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1,4,7-Triazacyclononane hemihydrate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
H-atom completeness 94%
R factor = 0.049
wR factor = 0.140
Data-to-parameter ratio = 12.2

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

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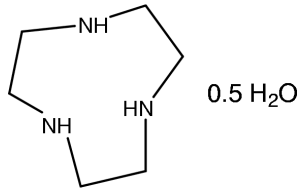
The title compound, $C_6H_{15}N_3\cdot0.5H_2O$, crystallizes in the high-symmetry trigonal space group $P\bar{3}c1$. This is, after more than 30 years of effort on this compound, the first reported structure of the free base of this macrocycle. Six N—H···O hydrogen bonds are formed between the water O atom occupying a special site at the origin and N atoms of six neighbouring 1,4,7-triazacyclononane molecules.

Comment

1,4,7-Triazacyclonone (tacn) and its derivatives form a very stable and diverse range of metal coordination compounds (Chaudhuri & Wieghardt, 1987; Daly & Martin, 2002) as a result of the propensity of tacn for facial coordination to metal ions. A survey of the Cambridge Structural Database (Version 5.25, update 3, July 2004; Allen, 2002) reveals around 1200 crystallographically characterized tacn compounds and complexes, the majority of these being metal coordination complexes. Although a recent publication (Warden *et al.*, 2004) describes some aspects of the interesting hydrogen-bonding and electrostatic interactions formed between protonated tacn molecules and anions, it is surprising that, after 30 or more years of intense study on this compound, the crystal structure of the free (uncoordinated, unprotonated) compound has not been determined. There are only a few crystallographically characterized examples of free base derivatives of uncoordinated tacn compounds (Clegg *et al.*, 1992; Blake *et al.*, 1994; Blake, Fallis, Gould *et al.*, 1996; Blake, Fallis, Heppeler *et al.*, 1996; Adam *et al.*, 1997; Pacchioni *et al.*, 2002), but the title compound, (I), is the first example of uncoordinated unprotonated tacn.



(I)

The compound crystallizes in the trigonal space group $P\bar{3}c1$, the asymmetric unit containing one-third of a tacn molecule and one-sixth of a water molecule. The tacn molecule contains the three N atoms oriented facially (Fig. 1), suitable for binding to metal ions. The water molecule occupies a special position at the origin. The H atoms on this molecule could not be located because of disorder. Six equivalent N—H···O hydrogen bonds are formed around the water molecule [N1—H1 = 1.00 (4) Å, N1···O1 = 3.0400 (13) Å and N1···O1 =

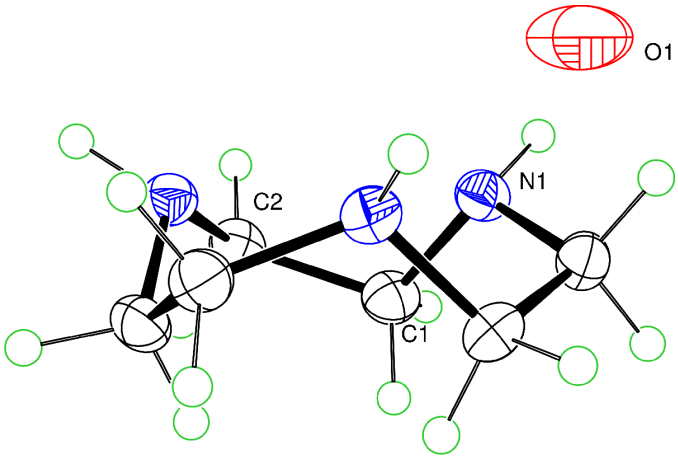


Figure 1
View of (I) (50% probability displacement ellipsoids).

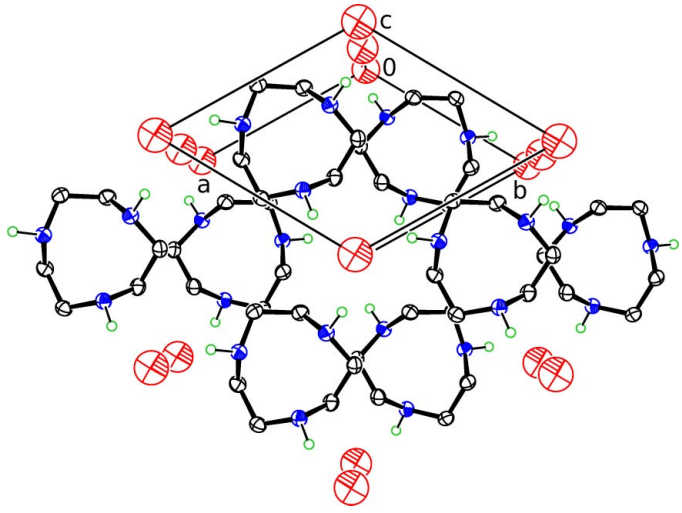


Figure 2
View of the packing in (I) (50% probability displacement ellipsoids). Carbon-bound H atoms have been omitted.

159 (9)°; symmetry codes for N1 and H1: (i) x, y, z; (ii) $-y, x-y, z$; (iii) $-x+y, -x, z$; (iv) $-x, -y, -z$; (v) $y, -x+y, -z$; (vi) $x-y, x, -z$.] The packing diagram (Fig. 2) shows the N—H···O hydrogen bonds and the alternating arrangement of hydrophobic and hydrophilic channels. The water molecules are located within the hydrophilic pockets.

Experimental

The compound was prepared using a modification (Johnson, 2004) of a published procedure (Richman & Atkins, 1974). Tritosyltacn (104.1 g, 0.17 mol) was added slowly to concentrated sulfuric acid (350 ml) and the mixture was heated at 373 K with stirring for 3 d. The reaction mixture was poured slowly into a cooled mixture of absolute ethanol (1 l) and diethyl ether (250 ml). The resulting white solid was filtered under a nitrogen blanket, washed with an 80:20 ethanol/diethyl ether mixture (300 ml) and diethyl ether (200 ml), and dried at 343 K *in vacuo*. The white solid was dissolved in the minimum amount of warm water and cooled to room temperature, at which point 48% HBr (100 ml) was added with stirring and the solution was left at 278 K overnight. The precipitate was filtered, washed with ethanol (200 ml) and diethyl ether (200 ml), and dried *in vacuo*. The solid was added to a rapidly stirred mixture of toluene (400 ml) and water (80 ml), and cooled in an ice bath. Sodium hydroxide (20 g) dissolved in water (60 ml) was added slowly to the rapidly stirred mixture, and the water was azeotropically removed using a Dean–Stark apparatus. The toluene fraction was then decanted through a cotton wool column and the volume was reduced under vacuum, affording 1,4,7-triazacyclonone in high purity as a colourless viscous oil (yield 15.6 g, 71%). MS: M^+ 129; ^{1}H NMR ($CDCl_3$, p.p.m.): 2.75 (12*H*), 2.05 (3NH, 0.5H_2O). Storage of this solid at 277 K afforded a crystalline solid, which melted at 318–323 K.

Crystal data

$C_6H_{15}N_3\cdot0.5H_2O$	Mo $K\alpha$ radiation
M_r = 138.22	Cell parameters from 7794 reflections
Trigonal, $P\bar{3}c1$	θ = 4.1–27.9°
a = 7.298 (1) Å	μ = 0.08 mm^{-1}
c = 16.560 (3) Å	T = 123 (2) K
V = 763.8 (2) Å^3	Block, colourless
Z = 4	0.87 × 0.25 × 0.25 mm
D_x = 1.202 Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.037
φ and ω scans	θ_{max} = 27.9°
Absorption correction: none	$h = -9 \rightarrow 9$
7794 measured reflections	$k = -9 \rightarrow 9$
610 independent reflections	$l = -21 \rightarrow 21$
523 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0781P)^2 + 0.2454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.049	
$wR(F^2)$ = 0.140	
S = 1.12	$(\Delta/\sigma)_{max} < 0.001$
610 reflections	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
50 parameters	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.4681 (18)	N1—C2^{vii}	1.4636 (19)
C1—C2	1.533 (2)		
N1—C1—C2	111.22 (11)	N1^{viii}—C2—C1	112.70 (11)
C2^{vii}—N1—C1	115.40 (11)		

Symmetry codes: (vii) $-y+1, x-y+1, z$; (viii) $-x+y, -x+1, z$.

H-atom parameters of the tacn molecule were refined. H atoms of the water molecule were not located.

Data collection: *COLLECT* (Hooft, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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