Molecular Recognition of Azobenzene Dicarboxylates by Acridine-Based Receptor Molecules; Crystal Structure of the Supramolecular Inclusion Complex of *trans*-3,3′-Azobenzene Dicarboxylate with a Cyclo-bis-intercaland Receptor

Predrag Cudic,[a] Jean-Pierre Vigneron,[a] Jean-Marie Lehn,*[a] Michèle Cesario,[b] and Thierry Prangé[c]

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The water soluble acyclic **1** and macrocyclic **2** receptor molecules, based on acridine units, form 1:1 complexes with the *cis*- or *trans*-2,2′ and 3,3′-azobenzene dicarboxylate substrates. The stability constants of these complexes, determined by ^{1}H NMR spectroscopy, cover a wide range from 30 to 10^5 M^{-1}, thus displaying very pronounced structure selectivity with respect to both substitution pattern and *cis*, *trans* configuration. The complexes of the cyclo-bis-intercaland receptor **2** are two or three orders of magnitude more stable than those of **1**. The inclusion complex of cyclo-bis-intercaland **2** with *trans*-3,3′- azobenzene dicarboxylate has been isolated and its structure has been determined by X-ray crystallography using synchrotron radiation, confirming the intercalation of the substrate between the acridine residues in the species formed.

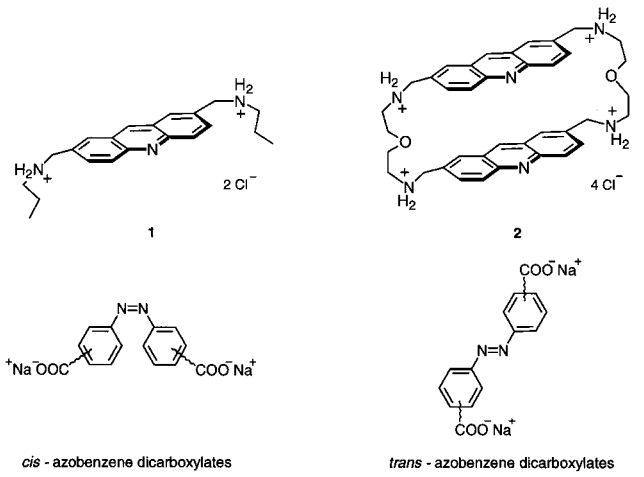
Introduction

One of the important goals of research in supramolecular chemistry is to achieve strong and selective binding of substrate molecules by suitably designed synthetic molecular receptors.[1,2] Such studies provide basic information about the factors controlling molecular recognition and self-assembly processes, and thus can also shed light on their operation in biological systems. On the other hand, these studies also contribute to the development of artificial receptor molecules of interest for catalysis or for applications in analytical and medicinal fields.

Previous reports from our laboratory have described the selective binding of flat aromatic substrates by macrocyclic receptors of the cyclo-bis-intercaland type. These receptors, designed in analogy to DNA intercalation phenomena, possess two planar subunits positioned at a distance suitable for the intercalation of flat substrate molecules. The synthesis and binding properties of cyclo-bis-intercaland receptors containing two porphyrine,[3,4] diazapyrene,[5] phenazine,[6] acridine,[7−13] phenanthridine,[14−16] or naphthalene[17,18] units have been reported. Using various spectroscopic methods, it has been shown that they bind flat aromatic substrates, and nucleotides and nucleosides by means of π−π stacking and electrostatic interactions. The intercalative binding of a nitrobenzene molecule,[5] and of terephthalate and isophthalate dianions[18] has been confirmed in the solid state by X-ray structure determinations.

Since in azobenzene, and its derivatives, *cis*/*trans* isomerization gives access to switching processes of interest for various applications in energy storage systems,[19] photochemical devices[20] or in supramolecular systems,[21] it is of much interest to achieve strong and selective binding of different structural and configurational isomers of substituted azobenzene molecules.

We report here on our studies of the complexation properties of the acyclic **1** and cyclo-bis-intercaland **2** receptor molecules towards the four isomers of the *cis*- and *trans*-2,2′- or 3,3′-azobenzene dicarboxylates by ^{1}H NMR spectroscopy and by determination of the crystal structure of the complex between **2** and the *trans*-3,3′ isomer.



Scheme 1. Structures of the receptors and substrates investigated

[a] Laboratoire de Chimie des Interactions Moléculaires, CNRS UPR 285, Collège deFrance,
11, Place Marcelin Berthelot, F-75231 Paris Cedex 05, France
Fax: (internat.) +33-1/4427-1356
E-mail: lehn@cdf.in2p3.fr
[b] Laboratoire de Cristallochimie, Institut de Chimie des Substances Naturelles, CNRS,
F-91198 Gif sur Yvette, Cedex France
[c] L.U.R.E., Bat. 209d, Université Paris-Sud,
F-91405 Orsay Cedex France

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Results and Discussion

Synthesis and Binding Properties of Cyclo-bis-intercaland Receptor 2

The cyclo-bis-intercaland receptor **2** was prepared according to the method previously described for the synthesis of the polyaza analogue containing diethylenetriamine bridges.[12] The key synthetic steps are the 2+2 condensation between 2,2′-oxybis(ethylamine) and acridine-2,7-carbaldehyde, followed by the $NaBH_4$ reduction of the corresponding tetraimine **3**. Compound **2** was isolated as its hexahydrochloride salt and is soluble in acidic aqueous solution. A structure such as **2** represents a molecular receptor providing a lipophilic cavity suitable for accommodation of planar organic molecules. One may thus expect intercalative binding of flat aromatic substrates in aqueous solution similar to that previously found for the polyaza analogue of **2**. Examination of CPK (Corey−Pauling−Koltun) models shows that azobenzene dicarboxylates may fit more or less well into the lipophilic cavity of the cyclo-bis-intercaland macrocycle **2**. Marked upfield shifts in the ^1H NMR spectrum of azobenzene dicarboxylate of up to 2 ppm in presence of the acridine receptors **1** or **2** indicated that complexation occurred.

The stability constants of the complexes between the acridine receptors **1**, **2** and *trans*-2,2′- or *trans*-3,3′-azobenzene dicarboxylate were determined by ^1H NMR titration experiments and are listed in Table 1. The data were analyzed by a nonlinear least-squares curve fitting procedure.[15] In all cases the best statistical fit has been obtained for the formation of 1:1 stoichiometry complexes as illustrated in Figure 1.

In the case of *cis*-2,2′- and *cis*-3,3′-azobenzene dicarboxylates, the stability constants were determined by ^1H NMR competition experiments between the *cis* and *trans* isomers. For the complexes of 1:1 stoichiometry the following equation can be derived:[22−24]

$$\frac{\Delta\delta^{i}_{cis}}{\Delta\delta^{j}_{trans}} = \frac{K_s^{trans} - K_s^{cis}}{K_s^{trans}\Delta^{j}_{trans}}\,\Delta\delta^{i}_{cis} + \frac{K_s^{cis}\Delta^{i}_{cis}}{K_s^{trans}\Delta^{j}_{trans}}$$

where $\Delta\delta^{i}_{cis}$ and $\Delta\delta^{j}_{trans}$ denote the differences in chemical shift of the substrate protons *i* and *j* in free and complexed form; K_s^{cis} and K_s^{trans} are the stability constants of the complexes between the acridine receptors **1**, **2** and the *cis* or *trans* substrates, respectively; Δ^{i}_{cis} and Δ^{j}_{trans} are the limiting values of the differences between the chemical shifts of free and fully complexed dicarboxylates. The stability constants for the *cis* isomers (K_s^{cis}) obtained on the basis of the above equation by linear regression are also collected in Table 1.

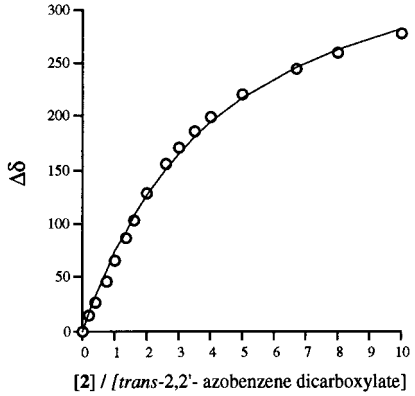

Figure 1. Experimental (O) and calculated (curve) ^1H NMR chemical shifts Δδ of the signal of the H6,6′ protons of *trans*-2,2′-azobenzene dicarboxylate as a function of the cyclo-bis-intercaland **2**/*trans*-2,2′-azobenzene dicarboxylate ratio

The 1:1 stoichiometry observed for all complexes and the fact that the K_s values for complexes with the acridine cyclo-bis-intercaland **2** are higher than those for the acyclic receptor **1** suggest a sandwich or intercalative type of binding in the case of **2** (Table 1). This was confirmed in the solid state by an X-ray structure analysis of the complex between *trans*-3,3′-azobenzene dicarboxylate and cyclo-bis-intercaland **2** (see below). The very strong and preferential binding of this substrate compared to the other three isomers reveals marked electrostatic and structural complementarity between host and guest. On the other hand, lower complementarity between receptor **2** and the (planar) *trans*-2,2′ or (nonplanar) *cis*-isomers results in weaker binding. The results show marked positional (3,3′ > 2,2′) and configurational (*trans* > *cis*) selectivity in the binding of the four substrates by receptor **2**. Indeed, molecular recognition of the substrate implies both geometrical and interactional complementarity between the associating partners, i.e., optimal information content of a receptor with respect to a given substrate. In the course of these complexation studies it was also found that binding led to an acceleration in *cis* to *trans* thermal isomerization[25]. This interesting effect is currently being studied and will be described in a later report.

Table 1. Stability constants (log K_s) for various 1:1 receptor/substrate complexes determined by ^1H NMR spectroscopy in D_2O solution (pD = 6.0)

Substrate	log K_s	
	Acyclic receptor **1**	Cyclo-bis-intercaland **2**
trans-3,3′-azobenzene dicarboxylate	2.7	5.4
cis-3,3′-azobenzene dicarboxylate	2.1	4.0
trans-2,2′-azobenzene dicarboxylate	1.5	3.1
cis-2,2′-azobenzene dicarboxylate	– [a]	2.7

[a] Because of fast *cis*/*trans* thermal isomerization in the presence of acyclic acridine receptor **1** this value could not be determined.

Molecular Structure of the Inclusion Complex

The X-ray structure of the complex between *trans*-3,3′azobenzene dicarboxylate and receptor **2** reveals an original host/guest association (Figures 2 and 3). The four positive charges of the macrocyclic receptor **2** are balanced by two azobenzoate dianions. Cocrystallized water molecules are also present in the supramolecular structure.

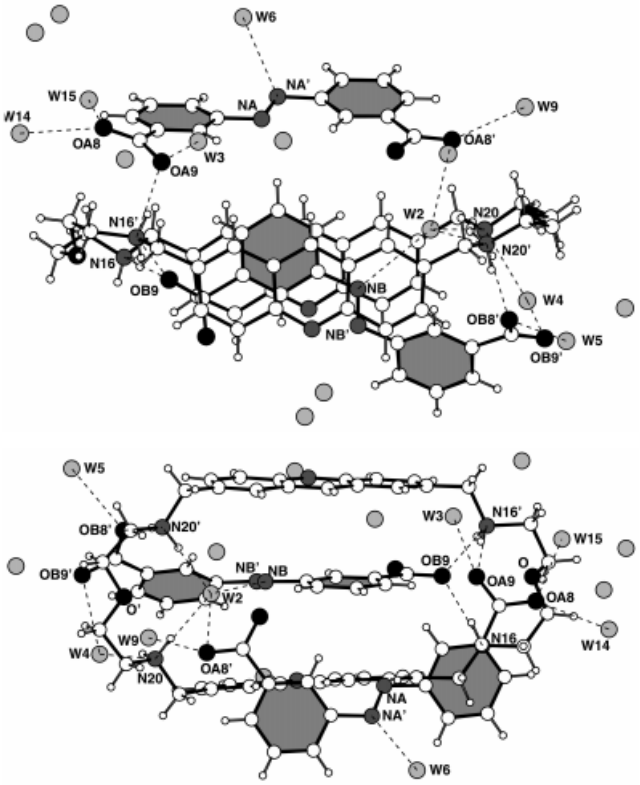

Figure 2. (a) Representation of the inclusion complex viewed normally to the acridine subunits, the macrocyclic receptor being surrounded by water molecules (hydrogen bonds are represented by dotted lines); (b) side view

One dianion is partially intercalated between the two acridine subunits of the macrocyclic receptor at a van der Waals contact distance of 3.5 Å. The second moiety of the dianion, tilted by 35° with respect to the inserted part of the substrate, extends out of the cavity of the macrocycle. The second charged guest, whose backbone is less distorted (10° between the two benzene rings), interacts with the macrocyclic framework from the outside, perpendicularly to the flat walls of the receptor.

Hydrogen-bond networks connect the different H-bond donors (NH_2^+), the acceptors (COO^-) and the donor/acceptor water molecules (Table 2). The external dianion is linked to the ligand through only one H-bond, the other H-bond interactions involving water molecules in the vicinity (Figures 2 and 3) The inserted dianion is bound to the ligand through three of the four protonated nitrogens of the macrocyclic receptor **2**, the other interactions of the oxygen atoms of the carboxylate groups are with water molecules. A complete fourfold connected H-bond arrangement of water molecules (range 2.73−3.15 Å) occurs in the hydrophilic channels of the structure.

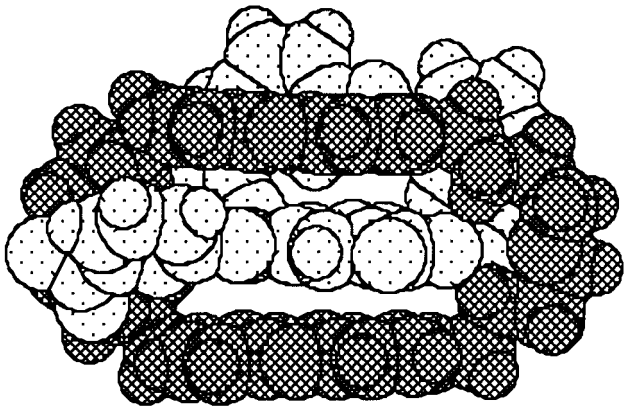

Figure 3. Crystal structure of the intercalative molecular complex in space filling representation

A striking point, revealed in the crystal structure, is the flexibility of the supramolecular arrangement. The size of the aromatic units of the receptor is not sufficient for a full sequestration. To achieve the best inclusion into the macrocyclic receptor as well as the most efficient anchoring to the polyammonium sites, the substrate adapts its length by rotation of the two benzene rings with regard to the Car−N=N−Car junction (internal dianion) or by rotation of the two carboxylate groups. Two different rotamers are observed in the molecular complex, for the external dianion and the inserted one (see Figures 2 and 3).

The binding of the second external substrate is too weak to be detected in the NMR spectroscopic studies in solution. In the solvated state, the complex is charge-stabilized (swamping effect) by the buffer, so that only the entity strongly bound by internal stacking is observed. In the crystal, charge stabilization is achieved by incorporating two dianions, one in the cavity and the other in the lattice.

Table 2. Details of hydrogen bonding features related to the macrocyclic receptor **2**, the substrates and the environment (Å)

Donor	Acceptor	N···O	H···O	< N−H···O
N(16)	O(B8)i	2.671(6)	1.80(1)	162
N(16)	O(B9)	2.787(6)	1.90(1)	167
N(16′)	O(A9)	2.805(6)	1.91(1)	170
N(16′)	O(B9)	2.858(6)	2.04(1)	151
N(20)	W(2)	2.985(6)	2.09(1)	170
N(20)	W(4)	2.768(6)	1.92(1)	157
N(20′)	O(B8′)	2.746(6)	1.85(1)	172
N(20′)	W(2)	2.905(6)	2.06(1)	155
W(15)	O(A8)	2.747(9)		
W(14)	O(A8)	2.919(8)		
W(3)	O(A9)	2.727(7)		
W(9)	O(A8′)	2.746(7)		
W(2)	O(A8′)	3.236(6)		
W(5)	OB8′)	2.796(6)		
W(4)	O(B9′)	2.806(7)		
W(6)	N(A′)	3.028(7)		
W(2)	N(B)	3.064(5)		

i = $-x$, $-y$, $2-z$.

The supramolecular assembly displays a very close packing. This indicates that the equilibrium spatial arrangement results from electrostatic interactions and stacking of the flat aromatic units as well as from staggering, a common feature observed in many aromatic compounds.[26] Stacking is observed both with the dianion inserted between the bis-acridine subunits, with a contact distance of 3.5 Å, and with the two centrosymmetrical external dianions, located in the crystal at an interplanar spacing of 3.8 Å. The staggering occurs with the external dianion, perpendicular to the acridine subunits.

Conclusion

The present results demonstrate the remarkable binding affinity and selectivity in water of the cyclo-bis-intercaland receptor **2** towards isomeric azobenzene dicarboxylates. The variation in the binding strength of the substrates with a change in configuration as well as in the position of the H-bond acceptors indicates that both stacking and electrostatic effects contribute to the stability of the complexes. The higher stability constants obtained for the cyclo-bis-intercaland **2** with respect to the acyclic receptor **1**, as well as the X-ray structure analysis of the complex between compound **2** and *trans*-3,3′-azobenzene dicarboxylate confirm that the binding is of intercalative type.

Studies of the effect of acridine receptors on the photochemical and thermal *cis*/*trans* isomerization of azobenzene dicarboxylates are in progress and will be described elsewhere.

Experimental Section

Materials and Methods: All commercially available chemicals employed were reagent grade and used without further purification. Melting points were determined on an Electrothermal digital melting-point apparatus. The microanalyses were performed at the Service Régional de Microanalyse de l'Université Pierre et Marie Curie (Paris). ^{1}H NMR spectra were recorded on Bruker AC 200 or Bruker AM 400 spectrometers. Cacodylate buffer (50 mM) was prepared by dissolving sodium cacodylate (Aldrich) in D_2O and pD was adjusted at 6.0 by adding DCl. *trans*-3,3′-Azodibenzoic acid disodium salt was prepared by glucose reduction of 3-nitrobenzoic acid in basic conditions according to the described method.[27] Crystallization from H_2O/acetone mixture afforded the pure product. Whereas reduction of 2-nitrobenzoic acid by glucose in basic conditions did not give the desired product, use of Zn instead of glucose as a reducing reagent afforded *trans*-2,2′-azodibenzoic acid.[28] The reaction mixture was extracted with diethyl ether. The organic layer was washed with water, dried (Na_2SO_4) and the solvent evaporated. Pure product was obtained by recrystallization from hot MeOH. Photostationary-state mixtures of *cis* and *trans* isomers of 2,2′- or 3,3′-azobenzene dicarboxylates for use in ^{1}H NMR competition experiments were obtained by UV (λ = 326 nm) irradiation of buffered solutions of their *trans* isomers. The *cis*/*trans* ratio was estimated on the basis of the area of the corresponding signals in the ^{1}H NMR spectra. Acridine-2,7-dicarbaldehyde and 2,7-(di-*n*-propylaminomethyl) acridine **1** were prepared as previously described.[12] 2,2′-Oxybis(ethylamine) was obtained from its dihydrochloride salt (Aldrich) by treatment with NaOH in methanol.

2,8,21,27-Tetraaza-5,24-dioxo[9,9](2,7)acridinophane-1,8,20,27-tetraene (3): A solution of 2,2′-oxybis(ethylamine) (222 mg, 2.13 mmol) in MeOH (100 mL) was added dropwise over 6 h at room temperature under argon to a well-stirred solution of acridine-2,7-dicarbaldehyde (500 mg, 2.13 mmol) in CH_2Cl_2/MeOH (1:1 mixture, 500 mL). The reaction mixture was stirred at the same temperature overnight. Evaporation of the solvent under reduced pressure without heating left an oily residue which was chromatographed (preparative TLC, neutral Al_2O_3) eluting with a gradient of MeOH in CH_2Cl_2 to obtain compound **3** (377 mg, 58% yield) as the main fraction which was not further purified. – R_f = 0.5 (neutral Al_2O_3, CH_2Cl_2/MeOH = 95:5). – ^{1}H NMR ($CDCl_3$ + CD_3OD): δ = 3.75 (m, CH_2, 4 H), 3.83 (m, CH_2, 4 H), 7.12 (s, Acridine-H1, -H8, 2 H), 7.57 (s, Acridine-H9, 1 H), 7.93 (d, Acridine-H4, -H5, 2 H, J = 9.2 Hz), 8.1 (m, CH, Acridine-H3, -H6, 4 H)

2,8,21,27-Tetraaza-5,24-dioxo[9,9](2,7)acridinophane (2): $NaBH_4$ (62 mg, 1.65 mmol) was added at 0°C to a solution of acridinophane **3** (200 mg, 0.33 mmol) in CH_2Cl_2/MeOH (1:1 mixture, 40 mL). After stirring for 1 hour at 0°C and 30 min at room temperature the solvent was evaporated, the residue dissolved in water and extracted with a CH_2Cl_2/MeOH (9:1) solvent mixture. The organic phase was dried (Na_2SO_4) and solvents evaporated. The oily residue was crystallized from a hot HCl/EtOH/THF mixture. Repeated recrystallization gave pure product **2** (yellow-green powder, 190 mg, 61% yield). – ^{1}H NMR (D_2O): δ = 3.35 (m, CH_2, 4 H), 3.76 (m, CH_2, 4 H), 4.06 (m, CH_2, 4 H), 7.68 (d, Acridine-H3, -H6, 2 H, J = 9.3 Hz), 7.9 (m, Acridine-H1, -H4, -H8, -H5, 4 H), 9.0 (s, Acridine-H9, 1 H). – $C_{38}H_{48}Cl_6N_4O_2 \cdot 6H_2O$: calcd. C 47.52, H 6.37, Cl 22.62, N 8.92, O 13.59; found C 47.90, H 6.31, Cl 20.06, N 8.33, O 12.83.

Stability Constants Determination: The stability constants of the complexes between the acridine receptors **1**, **2** and *trans*-2,2′-, or *trans*-3,3′-azobenzene dicarboxylates were determined by ^{1}H NMR spectroscopy in cacodylate buffer (50 mM, pD = 6.0) at ambient temperature. In these experiments the concentration of azobenzene dicarboxylates was kept constant (0.5 mM for titration with acyclic receptor **1**, and 0.25 mM for titration with cyclo-bis-intercaland receptor **2**), while the concentration of acridine receptors was varied from 25 to 0.5 mM for acyclic receptor **1**, and from 2.5 to 0.05 mM for cyclo-bis-intercaland receptor **2**. The stability constants of the complexes between the acridine receptors **1**, **2** and the *cis*-2,2′- or *cis*-3,3′-azobenzene dicarboxylates were determined by ^{1}H NMR competition experiments between the *cis* and *trans* isomers, under the same conditions as for the *trans* isomer. In all experiments the signal of the cacodylate protons in the ^{1}H NMR spectrum was used as internal standard.

X-ray Data of the Complex Between Receptor 2 and the *trans*-3,3′-Azobenzene Dicarboxylate: Crystallization of the complex from a water/acetone solution by slow evaporation at room temperature gave very small mica-shaped plates with a max. size of 0.3 mm and a thickness never exceeding 10 to 20 microns. They were unstable upon exposure to air and were mounted in Lindemann capillaries. A single yellowish micro crystal, 0.25 × 0.1 × 0.01 mm in size, was used for the complete X-ray data study. As the use of a standard diffractometer did not give enough observed reflections, X-ray data were recorded at the W-32 beam-line of the DCI synchrotron in Orsay, France,[29] using the rotation method on a MAR Research Image Plate detector (Ø 345 mm). Because of the small size of the

crystal and to reduce the background on the detector, the entrance slits at the beam-port were reduced to values of 0.15 × 0.15 mm. Each frame consists of a 3° rotation of the crystal around the spindle axis, with an exposure time of 30s. The crystal-to-detector distance (d = 9.5 cm) was set to achieve a resolution spacing of 1.0Å at the edge of the detector. The final data set comprises a total of one hundred frames (overall rotation of the crystal = 300°).

The processing of the data was done with the DENZO program.[30] The poor quality of the crystal was evident both from the shape of the spots and the difficulty in achieving a correct initial orientation matrix: extra Bragg reflections corresponding to a twinned region, or maybe a broken part of the crystal, were interfering during the auto-indexing step. This problem was overcome by interactively removing these extra-reflections. The intensities were corrected as usual from Lorentz and polarization effects and reduced to a unique set using the SCALA program of the CCP4 suite.[31] Finally, structure factors were derived by application of the French & Wilson method[32] as coded in the TRUNCATE program of the CCP4.

The structure was solved by direct methods using the SHELXS86 program[33] and anisotropically refined on F^2 for all reflections by least-squares procedures.[34] The asymmetric unit contains one macrocyclic receptor cation, two azodibenzoate anions, and fifteen water molecules. No signature for acetone was observed in the electron density.

In order to cope with the important number of parameters versus the data, a blocking strategy of the refinement was to divide the structure into three overlapping blocks of positional and thermal parameters. All the hydrogen atoms of the macrocyclic receptor and the dianions were located on difference-Fourier syntheses. Their positions were refined with distance restraints (C−H = 0.97Å, N−H = 0.90Å) and assigned isotropic thermal parameters equal to 1.3 times that of the bonded atom.

Table 3. Crystal data and summary of the refinement

Chemical formula	$[C_{38}H_{46}N_6O_2]$, $2[C_{14}H_8N_2O_4]$,$15H_2O$
Molecular weight	1425.50
No. of independent receptor (a.u.)	1
No. of independent anion (a.u.)	2
Solvent (a.u.)	15 water molecules
Space group	*P*-1(No.2)
a, Å	10.606(5)
b, Å	18.842(8)
c, Å	19.483(8)
α, °	71.27(3)
β, °	85.49(3)
γ, °	84.08(4)
V, Å^3	3663(3)
Z	2
D_{calc}, g cm^{-3}	1.292
Wavelength, Å	0.97
μ, mm^{-1}	0.10
F(000):	1516
No. of reflections in the refinement: total/observed[a]	6382/6124
No. of independent atoms	103
No. of parameters/restraints	924/50
wR_2 on I (%) all data/observed data[a]	25.0/24.7
wR_1 on F (%) all data/observed data	8.92/8.68
Min/Max in last difference-Fourier map (e/Å^3)	−0.20/+0.49

[a] Criterion for observed data: $I = 2\sigma(I)$.

Of the fifteen water molecules located in the structure, thirteen are fully ordered and correctly hydrogen-bonded to the model. The two last water molecules are disordered and distributed between two [70:30, W(10) and W(11)] or three [40:40:20, W(16), W(17) and W(18)] sites. They were all refined with anisotropic thermal factors, except the minor sites, which were kept isotropic.

In the final electron density map, two residual peaks of 0.49 and − 0.20 e Å^{-3} were observed in the vicinity of the [W(10)/W(11)] and [W(16)/W(17)/W(18)] regions. However, all attempts to model these peaks by disordered solvents failed to improve either the quality of the map or the agreement factors. The final statistics regarding the refinement are reported in Table 3.

The list of atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms, bond lengths and angles, atomic coordinates of hydrogen atoms, has been deposited with the Cambridge Crystallography Data Centre as supplementary publication number CCDC-133358. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk] and is also available as a standard cif file from the authors at cesario@icsn.cnrs-gif.fr.

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