Monoprotonated [2.2.2]cryptand picrate monohydrate

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The title compound, 4,7,13,16,21,24-hexaoxa-1-azonia-10-aza-bicyclo[8.8.8]hexacosane picrate monohydrate, $C_{18}H_{37}N_2O_6{}^+ \cdot C_6H_2N_3O_7{}^- \cdot H_2O$, is a salt of [2.2.2]cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) with picric acid (2,4,6-trinitrophenol). The monoprotonated cryptand cation encapsulates a water molecule through N—H···O and O—H···O hydrogen bonds.

Comment

There has been growing interest in the studies of charge-transfer complexes between macrocyclic crown ethers and a variety of acceptor molecules such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Semnani & Shamsipur, 1993; Hasani & Shamsipur, 1997), tetracyanoethylene (Hasani & Shamsipur, 1997), *p*-chloranil (Andrews & Keefer, 1988), 2,4,6-trinitrotoluene (Jayathirtha & Krishnan, 1981), picric acid (Rady, 1992) and iodine (Hirsch *et al.*, 1993; Semnani & Shamsipur, 1995, 1996, 1997; Sadeghi *et al.*, 1997). The cavity formed by the cyclic disposition of donating atoms in the macrocyclic crown ethers provides a very exciting feature to study their molecular encapsulation properties (Izatt *et al.*, 1992). In this paper, we have isolated the title compound, (I), and determined its crystal structure.

(I)
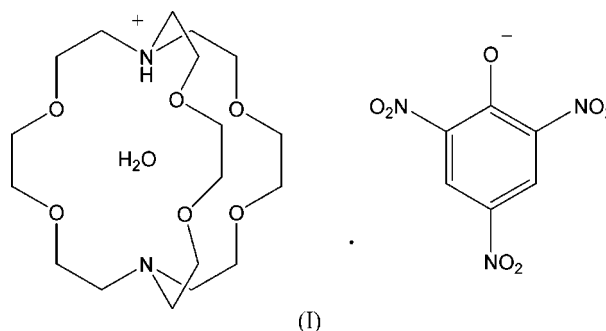
The asymmetric unit in (I) contains a monoprotonated [2.2.2]cryptand cation, a picrate anion and a water molecule (Fig. 1). The water molecule is encapsulated through N—H···O and O—H···O hydrogen bonds (Table 1), with the O atom (O14) deviating only 0.055 (2) Å from the mean plane formed by the C15/O11/O13/C21 atoms of the cryptand cation [mean deviation 0.0130 (15) Å]. The cation and anion are held together by C—H···O hydrogen bonds. The neighboring asymmetric units related by an inversion center are linked by bifurcated C—H···O hydrogen bonds (C7—H7A···O4ⁱ and C7—H7A···O5ⁱ; symmetry code i as in Table 1) and a π–π interaction between the benzene rings to form a dimeric unit;
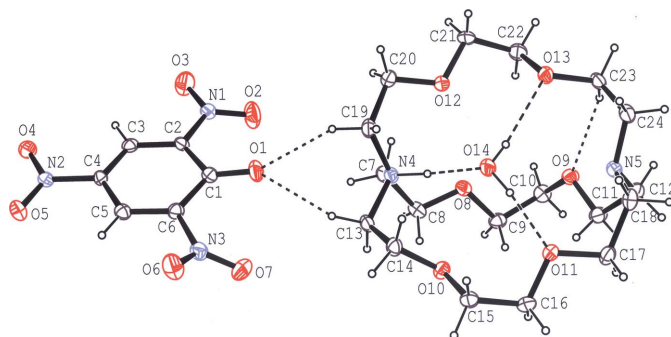
Figure 1
The asymmetric unit of (I), with the atomic labeling scheme. Displacement ellipsoids of non-H atoms are drawn at the 35% probability level. Hydrogen bonds are indicated by dashed lines.
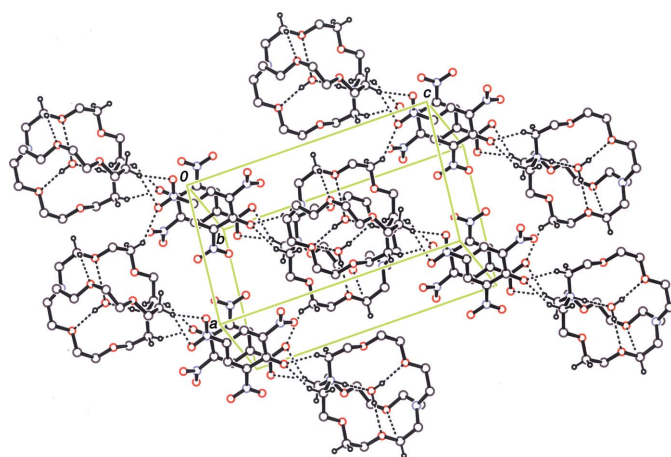

Figure 2
A packing diagram of (I), viewed approximately along the *b* axis. Hydrogen bonds are indicated by dashed lines. H atoms of the groups not involved in the hydrogen bonds have been omitted for clarity.

the centroid–centroid$(2 - x, 1 - y, 2 - z)$ and interplanar distances are 3.5560 (12) and 3.288 (2) Å, respectively (Fig. 2). These units are further connected by C—H···O hydrogen bonds to form a hydrogen-bonded network.

Experimental

To a solution of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (100 mg, 0.25 mmol) in CH_3OH (10 ml), a solution of picric acid (57.3 mg, 0.25 mmol) in $CHCl_3$ (10 ml) was added at room temperature. Light-orange crystals suitable for X-ray diffraction were obtained by slow evaporation of the mixed solution at room temperature.

Crystal data

$C_{18}H_{37}N_2O_6{}^+ \cdot C_6H_2N_3O_7{}^- \cdot H_2O$	$Z = 4$
$M_r = 623.61$	$D_x = 1.424$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.2633$ (3) Å	$\mu = 0.12$ mm^{-1}
$b = 19.2661$ (6) Å	$T = 150$ (2) K
$c = 16.3624$ (5) Å	Block, light orange
$\beta = 94.8805$ (11)°	$0.17 \times 0.16 \times 0.14$ mm
$V = 2909.57$ (16) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	27944 measured reflections
ω scans	6652 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	3809 reflections with $I > 2\sigma(I)$
$T_{min} = 0.855$, $T_{max} = 0.984$	$R_{int} = 0.067$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0486P)^2 + 0.9805P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.10$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
6652 reflections	$\Delta\rho_{min} = -0.36$ e Å^{-3}
401 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4N···O14	0.97 (3)	1.78 (3)	2.725 (2)	164 (2)
O14—H14C···O13	0.85 (3)	2.14 (3)	2.953 (2)	163 (3)
O14—H14D···O11	0.86 (3)	1.99 (3)	2.827 (2)	163 (3)
C7—H7A···O4^i	0.97	2.48	3.295 (3)	141
C7—H7A···O5^i	0.97	2.60	3.391 (3)	139
C13—H13A···O1	0.97	2.33	3.206 (3)	151
C19—H19A···O1	0.97	2.27	3.163 (3)	152
C19—H19B···O11^{ii}	0.97	2.42	3.350 (3)	160
C21—H21A···O4^{iii}	0.97	2.47	3.299 (3)	143
C23—H23A···O9	0.97	2.48	3.254 (3)	136

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

H atoms were located in a difference Fourier map and the H atom attached to the N atom was refined freely. The water H atoms were refined isotropically with a distance restraint of 0.85 (2) Å. Other H atoms were treated as riding, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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