organic compounds

A perchlorate salt of an octaprotonated cryptand

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The title compound, 1,4,8,11,14,18,23,27-octaaza-6,16,25(2,6)-tripyridinabicyclo[9.9.9]nonacosaphane(8+) octaperchlorate pentahydrate, $C_{33}H_{59}N_{11}^{8+} \cdot 8ClO_4^- \cdot 5H_2O$, is a salt of an octaprotonated cryptand in which one of the pyridine groups and the bridgehead tertiary amines remain unprotonated. The central cavity of the cryptand is not occupied, although the perchlorate ions are hydrogen bonded in clefts formed between the arms of the cryptand.

Comment

Protonated aminocryptands have previously been shown to be versatile hosts for polyatomic oxoanions (Morgan et al., 1995; Hynes et al., 2000; Maubert et al., 2001; Farrell et al., 2003). In these examples, either one or two anions are encapsulated within the cavity of the cryptand, most commonly by a mixture of direct (anion–protonated amine) and indirect (anion–water–protonated amine) hydrogen bonding. The hexaprotonated form of the pyridine-containing cryptand L has been shown to bind a single SiF_6^{2-} ion within the cavity via six (amine)N—H···F hydrogen bonds, while four BF_4^- ions are located in the lattice but are clearly outside the host.


(I)
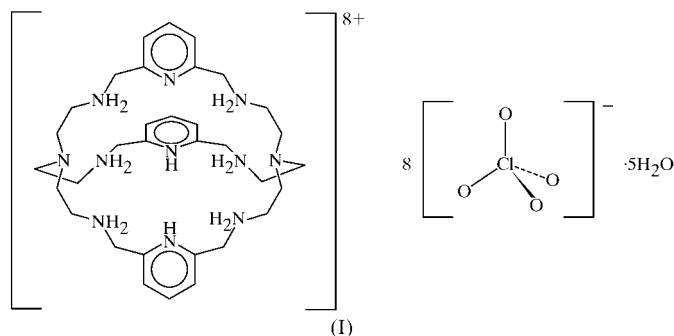
In contrast, the octaprotonated form of the host in the title compound, (I), binds three of the perchlorate anions in sites within clefts formed between the arms of the cryptand.

Fig. 1 shows the conformation of the protonated cryptand. The six secondary amine groups are protonated, but the

tertiary amine groups of the bridgeheads (N1 and N2) are not. Two of the pyridine groups are protonated (at N4A and N4C), and the planes of these rings are aligned tangentially to the body of the cryptand and are almost parallel to each other (Fig. 2). The H atoms attached to N4A and N4C were located from difference maps, and there is further support for this assignment in the observation of hydrogen bonding between these two pyridine groups and the perchlorate O atoms.
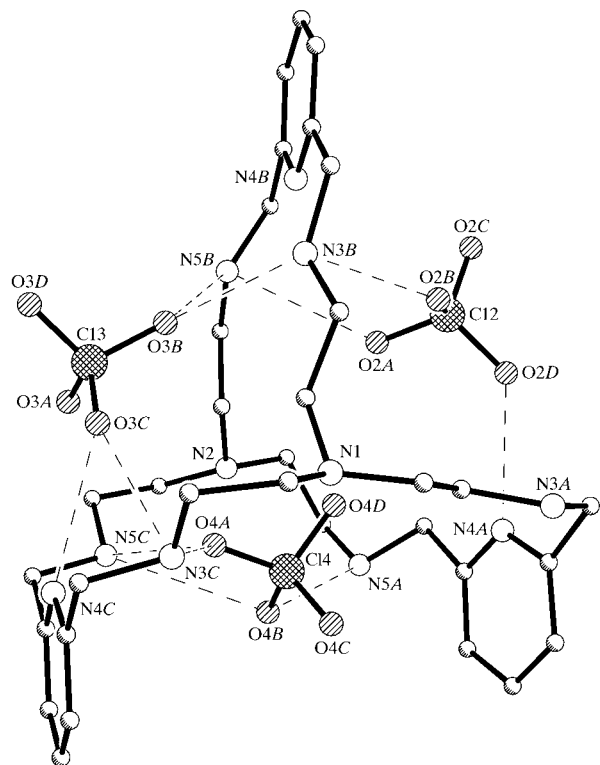
Protonation of the pyridine rings rather than the bridgehead N atoms would be surprising if the pK_a values of these groups were close to those of free pyridine and triethylamine (pK_a of 5.25 and 11.01, respectively). Within the constraints of the cage framework, however, this assumption appears not to hold. In part, this behaviour may be due to some flattening of the tetrahedral geometry at the bridgehead N atoms, which reflects a tendency towards sp^2 hybridization and therefore a decrease in basicity. However, geometric evidence for sp^2 hybridization is slight; the angle sums at N1 and N2 are 338 (8) and 337 (9)°, respectively. An alternative possibility is that, since protonation is stabilized by hydrogen bonding, the observed protonation pattern is a consequence of the hydrogen bonding in the lattice.

As with other reported anion cryptates (Morgan et al., 1995; Hynes et al., 2000; Maubert et al., 2001; Farrell et al., 2003), the hydrogen-bonding network that links the cation, anions and solvate water molecules is complex. The individual hydrogen
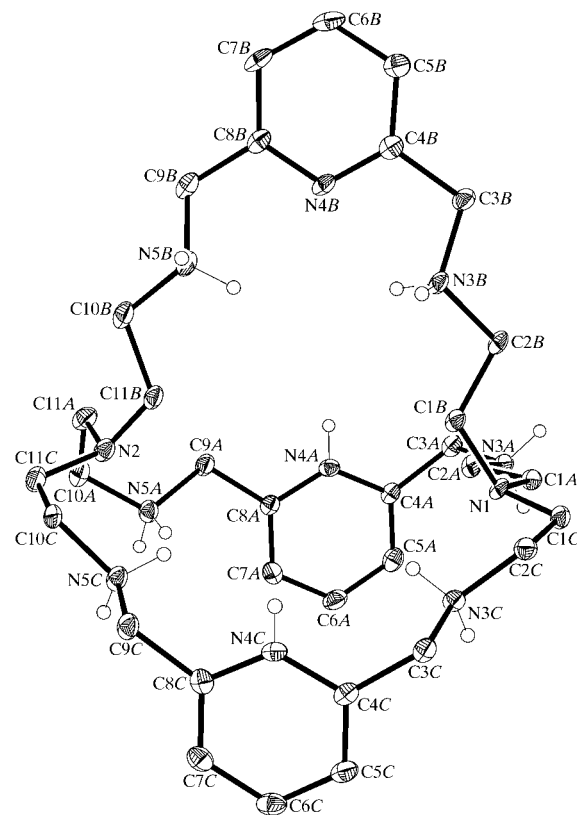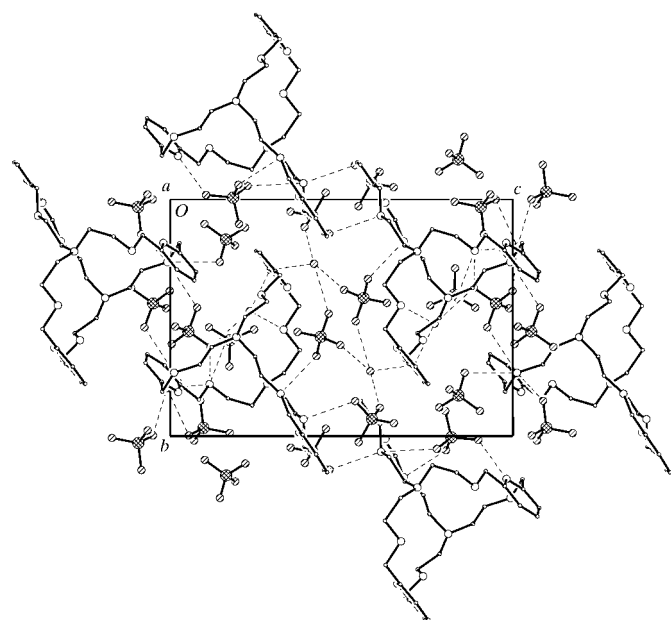

Figure 1
A perspective view of the title cation, showing ellipsoids at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity.

bonds are listed in Table 1, while Fig. 2 illustrates the binding of the three perchlorate anions most closely associated with the clefts between the arms of the cryptand. Each of the eight perchlorate anions forms at least one hydrogen bond to a protonated group of the cryptand, and each cryptand NH_2^+ group forms at least two hydrogen bonds (some are bifurcated) to O atoms of either the perchlorate anions or the water molecules. The solvate water molecules facilitate further hydrogen-bonding interactions that extend through the lattice (Fig. 3).

The hexaprotonated analogue of the cryptand can selectively encapsulate SiF_6^{2-} in preference to BF_4^- (Morgan et al., 1995). Although this observation can be partly explained on the basis of charge selectivity, taken in tandem with the present result this preference might also suggest that the cryptand does not favour tetrahedral guests. However, as it is equally possible that the octaprotonated cryptand adopts this geometry to maximize the hydrogen bonding and hence minimize the energy of the structure, the structures of other hexa- or octaprotonated cryptates of this ligand will be of much interest.

Figure 2
A perspective diagram showing the three perchlorate anions hydrogen bonded into the clefts between strands of the protonated cryptand. Hydrogen bonds are shown as dashed lines.

Experimental

The neutral cryptand was prepared according to the literature method of Marrs et al. (1993) and was dissolved in ethanol. Perchloric acid was added until the pH of the solution was approximately 2. Colourless crystals of the complex crystallized out of this solution over a period of approximately two weeks.

Figure 3
A projection of the unit cell along a, with hydrogen bonds shown as dashed lines.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3A-H3A1\cdots O1D$	0.92	1.93	2.850 (4)	173
$N3A-H3A2\cdots O5A^i$	0.92	2.11	2.889 (4)	142
$N4A-H4A\cdots O2D$	0.85 (4)	1.91 (4)	2.755 (4)	173 (4)
$N5A-H5A1\cdots O4B$	0.92	2.01	2.914 (4)	167
$N5A-H5A2\cdots O2W$	0.92	1.99	2.798 (4)	146
$N5A-H5A2\cdots O1C^{ii}$	0.92	2.51	2.987 (4)	113
$N3B-H3B1\cdots O2B$	0.92	2.16	2.829 (4)	129
$N3B-H3B2\cdots O6A$	0.92	2.15	2.850 (4)	132
$N3B-H3B2\cdots O3B$	0.92	2.32	2.974 (3)	128
$N5B-H5B1\cdots O7A$	0.92	1.98	2.874 (4)	162
$N5B-H5B2\cdots O2A$	0.92	2.42	2.998 (4)	121
$N5B-H5B2\cdots O3B$	0.92	2.45	2.976 (4)	117
$N3C-H3C1\cdots O1W$	0.92	1.81	2.672 (4)	155
$N3C-H3C1\cdots O8D$	0.92	2.56	3.114 (4)	119
$N3C-H3C2\cdots O4A$	0.92	2.29	3.121 (4)	150
$N3C-H3C2\cdots O3C$	0.92	2.43	2.956 (4)	116
$N4C-H4C\cdots O3C$	0.82 (4)	2.29 (4)	2.991 (4)	145 (3)
$N5C-H5C1\cdots O4A$	0.92	2.33	3.168 (4)	152
$N5C-H5C1\cdots O4B$	0.92	2.60	3.125 (4)	116
$N5C-H5C2\cdots O3W$	0.92	1.76	2.661 (4)	165
$O1W-H1WA\cdots O4C$	0.85 (5)	2.06 (5)	2.833 (4)	151 (4)
$O1W-H1WA\cdots O1A$	0.85 (5)	2.39 (4)	2.992 (4)	129 (4)
$O1W-H1WB\cdots O2W^{ii}$	0.91 (5)	2.03 (5)	2.840 (4)	147 (4)
$O2W-H2WA\cdots O5B$	0.87 (4)	1.92 (5)	2.781 (4)	167 (4)
$O2W-H2WB\cdots O1B^{ii}$	0.81 (4)	2.51 (4)	2.927 (4)	113 (3)
$O2W-H2WB\cdots O5A^{iii}$	0.81 (4)	2.62 (4)	3.281 (4)	140 (4)
$O3W-H3WA\cdots O1C^{ii}$	0.82 (5)	2.14 (5)	2.924 (4)	160 (4)
$O3W-H3WA\cdots O1D^{ii}$	0.82 (5)	2.61 (5)	3.237 (4)	135 (4)
$O3W-H3WB\cdots O4W$	0.90 (5)	1.83 (5)	2.667 (4)	155 (4)
$O4W-H4WA\cdots O5W^{iv}$	0.92 (5)	1.89 (5)	2.746 (5)	155 (4)
$O4W-H4WB\cdots O8B^v$	0.79 (5)	2.39 (5)	3.127 (6)	155 (5)
$O4W-H4WB\cdots O8C^v$	0.79 (5)	2.51 (5)	3.218 (6)	149 (5)
$O5W-H5WA\cdots O6C^{vi}$	0.84 (5)	2.04 (5)	2.871 (4)	171 (5)
$O5W-H5WB\cdots O7D$	0.87 (5)	2.00 (5)	2.846 (4)	161 (5)

Symmetry codes: (i) $2-x, 2-y, -z$; (ii) $2-x, 1-y, -z$; (iii) $1-x, 2-y, -z$; (iv) $1-x, 1-y, 1-z$; (v) $x-1, y, z$; (vi) $2-x, 1-y, 1-z$.

organic compounds

Crystal data

$C_{33}H_{59}N_{11}{}^{8+}\cdot 8ClO_4{}^-\cdot 5H_2O$
$M_r = 1495.59$
Triclinic, $P\bar{1}$
$a = 12.9265\ (13)$ Å
$b = 13.6798\ (14)$ Å
$c = 18.5310\ (19)$ Å
$\alpha = 84.258\ (9)°$
$\beta = 76.394\ (8)°$
$\gamma = 65.092\ (8)°$
$V = 2888.7\ (6)$ Å^3

$Z = 2$
$D_x = 1.719$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 36
  reflections
$\theta = 4.5–12.5°$
$\mu = 0.50$ mm^{-1}
$T = 128\ (2)$ K
Block, colourless
$0.82 \times 0.52 \times 0.36$ mm

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: ψ scan
  (SHELXTL/PC; Siemens, 1990)
  $T_{min} = 0.862$, $T_{max} = 0.972$
9513 measured reflections
9055 independent reflections
7315 reflections with $I > 2\sigma(I)$

$R_{int} = 0.105$
$\theta_{max} = 24.0°$
$h = 0 \rightarrow 14$
$k = -14 \rightarrow 15$
$l = -20 \rightarrow 21$
3 standard reflections
  every 97 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.113$
$S = 1.03$
9055 reflections
838 parameters
H atoms treated by a mixture of
  independent and constrained
  refinement

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2$
  $+ 4.792P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

H atoms bonded to C atoms or amine N atoms were inserted at calculated positions, the constrained C/N—H distances being 0.95, 0.99 and 0.92 Å for aryl, methylene and amine H atoms, respectively. H atoms bonded to O atoms or to the pyridine N atoms were located from difference maps and their coordinates were refined. All H atoms were refined with $U_{iso}(H) = 1.2U_{eq}(X)$, where X is the attached C, N or O atom.

Data collection: XSCANS (Siemens, 1990); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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