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Versatility in Inclusion Hosts. Unusual Conformation in the Crystal Structure of the *p*-*t*-Butylcalix[8]arene : Pyridine (1 : 8) Clathrate

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Abstract. Crystal structure analysis proves that the *p*-*t*-butylcalix[8]arene host sits around a symmetry center in the $P\bar{1}$ crystal lattice. The triclinic cell parameters and calculated volume are: $a = 10.034(2)$, $b = 17.434(2)$, $c = 18.321(2)$ Å, $\alpha = 113.86(1)°$, $\beta = 93.08(1)°$, $\gamma = 92.62(1)°$, $V = 2919(2)$ Å^3. For $Z = 1$ and F.W. = 1834.6 the calculated density is 1.04 g/cm^3. It is shown that the host macrocycle is in an open chairlike conformation and virtually leaves no cavity to be occupied by the guest molecule. Consequently the pyridine guest molecules are enclathrated through steric barriers into the crystal lattice, having only one of the guests in the asymmetric unit bound to the host. The open conformation of the host is facilitated by a break in the ring of O···O hydrogen bonds on the rim of the would-be calix. This structure also conveys essential information on the possible solution conformations of the host in pyridine.

Key words. Calix[8]arene, chairlike macrocycle shape, centrosymmetric, disorder.

Supplementary data relating to this article (bond distances and angles (Tables 4 and 5), anisotropic displacement parameters for non-hydrogen atoms (Table 6), atomic coordinates for hydrogen atoms (Table 7) and observed and calculated structure factors (Table 8)) are deposited with the British Library as Supplementary Publication No. SUP 82127 (28 pages).

1. Introduction

As an attempt to obtain a calix[8]arene complex with pyridine ligated Cu^+ ions, efforts were made to obtain co-crystals from these species. Recent publications indicate that such systems may well be useful tools for mimicking enzymic features as, for example, chiral recognition [1] or hopefully some activity related to the embedded metal ions. The crystal structure analysis proved unfortunately that copper ions are totally absent from the crystal lattice in this case.

2. Experimental

2.1. CHEMICAL PROCEDURES

The usual Schlenck-type glassware and inert gas techniques were used to prepare 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene [2] and $(CuClC_5H_5N)_n$ [3]. Pyridine was purified by storing over solid KOH and by subsequent distillation over CaH_2 under an argon atmosphere.

5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octa-hydroxycalix[8]arene (646 mg, 0.5 mmol) and $(CuClC_5H_5N)_n$ (356.2 mg, 0.5 mmol) were added to pyridine (15 mL) in a Schlenck tube under argon and stirred for over 15 min until a clear yellowish-green solution was obtained. The solution was kept at room temperature for a week while the resulting large colorless prisms deposited. After filtration and washing with small amounts of pyridine wet crystals were used for the X-ray structure determination. In vacuum these crystals quickly became opaque and decomposed into a white powder.

2.2. CRYSTALLOGRAPHY

Data Collection

A colorless prismatic crystal of the title compound having approximate dimensions of 0.15 × 0.25 × 0.30 mm was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with CuK_α radiation ($\lambda = 1.54184$ Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $20° < \theta < 25°$, measured by the computer controlled diagonal slit method of centering. The unit cell volume, chemical considerations and the lack of systematic absences indicated the space group to be $P\bar{1}$ (#2). The data were collected at a temperature of 300(1) K using the ω-2θ scan technique. The scan range was determined as a function of θ to correct for the separation of the K_α doublet [4] (see Table I).

Data Reduction

A total of 6271 reflections were collected of which 5230 were unique. As a check on crystal and electronic stability three representative reflections were measured every 60 min. The intensities of these standards remained constant, therefore no decay correction was applied. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 4.8 cm^{-1} for CuK_α radiation. An empirical spherical absorption correction [5] was applied. Relative transmission coefficients ranged from 0.813 to 1.264 with an average value of 0.959.

Structure Model and Refinement

The initial structure model was obtained by direct methods. Using 500 reflections (minimum E of 1.75) and 4434 relationships, a total of 32 phase sets were produced. Thirty-seven atoms were located from an E map prepared from the phase set with the best combined figure of merits. On inputting these atomic positions 57 non-hydrogen atoms were obtained from the subsequent weighted Fourier synthesis. Non-hydrogen atomic positions for the rest of the scattering model were obtained from difference electron density maps. Hydrogen atoms were positioned and added to the structure factor calculations but their parameters were not refined. The structure model in the space group $P\bar{1}$ is located around a center of symmetry,

Table I. Experimental details.

A. Crystal Data	*B. Intensity Measurements*
Formula: $C_{120}H_{152}N_8O_8$	Instrument: Enraf-Nonius CAD4 diffractometer
F.W.: 1834.6	Monochromator: Graphite crystal, incident beam
Crystal dimensions: 0.15 × 0.25 × 0.30 mm	Attenuator: Ni foil, factor 22.0
CuK_α radiation ($\lambda = 1.54184$ Å)	Scan type & rate: $\omega - 2\theta$; 1–20°/min (in θ)
Temperature = 300(1) K	Scan width: $0.4 + 0.140 \tan\theta$
Space group $P\bar{1}$	Maximum 2θ: 100.0°
$a = 10.034$ (2) Å	No. of refl. measured: 6271 total, 5230 unique
$b = 17.434$ (2) Å	Corrections: Lorentz-polarization, absorption
$c = 18.321$ (2) Å	
$\alpha = 113.86$ (1)°	
$\beta = 93.08$ (1)°	
$\gamma = 92.62$ (1)°	
$V = 2919$ (2) Å^3	
$Z = 1$, $D_c = 1.04$ mg/m^3	
$\mu = 4.8$ cm^{-1}	
C. Structure Solution and Refinement	
Solution: Direct methods	Unweighted agreement factor: 0.096
Hydrogen atoms: Included as fixed contribution to the structure factor	Weighted agreement factor: 0.146
Refinement: Full-matrix least-squares	R-Factor including unobs. data: 0.116
Minimization function: $w(\Sigma\lvert F_o\rvert - \lvert F_c\rvert)^2$	Esd of obs. of unit weight: 5.31
Anomalous dispersion: All non-hydrogen atoms	Convergence, largest shift: 4.02
Reflections included: 4313 with $F_o^2 > 3.0\sigma\ (F_o^2)$	High peak in final diff. map: 0.43 (7) e/Å^3
Parameters refined: 562	

i.e. the crystallographic asymmetric unit consists of only half of the molecule. Early in the model refinement positional disorder was revealed. It was manifested through blurred electron density and partly by resolved high electron density peaks (1–2 e Å^{-3}). This observation applies especially to some atoms of the pyridine molecules and for many of the rotationally disordered methyl termini in the t-butyl groups.

The structure model was refined in full-matrix least-squares where the function minimized was $w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma(F_o^2)^2$. The standard deviation on intensities, $\sigma(F_o^2)$, is defined as follows

$$\sigma(F_o^2) = ([S^2(C + R^2B) + (pF_o^2)^2]/L_p)^2$$

where S is the scan rate, C is the total integrated peak count, R^2 is the squared ratio of scan time to background counting time, B is the total background count, L_p is the Lorentz polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.045. Scattering factors were taken from Cromer and Waber [6]. Anomalous dispersion effects were included in F_c [7]; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer [8]. Only the 4313 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 562 variable parameters and converged with unweighted and weighted factors of:

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.096$$

$$R_2 = (\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w F_o^2)^{1/2} = 0.146$$

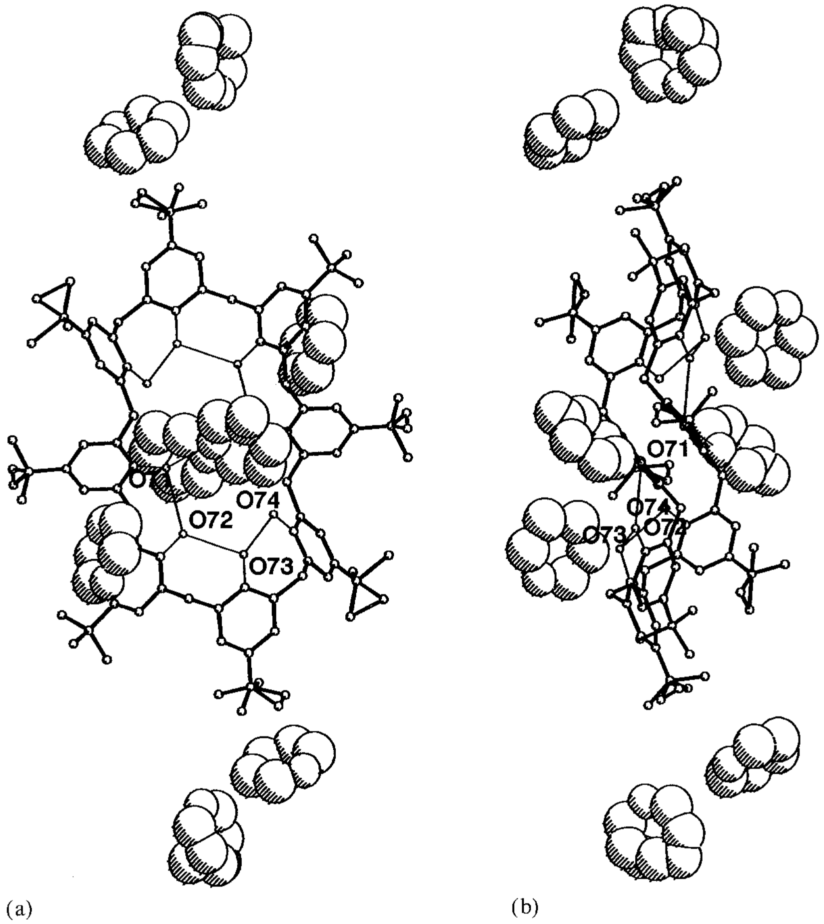
The highest peak in the final difference map had a height of 0.43 e/Å^3 with an estimated error based on ΔF[9] of 0.07.

As an alternative model the non-centrosymmetric space group was also used to test the centrosymmetrical structure hypothesis though there seemed to be little doubt as to the general shape of the host. Theoretically one could still envisage a dissymmetric arrangement of the eight independent guest pyridines, thereby giving rise to a non-centrosymmetrical lattice. Attempts to devise such models did not give noticeable improvement in the discrepancy factors over the centrosymmetric model. Thus, considering the unfavorable observations/enlarged parameter number ratio and all the related complexities associated with the problem we conclude that the probable space group is $P\bar{1}$. Therefore the resulting molecular model must be centrosymmetric as well.

All calculations were performed on a PDP-11/34 128 Kw minicomputer using SDP-PLUS and local programs [10].

3. Discussion

Atomic coordinates are in Table II, bonding parameters in Tables IV and V (deposited). As a result of the crystal structure analysis it is possible to establish the true stoichiometry of this crystal as 1 : 8. The molecular structure, as obtained from the crystal structure model, is shown in Figure 1. As alluded above the host molecule sits around a center of symmetry. One can also establish that the host has an open conformation [11, 12]. Both facts are remarkable since earlier X-ray results



(a) (b)

Fig. 1. (a) Molecular conformation and the relative disposition of the guest molecules (atoms of which were drawn with 0.45 van der Waals radii) in the crystal structure of the title clathrate as viewed in the central plane of the molecule. Possible O···O hydrogen bonds are indicated in thin lines. Hydrogen atoms of the host are omitted for clarity. (b) As in Fig. 1a but viewed 90 degrees rotated from the other view. The open conformation of the calix[8]arene host is clearly visible as well as the solvents offset from the cavity.

[12a] suggested the so called 'pleated loop' shape for the pure title host crystallized from the same solvent (pyridine), as a possible conformer in solution as well. The calix[8]ligand approximates in the backbone part (i.e. the linking methylene and phenol carbon atoms) the shape of a *chair* or *stairway*. Thus, it has three planes made up of four carbon atoms each that are closely rectangular to each other. Such a shape may be also derived from *two calix[4]* entities in a *partial cone* conformation. The aromatic group 1 and its symmetry mate are rotated concurrently along its adjoining bond out of the theoretical ring closure position. This also results in their offset from the cone into a quasi-equatorial position in the center of the calix[8]ligand. The observed host shape may also clear up some of the controversy between earlier postulates of Gutsche and Bauer [14] and the cited X-ray work [12a] as to the existence of the so called 'pinched' conformation, which was

Table II. Fractional atomic coordinates and Beq values with their e.s.d's for p-*t*-butylcalix[8]arene : pyridine (1 : 8). Crystallographic site populations other than unity are indicated accordingly.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eq)/*B*	
C(11)	0.7975(5)	−0.5444(3)	0.1462(2)	3.3(1)	
C(21)	0.7058(5)	−0.5966(3)	0.0854(2)	3.0(1)	
C(31)	0.7280(5)	−0.6805(3)	0.0421(2)	3.4(1)	
C(41)	0.8397(5)	−0.7125(3)	0.0654(3)	4.1(1)	
C(51)	0.9301(6)	−0.6616(3)	0.1304(3)	4.2(1)	
C(61)	0.9071(5)	−0.5789(3)	0.1679(2)	4.0(1)	
O(71)	0.5944(3)	−0.5607(2)	0.0715(1)	3.92(8)	
C(81)	0.7786(5)	−0.4520(3)	0.1929(2)	3.4(1)	
C(91A)	1.170(1)	−0.6333(8)	0.196(1)	13.8(4)	Mult = 0.75
C(91b)	1.183(2)	−0.651(1)	0.159(1)	5.6(5)	Mult = 0.25
C(101)	1.0832(9)	−0.7864(5)	0.0946(5)	10.4(2)	
C(111)	1.006(1)	−0.7167(5)	0.2296(4)	9.8(3)	
C(121)	1.0484(6)	−0.6997(4)	0.1588(3)	5.4(1)	
C(12)	0.5414(5)	−0.4236(3)	0.3564(3)	3.5(1)	
C(22)	0.5893(5)	−0.4421(3)	0.2817(2)	3.2(1)	
C(32)	0.7240(5)	−0.4312(3)	0.2733(2)	3.3(1)	
C(42)	0.8101(5)	−0.4048(3)	0.3416(3)	3.8(1)	
C(52)	0.7703(5)	−0.3883(3)	0.4168(2)	3.9(1)	
C(62)	0.6317(5)	−0.3970(3)	0.4228(2)	3.6(1)	
O(72)	0.4955(3)	−0.4705(2)	0.2158(1)	3.98(8)	
C(82)	0.3911(5)	−0.4301(3)	0.3664(3)	3.8(1)	
C(92)	0.8357(8)	−0.2687(4)	0.5498(4)	8.2(1)	
C(102)	0.8388(7)	−0.4221(4)	0.5349(3)	6.0(2)	
C(112)	1.0135(6)	−0.3649(4)	0.4707(3)	6.3(1)	
C(122)	0.8668(6)	−0.3607(3)	0.4925(3)	4.7(1)	
C(13)	0.1758(5)	−0.2813(3)	0.3150(3)	3.7(1)	
C(23)	0.2487(5)	−0.3496(3)	0.3069(2)	3.7(1)	
C(33)	0.3233(5)	−0.3544(3)	0.3712(2)	3.6(1)	
C(43)	0.3344(6)	−0.2804(3)	0.4452(3)	4.6(1)	
C(53)	0.2696(6)	−0.2084(3)	0.4556(3)	4.6(1)	
C(63)	0.1895(6)	−0.2112(3)	0.3900(3)	4.6(1)	
O(73)	0.2416(3)	−0.4155(2)	0.2308(1)	4.29(8)	
C(83)	0.0901(5)	−0.2788(3)	0.2461(3)	3.9(1)	
C(93a)	0.340(2)	−0.0595(9)	0.5157(8)	19.5(7)	Mult = 0.75
C(93b)	0.183(3)	−0.070(1)	0.531(1)	7.3(6)	Mult = 0.25
C(103a)	0.158(2)	−0.099(1)	0.562(1)	10.1(5)	Mult = 0.33
C(103b)	0.253(2)	−0.1540(9)	0.5958(6)	14.2(6)	Mult = 0.67
C(113)	0.434(1)	−0.1181(9)	0.5673(8)	20.0(4)	
C(123)	0.2840(7)	−0.1331(4)	0.5324(3)	7.4(1)	
C(14)	0.2864(5)	−0.2169(3)	0.1038(3)	3.9(1)	
C(24)	0.2350(5)	−0.2639(2)	0.1428(2)	3.3(1)	
C(34)	0.1540(5)	−0.2280(3)	0.2051(3)	3.8(1)	
C(44)	0.1311(5)	−0.1421(3)	0.2295(3)	4.4(1)	
C(54)	0.1846(5)	−0.0928(3)	0.1932(3)	4.2(1)	
C(64)	0.2602(5)	−0.1339(3)	0.1292(3)	4.0(1)	
O(74)	0.2632(3)	−0.3460(2)	0.1161(2)	4.47(8)	
C(84)	0.3635(5)	−0.2606(3)	0.0297(3)	4.0(1)	
C(94)	0.251(1)	0.0480(5)	0.1978(7)	13.5(4)	
C(104)	0.158(3)	0.0329(8)	0.306(1)	33(1)	
C(114a)	0.030(1)	0.0240(7)	0.248(1)	15.3(5)	Mult = 0.75

Table II. (continued)

Atom	x/a	y/b	z/c	B(eq)/B	
C(114b)	0.061(2)	−0.002(1)	0.140(1)	4.7(0)	Mult = 0.25
C(124)	0.1560(7)	−0.0035(4)	0.219(4)	7.4(1)	
N(1)	0.3554(4)	−0.6212(3)	−0.0137(2)	5.5(1)	
C(1p1)	0.2870(7)	−0.6953(4)	−0.0624(4)	7.5(1)	
C(2ap1)	0.133(1)	−0.719(1)	−0.087(1)	9.9(5)	Mult = 0.50
C(2bp1)	0.154(1)	−0.6972(5)	−0.0736(6)	5.0(2)	Mult = 0.50
C(3p1)	0.0800(6)	−0.6307(4)	−0.0366(3)	5.6(1)	
C(4p1)	0.1548(6)	−0.5540(3)	0.0112(3)	5.5(1)	
C(5p1)	0.2912(5)	−0.5532(3)	0.0204(3)	4.3(1)	
N(2)	0.5120(8)	−0.6733(4)	0.3794(4)	9.5(2)	
C(1p2)	0.4547(8)	−0.7221(6)	0.3161(5)	9.4(2)	
C(2p2)	0.501(1)	−0.7261(7)	0.2354(5)	10.9(3)	
C(3p2)	0.622(1)	−0.6683(5)	0.2467(4)	8.32(2)	
C(4p2)	0.674(1)	−0.6223(5)	0.3193(5)	9.6(2)	
C(5p2)	0.623(1)	−0.6294(5)	0.3832(5)	10.0(2)	
N(3)	0.2084(7)	0.1498(4)	0.6944(4)	9.6(2)	
C(1p3)	0.239(1)	0.1875(5)	0.6461(5)	9.7(3)	
C(2p3)	0.367(1)	0.2073(5)	0.6403(6)	10.0(2)	
C(3p3)	0.4630(8)	0.1924(6)	0.6851(6)	11.8(2)	
C(4p3)	0.432(1)	0.1487(7)	0.7343(5)	13.0(3)	
C(5p3)	0.295(1)	0.1316(5)	0.7362(5)	9.6(2)	
N(4)	0.346(1)	−0.0741(6)	0.8429(6)	16.1(3)	
C(1p4)	0.314(1)	−0.0920(8)	0.8983(7)	14.1(4)	
C(4p4)	0.352(1)	0.0676(7)	0.9039(7)	14.5(4)	
C(5p4)	0.357(1)	0.0019(8)	0.8464(7)	13.0(4)	

essentially based on the NMR data of this host in different solvents. The pure p-*t*-butylcalix[8]arene host [12a] was later thought to represent an intermediate conformation as found in a so called pleated loop form in the solid state. Also, that 'pleated loop' shaped molecule does not possess the center of symmetry as in [12b] and in this work. We believe that the high solvent content observed in our crystal is a close mimic of the spatial conditions of the given solvent/solute system at corresponding concentrations. The present structure seems also to corroborate the conclusions of Gutsche *et al.* [12a] as to the possible role of the solvent in breaking up the hydrogen bond circle between the phenolic —OH groups which are supposed to stabilize a conical conformation (*vide infra*).

It is also remarkable that the existence of this conformation in the solid state proves that a classic molecular inclusion host (cavitate) is capable of transforming itself into a typical clathrate (crystal lattice inclusion) host [15]. Correspondingly the pyridine 'guests' fill in interstitial voids of the lattice maintained by the huge chair-shaped form of the calix[8]arene host matrix. The guest molecules are very much freed from productive binding to the host matrix of the crystal lattice (cf. Table III) having only one such presumably O—H···N type hydrogen bond out of the four pyridine molecules in the asymmetric unit. This fact also underlines that this crystal structure is built *via* weak and mostly steric interactions, as also indicated by the very low density of this crystal. The only direct host···guest O···N

Table III. Interatomic distances (Å, possible hydrogen bond bridgehead distances) with their e.s.ds.

O(71)···N(1)	2.708(6)	O(72)···O(73)	2.752(5)
O(71)···O(72)	2.740(5)	O(73)···O(74)	2.831(6)

*Atoms N(2), N(3) and N(4) have no O···N contact distances below 3.0 Å.

contact is probably also driving the host molecule into the chairlike shape by breaking the otherwise continuous chain of hydrogen bonds between neighboring phenolic —OH groups. In fact this is the shortest hydrogen bond among those observed (Table III). Six (three) out of the eight (four) phenolic —OH groups on the rim of the molecule (the asymmetric unit) have appreciably shorter contacts than the sum of the O···O van der Waals radii (Table III). It did not escape our attention that qualitatively similar calix[8]arene ligand shapes were reported for several metal complexes [12d–f]. Indeed the title associate can be perceived as related to such structures to some extent due to the particular way of binding two molecules of pyridine. The rotational disorder in many of the terminal *t*-butyl groups of the host structure has been similarly observed in other calix[8]arene crystals [12]. The disorder is also heavily present in the guest models, where rotation around the pyridine ring center is apparent and makes even the proper atomic assignment questionable.

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