

Structures of the *p*-Xylylenediammonium Chloride and Calcium Hydrogensulfate Adducts of the Cavitand 'Cucurbituril', C₃₆H₃₆N₂₄O₁₂

BY WADE A. FREEMAN

Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680, USA

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Abstract

Structure determinations of two crystalline adducts of the cavitand cucurbituril, a cyclic hexameric dimethanoglycoluril of possible catalytic importance, are reported. Crystal data are also reported for 11 other adducts. Cucurbituril is a hexagonal cage with an internal cavity of diameter ~ 5.5 Å accessed by portals of diameter ~ 4 Å. In the *p*-xylylenediammonium chloride adduct of cucurbituril [C₃₆H₃₆N₂₄O₁₂·NH₂CH₂C₆H₄CH₂NH₂·2HCl·10H₂O, $M_r = 1386.1$, $F(000) = 1412$, $\mu = 2.16$ cm⁻¹, monoclinic, $P2_1/n$, $a = 12.071$ (4), $b = 15.757$ (4), $c = 14.485$ (6) Å, $\beta = 91.98$ (3)°, $V = 2753$ (2) Å³, $D_m = 1.63$, $D_x(Z = 2) = 1.67$ g cm⁻³] the *p*-xylylenediammonium ion is a guest inside the cucurbituril cage. The structure was refined to $R = 0.0624$ based on 3694 independent observed reflections collected at 302 K using Mo $K\alpha$ radiation. The second adduct [C₃₆H₃₆N₂₄O₁₂·2Ca(HSO₄)₂·13H₂O, $M_r = 1699.5$, $F(000) = 882$, $\mu = 4.26$ cm⁻¹, triclinic, $P\bar{1}$, $a = 11.948$ (4), $b = 10.392$ (6), $c = 15.669$ (6) Å, $\alpha = 92.15$ (8)°, $\beta = 115.18$ (5)°, $\gamma = 109.66$ (6)°, $V = 1620$ (3) Å³, $D_m = 1.78$, $D_x(Z = 1) = 1.74$ g cm⁻³] has a water molecule at the center of the otherwise empty cage; Ca^{II} ions lie at the two cage portals and link adjoining cages by coordination to carbonyl O atoms. This structure was refined to $R = 0.0643$ based on 3686 independent observed reflections collected at 294 K using Mo $K\alpha$ radiation.

Introduction

Other reports (Freeman, Mock & Shih, 1981; Mock & Shih, 1983; Mock, Irra, Wepsiec & Manimaran, 1983) discuss the history, preparation and binding capacity of the cyclic hexamer of formula (C₆H₆N₄O₂)₆. This compound has the trivial name cucurbituril. As a 'cavitand' (Moran, Karbach & Cram, 1982), cucurbituril (Fig. 1) forms a wide variety of crystalline adducts with aliphatic and aromatic mono- and diammonium salts and also with metal-ion salts. NMR evidence (Mock & Shih, 1983) has indicated that the organic diammonium salts thread into the cage's cavity and are bound there. The binding

most likely depends on charge-dipole attraction between the ammonium cations and the O atoms of the cucurbituril's carbonyl groups. Metal ions do not enter the cucurbituril's cavity but coordinate to the carbonyl O atoms at its portals.

A catalytic quantity of cucurbituril greatly accelerates the 1,3-cycloaddition of propargylamine to 2-azidoethylamine, giving 1-(2-aminoethyl)-4-aminoethyl-1,2,3-triazole and making the reaction regio-specific. This catalysis has several other enzyme-like features (Mock, Irra, Wepsiec & Manimaran, 1983). Binding energies in cucurbituril's host-guest complexes approximate those in common enzyme-substrate interactions, and the binding can be stereoselective – for example, the substitution pattern of arene diamines has a great effect on their binding to cucurbituril. Such specificity is not the case for analogous cyclodextrin host-guest complexes (Van Etten, Sebastian, Clowes & Bender, 1967). The details of cucurbituril's structure therefore hold considerable interest. This paper follows a preliminary structural report on cucurbituril (Freeman, Mock & Shih, 1981) and presents a new structure, in which the cavitand contains a guest molecule. Crystallographic data on 11 other adducts are also given.

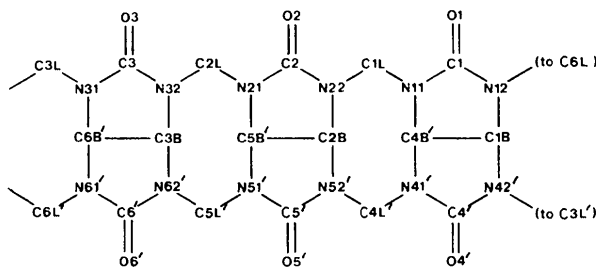


Fig. 1. Partial structural formula of the cyclic hexameric cavitand cucurbituril. In the structure determinations the cage molecule encircles a center of symmetry which generates the second half of the molecule from the asymmetric unit. The same numbering system is used in both structure determinations: methine C atoms are *B* (backbone), methylene C atoms are *L* (linking), and carbonyl C atoms are left without special designations. Primed designations refer to atoms transformed from the positions given in Tables 2 and 3, by the center of inversion at the cavitand's center.

Table 1. Crystal data for thirteen cucurbituril adducts

Adduced species and formula of adduct	$D_m; D_c$ (g cm ⁻³)	a (Å)	b (Å)	c (Å)	Crystal system and space group
(1) <i>p</i> -Xylylenediamine dihydrochloride cucurbituril. NH ₂ CH ₂ C ₆ H ₄ CH ₂ NH ₂ .2HCl.10H ₂ O	1.63; 1.671 ($Z = 2$)	12.071 (4)	15.757 (4) $\beta = 91.98$ (3)°	14.485 (6)	Monoclinic $P2_1/n$
(2) 1,4-Butanediamine dihydrochloride cucurbituril. NH ₂ (CH ₂) ₄ NH ₂ .2HCl.9H ₂ O	1.62; 1.660 ($Z = 2$)	11.659 (4)	15.681 (5) $\beta = 92.66$ (5)°	14.446 (5)	Monoclinic $P2_1/n$
(3) 1,5-Pentanediamine dihydrochloride cucurbituril. NH ₂ (CH ₂) ₅ NH ₂ .2HCl.9H ₂ O	1.61; 1.625 ($Z = 2$)	11.874 (6)	15.837 (7)	14.478 (7)	Orthorhombic $Pnnm$ or $Pnn2$
(4) 1,6-Hexanediamine dihydrochloride cucurbituril. NH ₂ (CH ₂) ₆ NH ₂ .2HCl.9H ₂ O	1.62; 1.624 ($Z = 2$)	12.126 (5) $\alpha = 92.08$ (7)°	15.947 (10)	14.256 (7)	Monoclinic* $P2_1/n$
(5) 1-(2-Aminoethyl)-4-aminoethyl-1,2,3-triazole dihydrochloride cucurbituril. C ₃ H ₃ N ₅ .2HCl.xH ₂ O	1.98; $\alpha = 93.0^\circ$	11.98	16.36	14.27	Monoclinic* $P2_1/n$
(6) Silver(I) nitrate cucurbituril. AgNO ₃ .12H ₂ O	1.78; 1.740 ($Z = 2$)	11.76	16.92	14.78	Orthorhombic $Pnn2$ or $Pnnm$
(7) Cadmium(II) nitrate cucurbituril. $\frac{1}{3}$ [Cd(NO ₃) ₂].9H ₂ O	1.81; 1.793 ($Z = 2$)	11.599 (7)	16.228 (11)	14.897 (11)	Orthorhombic $Pnn2$ or $Pnnm$
(8) Zinc(II) nitrate cucurbituril. $\frac{1}{2}$ [Zn(NO ₃) ₂].9H ₂ O	1.66; 1.720 ($Z = 2$)	11.63	16.12	14.68	Orthorhombic $Pnn2$ or $Pnnm$
(9) Nickel(II) nitrate cucurbituril. Ni(NO ₃) ₂ .12H ₂ O	1.68; 1.660 ($Z = 2$)	11.684 (6)	16.209 (7)	14.743 (5)	Orthorhombic $Pnn2$ or $Pnnm$
(10) Tetrahydrofurfurylamine hydrochloride cucurbituril. C ₅ H ₉ N. NO. HCl.xH ₂ O	<1.584; ($Z = 1$)	14.51	14.51	10.79	Hexagonal†
(11) Sulfuric acid cucurbituril. 9H ₂ SO ₄ .24H ₂ O	1.75; 1.768 ($Z = 1$)	15.441 (NO)	15.441 (4)	10.516 (4)	Hexagonal†
(12) Sodium tetrachloroaurate(III) cucurbituril. 3(NaAuCl ₄).18H ₂ O	2.19; 2.290 ($Z = 2$)	11.78	11.78	14.46	Trigonal $P321$ or $P\bar{3}m1$
(13) Calcium hydrogensulfate cucurbituril. 2[Ca(HSO ₄) ₂].13H ₂ O	1.78; 1.742 ($Z = 1$)	11.948 (4) $\alpha = 92.15$ (8)°	10.392 (6) $\beta = 115.18$ (5)°	15.669 (6) $\gamma = 109.66$ (6)°	Triclinic $P\bar{1}$

* The a axis is unique (non-standard cell) for comparison.

† Space group is $P622$, $P6mm$, $P6m2$, $P62m$ or $P6/mmm$.

Experimental

The 13 crystalline adducts were prepared by mixing and slow evaporation of acid solutions of cucurbituril with the various diamines or metal-ion salts (Shih, 1981).

All of the adducts were examined by X-ray precession photography. Crystal data are given in Table 1. Where standard deviations are given in Table 1 more accurate cell dimensions were obtained by least-squares fitting of the angular positions of 12 to 25 high- 2θ reflections. These data were obtained using Picker FACS-1 or Nicolet P3/F automatic diffractometers. Elemental analyses (C, H, and N) were satisfactory for the given formulas except for (5) and (10) where analysis was not available owing to the ready decomposition of the crystals; (2) analyzed as a tetrahydrate after drying at 373 K.

Determination of the structure of

C₃₆H₃₆N₂₄O₁₂.NH₂CH₂C₆H₄CH₂NH₂.2HCl.10H₂O

Preliminary precession photographs indicated the space group $P2_1/n$. The unconventional setting was used to show the crystallographic similarities among the adducts. Density determined by neutral buoyancy in CCl₄/CBr₄. Intensity data collected on a prismatic crystal approximately 0.2 × 0.2 × 0.35 mm, Nicolet P3/F automatic diffractometer, graphite-crystal monochromator. Cell dimensions determined by least-squares fitting to the location of 25 reflections (2θ range: 15 to 41°). Reflections collected to $2\theta = 50^\circ$ for $h, k, \pm l$ and corrected empirically for absorption

($T_{\max} = 0.712$; $T_{\min} = 0.668$). Three standard reflections (060, $\bar{1}05$, 5 $\bar{1}0$) monitored every 93 reflections, no systematic changes. 5144 reflections collected, not counting systematic absences; 1204 unobserved [$F < 2.5\sigma(F)$] and 246 symmetry equivalent ($R_{\text{merge}} = 0.038$). Based on the resulting 3694 independent reflections the structure was solved by direct methods using the *SHELXTL* program package (Sheldrick, 1981) which gave the locations of all the non-hydrogen atoms except those of the waters of crystallization.

Refinement minimized $\sum w(|F_o| - |F_c|)^2$ and used counting weights where $w^{-1} = \sigma^2(F_o) + gF_o^2$ and g was refined as a parameter (its final value was 0.00233). The refinement proceeded with conversion to anisotropic thermal parameters and the insertion of the H atoms of the cage molecule as 'riders' in calculated positions ($d_{C-H} = 0.96$ Å). The isotropic thermal parameters of these H atoms were allowed to vary independently. A difference Fourier synthesis showed three sites of higher electron density, which were associated with the O atoms of waters of crystallization [$W(1)$ – $W(3)$]. Partial-occupancy O atoms [$W(4)$ – $W(6)$] were then placed in three other positions of moderate ($2\text{--}3 \text{ e \AA}^{-3}$) density in the difference Fourier synthesis. The occupancies of the three atoms were set at 0.435, 0.435 and 0.13. Eight of the 10 waters of crystallization in the formula unit were thereby included in the model. Further refinement eventually allowed the location of all of the H atoms of the guest molecule and of the $W(1)$ – $W(3)$ water molecules. The positional parameters of these H atoms were varied independently while their thermal

parameters were held at a reasonable value. Final positional parameters for the non-hydrogen atoms are given in Table 2.* The final R and wR were 0.0624 and 0.0722, respectively. The last cycles of refinement involved 474 parameters; the mean Δ/σ in the last cycle was 0.333. The maximum height in the final difference Fourier synthesis was $0.95 \text{ e } \text{\AA}^{-3}$.

Determination of the structure of $\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}\cdot 2\text{Ca}(\text{HSO}_4)_2\cdot 13\text{H}_2\text{O}$

Preliminary precession photographs showed that the crystal structure was triclinic. Crystal density determined by neutral buoyancy in $\text{CCl}_4/\text{CBr}_4$. An irregular spherical fragment of approximate radius 0.20 mm used for intensity-data collection on a Picker FACS-1 automatic diffractometer. Cell dimensions determined from 14 reflections (2θ range: $37\text{--}41^\circ$). Data collected to $2\theta = 45^\circ$ for $h, \pm k, \pm l$ and corrected empirically for absorption. Three standard reflections (300, 050, 204) monitored every 50 reflections, no systematic changes. 4484 reflections collected of which 544 were unobserved [$F < 2.0\sigma(F)$] and 254 were symmetric equivalents ($R_{\text{merge}} = 0.051$). Using the resulting 3686 reflections the structure was solved by direct methods with *MULTAN* (Main, Woolfson, Lessinger & Germain, 1976).

The quantity minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ using counting weights where $w^{-1} = \sigma^2(F_o)$; Ca¹¹-ion scattering factors and neutral atomic scattering factors for all other atoms were used. The values were from Cromer & Waber (1965) for non-hydrogen atoms and from Stewart, Davidson & Simpson (1965) for H. Later stages of refinement included the use of anisotropic thermal parameters for all non-hydrogen atoms and the insertion of 'riding' H atoms as chemically appropriate on the atoms of the cucurbituril cage. Ten additional H atoms were inserted into the final model in chemically sensible positions near the water and sulfate O atoms. The positional parameters of these were not varied; their isotropic thermal parameters were grouped into two sets of five and assigned equal values. Members of each set were constrained to vary in the same way. Final positional parameters are given in Table 3 for non-hydrogen atoms.* The final R and wR were 0.0643 and 0.0846, respectively. The last, full-matrix cycles of refinement included 476 independent and 62 dependent parameters. The maximum Δ/σ in the

Table 2. Atom coordinates ($\times 10^4$) and equivalent values of the anisotropic temperature factors ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms in $\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}\cdot \text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2\cdot 2\text{HCl}\cdot 10\text{H}_2\text{O}$

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O(1)	2424 (2)	9213 (2)	2615 (2)	45
C(1)	1573 (2)	9470 (2)	2226 (2)	36
N(11)	736 (2)	8961 (2)	1868 (2)	37
N(12)	1281 (2)	10294 (2)	2080 (2)	35
C(1L)†	738 (3)	8053 (2)	1992 (2)	40
C(1B)†	318 (3)	10364 (2)	1462 (2)	35
O(2)	1668 (2)	7554 (2)	3770 (2)	43
C(2)	667 (2)	7506 (2)	3592 (2)	33
N(21)	-112 (2)	7218 (2)	4175 (2)	37
N(22)	150 (2)	7749 (2)	2774 (2)	37
C(2L)	154 (3)	6828 (2)	5050 (2)	37
C(2B)	-1016 (3)	7544 (2)	2753 (2)	35
O(3)	1595 (2)	7774 (2)	6322 (2)	46
C(3)	601 (3)	7702 (2)	6446 (2)	36
N(31)	62 (2)	7962 (2)	7204 (2)	36
N(32)	-153 (2)	7330 (2)	5841 (2)	37
C(3L)	620 (3)	8257 (2)	8049 (2)	40
C(3B)	-1233 (2)	7251 (2)	6243 (2)	33
O(4)	2324 (2)	9428 (2)	7625 (2)	43
C(4)	1455 (2)	9669 (2)	7939 (2)	36
N(41)	1158 (2)	10491 (2)	8093 (2)	35
N(42)	595 (2)	9155 (2)	8188 (2)	40
C(4L)	1956 (3)	11177 (2)	8045 (2)	37
C(4B)	131 (2)	10554 (2)	8585 (2)	35
O(5)	3100 (2)	11183 (2)	6327 (2)	44
C(5)	2371 (2)	11697 (2)	6481 (2)	33
N(51)	2058 (2)	12353 (2)	5919 (2)	35
N(52)	1745 (2)	11722 (2)	7253 (2)	36
C(5L)	2648 (2)	12564 (2)	5095 (2)	35
C(5B)	1191 (2)	12869 (2)	6301 (2)	35
O(6)	3193 (2)	11096 (2)	4004 (2)	45
C(6)	2446 (2)	11585 (2)	3762 (2)	33
N(61)	1851 (2)	11550 (2)	2948 (2)	33
N(62)	2101 (2)	12271 (2)	4248 (2)	37
C(6L)	2091 (3)	10968 (2)	2200 (2)	40
C(6B)	1099 (2)	12262 (2)	2827 (2)	34
Cl	2892 (1)	-84 (1)	101 (1)	60
N(X)	-2924 (2)	10584 (3)	4242 (2)	65
C(1)(X)	-2240 (3)	10666 (2)	5090 (2)	43
C(2)(X)	-1087 (2)	10316 (2)	5017 (2)	32
C(3)(X)	-732 (3)	9867 (3)	4273 (3)	48
C(4)(X)	-335 (3)	10451 (3)	5746 (3)	51
W(1)	5131 (3)	-17 (3)	1398 (3)	84
W(2)	1172 (3)	2178 (3)	98 (3)	89
W(3)	163 (3)	3778 (3)	120 (3)	96
W(4)	423 (4)	3972 (5)	1858 (5)	72
W(5)	-177 (4)	5867 (4)	1946 (4)	52
W(6)	118 (14)	4971 (11)	1691 (12)	45

† L refers to linking (methylene) C atoms; B refers to backbone (methine) C atoms.

last cycle was 0.03 and the maximum height in the final difference Fourier synthesis was $0.64 \text{ e } \text{\AA}^{-3}$.

Discussion

In the cucurbituril adducts (1) through (9) (Table 1) the cage molecules all lie at special positions in a primitive orthorhombic or monoclinic unit cell with edges $a \sim 12$, $b \sim 16$, $c \sim 14.5 \text{ \AA}$. This general pattern involves three related space groups, $Pnmm$, $Pnn2$ and $P2_1/n$. Crystals of (2), (3) and (4) neatly realize the

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances, bond angles and cavitant torsion angles for both title compounds, and a stereoview of the unit-cell contents for the first compound have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39123 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Atom coordinates ($\times 10^4$) and equivalent values of the anisotropic temperature factors ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms in $\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12} \cdot 2\text{Ca}(\text{HSO}_4)_2 \cdot 13\text{H}_2\text{O}$

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
O(1)	7043 (4)	9211 (4)	4443 (3)	36
C(1)	7711 (6)	8540 (5)	4423 (4)	24
N(11)	8827 (5)	8564 (5)	5185 (3)	26
N(12)	7472 (5)	7704 (4)	3629 (3)	27
C(1L)†	9398 (6)	9382 (5)	6151 (4)	26
C(1B)†	8476 (6)	7106 (5)	3833 (4)	26
O(2)	7445 (4)	9493 (4)	6741 (3)	30
C(2)	8165 (5)	8839 (5)	7101 (4)	23
N(21)	8241 (5)	8218 (5)	7858 (5)	26
N(22)	9020 (4)	8640 (4)	6798 (3)	23
C(2L)	7516 (6)	7516 (6)	8302 (5)	28
C(2B)	9799 (5)	7923 (5)	7417 (4)	25
O(3)	4752 (4)	7867 (4)	7222 (3)	40
C(3)	5083 (6)	6982 (6)	7638 (4)	28
N(32)	6353 (5)	7049 (5)	8150 (3)	30
N(31)	4195 (5)	5747 (5)	7675 (3)	26
C(3L)	2760 (6)	5367 (6)	7223 (4)	28
C(3B)	6387 (6)	5897 (6)	8643 (4)	25
O(4)	1821 (4)	6022 (4)	5352 (3)	39
C(4)	1617 (5)	4813 (6)	5447 (4)	26
N(41)	884 (5)	3658 (4)	4706 (3)	26
N(42)	2026 (5)	4397 (4)	6294 (3)	27
C(4L)	54 (6)	3736 (6)	3739 (4)	29
C(4B)	648 (5)	2386 (5)	5072 (4)	25
O(5)	1374 (4)	5734 (4)	2907 (3)	36
C(5)	1076 (5)	4486 (6)	2666 (4)	26
N(51)	1218 (5)	3858 (4)	1960 (3)	26
N(52)	517 (5)	3472 (5)	3054 (3)	26
C(5L)	1678 (6)	4631 (6)	1359 (4)	27
C(5B)	726 (6)	2350 (6)	1831 (4)	25
O(6)	3908 (4)	7191 (4)	2612 (3)	35
C(6)	4071 (6)	6260 (6)	2234 (4)	27
N(62)	3089 (5)	5008 (5)	1656 (3)	28
N(61)	5268 (5)	6306 (5)	2309 (3)	27
C(6L)	6448 (6)	7589 (6)	2669 (4)	30
C(6B)	5119 (6)	5060 (6)	1751 (4)	25
Ca ²⁺	7445 (1)	11862 (1)	6924 (1)	30
S(1)	971 (2)	2234 (2)	8598 (1)	34
S(2)	2997 (2)	7257 (2)	9587 (1)	46
O(1)[S(1)]	-146 (4)	2116 (5)	7692 (3)	43
O(2)[S(1)]	2119 (5)	3604 (5)	8881 (3)	53
O(3)[S(1)]	633 (5)	2010 (5)	9369 (3)	53
O(4)[S(1)]	1489 (5)	1160 (5)	8432 (3)	52
O(1)[S(2)]	2672 (11)	7631 (11)	8700 (7)	154
O(2)[S(2)]	3093 (12)	8243 (10)	10256 (7)	183
O(3)[S(2)]	4170 (7)	6968 (7)	9827 (7)	145
O(4)[S(2)]	1872 (7)	5902 (6)	9378 (7)	121
W(1)	8003 (5)	11726 (5)	8556 (3)	48
W(2)	7934 (5)	11816 (4)	5588 (3)	47
W(3)	5202 (5)	10020 (5)	6318 (4)	64
W(4)	3483 (6)	11082 (6)	9957 (5)	80
W(5)	2929 (6)	9070 (6)	7336 (5)	86
W(6)	4490 (10)	7800 (10)	4661 (7)	148
W(I)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	156

† L refers to linking (methylene) C atoms; B refers to backbone (methine) C atoms.

possibilities of the space-group relationship: (2) is monoclinic, $P2_1/n$, b unique; (3) is orthorhombic, $Pnmm$ or $Pnn2$; (4) is monoclinic, $P2_1/n$, a unique. The pattern holds for metal-ion adducts [(6)–(9)] as well as organic diammonium adducts [(1)–(5)]. In adducts (10)–(12) the crystals are hexagonal or trigonal and there is only one cucurbituril per primi-

tive unit cell with no translational elements of symmetry. The hexamers stack up along a threefold or sixfold axis passing through their centers.

A structure determination of (1) proves that the organic ion is a guest in the interior of the cucurbituril cage (Fig. 2). In addition to the similarities between (1) and (2)–(5) in cell dimensions and symmetries, there is NMR evidence that this type of interaction occurs in all the organic adducts (Mock & Shih, 1983). In structures with one guest organic ion per host, most guests must occupy special positions having higher site symmetry than their molecular symmetry and must therefore be disordered. The one exception to the general pattern of disorder among the organic adducts is the *p*-xylylenediammonium adduct, in which the guest organic molecule has a center of symmetry.

Metal ions do not occupy the cage although their adducts with cucurbituril crystallize in patterns involving as much disorder as the organic adducts. Indeed (13) was chosen for a complete structure determination because it did not follow the structural pattern of the other adducts and seemed therefore less likely to present problems of structural disorder. The stoichiometry (Table 1) of five of the six metal-ion-containing adducts ranges up to two metal ions per cage. This suggests that the metal ion to cucurbituril interaction occurs at the two portals of the cavity. The complete structure determination of (13) shows that the metal ions are outside the cucurbituril portals and shared between adjacent cavities. Fig. 3 displays this sharing. A partial structural analysis, based on 1025 diffractometer data, of (9) also clearly shows the metal ions to be outside the cage. [The Ni^{II} ions in (9) apparently partially occupy two different general positions near the cage portals; they have site-occupancy factors of less than $\frac{1}{2}$.]

In (12) there are three metal atoms per cage. This adduct differs from the others by having the metal

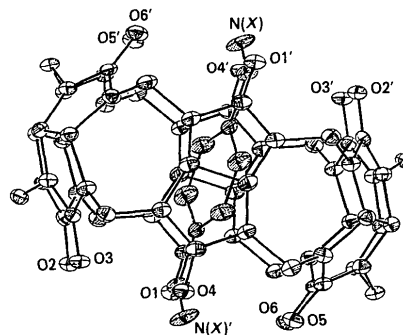


Fig. 2. Perspective view of the host-guest interaction between the cucurbituril cage and the *p*-xylylenediammonium ion. The guest, which occupies the internal cavity of the host molecule, has stippled atoms in this representation. Primes refer to atoms related by the center of inversion at the center of the cavity. H atoms are omitted.

held in the negatively charged complex ion AuCl_4^- . Based on the rhombohedral form and $\bar{3}m1$ Laue symmetry of the crystals the space group is either $P321$ or $P\bar{3}m1$. The single cucurbituril molecule in the unit cell would have 32 site symmetry in the first of these and $3m$ site symmetry in the second. The square-planar AuCl_4^- ions then would lie well outside the cage on twofold axes in $P321$ or at $2/m$ sites in $P\bar{3}m1$; only these arrangements are possible without disorder.

Another of the more symmetrical of the crystalline adducts of cucurbituril merits special mention, too. The striking 1:9:24 stoichiometry in (11) means that in this hexagonal crystal the cage molecule has associated with it 33 small molecules having approximately 131 per cent of its own mass. $1.2 \text{ mol liter}^{-1}$ of cucurbituril has crystallized with the equivalent of 10 M aqueous H_2SO_4 solution in the crystal.

It is useful to compare the structure of the cage in the (nearly) empty [(13)] and full [(1)] conditions. The average bond distances and angles (Table 4) differ little between the structures and are comparable to those in glycoluril (Blessing & DeTitta, 1984). The only significant difference between (13) and (1) occurs with the O-C-N angles. Two of the cross-cage diameters increase [from 10.023 (12) to 10.319 (6) Å and from 9.938 (12) to 10.129 (6) Å] and the third decreases [from 10.206 (12) to 9.782 (6) Å] going from (13) to (1). The last, shortest diameter is nearly perpendicular ($\sim 93^\circ$) to the plane of the guest's benzene

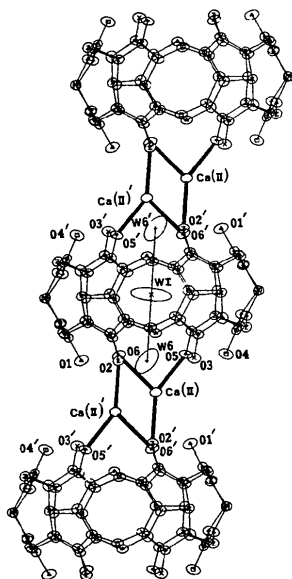


Fig. 3. Arrangement of Ca^{11} ions and cucurbituril molecules in the crystal structure of cucurbituril. $2\text{Ca}(\text{HSO}_4)_2 \cdot 13\text{H}_2\text{O}$. Each Ca^{11} is shared between cucurbituril molecules, coordinated (heavy line) to carbonyl O atoms. The chain runs along the b direction in the crystal. Also shown (in the center molecule only) is the way water molecules occupy the cage center and portals. The sulfates, other waters of crystallization and all H atoms are omitted.

Table 4. Mean bond distances (Å), mean bond angles ($^\circ$) and mean torsion angles ($^\circ$) of cucurbituril in two different adducts

	Number of unique instances	<i>p</i> -Xylylene-diammonium adduct (1)	$\text{Ca}(\text{HSO}_4)_2$ adduct (13)
O-C	6	1.224 (2)	1.228 (3)
C-N	12	1.367 (1)	1.362 (2)
CL-N*	12	1.446 (1)	1.444 (3)
CB-N*	12	1.449 (1)	1.450 (3)
CB-CB	3	1.547 (3)	1.545 (5)
O-C-N	12	125.6 (1)	123.6 (1)
N-C-N	6	108.7 (2)	108.5 (1)
CL-N-CB	12	123.7 (1)	123.6 (1)
C-N-CB	12	112.1 (1)	112.1 (1)
C-N-CL	12	123.0 (1)	122.7 (1)
N-CB-N	6	114.4 (2)	114.6 (1)
N-CB-CB	12	103.3 (1)	103.3 (1)
N-CL-N	6	114.1 (2)	114.0 (1)
N-CB-CB-N†	6	119.7 (3.1)	119.5 (2.4)
N-CB-CB-N	6	0.1 (3.0)	0.1 (2.4)
C-N-CL-N	12	105.1 (1.9)	103.6 (1.8)
CB-N-CL-N	12	87.1 (1.0)	87.0 (1.0)
N-C-N-CL	12	173.5 (1.8)	172.4 (1.5)
N-C-N-CB	12	4.7 (1.0)	2.0 (1.0)
O-C-N-CL	12	6.2 (1.7)	6.2 (1.5)
O-C-N-CB	12	175.0 (0.8)	176.9 (1.0)
C-N-CB-N'	12	114.9 (1.8)	112.6 (1.4)
C-N-CB-CB	12	1.1 (2.0)	0.1 (1.5)
CL-N-CB-CB	12	171.6 (1.1)	171.6 (1.1)
CL-N-CB-N'	12	76.8 (1.1)	77.0 (1.1)

* *L* refers to linking (methylene) C atoms; *B* refers to backbone (methine) C atoms.

† Primes refer to designations in Fig. 1.

ring in (1). Also the distance between the best least-squares planes of the six O atoms which are nearly coplanar at each portal of the cavitant increases when the cavity is filled. It is 5.990 (16) Å in (13) but 6.080 (8) Å in each (1). Therefore, the cavitant deforms to accommodate the guest molecule. Consideration of the torsion angles of the cavitant shows how this deformation occurs.

The 132 independent torsion angles of cucurbituril in (1) and (13) fall into 12 types (Table 4). There is considerable variation within every type in both (1) and (13). Thus, the six torsions of the type N-CB-CB-N' average near the nominal 120° in both (1) and (13) but range widely. The range of values of this torsion type is much increased by occupancy: from 13.6° [in (13)] to 20.3° [in (1)]. In more precise terms, σ_2 (defined as $\{[\sum(a_i^2/\sigma_i^2)]/\sum(1/\sigma_i^2) - \bar{a}^2\}/(N-1)\}^{1/2}$) rises from 2.4° in (13) to 3.1° in (1) for the N-CB-CB-N' torsion type. Lesser but significant increases in σ_2 occur going from (13) to (1) with the N-CB-CB-N, C-N-CB-N', and C-N-CB-CB torsion types. All of these types involve CB's; none involves CL's. In contrast there is no increase in σ_2 going from (13) to (1) for the CB-N-CL-N and CL-N-CB-N' torsion types, and there are only slight increases for the O-C-N-CL and C-N-CL-N torsion types. Also, the largest changes in mean torsion angle going from (13) to (1) occur with the N-C-N-CB and C-N-CB-N' torsions whereas mean torsion angles of types involving CL experience only smaller changes. The changes

upon occupancy of the cavity thus appear mainly within the glycoluril moieties, not at the links between them. These alterations may represent the full extent of cucurbituril's possible response to occupancy inasmuch as the *para*-disubstituted benzene ring is at the upper limit of size that the cucurbituril cavity accommodates (Mock & Shih, 1983).

In (1) each Ca^{II} ion is coordinated to three carbonyl O atoms – two at a portal of one cage and the third at a portal of an immediate neighbor (Fig. 3). The distances are 2.358 (4) and 2.475 (4) Å [to O(5) and O(6) of one cage] and 2.468 (4) Å [to O(2') of the other]. The perpendicular distance between the best least-squares planes of the portal O atoms of two such neighbors is 4.153 (16) Å. Octacoordination at the Ca^{II} is completed with W(1), W(2), W(3) and W(6) at 2.386 (4), 2.404 (5), 2.448 (5) and 2.713 (10) Å and O(1)[S(1)] at 2.514 (4) Å. One water of crystallization [W(6)] lies hydrogen-bonded 0.17 Å above the O(1)–O(6) plane and nearly equidistant from the six portal O atoms. At the center of inversion inside the cavity is found a single water molecule, a feature which recalls the encirclement of water by neutral crown compounds, first reported by Newkome, Hellen, Fronczek, DeLord, Kohli & Vogtle (1981). Thus a chain of hydrogen-bonded water molecules, W(6)–W(1)–W(6'), passes through the center of the 'empty' cage in (13).

In (1) there is also important hydrogen bonding at the portals of the cucurbituril cage. Each ammonium nitrogen, N(X), protrudes 0.630 (7) Å outside the plane of the six portal carbonyl O atoms and lies

off-center (Fig. 2), making close approaches to O(4) and O(5) [2.822 (4) and 2.914 (4) Å], and intermediate approaches to O(3) and O(6). N(X) also lies significantly close to W(5), W(3) and W(6) [distances are 2.856 (6), 2.869 (6) and 3.10 (3) Å].

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Dynamic Processes in Crystals Examined Through Difference Vibrational Parameters ΔU : The Low-Spin–High-Spin Transition in Tris(dithiocarbamato)iron(III) Complexes

BY K. CHANDRASEKHAR AND H. B. BÜRGI

Laboratorium für Chemische und Mineralogische Kristallographie der Universität, CH-3012 Bern, Switzerland

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Abstract

Difference vibrational parameters $\Delta U(z)$ evaluated along internuclear directions between bonded atoms contain physical information on internal molecular motion. For a number of metal complexes, showing small-amplitude motion, ΔU 's from diffraction experiments are found to be in good agreement with ΔU 's calculated from vibrational force fields. Typical values are in the range 0.002–0.003 Å². For molecules showing large-amplitude deformations of bond

length, experimental ΔU 's agree with those calculated from simple models. As an example, data for tris(dithiocarbamato)iron(III) complexes [(R₂NCS₂)₃Fe^{III}], taken from the literature, are analysed in detail. This class of compounds shows a spin equilibrium in the solid state which depends on temperature, on the substituents attached to the dithiocarbamate skeleton, and on solvate molecules, if any. The Fe–S bond distance varies between ~2.30 Å in the low-spin state and ~2.45 Å in the high-spin state, the exact value depending on the