Journal of Inclusion Phenomena and Macrocyclic Chemistry (2005) 51: 181–189
DOI 10.1007/s10847-005-2498-5

Crystal Structures of 1,5,9,18,22,26-Hexaaza[11.11]-*p*-cyclophane Adducts; Two-dimensional Supramolecular Networks

TERESA BOROWIAK[1,*], MACIEJ KUBICKI[1], GRZEGORZ DUTKIEWICZ[1], MAREK PIETRASZKIEWICZ[2] and OKSANA PIETRASZKIEWICZ[2]
[1]*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780, Poznań, Poland;* [2]*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warszawa, Poland*

(Received: 18 February 2004; in final form: 17 February 2005)

Key words: hydrogen bonding, macrocyclic amines, molecular recognition, two-dimensional supramolecular frameworks, weak and strong acid adducts of, X-ray diffraction

Abstract

Two newly identified supramolecular structures arise from self-assembly of the macrocyclic 1,5,9,18,22,26-hexaaza[11.11]-*p*-cyclophane salts with *o*-nitrophenol $(C_{28}H_{50}N_6)^{4+}\cdot 4(C_6H_4NO_2O)^-$ (**1**) and with HCl $(C_{28}H_{52}N_6)^{6+}\cdot 6Cl^-\cdot 4H_2O$ (**2**). In both cases two-dimensional supramolecular sheets are formed.

Introduction

Macrocyclic polyamines are versatile building blocks in supramolecular chemistry, e.g. symmetrical polyaza-macrocycles of large size can be highly protonated in acidic media and can form supramolecular assemblies with different anions. The salts of 1,4,8,11-tetraazacyclotetradecane $C_{10}H_{24}N_4$, Scheme 1 (a), with their architectures ranging between one-dimensional to three-dimensional aggregates are a good example [1–3]. A similar diversity of supramolecular structures has been found for the salts of 1,4,7,16,19,22-hexaaza[9.9]-*p*-cyclophane, $C_{24}H_{38}N_6$, Scheme 1 (b), (hereafter MAC-7) whose supramolecular aggregates with different anions were extensively studied by X-ray diffraction [4–8]. No structural information is available on larger symmetrical hexaaza macrocyclic amines and their salts [9], so we have commenced a new investigation into the use of 1,5,9,18,22,26-hexaaza[11.11]-*p*-cyclophane (hereafter MAC-9, Scheme 1 (c), as a flexible macrocyclic molecular receptor. MAC-9 is similar in its constitution to MAC-7 but the aliphatic chains are longer as they contain two identical N(3-aminopropyl)-1,3-propanediamine moieties between two *p*-xylyl spacers. MAC-9 should show higher flexibility than that observed for the MAC-7 macrocycle. Similar to MAC-7, also MAC-9 forms adducts even with weak acids like phenols. In this paper we report the results of the X-ray investigation of two adducts formed between MAC-9 and some acidic compounds: *o*-nitrophenol and hydrochloric acid. These two structures demonstrate flexibility of the macrocycle conformations, sites of protonation and two-dimensional networks. The adduct of MAC-9 with *o*-nitrophenol proved to be the salt $[(C_{28}H_{50}N_6)^{4+}]\cdot 4[(O_2N{-}C_6H_4O)^-]$ in which the cation is tetra-protonated (hereafter **1**) and the adduct with hydrochloric acid is a hydrated hexa-protonated salt $[(C_{28}H_{52}N_6)^{6+}]\cdot 6Cl^-\cdot 4H_2O$ (hereafter **2**).

* Author for correspondence. E-mail: borowiak@amu.edu.pl

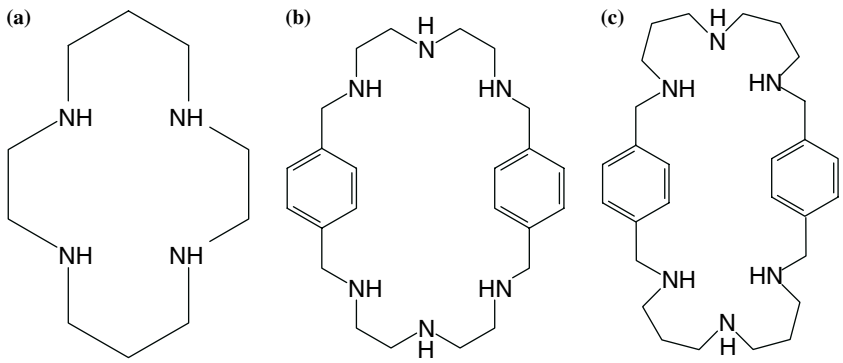
Experimental

Synthesis

The macrocycle MAC-9 was prepared using method reported by Pietraszkiewicz and Gąsiorowski [10]. *o*-Nitrophenol (Sigma-Aldrich), hydrochloric acid (Chempur), acetonitrile (Fluka) and ethanol (96%, Chempur) all were of analytical grade. The ^{1}H-NMR spectra for the adduct of MAC-9 with *o*-nitrophenol and hydrochloric acid were recorded on a Varian 400 MHz spectrometer in $CDCl_3$ (TMS as reference) and on a Bruker 500 MHz spectrometer in D_2O (DSS as reference), respectively.

Thermogravimetry measurements were run on the Du Pont Thermal Analyst 2100 equipped with TGA 951 module. Runs were performed at a scan rate of 10 K min^{-1} under Ar.

Synthesis of the MAC-9 adduct with o-nitrophenol
Solution of *o*-nitrophenol (1.5 mM, 0.208 g) in 2 cm^3 of acetonitrile was added to 0.25 mM of MAC-9 (0.1165 g) dissolved in 2 cm^3 of hot acetonitrile. A yellow precipitate was formed. After cooling the reaction mixture, the precipitate was filtered off, washed with small amount of acetonitrile and dried.



Scheme 1. Formulas of macrocyclic amines: (a) 1,4,8,11-tetraazacyclotetradecane, (b) 1,4,7,16,19,22-hexaaza[9.9]-*p*-cyclophane (MAC-7), (c) 1,4,9,18,22,26-hexaaza[11.11]-*p*-cyclophane (MAC-9).

^{1}H-NMR δ (ppm), ($CDCl_3$): 8.10 (dd, 4H, 4 × *o*-nitrophenyl), 7.58 (m, 4H, 4 × *o*-nitrophenyl), 7.25 (s, 8H, 2 × Ar), 7.16 (dd, 4H, 4 × *o*-nitrophenyl), 6.97 (m, 4H, 4 × *o*-nitrophenyl), 3.70 (s, 8H, 4 × $\mathbf{CH_2}$Ar), 2.68 (dt, 16H, 8 × $\mathbf{CH_2}CH_2\mathbf{CH_2}$), 2.01 (q, 8H, 4 × $CH_2\mathbf{CH_2}CH_2$).

Elemental analysis: Calculated for $C_{52}H_{66}N_{10}O_{12}$: C – 61.04%; H – 6.50%; N –13.69%. Found: C – 61.11%; H – 6.61%; N – 13.56%. Crystals suitable for X-ray measurements were prepared by dissolution of precipitate in hot ethanol (96%, p.a.) and slow cooling. Dark yellow crystals of prism shape were obtained after a few days.

Synthesis of the MAC-9 adduct with hydrochloric acid

For synthesis of this adduct 0.25 mM of MAC-9 (0.1165 g) was dissolved in 1 cm^3 of water then hydrochloric acid was added dropwise to pH 2. Then ethanol (3 cm^3) was added and white precipitate was filtered off and washed with ethanol. Crystals, colorless prisms, suitable for X-ray structure were crystallized from water.

^{1}H-NMR δ (ppm), (D_2O): 7.56 (s, 8H, Ar), 4.32 (s, 8H, 4 × $\mathbf{CH_2}$Ar), 3.03 (q, 16H, 4 × $\mathbf{CH_2}CH_2\mathbf{CH_2}$), 2.06 (m, 8H, 4 × $CH_2\mathbf{CH_2}CH_2$).

Elemental analysis: Calculated for $C_{28}H_{52}N_6.4H_2O$: C – 44.39%; H – 7.98%; N – 11.09%. Found: C – 44.26%; H – 8.06%; N – 10.95%. TGA: mass loss 9.92% in the range of temperatures 56–124 °C was assigned to the loss of 4.2 water molecules.

Data collection, structure solution and refinement

A yellow prism of dimensions 0.1 × 0.1 × 0.35 mm for **1** and a colorless prism of dimensions 0.2 × 0.3 × 0.5 mm for **2** were chosen for X–ray diffraction experiments. Diffraction data were collected on a KUMA KM4CCD diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 100(1) K for **1** and at room temperature for **2** [11]. Low temperature was controlled with Oxford Cryosystem cooling device. The measurements were done in six separate runs in order to cover the symmetry-independent part of the reciprocal space. The ω-scan was used with the step of 0.75° for **1** and 0.6° for **2**, two reference frames were measured after every 50 frames, they did not show any systematical changes neither in the peak positions nor in their intensities. Total of 782 frames for **1** and 956 frames for **2** were collected. The unit-cell parameters were determined by least squares treatment of the setting angles of 2442 (**1**) and 5193 (**2**) highest intensity reflections, chosen from the whole experiment. The Lorentz and polarization corrections were applied [12] as well as the absorption corrections (multi scan method [13]). The structures were solved by direct methods with SHELXS-97 program [14] and refined by full matrix least squares on F^2, using SHELXL-97 program [15]. Scattering factors incorporated in SHELXL-97 were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized with $w^{-1} = [\sigma^2(F_o)^2]$ and $w^{-1} = [\sigma^2(F_o)^2 + (0.153P)^2 + 2.1P]$ for **1** and **2**, respectively, where $P = (F_o^2 + 2F_c^2)/3$. Molecular graphics were performed with standard programs [16]. Relevant crystallographic data together with data collection and structure refinement details are listed in Table 1. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **1** were located in the subsequent ΔF maps and then their positional parameters and U_{iso} were refined. One common U_{iso} factor for each hydrogen atom of CH_2 groups was used and refined. Positions of all hydrogen atoms for **2** were calculated in their idealized positions first, and then the positional parameters of the hydrogen atoms involved in hydrogen bonding were refined. The positions of the remaining hydrogen atoms were refined using a riding model. Isotropic displacement parameters were fixed at 1.2 of U_{eq} of their parent non-hydrogen atoms.

Two different peaks in **2** of about 1.5 e/Å^3 each, have been interpreted as oxygen atoms of water molecules. They were refined isotropically, and their U_{izo} are as high as 0.30–0.31 Å^2, a few times higher than U_{eq} for non-hydrogen atoms of the macrocycle. These high values are caused probably by disorder of water molecules in the channels of the structure (Figure 6). In consequence of low precision of oxygen parameters, the water hydrogen atoms haven't been found. Disorder of the water molecules has brought about a low precision of the structure model for **2**, all the statistical indicators adopt high values, Table 1.

Table 1. Crystal data, data collection and structure refinement

Compound	**1**	**2**
Formula	$(C_{28}H_{50}N_6)^{4+}\cdot 4(C_6H_4NO_3)^-$	$(C_{28}H_{52}N_6)^{6+}\cdot 6Cl^-\cdot 4H_2O$
Formula weight	1023.15	749.46
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/m$
a (Å)	10.9376(14)	7.2402(8)
b (Å)	10.9561(14)	30.582(2)
c (Å)	11.9447(15)	10.6386(6)
α (°)	107.202(11)	90
β (°)	108.963(12)	109.585(8)
γ (°)	91.908(10)	90
V (Å^3)	1279.7(6)	2219.3(4)
Z	1	2
D_x (g cm^{-3})	1.33	1.12
$F(000)$	544	792
μ (mm^{-1})	0.1	0.42
θ range (°)	2–27	2–25
hkl range	$-13 \le h \le 13$	$-8 \le h \le 6$
	$-13 \le k \le 12$	$-34 \le k \le 36$
	$-12 \le l \le 15$	$-12 \le l \le 12$
Temp. (K)	100	295
Reflections		
Collected	11536	17028
Unique (R_{int})	5528 [0.066]	4005 [0.056]
With $I > 2\sigma(I)$	4206	3184
Number of parameters	448	196
$R(F)$	0.0441	0.0825
$wR(F^2)$	0.0423	0.2626
Goodness of fit	0.716	1.113
max/min $\Delta\rho$ (e Å^{-3})	0.247/−0.201	1.164/−0.529

The ionic components of **1** and **2** together with the labelling scheme are shown in Figures 1 and 2, respectively.

Results and discussion

1,5,9,18,22,26-Hexaaza[11.11]-*p*-cyclophane (MAC-9) contains two N(3-aminopropyl)-1,3-propanediamine sets that make it highly basic in water ($\log K_1 \div \log K_6 : 10.27 \div 6.39$) [17]. Exact assignment of protonation sequence in macrocyclic polyamines in solutions is a rather hard task. Based on ^{1}H and ^{13}C NMR spectra we could not draw reliable conclusions about protonation sequence for MAC-9 at room temperature. The proton exchange was fast enough, leading to time-averaged signals. The other researchers have also reported problems with protonation sequences for polyazamacrocycles [18].

Due to its high basicity, MAC-9 forms adducts even with rather weak acids, like phenols. We observed formation of yellow adducts with stoichiometry of 1:4 for *o*-nitrophenol (pK_a 7.21) and 1:6 for *p*-nitrophenol (pK_a 7.16) in the solid state. Only adducts with *o*-nitrophenol gave crystals suitable for X-ray measurements.

Constitution of the compounds in the solid state

Compound 1. In **1** the macrocyclic amine captures four protons to form a cation $[C_{28}H_{50}N_6]^{4+}$ in which N(8), N(12), N(8a) and N(12a) are protonated. Thus, there are eight N–H bonds directed out of the macrocycle, Figure 1, and hence this tetra-cation can act as an eightfold donor in intermolecular hydrogen bond formation. Such conformation of the tetra-protonated hexaaza-*p*-cyclophane (MAC-9) makes it a versatile building block for crystal engineering purposes. On the other hand, the N–H bonds at N(16) and N(16a) are directed towards the macrocycle interior (see Figure 3) and for this reason they play only a secondary role in the supramolecular arrangement being connected by weak hydrogen bonds with the oxygen atoms of the nitro groups. Moreover, N(16) and N(16a) remain unprotonated. The cation occupies a special position at an inversion center and is perfectly ordered. Careful examination of difference maps showed no disorder, neither in the positions of the skeletal carbon and nitrogen atoms, nor in the positions of the H atoms.

The *o*-nitrophenol is present as the mono-anion $(O_2NC_6H_4O)^-$, so the ionic synthon is built from four phenolate anions and one centrosymmetric tetra-protonated cation. The asymmetric unit contains a half of the cation

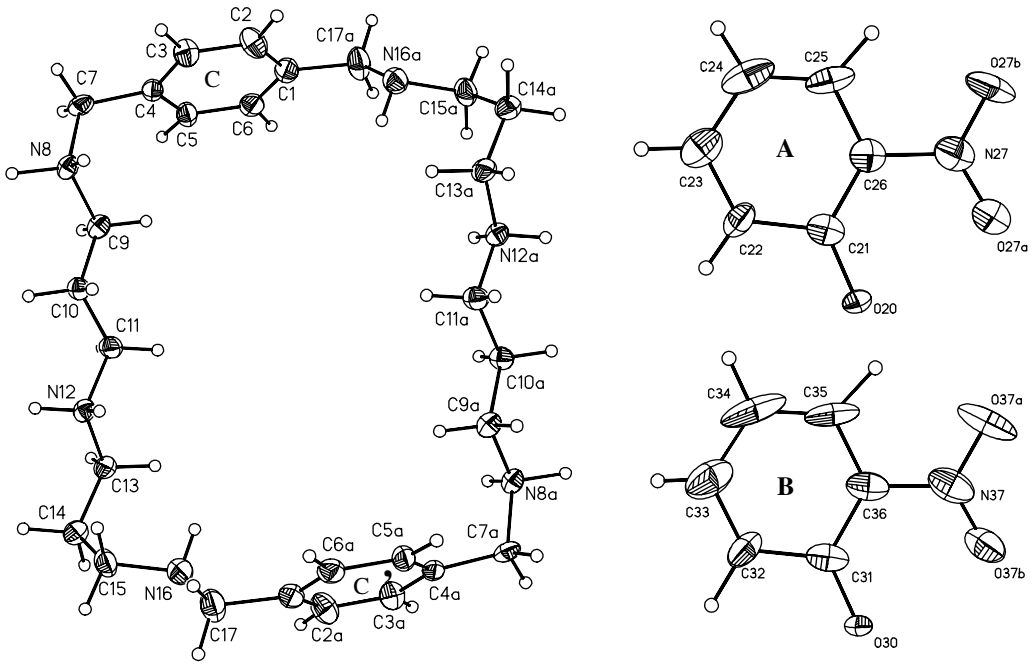


Figure 1. The ionic components of **1** showing the atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level.

and two independent anions, confirming the 1:4 molar ratio of the macrocycle to phenol, deduced from the elemental analysis. Moreover, **1** crystallizes without any solvent molecules. Within the cation, there is a clear difference between the C–N bond lengths involving protonated and unprotonated N atoms, Table 2. The observed ranges here are very similar to those for the corresponding types of bonds in the cations of MAC-7 [4, 6]. Bond lengths and bond angles within two phenolate anions agree with those for *o*-phenolate anion as found by Andersen and Andersen [19].

Compound 2. The ionic components of **2** comprise a six-protonated cation $(C_{28}H_{52}N_6)^{6+}$, lying across a plane of symmetry in $P2_1/m$, and six chloride anions;

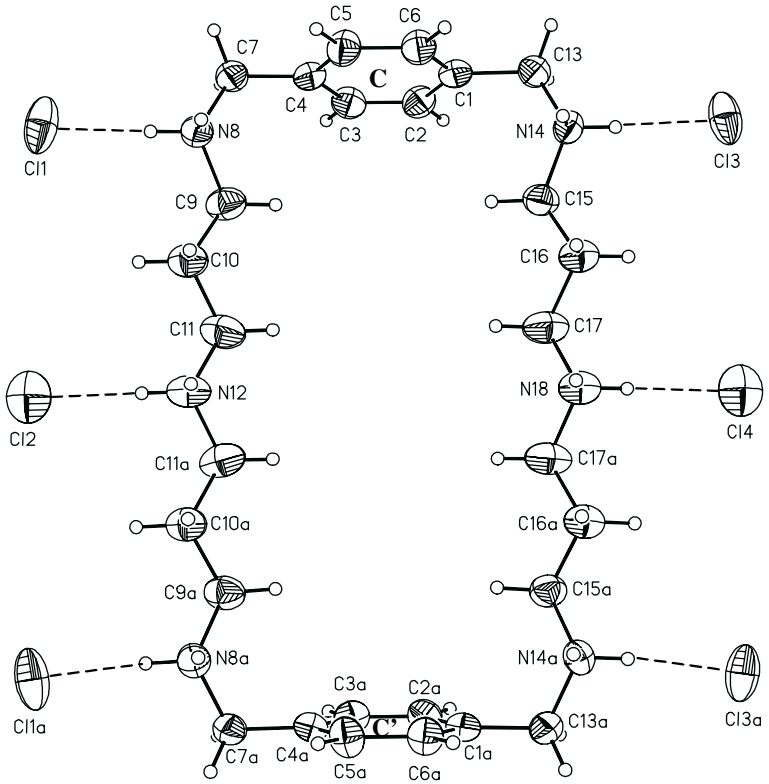


Figure 2. The ionic components of **2** showing the atom labeling scheme. Displacement parameters are drawn at 50% probablity level. The hydrogen bonds are indicated by broken lines.

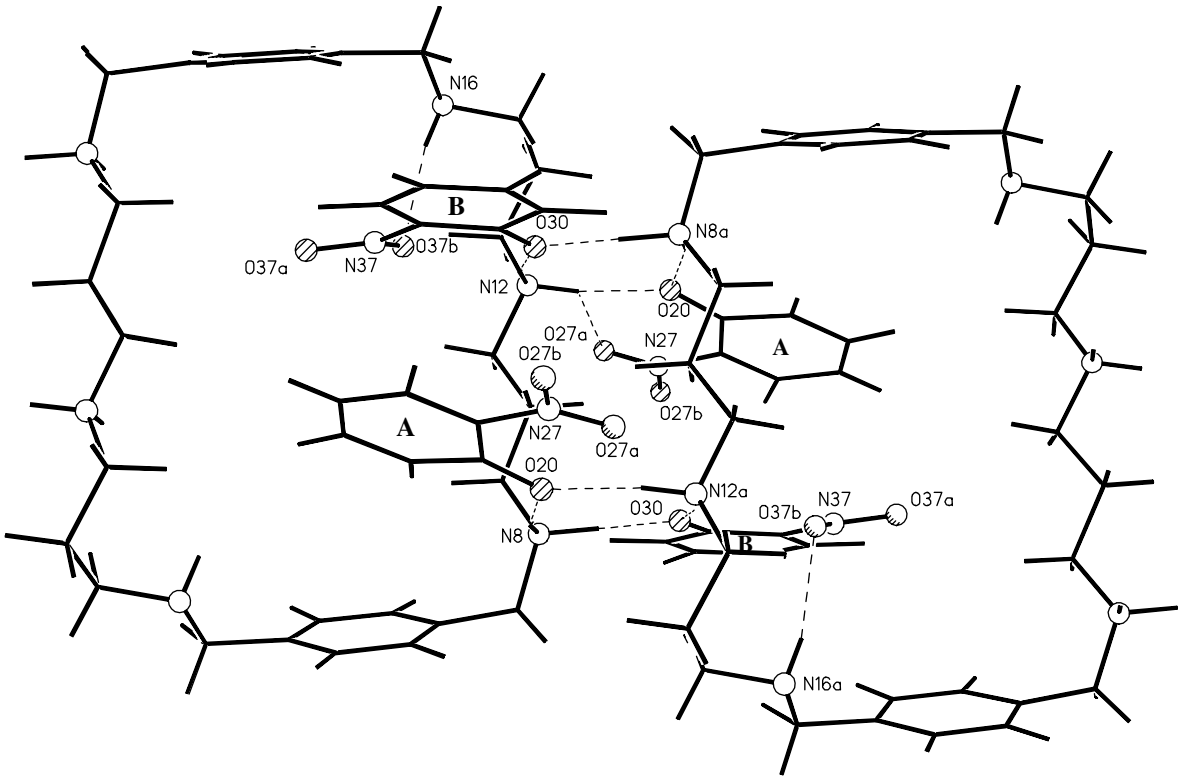


Figure 3. The ionic synthon of **1** built from two MAC-9 cations and four phenolate anions.

$N^+(12)$ and $N^+(18)$ occupy the special positions on the mirror plane, also, two anions are located at the same mirror plane and four are located in general positions, Figure 2.

All twelve N–H bonds are directed out of the macrocycle, six of them are roughly normal to the macrocyclic ring and the other six are located approximately in the average plane of the macrocycle, Figure 2. This hexa-protonated cation can act as a twelvefold donor in hydrogen bond formation. Four water molecules occupy general positions. The overall stoichiometry of cationic amine:chloride:water is thus 1:6:4. The asymmetric unit contains a half of the cation, two chloride anions in general positions and two halves lying across the plane of symmetry, and two water molecules. Also, as in the case of **1**, the cation in the adduct **2** is perfectly ordered. The observed ranges of C–N bond lengths confirm protonation of all N atoms, Table 2.

Conformation of the cations

Compound 1. The cation is centered at the cell center of inversion at 0 1/2 0 and adopts a chair-like conformation, with one N(3-aminopropyl)-1,3-propanediamine moiety flipped down and the other flipped up. The non-H atoms in the aliphatic part show almost perfect staggering about all of the C–C and C–N bonds, with the antiperiplanar (*ap*) torsional angles all within 10° of 180°, and the synclinal (*sc*) torsional angles all within 12° of ±60°. The two phenyl rings are parallel in the consequence of the centrosymmetry of the macrocyclic ring. Three other parameters have been used to provide a measure of the conformation: the distance between the ring centroids Ct(C)···Ct(C′) which indicates the 'length' of the macrocycle and the distance C(11)···C(11a) provides a measure of the 'width' of the macrocycle. The perpendicular distance between the two phenyl ring centroids provides a measure of the shift of the aryl rings relative to the saturated framework. These parameters are as follows: the Ct(C)···Ct(C′) is 10.77(1) Å, the 'width' of the macrocycle is 7.60(1) Å and the shift is 2.1(1) Å.

Compound 2. Two unexpected features of the cation structure have been found. The first one concerns the protonation sites described earlier, the second one concerns the cation conformation. It differs from that in **1** and its symmetry is close to C_{2v} (mm) point symmetry with the additional, non-crystallographic plane of symmetry perpendicular to the crystallographic one. As in the case of the cation in **1**, the non-H atoms in the aliphatic part show almost perfect staggering about all of the C–C and C–N bonds, with the antiperiplanar (*ap*) torsional angles all within 4° of 180°, and the synclinal (*sc*) torsional angles all within 8° of ±60°. The shape of the cation is close to a perfect slender rectangle with the height – the distance between ring centroids of 12.31(1) Å and the width – the N(12)···N(18) distance of 7.23(2) Å. Due to the crystallographic symmetry no shift between the centroids of the phenyl rings exists, although they are oriented in the antiparallel mode with the angle between their planes of 17.1(1)°.

Table 2. Selected molecular dimensions (Å, °)

Compound **1**	
N(8)–C(7)	1.506(3)
N(8)–C(9)	1.482(3)
N(12)–C(11)	1.491(3)
N(12)–C(13)	1.498(3)
N(16)–C(15)	1.480(3)
N(16)–C(17)	1.463(3)
N(8)–C(7)–C(4)–C(5)	91.2(3)
N(8)–C(7)–C(4)–C(3)	−85.6(3)
N(16a)^{i}–C(17a)^{i}–C(1)-C(2)	48.3(4)
N(16a)^{i}–C(17a)^{i}–C(1)–C(6)	−129.1(3)
Ct(C)–Ct(C′)	10.77(1)
Width	7.60(1)
Shift	2.1(1)
Compound **2**	
N(8)–C(7)	1.495(5)
N(8)–C(9)	1.475(5)
N(12)–C(11)	1.472(5)
N(14)–C(13)	1.491(5)
N(14)–C(15)	1.491(5)
N(18)–C(17)	1.484(5)
N(8)–C(7)–C(4)–C(5)	−74.2(4)
N(8)–C(7)–C(4)–C(3)	106.7(4)
N(14)–C(13)–C(1)–C(2)	−104.9(4)
N(14)–C(13)–C(1)–C(6)	74.8(4)
Ct(C)–Ct(C′)	12.31(1)
Width	7.23(2)
Slope	17.1(1)

Symmetry code: (*i*) $-x, -y-1, -z$
Ct(C), Ct(C′) are the centroids of the aromatic rings; 'width' is the distance C(11) ··· (11a) in **1** and N(12) ··· N(18) in **2**; 'shift' is the perpendicular distance between the phenyl ring centroids; 'slope' is the angle between the aromatic ring planes.

Supramolecular structures

Compound 1. The macrocyclic cation contains 10 N–H bonds, five of them are symmetrically independent and all of them participate in hydrogen bonding. Each of the symmetrically independent cationic N atoms, $N^+(8)$ and $N^+(12)$, acts as a double donor of two hydrogen bonds to two different anions: $N^+(8)$ is linked to the deprotonated *o*-nitrophenol $O^-(20)$ ($x-1, y-1, z$) and deprotonated *o*-nitrophenol $O^-(30)$ (x, y, z) by means of strong ionic N^+–H···O^- hydrogen bonds, Table 3, Figure 3. Also $N^+(12)$ forms two hydrogen bonds to the deprotonated $O^-(20)$ ($-x+1, -y+1, -z$) and $O^-(30)$ ($-x, -y, -z$). Thus, each of two deprotonated $O^-(20)$ and two deprotonated $O^-(30)$ participates in bifurcated hydrogen bonds which close two eight membered rings connecting two neighbouring macrocycles with the atomic sequence as follows: $N^+(8)$–H(8a)···$O^-(20)$···H(12b)–$N^+(12)$–H(12a)···$O^-(30)$···H(8b)–$N^+(8)$, Figure 3. One of the rings is located approximately at the level of one third of the macrocycle height and the other one, at the level of two thirds. Thus, the ionic synthon is built from two macrocyclic cations and four phenolate anions. It propagates into chains running parallel to the [010] direction, Figure 4.

The strong hydrogen bonds just described are crucial to the packing mode in crystals of **1**. They play a steering role in their subsequent organization. Firstly, in spite of heterogenous chains formed by hydrogen bonded macrocyclic cations and phenolate anions, there are also homogenous chains built from the two crystallographically independent anions only. The anions are hydrogen bonded by weak C–H···O bonds formed between the aromatic C–H groups and O atoms of the nitro groups. Secondly, the phenolate chains expand into sheets that the eight-membered hydrogen bonded rings are built in, Figure 4. There are two such rings between two macrocyclic cations, one above another, each macrocyclic cation participates in making two sheets, related by inversion centers, Figure 5. The sheets are slightly folded.

There are also some other hydrogen bonds that can be qualified as artefacts only, with no meaning for the packing modes, namely, the unprotonated N(16) acts as proton donor to the N(16)–H(16)···O(37b) hydrogen bond. Also, both, H(12a) and H(12b) participate in bifurcated hydrogen bonds, the strong ones mentioned above and weaker, to oxygen atoms of nitro-groups, $N^+(12)$–H(12a)···O(37b) and $N^+(12)$–H(12b)···O(27a), Table 3. The phenolate anions are not located in the macrocyclic cage, two of them 'hang' over the cage, two are located below the cage.

In the third direction there are only weak van der Waals interactions between macrocycles, so the supramolecular structure generated by specific intermolecular interactions is limited to two dimensions only. Due to deficiency of proton donors in this structure, a three-dimensional supramolecular arrangement cannot be created.

Compound 2. All N atoms of the macrocycle in **2** are protonated. Thus, the macrocyclic cation contains twelve N–H bonds, six of them are symmetrically independent. All Cl^- anions interact with the cationic nitrogen atoms by means of strong hydrogen bonds N^+–H···Cl^-, Figure 2, Table 3. The ionic synthon formed in this way propagates into sheets with the thickness of one macrocycle, i.e. of about 12 Å, Figure 6. The structure of one sheet conforms to the non-directional nature of ionic interactions. Each Cl^- anion is hydrogen bonded to two N^+–H groups coming from different cations; there are also some weak interactions to each Cl^- anion, namely three hydrogen bonds C–H···Cl^- and probably one O–H···Cl^- hydrogen bond to the water molecule, Figure 6, Table 3. The total number of interactions to each anion is six, the same as in the structure of NaCl, although the coordination mode is far from a regular octahedron. As a result of non-directionality of ionic interactions to Cl^-, two kinds of channels in each sheet are formed. One of them is filled with three Cl^- anions (the ionic radius of Cl^- is 1.81 Å) and the other holds four disordered water molecules whose hydrogen atoms have not been

Table 3. Hydrogen-bond dimensions (Å, °)

Compound **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	< D–H···A
$N^+(8)$–H(8a) $O^-(30)$ ^{i}	0.96(3)	1.80(3)	2.722(3)	160(3)
$N^+(8)$–H(8b)···$O^-(30)^{ii}$	1.12(3)	1.54(3)	2.659(3)	177(2)
$N^+(12)$–H(12a)···$O^-(30)^{iii}$	0.92(2)	1.87(2)	2.759(3)	162(2)
$N^+(12)$–H(12b)···$O^-(20)^{iv}$	0.98(2)	1.78(2)	2.749(3)	168(2)
$N^+(12)$–H(12a)···O(37b)^{iii}	0.92(2)	2.35(2)	2.931(3)	122(2)
$N^+(12)$–H(12b)···O(27a)^{iv}	0.98(2)	2.34(2)	2.860(3)	112(2)
N(16)–H(16)··· O(37b)^{iii}	0.87(2)	2.32(3)	3.148(4)	159(2)
C(23)–H(23)··· O(37b)^{v}	1.00(2)	2.38(3)	3.324(4)	159(2)
C(33)–H(33)··· O(27a)^{vi}	0.92(3)	2.55(3)	3.429(4)	160(3)

Compound **2**

D–H···A	d(D–H)	d(H···A)	d(D···A)	< D–H···A
$N^+(8)$–H(8a)···$Cl^-(1)$	0.78(4)	2.33(4)	3.103(4)	176(4)
$N^+(8)$–H(8b)···$Cl^-(3)^{i}$	0.97(6)	2.18(6)	3.101(4)	158(4)
$N^+(12)$–H(12a)···$Cl^-(2)$	0.92(7)	2.20(8)	3.103(7)	168(6)
$N^+(12)$–H(12b)···$Cl^-(4)^{i}$	0.92(6)	2.19(6)	3.107(5)	175(5)
$N^+(14)$–H(14a)···$Cl^-(1)^{ii}$	0.88(5)	2.27(5)	3.094(3)	156(4)
$N^+(14)$–H(14b)···$Cl^-(3)$	1.04(5)	2.05(5)	3.083(3)	175(3)
$N^+(18)$–H(18a)···$Cl^-(2)^{ii}$	1.17(9)	1.93(9)	3.104(5)	175(7)
$N^+(18)$–H(18b)···$Cl^-(4)$	0.92(8)	2.18(8)	3.093(7)	171(6)
C(2)-H(2a)···$Cl^-(1)^{iii}$	1.04(4)	2.77(4)	3.759(4)	160(3)
C(6)–H(6a)···$Cl^-(1)^{ii}$	0.93(4)	3.06(4)	3.887(4)	148(3)
C(3)-H(3a)···$Cl^-(3)^{iv}$	1.10(4)	2.76(4)	3.800(4)	157(3)
C(5)-H(5a)···$Cl^-(3)^{i}$	0.95(4)	3.02(4)	3.870(4)	149(3)
C(13)–H(13a)···Cl^- $(1)^{iii}$	0.96(4)	2.90(4)	3.772(5)	151(3)
C(7)–H(7b)···Cl^- $(3)^{iv}$	0.86(4)	2.99(4)	3.763(5)	150(3)
O(102)···$Cl^-(1)$	3.20(2)	$Cl^-(1)$···O(102) ··· O(101)	128(1)	
O(102)···$Cl^-(2)$	3.31(1)	$Cl^-(1)$···O(102) ··· $Cl^-(2)$	107(1)	
O(101)···$Cl^-(3)$	3.17(2)	$Cl^-(2)$···O(102) ··· O(101)	124(1)	
O(101)···$Cl^-(4)$	3.35(2)	$Cl^-(3)$···O(101) ··· O(102)	129(1)	
		$Cl^-(3)$···O(101) ··· $Cl^-(4)$	107(1)	
O(101)···O(102)	2.99(3)	$Cl^-(4)$···O(101) ··· O(102)	123(1)	

Symmetry transformations used to generate equivalent atoms: $^{i}x-1, y-1, z$; ^{ii} x, y, z; ^{iii} $-x, -y, -z$; $^{iv}-x+1, -y+1, -z$; ^{v} $x, y-1, z$; ^{vi} $x+1, y, z$
Symmetry transformations used to generate equivalent atoms: ^{i} $x, y, z+1$; ^{ii} $x-1, y, z-1$; ^{iii} $x, y, z-1$; ^{iv} $x+1, y, z+1$;

modelled. Figure 6 shows the structure of one sheet in two projections. As in adduct **1**, the supramolecular structure generated by specific strong interactions is limited to two dimensions only. In the third direction the sheets are superimposed by means of weak van der Waals interactions only.

Conclusions

The amine molecule has captured four protons in the adduct of the hexaaza-unit with *o*-nitrophenol. The all eight N–H bonds at protonated nitrogen atoms are directed out of the macrocycle and for this reason are disposed towards intermolecular hydrogen bond formation. The unprotonated nitrogen atoms are located in a more sterically hindered part of the macrocycle and hence are less available to the protons. As the molecule of *o*-nitrophenol has a deficit of protons which are capable of strong hydrogen bond formation, only a two-dimensional supramolecular structure has arisen.

The combination of the hexaaza-unit with hydrogen chloride, a considerably stronger acid than phenols, leads to the formation of a hexa-protonated cation with all twelve N–H bonds directed out of the macrocycle and hence it can act as a twelvefold donor in the intermolecular hydrogen-bonds. The conformation of the macrocyclic cation is dramatically different in comparison with that in the supramolecular aggregate with *o*-nitrophenol. Moreover, as the hydrogen bonds are formed to Cl^- anions, the geometric arrangement of the hydrogen bonds and the resulting two-dimensional supramolecular structure could be pre-determined.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 229474 for compound **1** and 229475 for compound **2**. Copies of the information may be obtained free of charge from the Director, CCDC,

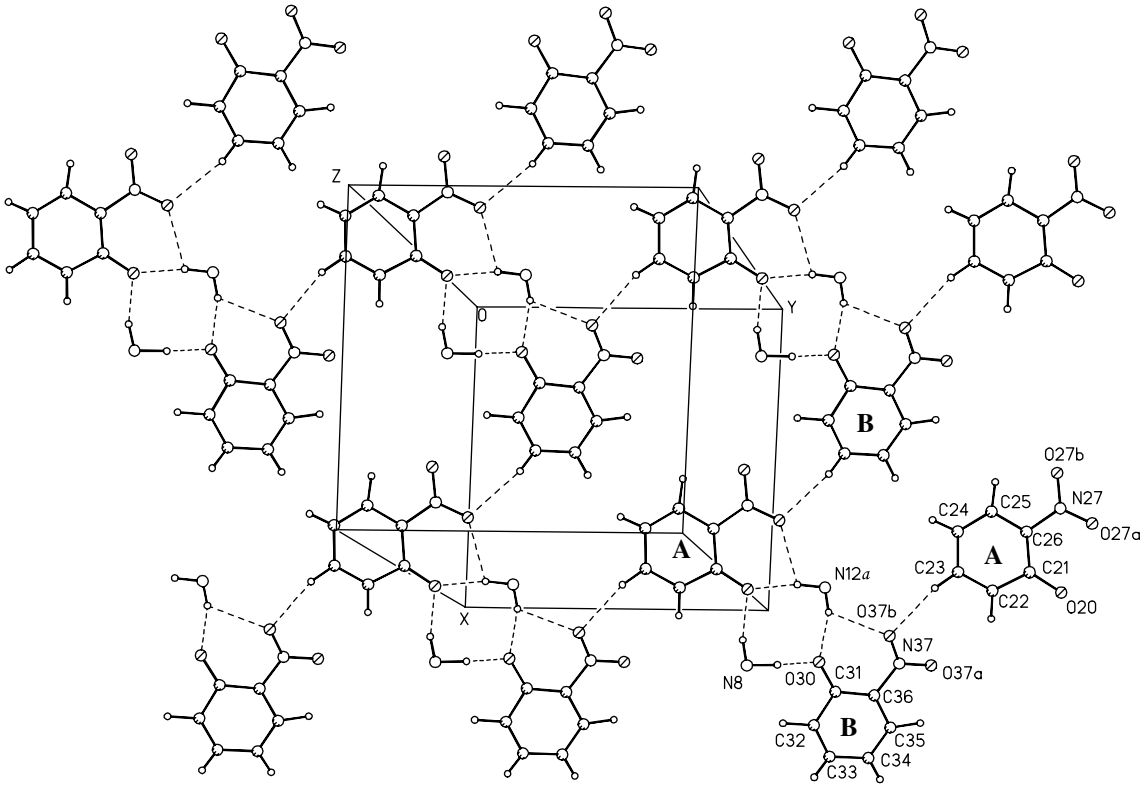


Figure 4. The structure of one sheet in **1** built from phenolate anionic chains and eight-membered rings. The rings are formed by hydrogen bonds between the proton donors, $N(8)^+$ and $N(12)^+$ and proton acceptors, $O(20)^-$ and $O(30)^-$. For the sake of clarity the cations are omitted, only $N(8)^+$ and $N(12)^+$ of the cations and their hydrogen atoms are presented.

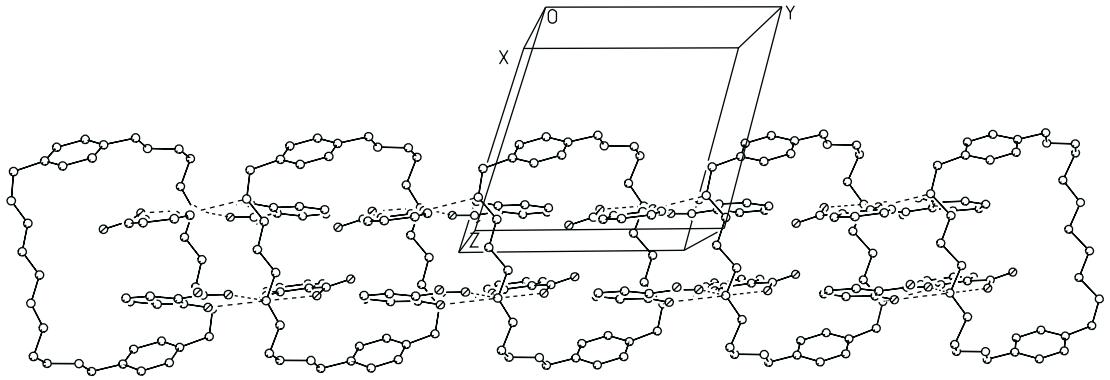


Figure 5. Two-dimensional supramolecular structure in **1**. The hydrogen-bonded eight-membered rings are a starting point for generating two-dimensional sheets. The sheets are situated at one-third and two-thirds of the macrocycle height. For the sake of clarity only eight-membered rings in one heterogenic chain are indicated (cf. Figure 5).

12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk <mailto:deposit@ccdc.cam.ac.uk> or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland and the Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland.

References

1. G. Ferguson, R.M. Gregson, and Ch. Glidewell: *Acta Cryst*. **C55**, 815 (1999).
2. R.M. Gregson, Ch. Glidewell, G. Ferguson, and A.J. Lough: *Acta Cryst*. **B56**, 39 (2000).
3. G. Ferguson, Ch. Glidewell, R.M. Gregson, and P.R. Meehan: *Acta Cryst*. **B54**, 139 (2000).
4. Ch. Glidewell, G. Ferguson, R.M. Gregson, and A.J. Lough: *Acta Cryst*. **B56**, 287 (2000).
5. W.-J. He, Z.-F. Ye, Y. Xu, Z.-J. Guo, and L.-G. Zhu: *Acta Cryst*. **C56**, 1019 (2000).
6. C.J. Burchell, G. Ferguson, A.J. Lough, and Ch. Glidewell: *Acta Cryst*. **C57**, 88 (2001).

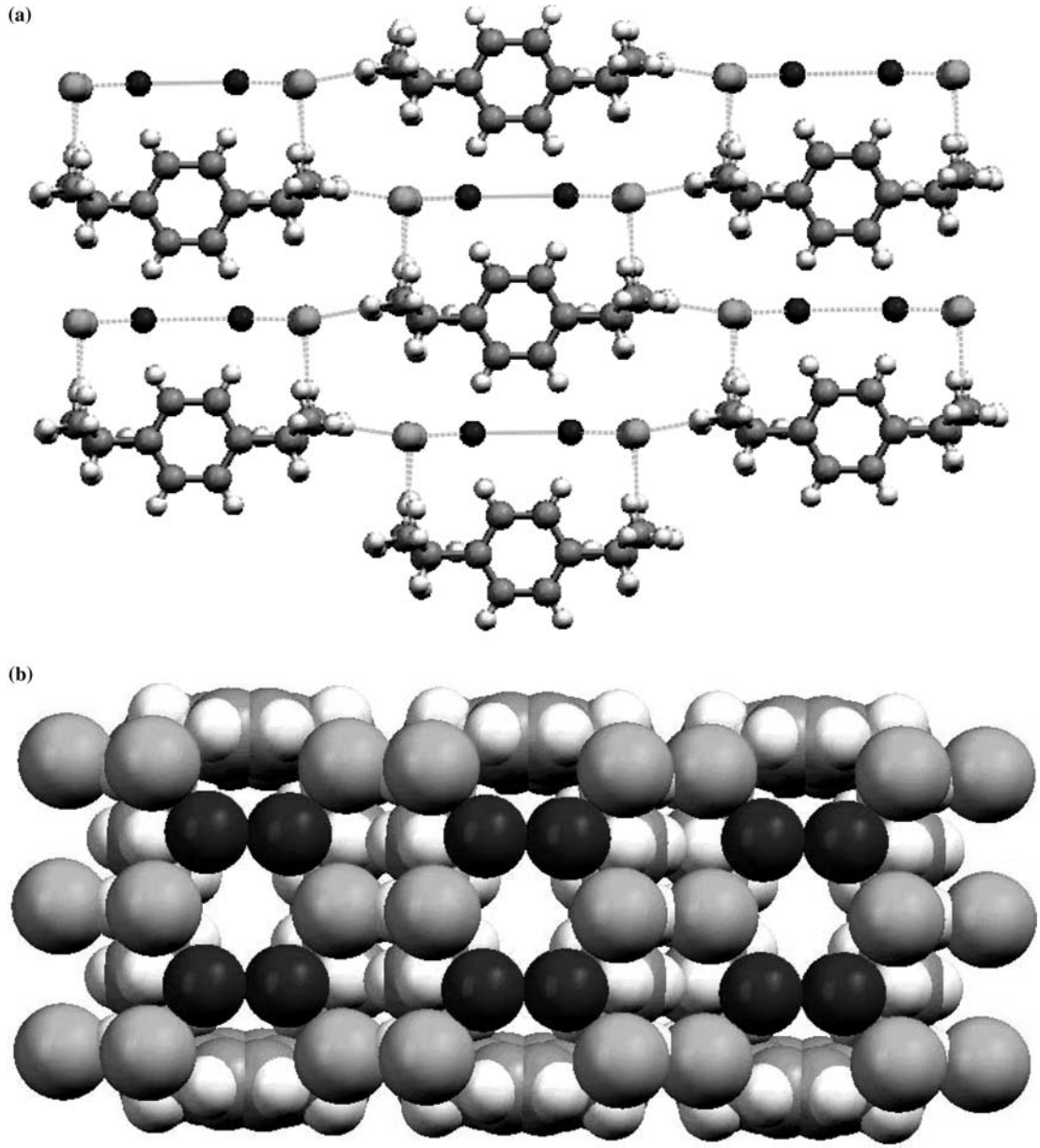


Figure 6. The structure of one sheet in **2** built from the hexa-protonated macrocycles, Cl^- anions (in green) and water molecules (in red). (a) The projection perpendicular to the phenyl ring planes. (b) After rotation by 90°. The height of a sheet corresponds to the height of the macrocycle, i.e. about 12 Å.

7. M.G. Basallote, J. Durán, M.J. Fernández-Trujillo, M.A. Máñez, M. Quirós, and J.M. Salas: *Polyhedron* **20**, 297 (2001).
8. L.-G. Zhu, A.M. Ellern, and N.M. Kostić: *Acta Cryst*. **C58**, o129 (2002).
9. F.H. Allen: *Acta Cryst*. **B58**, 380 (2002).
10. M. Pietraszkiewicz, and R. Gąsiorowski: *Chem. Ber*. **123**, 405 (1990).
11. CrysAlis CCD, ver. 1.162, KUMA Diffraction Instruments GmbH (1999).
12. CrysAlis Red., ver. 1.169, KUMA Diffraction Instruments GmbH (1999.).
13. R.H. Blessing: *J. Appl. Cryst*. **22**, 396 (1989).
14. G.M. Sheldrick, SHELXS-97. University of Göttingen (1997).
15. G.M. Sheldrick, SHELXL-97, University of Göttingen (1997).
16. Siemens, Stereochemical Workstation. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, (1989).
17. O. Pietraszkiewicz, M. Pietraszkiewicz, In: H. Takemura (ed.) *Cyclophane Chemistry for 21st Century*, Kerala, India, 2002, p. 217.
18. I. Alfonso, B. Dietrich, F. Rebolledo, V. Gotor, and J.-M. Lehn: *Helv. Chim. Acta* **84**, 280 (2001).
19. E.K. Andersen, and I.G.K. Andersen: *Acta Cryst*. **B31**, 391 (1975).