in which the ligand molecule forms hydrogen-bonded dimers. Atoms C(5) and C(72) of two peripheral cyclic urea rings in the ligand-dimer have particularly high amplitudes of thermal vibrations, possibly indicating a dynamic conformational inversion of the rings. Positions of the perching H_2O and CH_2Cl_2 guests are well defined. However, the second molecule of CH_2Cl_2 which lies close to the bound water is orientationally disordered. This disorder was approximated in the refinement by two possible orientations with occupancies of 0.70(1) (atoms Cl(82) and Cl(83)) and 0.30 (Cl(86) and Cl(87)). Two additional significant peaks appeared on difference-Fourier maps at final stages of the refinement. The first one is believed to represent an oxygen atom of a second water molecule, which in the subsequent refinement showed only partial occupancy of 0.62(1). The second peak represents a methyl substituent on atom C(28) with a refined occupancy of 0.31(1); it most probably originated from an impure mixture of starting materials, a suspicion confirmed by reinspection of MS spectra after the crystal structure analysis was completed.

In an effort to improve the results, two additional crystallization attempts of compound **III** were made from solvent mixtures of different composition. Analyses of the corresponding intensity data sets led, however, to similar results. They showed isomorphous structures which in addition to the H_2O and CH_2Cl_2 host–bound guests contained a disordered molecule of CH_2Cl_2 or THF, mol-fraction of water (O(85)) and the methyl substituent (C(84)) with minor occupancy. The data given in this paper represent the best structural model that could be obtained from the least-squares refinements of the three independent data sets. The final difference Fourier maps showed no indication of incorrectly placed or missing atoms; several relatively high and diffused peaks (< 1 e · Å^{-3}) appeared only in the vicinity of the disordered fragments of structures **II** and **III**.

3. Results

Final atomic coordinates of the four compounds are listed in Tables II–V; lists of anisotropic thermal parameters and H-atom coordinates have been deposited. The covalent bond lengths and bond angles obtained for the various molecules exhibit no extraordinary features. The conformational and configurational details of the corresponding ligands will be, however, emphasized in the discussion that follows, as they have a direct influence on the geometry of host–guest interaction.

Compound I. The asymmetric unit of this structure contains two molecules of the ligand and four molecules of water. They compose two slightly different host–guest complexes, as illustrated in Figure 2. The macrocyclic ligand has a preorganized configuration in which the aliphatic O—$(CH_2)_3$—O bridge and the dimethyl-substituted part of the biphenylene spacer lie on the same side of the ligand. In both molecules at least one of the methylenes and one of the methyls turn inward, shielding the lower convex face of the host by hydrocarbon groups. The three carbonyls are tilted toward the upper side of the macroring, and provide an effective receptor site for proton-donating guests. In previous examples such a converging arrangement was found to be well suited for the formation of a tripod of hydrogen bonds with a single alkylammonium ion [11]. However, in the presence of smaller and uncharged guests the same space on the molecular surface, divided into smaller sites between the centered cyclic urea oxygen (O(21)) and either one of the flanking ones (O(8) and O(34)), can be occupied by more than one species. In fact, in complex (a) of this structure two water molecules $H_2O(2)$ and $H_2O(3)$ are located within these sites (Figure 2), each H_2O hydrogen bonding in a 'dipode' fashion to two adjacent carbonyls of the host. All binding sites are ideally arranged for an optimized interaction of this type: the guest molecules lie in a perching position 1.57 and 1.68Å above the plane of the three carbonyl O's, and form nearly linear hydrogen bonds to them. Geometric details of all H-bonding interactions are given in Table VI. In complex (b) only one molecule of water $H_2O(1)$ is directly associated with the ligand (between O(8)* and O(21)*) through hydrogen bonds in a similar manner. The second part of the cavity remained empty. The $H_2O(4)$ molecule is located in the crystal between the two complexes, interacting from outside with the free carbonyl O(34)* of complex (b) as well as with the bound $H_2O(3)$ of complex (a) (Figure 3).

As a result of the asymmetry in host–guest interaction the conformational details of the two ligands are different. Relevant data are summarized in Table VII. They show that in complex (b) the torsion angles about bonds connecting the cyclic urea units to the phenylene spacers and about bonds in the aliphatic bridge deviate significantly from the symmetric sequence (with respect to the centered urea ring) observed in complex (a). Correspondingly, the O···O distances between carbonyls in the occupied sites are markedly shorter than those in the guest-free site: O(8)···O(21) = 4.43, O(21)···O(34) = 4.68, O(8)*···O(21)* = 4.37 and O(21)*···O(34)* = 4.98 Å. Other structural differences between the two hosts, including

Table II. Atomic coordinates and isotropic thermal parameters of **I**. $U_{eq.}$ is one third of the trace of the orthogonalized $\mathbf{U}^{ij}$ tensor. OW(*i*) and HW(*i*) denote atoms of the guest molecules of water.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{eq.}$
C(1)	-0.2594(5)	0.1778(5)	0.7142(3)	0.0285(31)
N(2)	-0.2179(4)	0.1266(4)	0.6665(2)	0.0278(25)
C(3)	-0.2922(5)	0.0610(5)	0.6571(3)	0.0308(30)
C(4)	-0.2537(5)	0.0291(5)	0.5954(3)	0.0308(31)
C(5)	-0.1368(5)	0.0193(5)	0.5880(3)	0.0342(34)
N(6)	-0.0905(4)	0.1128(4)	0.5788(2)	0.0268(25)
C(7)	-0.1317(5)	0.1642(5)	0.6198(3)	0.0274(32)
O(8)	-0.0900(3)	0.2402(3)	0.6161(2)	0.0295(21)
C(9)	0.0106(5)	0.1396(5)	0.5403(3)	0.0272(34)
C(10)	0.0237(5)	0.2051(5)	0.4759(3)	0.0326(35)
C(11)	0.1232(5)	0.2366(5)	0.4395(3)	0.0329(30)
C(12)	0.2087(5)	0.2034(5)	0.4710(3)	0.0329(34)
C(13)	0.1981(5)	0.1372(5)	0.5360(3)	0.0283(32)
C(14)	0.0977(5)	0.1011(4)	0.5694(3)	0.0243(30)
N(15)	0.2857(4)	0.1043(3)	0.5686(2)	0.0261(24)
C(16)	0.3706(5)	0.0660(5)	0.5307(3)	0.0296(31)
C(17)	0.4663(5)	0.0559(5)	0.5649(3)	0.0285(31)
C(18)	0.4353(5)	0.0003(5)	0.6398(3)	0.0282(31)
N(19)	0.3565(4)	0.0525(3)	0.6707(2)	0.0243(25)
C(20)	0.2854(5)	0.1063(5)	0.6349(3)	0.0308(32)
O(21)	0.2255(3)	0.1554(3)	0.6589(2)	0.0325(20)
C(22)	0.3434(5)	0.0320(4)	0.7434(3)	0.0267(32)
C(23)	0.4223(5)	0.0577(5)	0.7731(3)	0.0314(34)
C(24)	0.4111(5)	0.0351(5)	0.8438(3)	0.0344(35)
C(25)	0.3195(5)	-0.0087(5)	0.8863(3)	0.0320(32)
C(26)	0.2406(5)	-0.0334(4)	0.8565(3)	0.0272(32)
C(27)	0.2527(5)	-0.0151(5)	0.7855(3)	0.0270(32)
N(28)	0.1427(4)	-0.0673(4)	0.8977(3)	0.0318(27)
C(29)	0.1121(6)	-0.1669(5)	0.9166(4)	0.0397(36)
C(30)	0.0028(6)	-0.1770(5)	0.9066(4)	0.0454(39)
C(31)	-0.0690(5)	-0.1228(5)	0.9434(3)	0.0340(35)
N(32)	-0.0303(4)	-0.0248(4)	0.9236(2)	0.0292(27)
C(33)	0.0729(5)	-0.0009(5)	0.9044(3)	0.0336(38)
O(34)	0.1024(3)	0.0819(3)	0.8942(2)	0.0328(21)
C(35)	-0.1004(5)	0.0487(5)	0.9349(3)	0.0302(34)
C(36)	-0.1168(5)	0.1264(4)	0.8699(3)	0.0262(31)
C(37)	-0.0686(5)	0.2142(5)	0.8554(3)	0.0325(33)
C(38)	-0.0793(5)	0.2878(5)	0.7977(3)	0.0346(34)
C(39)	-0.1389(5)	0.2746(5)	0.7518(3)	0.0292(31)
C(40)	-0.1889(5)	0.1871(5)	0.7631(3)	0.0293(32)
C(41)	-0.1793(5)	0.1132(4)	0.8233(3)	0.0235(31)
C(42)	-0.2315(5)	0.0191(5)	0.8389(3)	0.0291(31)
C(43)	-0.3161(5)	-0.0129(5)	0.8929(3)	0.0315(33)
C(44)	-0.3621(5)	-0.1014(5)	0.9095(3)	0.0356(33)
C(45)	-0.4486(6)	-0.1373(5)	0.9693(4)	0.0440(35)
C(46)	-0.3270(6)	-0.1577(5)	0.8682(4)	0.0395(36)
C(47)	-0.2446(5)	-0.1271(5)	0.8145(3)	0.0322(32)
C(48)	-0.2124(6)	-0.1857(5)	0.7685(4)	0.0404(36)
C(49)	-0.1958(5)	-0.0392(4)	0.8018(3)	0.0280(30)
O(50)	0.0827(3)	0.0297(3)	0.6322(2)	0.0290(21)
C(51)	0.1128(5)	-0.0618(5)	0.6267(3)	0.0304(31)
C(52)	0.1047(5)	-0.1329(5)	0.6984(3)	0.0308(33)

Table II (continued)

Atom	*x/a*	*y/b*	*z/c*	$U_{eq.}$
C(53)	0.1907(5)	−0.1240(5)	0.7367(3)	0.0344(33)
C(54)	0.1728(3)	−0.0401(3)	0.7585(2)	0.0316(21)
C(1)*	0.6599(5)	0.6631(5)	0.7107(3)	0.0280(30)
N(2)*	0.6320(4)	0.6089(3)	0.6674(2)	0.0256(24)
C(3)*	0.6884(6)	0.5220(5)	0.6704(4)	0.0455(37)
C(4)*	0.7010(7)	0.5049(7)	0.6051(5)	0.0700(52)
C(5)*	0.6123(6)	0.5223(6)	0.5685(4)	0.0533(46)
N(6)*	0.5624(4)	0.6087(4)	0.5703(3)	0.0301(25)
C(7)*	0.5743(5)	0.6530(4)	0.6180(3)	0.0246(31)
O(8)*	0.5373(3)	0.7297(3)	0.6140(2)	0.0338(21)
C(9)*	0.4783(5)	0.6374(4)	0.5333(3)	0.0256(29)
C(10)*	0.4938(5)	0.6895(4)	0.4646(3)	0.0263(31)
C(11)*	0.4102(5)	0.7148(5)	0.4293(3)	0.0305(31)
C(12)*	0.3086(5)	0.6892(4)	0.4645(3)	0.0261(31)
C(13)*	0.2920(5)	0.6369(4)	0.5330(3)	0.0219(29)
C(14)*	0.3764(5)	0.6083(5)	0.5673(3)	0.0266(29)
N(15)*	0.1882(4)	0.6094(4)	0.5678(2)	0.0256(27)
C(16)*	0.1278(5)	0.5507(5)	0.5405(3)	0.0317(33)
C(17)*	0.0183(5)	0.5299(5)	0.5781(3)	0.0373(36)
C(18)*	0.0167(5)	0.5011(5)	0.6544(3)	0.0349(33)
N(19)*	0.0670(4)	0.5771(4)	0.6696(2)	0.0271(25)
C(20)*	0.1553(5)	0.6251(5)	0.6292(3)	0.0274(31)
O(21)*	0.2015(3)	0.6824(3)	0.6467(2)	0.0314(22)
C(22)*	0.0466(5)	0.5769(5)	0.7400(3)	0.0288(32)
C(23)*	−0.0312(5)	0.6326(5)	0.7598(3)	0.0387(33)
C(24)*	−0.0470(6)	0.6337(6)	0.8273(3)	0.0452(38)
C(25)*	0.0153(5)	0.5866(5)	0.8726(3)	0.0374(35)
C(26)*	0.0938(5)	0.5315(5)	0.8537(3)	0.0304(31)
C(27)*	0.1095(5)	0.5247(5)	0.7872(3)	0.0257(31)
N(28)*	0.1627(4)	0.4860(4)	0.9009(2)	0.0323(27)
C(29)*	0.1570(7)	0.3819(5)	0.9299(4)	0.0547(43)
C(30)*	0.2207(6)	0.3530(5)	0.9873(4)	0.0435(37)
C(31)*	0.3281(6)	0.3977(5)	0.9625(3)	0.0401(35)
N(32)*	0.3232(4)	0.5011(4)	0.9336(2)	0.0294(25)
C(33)*	0.2378(5)	0.5442(5)	0.9093(3)	0.0311(32)
O(34)*	0.2282(3)	0.6288(3)	0.8922(2)	0.0337(22)
C(35)*	0.4078(5)	0.5619(5)	0.9383(3)	0.0314(35)
C(36)*	0.4557(5)	0.6336(5)	0.8713(3)	0.0287(32)
C(37)*	0.4224(5)	0.7270(5)	0.8554(3)	0.0293(33)
C(38)*	0.4616(5)	0.7953(5)	0.7942(3)	0.0331(31)
C(39)*	0.5343(5)	0.7722(5)	0.7472(3)	0.0324(32)
C(40)*	0.5726(5)	0.6827(5)	0.7616(3)	0.0261(29)
C(41)*	0.5345(5)	0.6121(5)	0.8252(3)	0.0268(30)
C(42)*	0.5828(5)	0.5171(5)	0.8435(3)	0.0275(30)
C(43)*	0.6712(5)	0.5034(5)	0.8748(3)	0.0308(32)
C(44)*	0.7182(5)	0.4168(5)	0.8933(3)	0.0350(33)
C(45)*	0.8140(6)	0.4034(5)	0.9273(4)	0.0467(38)
C(46)*	0.6748(5)	0.3419(5)	0.8790(3)	0.0343(34)
C(47)*	0.5859(5)	0.3526(5)	0.8485(3)	0.0354(33)
C(48)*	0.5411(6)	0.2701(5)	0.8342(4)	0.0498(42)
C(49)*	0.5411(5)	0.4392(5)	0.8320(3)	0.0352(35)
O(50)*	0.3669(3)	0.5547(3)	0.6344(2)	0.0382(23)
C(51)*	0.3314(6)	0.4599(5)	0.6512(3)	0.0416(35)

Table II (continued)

Atom	x/a	y/b	z/c	$U_{eq.}$
C(52)*	0.3354(6)	0.4138(6)	0.7261(4)	0.0581(43)
C(53)*	0.2822(6)	0.4719(6)	0.7707(4)	0.0531(45)
O(54)*	0.1775(3)	0.4670(3)	0.7653(2)	0.0394(23)
OW(1)	0.3528(3)	−0.1699(3)	0.5827(2)	0.0412(24)
OW(2)	0.1160(4)	0.3217(3)	0.5936(3)	0.0554(27)
OW(3)	0.2026(5)	0.2189(4)	0.7747(3)	0.0796(35)
OW(4)	0.2735(5)	0.2022(4)	0.8981(3)	0.0792(36)
HW(1a)	0.4154	−0.2000	0.5962	0.0500
HW(1b)	0.2829	−0.2099	0.6040	0.0500
HW(2a)	0.0462	0.2933	0.5962	0.0500
HW(2b)	0.1513	0.2702	0.6320	0.0500
HW(3a)	0.1538	0.1600	0.8077	0.0500
HW(3b)	0.2282	0.1859	0.7347	0.0500
HW(4a)	0.2621	0.2001	0.8487	0.0500

conformations of the individual urea cycles, seem to be mostly affected by intramolecular (on the bottom face of the complexes) and intermolecular steric interactions.

Compound **II**. The molecular structure of this compound is illustrated in Figure 4. It involves the second isomer of the host species where the dimethyl substituted phenyl and the three urea carbonyl groups are located on the upper face of the ligand. In many respects the observed structure resembles that of complex (b) in the previous example. Thus, only one molecule of water is directly bound to the polar surface of the host consisting of the converging carbonyls. The guest lies between and hydrogen-bonds in a characteristic manner to O(8) and O(21) (Table VI), the O(8)···O(21) distance being here 4.43 Å. The O(43) carbonyl is not involved in any strong interaction. The presence of empty space in the uncomplexed site between O(21) and O(34) is partially compensated for by a decreased tilt upward of the latter and consequently a shorter O(21)···O(34) distance of only 3.88 Å. The inward turning methyl substituent covers the remaining space between O(8) and O(34) (4.94 Å) on the upper side of the cavity. The bottom surface of the complex consists, as in the previous structure, of hydrocarbon phenylene and methylene groups. The coordination sphere of the bound water is supplemented in this compound by a molecule of CH_2Cl_2 which hydrogen-bonds to the water oxygen from outside the complex (Figure 5). There are no additional intermolecular interactions other than through dispersion forces.

Compound **III**. The bridged noncyclic ligand **3** takes part in a more complexed molecular inclusion type structure. In this host the terminal cyclic urea units provide additional proton-donating sites of bonding. The crystallographic analysis revealed, however, that these sites are used for H-bonded dimerization of **3** rather than for association with potential guest species. As shown in Figure 6, the dimer is stabilized by two pairs of circular H-bonds between the terminal urea units of the two molecules of the ligand. The formation of dimers imparts more rigidity to the ligand system; geometrically, it requires that one of the terminal carbonyl groups on each monomer be turned outward. The dimeric entity contains a polar cavity at each end; the two sites being separated from each other by a lipophilic barrier of methylene groups from the outward-turned cyclic urea units. Only two carbonyls converge

Table III. Atomic coordinates and isotropic thermal parameters of **II**. $U_{\mathrm{eq.}}$ is one third of the trace of the orthogonalized $\mathbf{U}^{ij}$ tensor. Atoms 55–57 and 58 denote the CH_2Cl_2 and H_2O guest species, respectively.

Atom	x/a	y/b	z/c	$U_{\mathrm{eq.}}$
C(1)	0.5354(2)	−0.0444(6)	0.4476(3)	0.0509(28)
N(2)	0.5349(2)	−0.1165(4)	0.4953(2)	0.0471(25)
C(3)	0.5077(2)	−0.2253(6)	0.4826(3)	0.0526(30)
C(4)	0.5333(2)	−0.3171(6)	0.5276(3)	0.0559(30)
C(5)	0.5462(2)	−0.2714(6)	0.5883(3)	0.0578(34)
N(6)	0.5665(2)	−0.1531(4)	0.5954(2)	0.0426(22)
C(7)	0.5598(2)	−0.0769(6)	0.5508(3)	0.0452(28)
O(8)	0.5774(1)	0.0225(4)	0.5602(2)	0.0462(20)
C(9)	0.5918(2)	−0.1101(5)	0.6544(3)	0.0372(29)
C(10)	0.5684(2)	−0.0632(6)	0.6843(3)	0.0498(36)
C(11)	0.5920(2)	−0.0207(6)	0.7406(3)	0.0459(31)
C(12)	0.6397(2)	−0.0205(5)	0.7665(3)	0.0392(31)
C(13)	0.6634(2)	−0.0674(5)	0.7380(3)	0.0304(24)
C(14)	0.6397(2)	−0.1178(5)	0.6818(3)	0.0341(25)
N(15)	0.7125(2)	−0.0707(4)	0.7660(2)	0.0287(20)
C(16)	0.7341(2)	−0.1707(5)	0.8054(2)	0.0328(25)
C(17)	0.7847(2)	−0.1471(5)	0.8401(2)	0.0315(24)
C(18)	0.8059(2)	−0.1243(5)	0.7989(2)	0.0300(23)
N(19)	0.7809(1)	−0.0277(4)	0.7582(2)	0.0258(19)
C(20)	0.7353(2)	−0.0037(5)	0.7419(2)	0.0285(25)
O(21)	0.7153(1)	0.0774(3)	0.7069(2)	0.0327(15)
C(22)	0.8040(2)	0.0300(5)	0.7282(2)	0.0281(25)
C(23)	0.8437(2)	0.0923(5)	0.7603(3)	0.0288(24)
C(24)	0.8676(2)	0.1469(5)	0.7329(3)	0.0352(27)
C(25)	0.8501(2)	0.1437(5)	0.6727(3)	0.0321(26)
C(26)	0.8104(2)	0.0814(5)	0.6398(2)	0.0321(27)
C(27)	0.7884(2)	0.0192(5)	0.6680(2)	0.0301(25)
N(28)	0.7936(2)	0.0741(4)	0.5780(2)	0.0322(21)
C(29)	0.8263(2)	0.0394(5)	0.5550(3)	0.0401(27)
C(30)	0.8013(2)	−0.0214(6)	0.4974(3)	0.0478(31)
C(31)	0.7619(2)	0.0522(6)	0.4568(3)	0.0473(31)
N(32)	0.7320(2)	0.0853(4)	0.4846(2)	0.0405(22)
C(33)	0.7490(2)	0.1076(5)	0.5435(2)	0.0346(28)
O(34)	0.7246(1)	0.1550(3)	0.5637(2)	0.0390(17)
C(35)	0.6847(2)	0.1142(6)	0.4481(3)	0.0444(29)
C(36)	0.6516(2)	0.0149(5)	0.4431(2)	0.0432(30)
C(37)	0.6646(2)	−0.1018(6)	0.4390(3)	0.0528(32)
C(38)	0.6352(3)	−0.1955(6)	0.4349(3)	0.0549(34)
C(39)	0.5944(3)	−0.1749(6)	0.4368(3)	0.0560(33)
C(40)	0.5804(2)	−0.0592(5)	0.4418(2)	0.0437(27)
C(41)	0.6087(2)	0.0361(5)	0.4432(2)	0.0392(27)
C(42)	0.5934(2)	0.1611(5)	0.4428(2)	0.0368(24)
C(43)	0.5697(2)	0.2184(6)	0.3905(3)	0.0418(28)
C(44)	0.5558(2)	0.3365(6)	0.3882(3)	0.0446(27)
C(45)	0.5304(3)	0.3979(7)	0.3294(3)	0.0660(38)
C(46)	0.5659(2)	0.3950(5)	0.4398(3)	0.0401(27)
C(47)	0.5895(2)	0.3394(5)	0.4935(3)	0.0359(22)
C(48)	0.5993(2)	0.4033(6)	0.5505(3)	0.0433(30)
C(49)	0.6037(2)	0.2229(5)	0.4947(2)	0.0366(23)
O(50)	0.6656(1)	−0.1785(3)	0.6605(2)	0.0395(17)
C(51)	0.6645(2)	−0.1508(5)	0.6040(3)	0.0422(26)

Table III (continued)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{eq.}$
C(52)	0.7041(2)	- 0.2154(5)	0.6004(2)	0.0420(28)
C(53)	0.7504(2)	- 0.1711(5)	0.6443(3)	0.0402(26)
O(54)	0.7502(1)	- 0.0451(3)	0.6330(2)	0.0350(16)
C(55)	0.9185(3)	0.1841(8)	0.2784(4)	0.0899(51)
Cl(56)	0.8967(1)	0.2049(3)	0.2035(1)	0.1013(14)
Cl(57)	0.9785(1)	0.2212(3)	0.3124(1)	0.1136(16)
O(58)	0.6262(1)	0.1768(3)	0.6498(2)	0.0419(17)
H(58a)	0.6557	0.1376	0.6745	
H(58b)	0.6067	0.1191	0.6194	

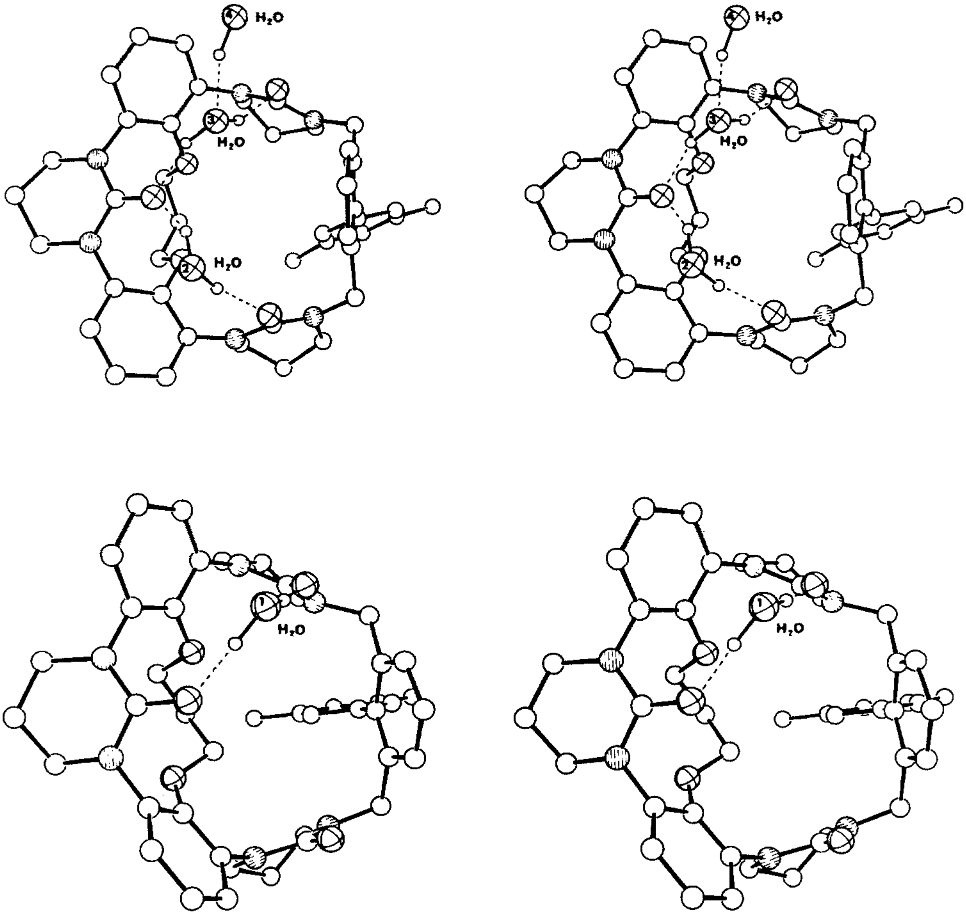

Fig. 2. Stereoview of the two complexes (a) and (b) in the asymmetric unit of I.

Table IV. Atomic coordinates and isotropic thermal parameters of **III**. $U_{eq.}$ is one third of the trace of the orthogonalized $\mathbf{U}^{ij}$ tensor. Atoms 77–79 and 80 denote the host-included CH_2Cl_2 and H_2O guests, respectively. Atoms C(81) and Cl(82), Cl(83), Cl(86) and Cl(87) (with fractional occupancies) represent the disordered outer CH_2Cl_2. Atoms C(84) and O(85) denote the methyl impurity and the second water molecule with partial occupancies (see text).

Atom	*x/a*	*y/b*	*z/c*	$U_{eq.}$
O(1)	0.0452(3)	-0.1485(3)	0.0135(2)	0.0353(15)
C(2)	0.0409(4)	-0.0926(5)	0.0533(3)	0.0341(19)
N(3)	-0.0163(3)	-0.0890(4)	0.0947(3)	0.0383(17)
C(4)	-0.0176(5)	-0.0402(6)	0.1533(4)	0.0628(23)
C(5)	0.0467(8)	0.0169(9)	0.1601(6)	0.1513(29)
C(6)	0.0838(7)	0.0357(6)	0.0999(5)	0.0882(25)
N(7)	0.0925(4)	-0.0313(4)	0.0564(3)	0.0387(18)
C(8)	0.1684(4)	-0.0461(4)	0.0388(3)	0.0307(19)
C(9)	0.2006(5)	0.0012(5)	-0.0081(4)	0.0417(22)
C(10)	0.2752(4)	-0.0094(5)	-0.0216(3)	0.0420(23)
C(11)	0.3202(4)	-0.0660(5)	0.0131(3)	0.0375(19)
C(12)	0.2894(4)	-0.1140(4)	0.0608(3)	0.0317(20)
C(13)	0.2115(4)	-0.1049(4)	0.0725(3)	0.0310(19)
O(14)	0.1781(3)	-0.1463(3)	0.1202(2)	0.0311(14)
C(15)	0.1683(4)	-0.2307(4)	0.1120(3)	0.0311(19)
C(16)	0.1256(4)	-0.2588(5)	0.1710(3)	0.0339(19)
C(17)	0.1698(4)	-0.2390(5)	0.2351(3)	0.0320(19)
O(18)	0.2392(3)	-0.2862(3)	0.2365(2)	0.0323(15)
C(19)	0.2956(4)	-0.2680(4)	0.2834(3)	0.0327(19)
N(20)	0.3359(3)	-0.1718(4)	0.0954(2)	0.0295(16)
C(21)	0.3646(4)	-0.2387(5)	0.0560(3)	0.0372(18)
C(22)	0.4242(4)	-0.2858(5)	0.0950(3)	0.0437(21)
C(23)	0.3942(5)	-0.3076(5)	0.1609(3)	0.0425(20)
N(24)	0.3766(3)	-0.2333(4)	0.1945(3)	0.0315(17)
C(25)	0.3427(4)	-0.1688(5)	0.1631(3)	0.0308(18)
O(26)	0.3204(3)	-0.1099(3)	0.1924(2)	0.0376(16)
C(27)	0.3659(4)	-0.2419(5)	0.2637(3)	0.0318(19)
C(28)	0.4270(4)	-0.2281(5)	0.3088(3)	0.0381(20)
C(29)	0.4171(5)	-0.2404(5)	0.3754(3)	0.0402(20)
C(30)	0.3470(4)	-0.2660(5)	0.3953(3)	0.0373(20)
C(31)	0.2865(4)	-0.2803(5)	0.3506(3)	0.0334(20)
N(32)	0.2155(3)	-0.3109(4)	0.3707(3)	0.0307(17)
C(33)	0.2003(5)	-0.3973(5)	0.3590(4)	0.0424(23)
C(34)	0.1149(5)	-0.4134(5)	0.3562(4)	0.0427(20)
C(35)	0.0820(4)	-0.3758(5)	0.4150(4)	0.0433(21)
N(36)	0.1007(3)	-0.2904(4)	0.4183(3)	0.0365(19)
C(37)	0.1667(4)	-0.2597(5)	0.3986(3)	0.0335(20)
O(38)	0.1821(3)	-0.1869(3)	0.4039(2)	0.0369(16)
O(39)	-0.0096(3)	-0.1752(3)	0.4611(2)	0.0396(15)
C(40)	-0.0104(5)	-0.1102(5)	0.4312(3)	0.0392(20)
N(41)	0.0509(4)	-0.0859(4)	0.4000(3)	0.0420(20)
C(42)	0.0515(5)	-0.0192(6)	0.3538(4)	0.0553(21)
C(43)	-0.0292(5)	0.0099(6)	0.3356(4)	0.0601(24)
C(44)	-0.0681(5)	0.0192(5)	0.3970(5)	0.0562(22)
N(45)	-0.0717(4)	-0.0590(4)	0.4298(3)	0.0392(18)
C(46)	-0.1450(4)	-0.0887(5)	0.4427(3)	0.0420(21)
C(47)	-0.1867(5)	-0.0513(5)	0.4907(4)	0.0497(20)
C(48)	-0.2607(5)	-0.0739(6)	0.4984(4)	0.0559(23)
C(49)	-0.2945(5)	-0.1312(6)	0.4600(4)	0.0496(21)

Table IV (continued)

Atom	*x/a*	*y/b*	*z/c*	$U_{eq.}$
C(50)	-0.2548(4)	-0.1702(5)	0.4112(4)	0.0427(22)
C(51)	-0.1794(4)	-0.1493(5)	0.4036(3)	0.0366(19)
O(52)	-0.1372(3)	-0.1800(3)	0.3547(2)	0.0372(16)
C(53)	-0.1183(4)	-0.2643(5)	0.3565(3)	0.0380(19)
C(54)	-0.0727(4)	-0.2809(5)	0.2984(3)	0.0397(20)
C(55)	-0.1182(4)	-0.2668(5)	0.2338(3)	0.0390(19)
O(56)	-0.1790(3)	-0.3249(3)	0.2280(2)	0.0423(15)
C(57)	-0.2380(4)	-0.3092(5)	0.1813(3)	0.0397(20)
N(58)	-0.2924(3)	-0.2317(4)	0.3735(3)	0.0448(18)
C(59)	-0.3169(5)	-0.3025(6)	0.4092(4)	0.0562(24)
C(60)	-0.3649(7)	-0.3556(8)	0.3689(5)	0.0881(25)
C(61)	-0.3343(6)	-0.3703(6)	0.3029(4)	0.0666(26)
N(62)	-0.3212(4)	-0.2919(4)	0.2722(3)	0.0437(18)
C(63)	-0.2964(4)	-0.2260(5)	0.3060(3)	0.0391(20)
O(64)	-0.2798(3)	-0.1631(4)	0.2779(2)	0.0457(16)
C(65)	-0.3100(4)	-0.2927(5)	0.2030(3)	0.0416(21)
C(66)	-0.3711(4)	-0.2802(5)	0.1584(3)	0.0441(21)
C(67)	-0.3611(4)	-0.2840(6)	0.0910(4)	0.0471(22)
C(68)	-0.2905(4)	-0.3002(5)	0.0705(3)	0.0426(20)
C(69)	-0.2282(4)	-0.3128(5)	0.1149(3)	0.0385(22)
N(70)	-0.1549(3)	-0.3308(4)	0.0915(3)	0.0374(18)
C(71)	-0.1283(6)	-0.4127(6)	0.0966(5)	0.0658(25)
C(72)	-0.0683(6)	-0.4301(6)	0.0513(7)	0.1139(27)
C(73)	-0.0119(5)	-0.3663(5)	0.0413(4)	0.0503(23)
N(74)	-0.0448(3)	-0.2863(4)	0.0460(3)	0.0367(18)
C(75)	-0.1135(4)	-0.2691(5)	0.0686(3)	0.0346(20)
O(76)	-0.1373(3)	-0.1982(3)	0.0688(2)	0.0399(16)
C(77)	-0.1946(5)	-0.4412(5)	-0.1624(4)	0.0561(21)
Cl(78)	-0.2557(2)	-0.5221(2)	-0.1835(1)	0.0868(11)
Cl(79)	-0.1058(2)	-0.4811(2)	-0.1292(2)	0.0946(11)
O(80)	0.2244(4)	0.1004(4)	0.8450(3)	0.0810(19)
C(81)	0.0955(11)	0.5571(13)	0.6882(10)	0.1240(30)
Cl(82)	0.0440(3)	0.5651(4)	0.6068(3)	0.1346(20)
Cl(83)	0.0356(3)	0.5368(4)	0.7504(3)	0.1223(20)
C(84)	0.5028(15)	-0.2009(16)	0.2920(13)	0.0500
O(85)	0.2339(8)	0.0069(9)	0.7019(7)	0.1114
Cl(86)	0.1087(5)	0.4839(6)	0.6866(4)	0.0700
Cl(87)	0.0777(8)	0.5009(9)	0.6263(7)	0.0700
H(3)	-0.0574	-0.1249	0.0881	0.0500
H(36)	0.0662	-0.2503	0.4325	0.0500
H(41)	0.0941	-0.1146	0.4077	0.0500
H(74)	-0.0167	-0.2402	0.0352	0.0500
H(77a)	-0.1858	-0.4079	-0.2030	0.0500
H(77b)	-0.2183	-0.4061	-0.1284	0.0500
H(80a)	0.2040	0.1437	0.8677	0.0500
H(80b)	0.2278	0.1270	0.8029	0.0600

now on each site (Figure 6). The aliphatic O—$(CH_2)_3$—O bridges lie on the bottom part of the molecular surface, which is covered by a lipophilic skin of C—C and C—H bonds.

In the observed structure two different guests interact directly with the two cavities; CH_2Cl_2 beautifully occupies one site between O(26) and O(38) (O···O = 5.26 Å), while a water

Table V. Atomic coordinates and isotropic thermal parameters of **IV**. $U_{eq.}$ is one third of the trace of the orthogonalized $\mathbf{U}^{ij}$ tensor.

Atom	*x/a*	*y/b*	*z/c*	$U_{eq.}$
C(1)	0.4944(2)	0.2993(2)	0.2171(1)	0.0267(7)
N(2)	0.4563(1)	0.3549(2)	0.2648(1)	0.0253(7)
C(3)	0.5030(2)	0.3301(2)	0.3437(1)	0.0380(9)
C(4)	0.5064(2)	0.4169(3)	0.3904(1)	0.0461(10)
C(5)	0.4026(2)	0.4702(3)	0.3614(1)	0.0490(11)
N(6)	0.3694(1)	0.4954(2)	0.2832(1)	0.0280(7)
C(7)	0.3958(1)	0.4374(2)	0.2355(1)	0.0249(7)
O(8)	0.3682(1)	0.4594(1)	0.1702(1)	0.0294(6)
C(9)	0.2847(2)	0.5670(2)	0.2533(1)	0.0239(8)
C(10)	0.2981(2)	0.6603(2)	0.2851(1)	0.0292(9)
C(11)	0.2147(2)	0.7280(2)	0.2570(1)	0.0352(9)
C(12)	0.1167(2)	0.7038(2)	0.1976(1)	0.0306(9)
C(13)	0.1021(2)	0.6093(2)	0.1681(1)	0.0229(7)
C(14)	0.1868(2)	0.5412(2)	0.1951(1)	0.0238(7)
N(15)	0.0014(1)	0.5819(2)	0.1094(1)	0.0231(6)
C(16)	-0.0558(2)	0.6538(2)	0.0509(1)	0.0322(9)
C(17)	-0.1256(2)	0.6024(2)	-0.0202(1)	0.0314(8)
C(18)	-0.1970(2)	0.5271(2)	-0.0086(1)	0.0302(8)
N(19)	-0.1313(1)	0.4600(2)	0.0525(1)	0.0254(6)
C(20)	-0.0413(2)	0.4916(2)	0.1143(1)	0.0224(7)
O(21)	-0.0005(1)	0.4388(1)	0.1695(1)	0.0290(5)
C(22)	-0.1673(2)	0.3611(2)	0.0512(1)	0.0235(8)
C(23)	-0.2777(2)	0.3416(2)	0.0283(1)	0.0305(8)
C(24)	-0.3115(2)	0.2448(2)	0.0271(1)	0.0349(9)
C(25)	-0.2385(2)	0.1670(2)	0.0470(1)	0.0329(8)
C(26)	-0.1282(2)	0.1877(2)	0.0697(1)	0.0271(8)
C(27)	-0.0939(2)	0.2842(2)	0.0713(1)	0.0245(7)
N(28)	-0.0514(1)	0.1079(2)	0.0941(1)	0.0258(7)
C(29)	-0.0433(2)	0.0544(2)	0.1606(1)	0.0369(9)
C(30)	0.0165(2)	-0.0398(2)	0.1665(1)	0.0316(8)
C(31)	0.1278(2)	-0.0195(2)	0.1693(1)	0.0312(8)
N(32)	0.1200(1)	0.0490(2)	0.1094(1)	0.0235(6)
C(33)	0.0306(2)	0.1044(2)	0.0696(1)	0.0229(8)
O(34)	0.0237(1)	0.1496(1)	0.0140(1)	0.0306(6)
C(35)	0.2009(2)	0.0379(2)	0.0795(1)	0.0266(8)
C(36)	0.2726(2)	0.1253(2)	0.0823(1)	0.0226(7)
C(37)	0.2869(2)	0.1445(2)	0.0175(1)	0.0261(8)
C(38)	0.3614(2)	0.2136(2)	0.0169(1)	0.0292(8)
C(39)	0.4236(2)	0.2661(2)	0.0809(1)	0.0269(8)
C(40)	0.4119(2)	0.2489(2)	0.1469(1)	0.0239(7)
C(41)	0.3351(1)	0.1788(2)	0.1469(1)	0.0202(7)
C(42)	0.3184(1)	0.1642(2)	0.2162(1)	0.0221(7)
C(43)	0.3815(2)	0.0989(2)	0.2708(1)	0.0244(8)
C(44)	0.3646(2)	0.0883(2)	0.3357(1)	0.0264(7)
C(45)	0.4317(2)	0.0167(2)	0.3953(1)	0.0379(9)
C(46)	0.2850(2)	0.1444(2)	0.3439(1)	0.0276(8)
C(47)	0.2230(2)	0.2129(2)	0.2902(1)	0.0263(7)
C(48)	0.1395(2)	0.2769(2)	0.3003(1)	0.0383(9)
C(49)	0.2410(2)	0.2214(2)	0.2265(1)	0.0260(7)

Table VI. Geometry of the hydrogen bonds in host-guest compounds **I–III**

Donor (RH)	Acceptor (R′)	R–H (Å)	R···R′ (Å)	H···R′ (Å)	R–H···R′ (deg.)
Compound **I**					
H_2O(W1a)	O(8)*	0.96	2.868(7)	1.91	171.4
H_2O(W1b)	O(21)*	1.05	2.826(6)	1.83	156.0
H_2O(W2a)	O(8)	1.00	2.883(7)	1.89	170.5
H_2O(W2b)	O(21)	1.07	2.895(7)	1.92	149.2
H_2O(W3a)	O(34)	1.07	2.805(7)	1.83	149.8
H_2O(W3b)	O(21)	1.07	2.935(9)	1.81	158.8
H_2O(W4a)	O(W3)	1.07	2.799(11)	1.77	158.9
H_2O(W4b)	O(34)*	–	2.923(10)[a]	–	–
Compound **II**					
H_2O(58a)	O(21)	0.99	2.828(5)	1.86	165.9
H_2O(58b)	O(8)	1.00	2.753(5)	1.76	171.4
CCl_2H_2(55b)	O(58)	1.04	3.184(12)	2.15	170.9
Compound **III**					
NH(3)	O(76)	0.94	2.823(8)	1.88	175.9
NH(36)	O(39)	0.96	2.905(8)	1.95	175.7
NH(41)	O(38)	0.90	2.851(9)	1.97	166.6
NH(74)	O(1)	0.95	2.892(8)	1.95	177.4
H_2O(80a)	O(76)	0.94	2.911(8)	2.02	156.5
H_2O(80b)	O(64)	0.98	2.951(8)	2.03	155.7
CCl_2H_2(77a)	O(26)	1.02	3.124(9)	2.17	153.9
CCl_2H_2(77b)	O(38)	1.02	3.389(10)	2.46	151.0
CCl_2H_2(81)	O(64)	–	3.283(12)[b]	–	–
CCl_2H_2(81)	O(80)	–	3.357(13)[b]	–	–
H_2O(85)	O(64)	–	2.752(12)[b]	–	–

[a] Atom H(W4b) in **I** has not been located.

[b] The H-atoms of the disordered CH_2Cl_2 and the fractional H_2O have not been located. The marked distances only indicate possible hydrogen-bonding interactions.

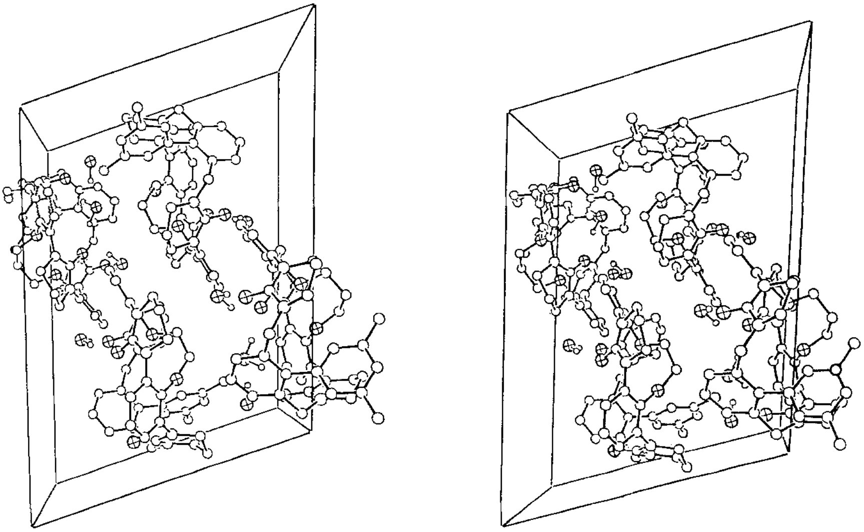

Fig. 3. Crystal structure of **I**, viewed approximately down **a**.

Table VII. Conformational details of the ligands

(a) *Torsion angles (°) about bonds connecting the cyclic urea and phenylene fragments*

	I	I*	II	IV
C7—N6—C9—C14	89.0(9)	-73.5(9)	-87.1(8)	46.1(3)
C14—C13—N15—C20	-52.4(10)	52.1(10)	67.8(7)	45.3(3)
C20—N19—C22—C27	58.4(10)	-70.6(9)	-57.7(8)	-46.4(3)
C27—C26—N28—C33	-86.3(9)	101.4(8)	58.2(8)	-46.6(3)

	III		III
C2—N7—C8—C13	-58.3(9)	C40—N45—C46—C51	103.2(8)
C13—C12—N20—C25	-57.3(9)	C51—C50—N58—C63	-57.1(10)
C25—N24—C27—C19	74.5(9)	C63—N62—C65—C57	77.4(9)
C19—C31—N32—C37	-105.0(8)	C57—C69—N70—C75	-103.0(8)

(b) *Torsion angles (°) within the* O—$(CH_2)_3$—O *aliphatic bridge*

	I	I*	II
C14—O50—C51—C52	174.0(6)	175.6(7)	167.9(5)
O50—C51—C52—C53	-75.3(8)	50.0(9)	-65.4(6)
C51—C52—C53—O54	74.1(8)	67.3(9)	-56.3(6)
C52—C53—O54—C27	-171.2(6)	-167.5(7)	178.7(5)

	III		III
C13—O14—C15—C16	-176.9(5)	C51—O52—C53—C54	-179.9(6)
O14—C15—C16—C17	-58.6(7)	O52—C53—C54—C55	-63.6(7)
C15—C16—C17—O18	-65.2(7)	C53—C54—C55—O56	-65.7(7)
C16—C17—O18—C19	167.9(6)	C54—C55—O56—C57	163.8(6)

(c) *Dihedral angles (°) between planes of the phenyl rings within the dimethyl substituted biphenylene fragment*

I	I*	II	IV
109.3(2)	86.7(2)	89.7(2)	91.8(1)

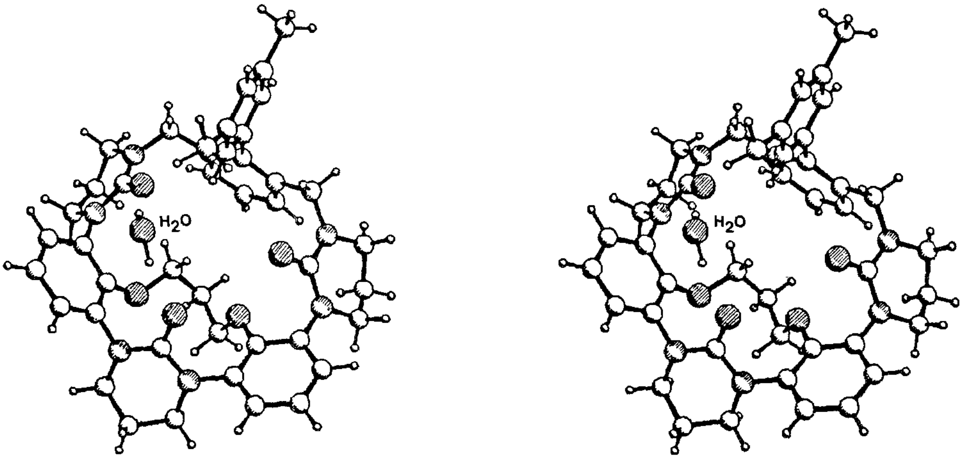

Fig. 4. Stereoview of the host–guest complex in compound **II**.

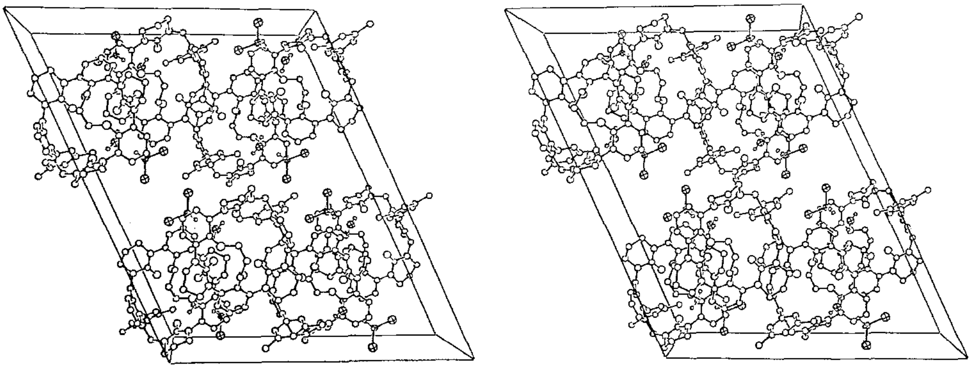

Fig. 5. Crystal structure of **II**, viewed approximately down **b**.

molecule is located in the second cavity between O(64) and O(76) (O···O = 5.14 Å). Geometrical parameters related to the hydrogen bonding and the host conformation are included in Tables VI and VII, respectively.

The crystal structure of this compound (Figure 7) contains two additional species, a disordered CH_2Cl_2 and fractional H_2O. Both, lie outside the complex within hydrogen

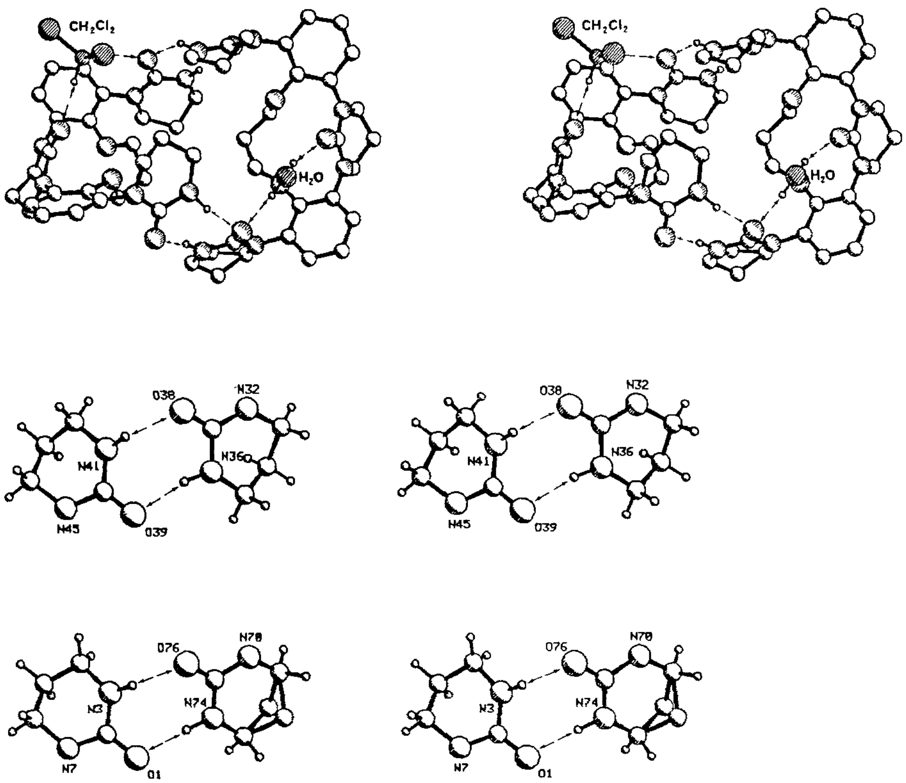

Fig. 6. Stereoviews of: (a) the host–guest complex in **III**, and (b) the hydrogen bonding between monomers of the ligand-dimer, illustrating a possible conformational disorder in one of the rings (see Table VI).

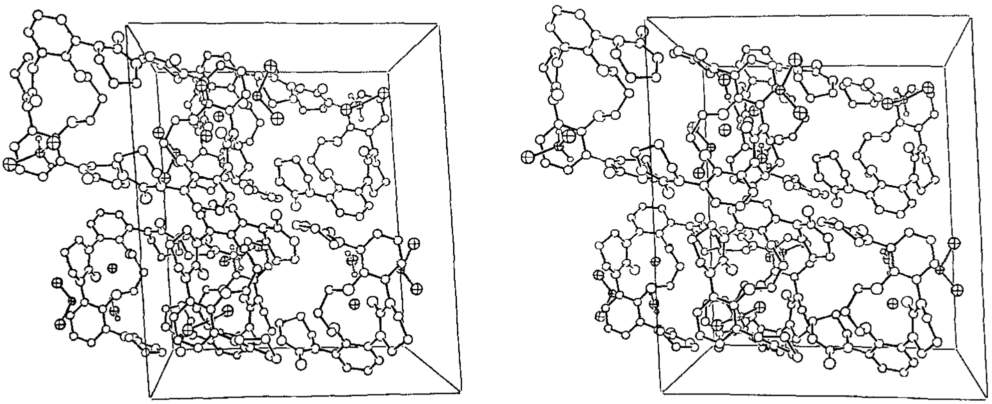

Fig. 7. Crystal structure of **III**, viewed approximately down **b**.

bonding distance from the bound water and from a carbonyl O(64) of an adjacent cyclic urea. In this region of the crystal the complexed dimers appear to be less densly packed than in other parts of the structure. The tendency to fill the empty intermolecular space could also be the main driving force for co-crystallization with the 'impure' molecule of **3** containing a methyl substituent on C(28) (see Experimental), as this methyl (C(84)) was found to be located in the same region close to the disordered molecule of CH_2Cl_2.

Compound **IV**. The molecular structure of the macrocyclic unbridged ligand **4**, which did not form complexes upon crystallization from similar solutions, is illustrated in Figure 8. This molecule has a nearly perfect mirror symmetry. While the central cyclic urea is tilted towards one side of the molecular framework, the two flanking carbonyls are tilted towards the opposite side. One face of the molecule has a convex form, being covered also by CH_2 groups and the dimethyl-substituted phenyl. The other face with O(8) and O(34) on it has a form of a concave and polar surface. The distance between the two oxygens is 6.08 Å, apparently too large for an effective complexation of either CH_2Cl_2 or H_2O (no other species of more suitable shape and size were present in the solution). Instead, the crystal structure consists

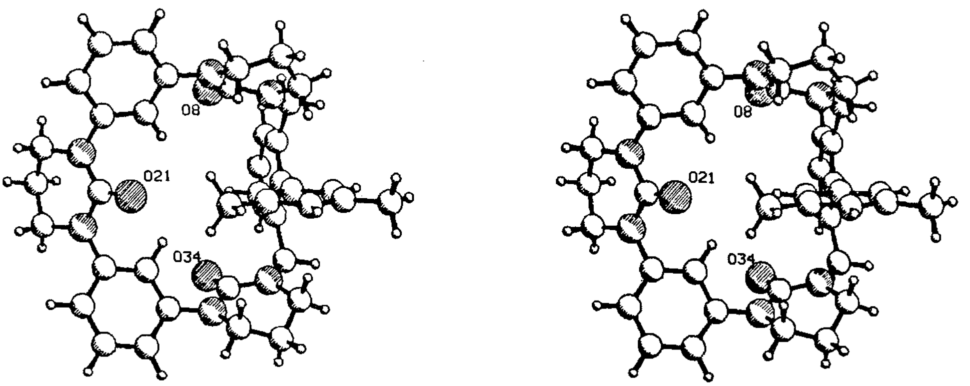

Fig. 8. Molecular structure of the uncomplexed ligand **4**.

of efficiently packed ligand molecules with the thin end (the outer part of the central cyclic urea) of one species at x, y, z well fitting into the concave space of an adjacent molecule at $-x, 1-y, -z$. This is reflected in relatively short nonbonding distances between the two fragments: O(8)···C(18) = 3.08, O(8)···H(18a) = 2.3 Å, C(18)–H(18a)···O(8) = 128° and O(34)···C(16) = 3.07, O(34)···H(16b) = 2.3 Å, C(16)–H(16b)···O(34) = 129°. The conformational features of the molecular structure are also described in Table VII.

4. Discussion

The present results show that small uncharged guest species can form stable complexes with hosts containing only cyclic urea (carbonyl) binding sites. Bidentate guests with acidic CH and OH groups such as water and CH_2Cl_2 require only two carbonyl acceptors for such complexation donating their protons in a 'dipode' fashion. The ligands involved in **1–3** contain concave cavities with carbonyl groups lined on the surface and held in convergent positions by the molecular framework. In the complexed sites the distance between adjacent carbonyl oxygens vary from 4.4 Å in **I** to 5.2 Å in **III**. The guest molecules were found to perch on the binding sites, directing their protons at the oxygen acceptors; all the hydrogen bonds between the interacting components are close to linear (Table VI). The structure of complex **III**, in which the H_2O and CH_2Cl_2 are bound simultaneously to the ligand, suggests that both guests are suited for complexation. Binding of water is, however, much stronger than binding of the less polar CH_2Cl_2, as is reflected by the average distances: $H_2O\cdots O{=}C$ 2.95 Å in **III** and 2.85 Å in all compounds, and $Cl_2H_2C\cdots O{=}C$ 3.25 Å. Nevertheless, at the low temperature of the experiment all guests which are directly bound to the corresponding hosts appeared ordered and thermally stable.

The host–guest complexes are stabilized by multiple O—H···O and C—H···O interactions in a similar manner to that observed in complexes of crown ethers with uncharged species. Relevant comparison can be made, for example, with complexes of 18-crown-6 with water [14] and with CH-acidic guests such as malonodinitrile [15], nitromethane [16], dimethyl sulfone [17] and dimethyl acetylenedicarboxylate [18]. Indeed, in all the various complexes the geometric details of the individual hydrogen bonds are very similar to the data of this work shown in Table VI. Due to the large number of oxygen sites and the roughly planar shape of the cavity in 18-crown-6, the hexaether ring is usually coordinated from opposite sides by two proton donating units of the neutral guest species [6]. The cyclic urea ligands in the present structures contain binding sites of more concave shapes, which leads to a better spatial complementarity between the host and guest constituents.

Crystallographic evidence from X-ray and neutron diffraction studies for the C—H···O interactions has repeatedly been described in recent literature [19,20]. On the basis of geometrical and statistical considerations it has been concluded that these interactions are attractive in nature, and can reasonably be referred to as hydrogen bonds [20]. In the present study such C—H···O bonds have been observed in various environments. The attraction of the CH_2Cl_2 guest to the molecular surface of the ligand dimer in **III**, encountered consistently in three different crystallization experiments, provides an additional indication that C—H···O bonds play an important role in intermolecular interactions. Significant host–host interactions between the $>CH_2$ and C=O groups have also been observed in compound **IV**. The corresponding donor-acceptor distances between adjacent molecules related to one another by inversion are even shorter than the host–guest distances in **III**. The C···O distances in **IV** (3.07 and 3.08 Å) are also considerably shorter than those between the H_2O guests and the external CH_2Cl_2's in **II** (3.18 Å) and in **III** (3.36 Å). This is in agreement with previous findings that C—H groups adjacent to nitrogen atoms tend to participate in short C—H···O interactions [20]. Furthermore, inspection of Figures 6 and 8 shows another feature which is consistent with the attractive character of the $CH_2\cdots O{=}C$ interactions in compounds **III** and **IV**; it appears that the CH protons lie near the plane containing the lone pair orbitals of the oxygen, the H···O=C angles being 129–138° in **III** and 145–150° in **IV**.

The four compounds described in this paper were crystallized from similar but not identical solvent mixtures. Compounds **I–III** represent *molecular inclusion* type structures with respect to some of the guest species, including additional molecules of the solvent in between the various complexed entities. The full contents of each crystal type as well as conformational features of the ligands are affected by the different patterns of crystal packing that are significant in the individual structures. Thus, the two complexes contained in the asymmetric unit of **I** are of different stoichiometry, and only one out of the three ligand-bound H_2O's is further coordinated from outside by another molecule of water. Compound **II** resembles a ternary complex. The ligand is directly associated with only one molecule of water, which attracts also from the other side an additional molecule of CH_2Cl_2. In compound **III** the bound water exhibits a similar secondary interaction with another molecule of CH_2Cl_2, as in **II**.

Molecular structures of the ligands deserve some further discussion. The unbridged ligand **4** is characterized by the least-strained conformation. With respect to the mean plane of the macroring, the central carbonyl group and the two flanking C=O groups are tilted in opposite directions. The two phenylene spacers are roughly coplanar with the ring, while the substituted biphenylene group is perpendicular to it. The nonbonding distance between the side oxygens is too large for the inclusion of either H_2O or CH_2Cl_2. Introduction of the $O{-}(CH_2)_3{-}O$ bridge between the phenylenes directs the three carbonyls toward the same face of the ligand creating a more organized polar surface which is more attractive for the potential guest candidates. In the two macrocyclic isomers **1** and **2** water binds preferably between the central (O(21)) and one of the side (O(8) and O(34)) carbonyls; in each molecule of the complex the distance between the latter is largests, 6.27 and 6.40 in **I** and 4.94 Å in **II**. The aromatic rings of the biphenylene fragment are nearly perpendicular to one another in the three macrocyclic ligands (Table VII). Dimerization of the unbridged ligand **3** evidently adds to the organization of this host structure as well, leading to the formation of two convergently arranged carbonyl binding sites. The overall conformation of the ligands is, however, not entirely rigid. Rather, it is adjusted differently in each one of the host molecules to energetically optimize intra- and intermolecular interactions in the individual structures. The observed conformational variations do not indicate any specific regularity. For example, some of ethereal O's in the bridging units point towards the lower face of the ligand while others turn upward, irrespective of whether they lie close to a complexed or an uncomplexed site of the host (Figures 2, 4 and 6). None of these oxygens takes part in specific interactions. There is also no apparent consistency in the puckering parameters of the individual rings of the cyclic urea.

The above results are in good agreement with previous observations that a suitable organization of potential binding sites in the host structures is an important factor in the design of molecular complexes with functionally complementary guests [11]. They further show that host–guest type complexes of hosts containing only cyclic urea binding sites can also be used as models for studies of weak intermolecular interactions. Further efforts should be made to crystallize complexes with other guest functions from water-free solvents in order to elucidate additional types of host–guest interaction.

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