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Cucurbit[6]uril *p*-phenylenediammonium diiodide decahydrate inclusion complex

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Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.085
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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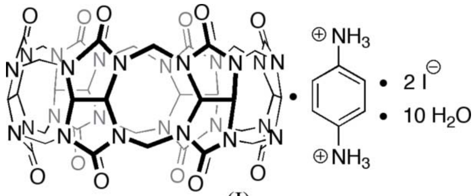
The inclusion complex, $C_6H_{10}N_2^{2+}\cdot 2I^-\cdot C_{36}H_{36}N_{24}O_{12}\cdot 10H_2O$, displays a large ellipsoidal deformation of the cucurbit[6]uril skeleton upon complex formation. The cucurbit[6]uril molecule and the phenylenediammonium dication are each disposed about a center of inversion.

Comment

The supramolecular chemistry of the cucurbit[*n*]uril (CB[*n*]) family (Lagona *et al.*, 2005; Kim *et al.*, 2000) of macrocycles has received widespread attention in recent years because its members bind to hydrophobic species in water with high affinity and selectivity (Liu, Ruspic *et al.*, 2005; Liu, Zavalij & Isaacs, 2005; Isaacs *et al.*, 2005). These outstanding recognition processes have been exploited in numerous advanced applications including ion-channels (Jeon *et al.*, 2004), self-assembling dendrimers (Moon *et al.*, 2004), 'molecular' molecular sieves (Miyahara *et al.*, 2002), crystal engineering (Sokolov *et al.*, 2000), photochemical stabilizers (Mohanty & Nau, 2005), chemical sensors (Sindelar *et al.*, 2005; Bush *et al.*, 2005; Lagona *et al.*, 2006), and as components of self-sorting systems (Mukhopadhyay *et al.*, 2004, 2006). Despite its seemingly rigid polycyclic structure, CB[6] undergoes substantial deformations in its transition states for ingression and egression (Marquez *et al.*, 2004) as well as in the ground states (Samsonenko *et al.*, 2002) of its host–guest complexes.



(I)

The asymmetric unit of (I) comprises one half of a CB[6] molecule, disposed about a center of inversion, one half of a 1,4-phenylenediammonium cation, disposed about a center of inversion, an iodide counter-ion and five water molecules. Interestingly, each NH_3^+ group forms two hydrogen bonds to the ureidyl C═O portal of CB[6] (Fig. 1 and Table 1). The remaining NH group hydrogen bonds to a water molecule which, in turn, hydrogen bonds to the C═O portal of CB[6]. Several other water molecules are present in the structure of (I); these water molecules form hydrogen-bonded chains that are terminated by hydrogen bonding to the iodide counter-ions. The majority of the geometrical features of (I) are as expected, given the molecular structures of their components. One feature of the crystal structure of complex (I) that is

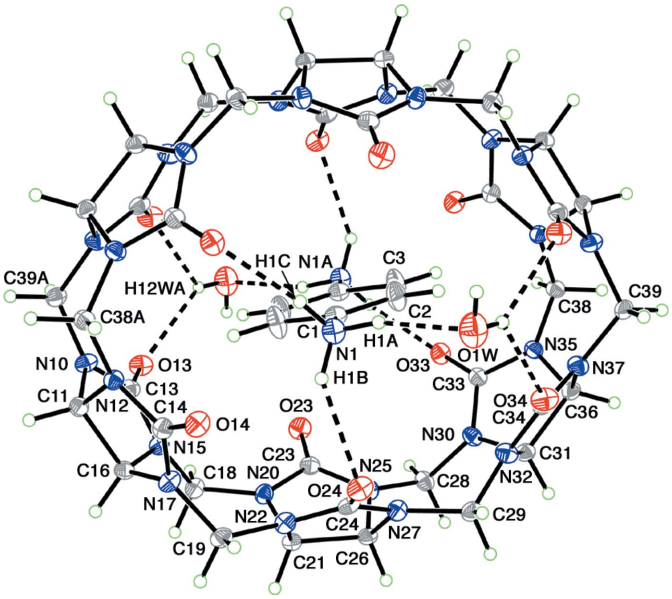


Figure 1
The molecular structure of complex (I), showing the atom-labeling scheme and displacement ellipsoids drawn at the 30% probability level. The iodide counter-ion and four of the five unique water molecules have been omitted for clarity. Dashed lines indicate hydrogen bonds.

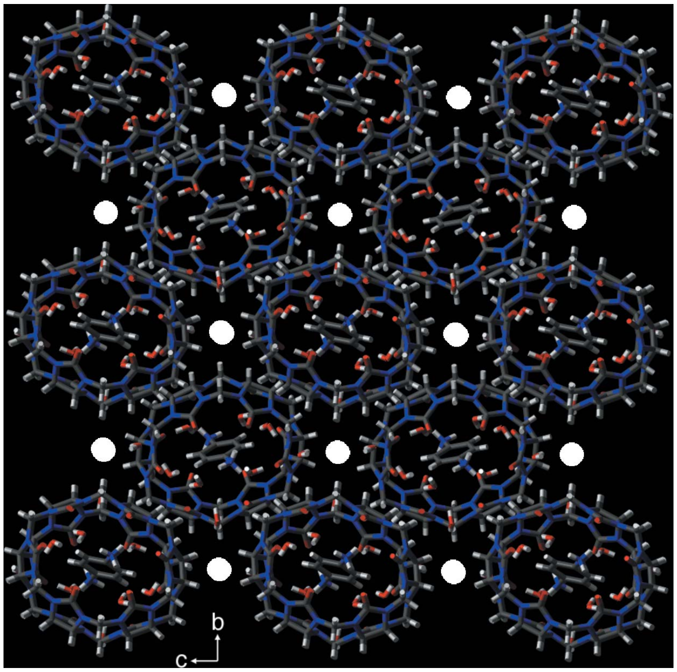


Figure 2
Illustration of the packing of complex (I) in the *bc* plane of the crystal structure. Color coding: C gray, H white, N blue, O red and I purple.

unusual is the observed ellipsoidal deformation of the CB[6] skeleton. We follow the suggestion of Samsonenko *et al.* (2002) and quantify this distortion as the maximum difference observed between the opposing non-bonded carbon–carbon distance along the equator of the CB[6] molecule. By this definition, the CB[6] component of (I) exhibits an ellipsoidal deformation of 1.34 Å (non-bonded C–C range 9.51–10.85 Å).

Interestingly, complex (I) forms slabs based on a rectangular motif in the *bc* plane (Fig. 2). To fill space efficiently, these slabs are offset with respect to one another upon progression along the *a* axis. The I^- counter-ions are located at the interface of these slabs and act as hydrogen-bond acceptors for the water molecules (Table 1).

Previously, Fedin and co-workers (Samsonenko *et al.*, 2002) have shown that ellipsoidal deformation of the CB[6] skeleton of up to 1.31 Å can be achieved. The significant ellipsoidal deformation observed in complex (I) (1.34 Å) places it amongst the largest known. In combination, these results suggest that CB[6] – and, by analogy, other members of the CB[*n*] family (Lagona *et al.*, 2005; Huang *et al.*, 2006) – have the ability to respond to the sizes and shapes of their guest molecules.

Experimental

Complex (I) was prepared by mixing cucurbit[6]uril (Freeman *et al.*, 1981) with 1,4-phenylenediamine dihydrochloride in water according to a literature procedure (Liu, Ruspic *et al.*, 2005) followed by the addition of KI. Single crystals suitable for structure determination were obtained by allowing an aqueous solution of complex (I) to stand at room temperature for several days.

Crystal data

$C_6H_{10}N_2^{2+}\cdot 2I^-\cdot C_{36}H_{36}N_{24}O_{12}\cdot 10H_2O$
$M_r = 1541.01$
Monoclinic, $P2_1/n$
$a = 11.854$ (3) Å
$b = 15.460$ (4) Å
$c = 15.279$ (4) Å
$\beta = 90.447$ (4)°
$V = 2800.1$ (11) Å^3
$Z = 2$
$D_x = 1.828$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.23$ mm^{-1}
$T = 223$ (2) K
Prism, yellow
0.32 × 0.23 × 0.21 mm

Data collection

Bruker SMART CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.720$, $T_{\max} = 0.773$
31829 measured reflections
6417 independent reflections
5677 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.085$
$S = 1.00$
6417 reflections
446 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 9.444P]$, $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.83$ e Å^{-3}
$\Delta\rho_{\min} = -0.94$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1$W^{\rm i}$	0.90	1.85	2.728 (4)	165
N1—H1B···O24	0.90	2.19	2.945 (3)	141
N1—H1C···O33$^{\rm i}$	0.90	1.95	2.840 (3)	169
O1W—H11W···O2$W^{\rm i}$	0.841 (10)	2.04 (3)	2.716 (5)	137 (4)
O1W—H12W···O34$^{\rm i}$	0.829 (10)	2.19 (3)	2.765 (4)	127 (3)

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$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O1W—H12W\cdots O13$	0.829 (10)	2.21 (3)	2.911 (3)	143 (4)
$O2W—H21W\cdots O5W^{i}$	0.844 (10)	2.03 (3)	2.831 (5)	158 (6)
$O2W—H22W\cdots O33^{ii}$	0.844 (10)	1.923 (19)	2.741 (4)	163 (5)
$O3W—H31W\cdots O1W^{i}$	0.830 (10)	2.02 (3)	2.793 (4)	156 (6)
$O3W—H32W\cdots I1^{iii}$	0.826 (10)	3.03 (3)	3.740 (4)	146 (4)
$O4W—H41W\cdots O14$	0.849 (10)	2.49 (4)	2.948 (4)	114 (3)
$O4W—H42W\cdots O23^{ii}$	0.842 (10)	2.13 (3)	2.898 (4)	152 (5)
$O5W—H51W\cdots I1$	0.832 (10)	2.769 (15)	3.592 (4)	171 (5)
$O5W—H52W\cdots I1^{iv}$	0.834 (10)	2.86 (2)	3.668 (3)	163 (6)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $-x, -y+1, -z$.

N- and C-bound H atoms were included in the riding-model approximation, with N—H = 0.90 and C—H = 0.98–0.99 Å, and with $U_{iso}(H) = 1.5U_{eq}(N)$ and $U_{iso}(H) = 1.2U_{eq}(C)$. O-bound H atoms were refined with soft constraints of O—H = 0.83 (1) Å and H$\cdots$H = 1.32 (2) Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSHELL* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

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