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1,4,10,16,21-Pentaaza-7,13,24-triazoniabicyclo[8.8.8]hexacosane monohydrate clathrate trichloride hexahydrate

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The title compound, $C_{18}H_{59}N_8^{3+}\cdot 3\,Cl^-\cdot 7H_2O$, is a chloride salt of a triprotonated cryptand. One of the water molecules is located inside the crypt and makes six hydrogen bonds to the crypt (two as donor and four as acceptor). The coordination geometry about the bound water molecule is trigonal prismatic.

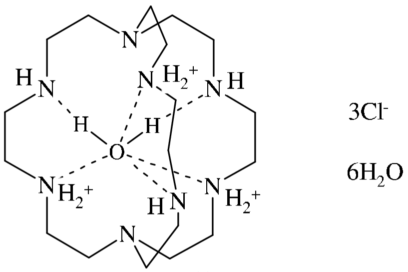
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.102
Data-to-parameter ratio = 14.2

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

Comment

The small cryptand 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]-hexacosane is a versatile host for cations (Coyle *et al.*, 1997, 2004; McKee *et al.*, 2001) and also, in the hexaprotonated form, for anions (Dietrich *et al.*, 1996; Hossain *et al.*, 2002). In this paper, we report the structure, (I), of a triprotonated form of the cryptand, which encapsulates a neutral water molecule as guest in the cavity. A similar complex formed from the tetraprotonated ligand has been reported recently (Hossain *et al.*, 2002).



(I)

The structure of the $[C_{18}H_{59}N_8(H_2O)]^{3+}$ cation is shown in Fig. 1. H atoms bonded to O or N atoms were located in difference maps. The highest residual peaks are in the region of the chloride anions and not close to the amines; the protonated amines are N3*B*, N4*A* and N4*C*. The water molecule makes six hydrogen bonds to the cryptand (Table 1), two as donor (to N3*A* and N3*C*), and four as acceptor (from the three protonated amines and from N4*B*). These hydrogen bonds cover a wide range [2.680 (2)–3.022 (2) Å]; the shortest are those where the encapsulated water molecule acts as donor to the neutral amines N3*A* and N3*C*, and the longest is that with neutral amine N4*B* as donor. Taken in isolation, it is surprising that the shortest hydrogen bonds are not the charge-assisted interactions involving the protonated amines; however, this is likely to be due to mutual constraints within the extended hydrogen-bond network (Fig. 2). All the secondary amine groups, protonated or not, make two hydrogen bonds, one to the central water molecule (O1) and the other to either a chloride anion or a water molecule of crystallization (Table 1). Within each of the three clefts

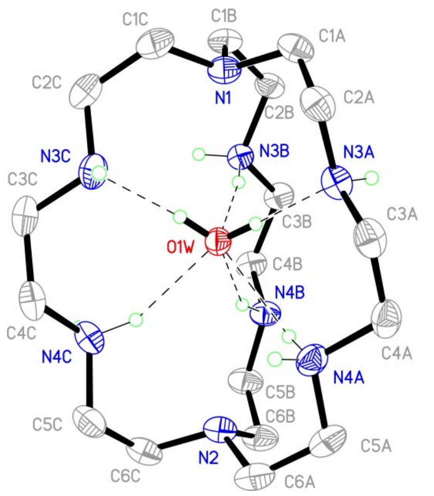


Figure 1

A perspective view of the $[C_{18}H_{59}N_8(H_2O)]^{3+}$ cation. H atoms bonded to C atoms have been omitted for clarity and displacement ellipsoids are drawn at the 50% probability level. The protonated N atoms are N3*B*, N4*A* and N4*C*.

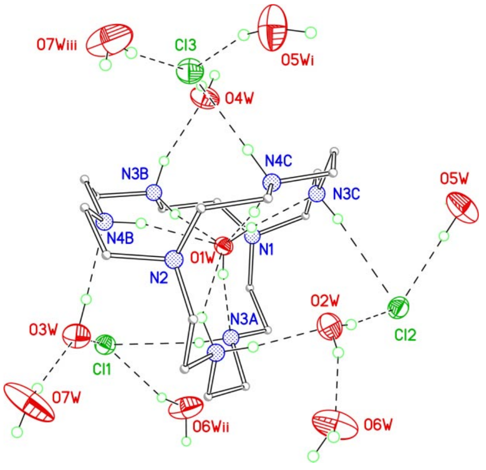


Figure 2

The hydrogen bonding about the cryptate (dashed lines); displacement ellipsoids for the Cl and O atoms are drawn at the 50% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $\frac{5}{2} - x, y - \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.]

formed by the cryptand is an amine–chloride–water–amine hydrogen-bonded chain and the hydrogen bonding extends in three dimensions throughout the crystal structure.

The coordination geometry at the encapsulated water O atom (O1*W*) is close to trigonal prismatic (Fig. 2). The arrangement of the six hydrogen bonds is remarkably similar to that observed for the encapsulated water molecule in the tetraprotonated analogue $[C_{18}H_{60}N_8(H_2O)]^{4+}$, although in that case (Hossain *et al.*, 2002) the geometry was described as tetrahedral.

Experimental

The unsubstituted cryptand was prepared as described previously (Smith *et al.*, 1993). The protonated product was obtained in an attempt at part-tosylation of the amine N atoms. To one millimole of free cryptand in dichloromethane (50 ml) was added 4-methoxybenzene sulfonyl chloride (4 mmol) and triethylamine (4 mmol). The mixture was stirred overnight and evaporated to dryness. The white solid obtained was redissolved and subjected to alumina chromatography using as eluant dichloromethane/1% MeOH, which had been treated with ammonia gas beforehand. The crystals were obtained on slow evaporation of the eluant.

Crystal data

$C_{18}H_{45}N_8^{3+}\cdot 3Cl^-\cdot 7H_2O$
$M_r = 606.08$
Orthorhombic, *Pbca*
$a = 14.2710$ (6) Å
$b = 14.9228$ (6) Å
$c = 29.8597$ (12) Å
$V = 6359.0$ (4) Å^3
$Z = 8$
$D_x = 1.266$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 12 824 reflections
$\theta = 2.4–27.5°$
$\mu = 0.34$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.36 × 0.30 × 0.29 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.826$, $T_{max} = 0.907$
43 473 measured reflections
5604 independent reflections
4323 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 16$
$k = -17 \rightarrow 17$
$l = -35 \rightarrow 35$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.102$
$S = 1.03$
5604 reflections
394 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 5.7025P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3*A*—H3*A*4···Cl1	0.86 (3)	2.55 (3)	3.4000 (19)	172 (2)
N3*B*—H3*B*3···O4*W*	0.86 (3)	1.96 (3)	2.787 (3)	161 (3)
N3*B*—H3*B*4···O1*W*	0.96 (3)	1.91 (3)	2.859 (2)	170 (2)
N3*C*—H3*C*3···Cl2	0.80 (3)	2.62 (3)	3.420 (2)	173 (3)
N4*A*—H4*A*3···O2*W*	0.89 (3)	1.86 (3)	2.743 (3)	170 (3)
N4*A*—H4*A*4···O1*W*	0.91 (3)	2.19 (3)	2.954 (2)	141 (2)
N4*B*—H4*B*4···O1*W*	0.87 (3)	2.21 (3)	3.022 (2)	154 (2)
N4*C*—H4*C*3···O1*W*	0.90 (3)	2.04 (3)	2.888 (2)	156 (2)
N4*C*—H4*C*4···Cl3	0.93 (3)	2.22 (3)	3.144 (2)	173 (2)
O1*W*—H1*WA*···N3*C*	0.845 (9)	1.842 (11)	2.680 (2)	171 (3)
O1*W*—H1*WB*···N3*A*	0.838 (10)	1.861 (10)	2.696 (2)	174 (3)
O2*W*—H2*WA*···O6*W*	0.833 (10)	1.908 (12)	2.709 (3)	161 (3)
O2*W*—H2*WB*···Cl2	0.831 (9)	2.314 (11)	3.1240 (18)	165 (2)
O3*W*—H3*WA*···Cl1	0.844 (10)	2.313 (10)	3.1531 (19)	174 (2)
O3*W*—H3*WB*···N4*B*	0.851 (10)	1.968 (10)	2.818 (3)	177 (2)
O4*W*—H4*WB*···Cl2^{iv}	0.837 (9)	2.328 (11)	3.1410 (19)	164 (2)
O4*W*—H4*WA*···Cl3	0.835 (9)	2.295 (11)	3.1087 (19)	165 (2)
O5*W*—H5*WA*···Cl3^{v}	0.851 (10)	2.423 (12)	3.257 (2)	166 (2)
O5*W*—H5*WB*···Cl2	0.850 (10)	2.340 (10)	3.187 (2)	174 (2)
O6*W*—H6*WA*···O7*W*^{vi}	0.867 (10)	1.893 (11)	2.734 (3)	163 (2)
O6*W*—H6*WB*···Cl1^{vii}	0.847 (10)	2.319 (11)	3.147 (2)	166 (2)
O7*W*—H7*WA*···Cl3^{viii}	0.832 (10)	2.408 (10)	3.228 (2)	169 (2)
O7*W*—H7*WB*···O3*W*	0.824 (10)	1.941 (11)	2.743 (3)	164 (3)

Symmetry codes: (iv) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (vi) $-x + 2, -y + 1, -z + 1$; (vii) $-x + \frac{5}{2}, y + \frac{1}{2}, z$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

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H atoms bonded to C atoms were placed at calculated positions and refined using a riding model. The C—H distances were constrained to 0.99 Å and were refined with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). H atoms bonded to O or N were located in difference maps and assigned a common $U_{\rm iso}$(H) value of 0.05 Å^2; their coordinates were refined freely, except that DFIX restraints were applied to the O—H distances [0.84 (2) Å] and H—O—H angles [by restraining the H···H distances to 1.37 (1) Å] (Sheldrick, 2001).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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