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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1474). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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10H^+-2,3-Benzo-1,4-dioxa-7,10,13-triazacyclopentadec-2-ene-6,14-dione Picrate Hydrate (1/1/1)

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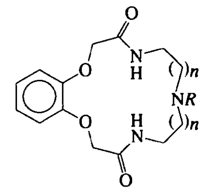
Abstract

The title compound, $C_{14}H_{20}N_3O_4^+.C_6H_2N_3O_7^-.H_2O$, contains a 15-membered macrocycle which has two ether O atoms, two pairs of amide N and O atoms, and an amine N atom as potential donor atoms. The macrocycle has undergone protonation at the amine N atom. The picrate ion interacts through its phenolic O atom with the NH_2 group *via* an N—H···O hydrogen bond. The water molecule is linked in an endocyclic manner to the macrocyclic ring through both the amide groups by an O···H—N hydrogen bond. The ether O atoms do not participate in any hydrogen-bonding interactions. The water molecule is also intermolecularly linked to one symmetry-related nitro group O atom of the picrate and to one amide O atom.

Comment

Host–guest chemistry is primarily based on the complementarity of the sites of the host with those of the guest. A small change in structure can alter this complementarity (Cram, 1986, 1988) and thus the binding properties of the host. In diamide–diether–amine macrocycles (1*a*)–(1*c*), the cavities possess three electron-rich centres (two O atoms and one NH amine atom) and two electron-deficient centres (two NH amide atoms). These macrocycles can therefore interact with electron-rich molecules such as water or alcohols through their amide N atoms and with cations through the ether O atoms and the amine. The previously reported extraction results (Kumar, Singh & Singh, 1992) show a much higher extraction of Pb^{2+} by (1*a*) and (1*b*) than is seen for (1*c*). The X-ray results show that in (1*c*), water enters the cavity, whereas in (1*b*), it remains in the lattice (Hundal, Hundal, Kumar, Singh & Sanz-Aparicio, 1995; Hundal *et al.*, 1996). Based on these results, we envisaged that the conversion of (1*a*) and (1*b*) into their ammonium salts would render the cavities more electron-deficient and would thus facilitate the encapsulation of small electron-rich molecules like water and simple alcohols.



(1*a*) $n = 1$; $R = H$
(1*b*) $n = 2$; $R = H$
(1*c*) $n = 2$; $R = CH_2CH_2CN$

We present here the results of a structure determination of (1*a*) picrate hydrate, where a water O atom forms hydrogen bonds with two amide NH units in the cavity of (1*a*) and water H atoms remain hydrogen bonded with amide O atoms and the *p*-nitro unit of picrate from two different neighbouring molecules. Extensive hydrogen bonding between the ammonium unit of the macrocycle and the picrate anion is also observed. All the bond distances and angles are as expected (Hundal *et al.*, 1996). The structure solution reveals that the picric acid loses its proton to form the picrate anion. The proton

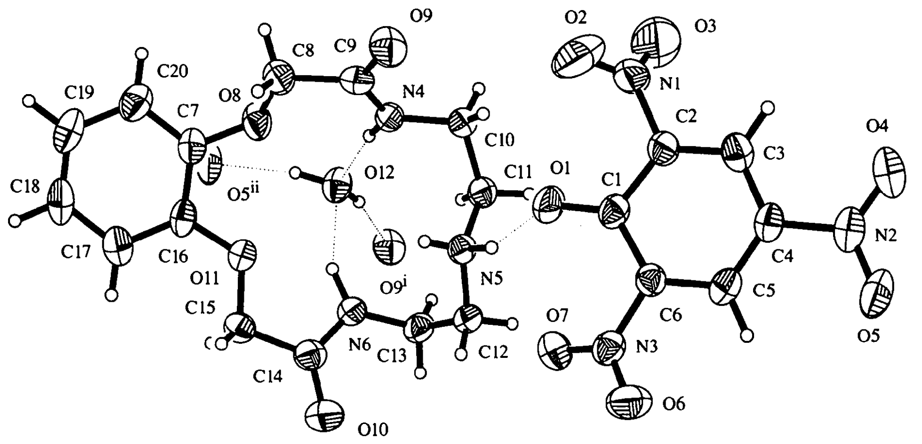


Fig. 1. A view of the title compound showing the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the H atoms have been assigned arbitrary radii.

is taken up by the amine group of the macrocyclic ring to form an ammonium group. The interaction between the macrocyclic ring and the picrate anion is through an N5—H52···O1 intramolecular hydrogen bond. Comparison with the structure of the free macrocycle (Hundal *et al.*, 1996) indicates that there are two water molecules in the free molecule; both are exocyclic and involved in extensive hydrogen bonding with the macrocycle. In the present complex, one water molecule has been replaced by the picrate anion. As a consequence of this change, the other water molecule moves into the centre of the macrocyclic cavity; it is involved in both the inter- and intramolecular hydrogen bonding. It behaves as a hydrogen-bond donor towards the amide O9 atom and the O5 atom of one of the nitro groups, forming two intermolecular hydrogen bonds, O12—H121···O9^{i} and O12—H122···O5^{ii} [symmetry codes: (i) $x+1$, y, z; (ii) $-x+1$, $-y$, $z-\frac{1}{2}$] (Table 2). O12 behaves as a hydrogen-bond acceptor forming two intermolecular hydrogen bonds, N4—H41···O12 and N6—H61···O12. In (1*a*), the torsion angles O8—C7—C16—O11, C8—O8—C7—C16 and C15—O11—C16—C7 are 2.3 (6), −123.0 (4) and 172.6 (4)°, respectively. The interaction with the picrate ion, the endocyclic water molecule and the conversion of amine to ammonium causes significant changes to the macrocyclic conformation. The free ligand (1*c*) has the two ether O atoms, the two pairs of amide NO atoms and the amine N atom in one plane. The conformation of the ring is an envelope with $-CH_2-CH_2-NH-CH_2-CH_2-$ forming the flap of the envelope and the segment $-CH_2-NH-CH_2-$ forming a 'V' on the flap. Comparison with the uncomplexed ligand indicates that there is a twist of about 50° (Allen & Rogers, 1969) about the C7—O8 bond. Similarly, there is a twist of about 100° about the C12—C13 bond. As a result of these conformational changes, the five donor atoms deviate significantly from a least-squares plane [deviations are 0.05 (1), −0.39 (1), 0.50 (1), −0.39 (1) and 0.22 (1) Å for O8, O11, N6, N5 and N4, respectively], indicating that the energy barriers between various conformations are very small.

Our attempts to isolate (1*a*) picric acid.*R*OH (*R* = Me, Et, Pr, Bu) complexes failed, the main reason being that the presence of one alkyl unit in place of a water H atom removes one hydrogen-bonding interaction and sterically disfavours the other intermolecular hydrogen-bond interaction.

Experimental

The macrocycle was synthesized according to a published method (Kumar, Singh & Singh, 1992). The title compound was prepared by direct reaction between picric acid and the macrocycle in an aqueous medium, with crystals forming immediately.

Crystal data

$C_{14}H_{20}N_3O_4^+.C_6H_2N_3O_7^-.H_2O$
$M_r = 540.45$
Orthorhombic
$Pna2_1$
$a = 7.4948\ (3)$ Å
$b = 11.5989\ (6)$ Å
$c = 27.147\ (3)$ Å
$V = 2359.9\ (3)$ Å^3
$Z = 4$
$D_x = 1.521$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 3$–$20°$
$\mu = 1.102$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.3 × 0.1 × 0.1 mm
Yellow

Data collection

Siefert diffractometer
$2\theta-\theta$ scans
Absorption correction: none
2056 measured reflections
2056 independent reflections
1869 reflections with $I > 2\sigma(I)$

$\theta_{max} = 60°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 31$
3 standard reflections every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0399$
$wR(F^2) = 0.1071$
$S = 1.089$
2056 reflections
344 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 1.11P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0048 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.1 (3), not reliably determined

Table 1. *Selected torsion angles (°)*

C8—O8—C7—C16	−123.0 (4)	O8—C7—C16—O11	2.3 (6)
C15—O11—C16—C7	172.6 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H41···O12	0.92	2.09	2.980 (4)	171
N6—H61···O12	0.96	2.02	2.896 (5)	150
N5—H51···O1	1.02	1.76	2.723 (5)	154
O12—H122···O9$^{\rm i}$	0.83	1.87	2.697 (4)	168
O12—H121···O5$^{\rm ii}$	0.96	2.01	2.961 (5)	170

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

The poor quality of the available crystals limited the resolution of the data and led in turn to a lower data/parameter ratio (6:1) than was hoped for. At convergence, the mean s.u. on a C—C bond was 0.006 Å. The amide, ammonium and water H atoms were located by difference Fourier synthesis, but were refined with restraints to maintain the geometry derived from the difference map. All other H atoms were placed geometrically. The hydrogen-bonding calculations were performed using *PARST* (Nardelli, 1983).

Data collection: *CRYSOM* (Siefert, 1996). Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *XRAY-80* (Stewart, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(1,3-Benzothiazol-2-yl)-2-(2-bromo-5-nitrophenyl)ethanone

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Abstract

The title compound, $C_{15}H_9BrN_2O_3S$, was isolated as an unexpected product from the reaction of the anion of sodium 2-(1,3-benzothiazolyl)ethanonitrile with α,2-dibromo-5-nitrotoluene. Its structure features a benzothiazole fragment and a bromo- and nitro-substituted phenyl ring linked by a methyl ketone group. The dihedral angle between the benzothiazole and phenyl rings is 103.7 (2)°. The benzothiazole fragment is planar, with a maximum deviation of 0.021 (2) Å. The nitro group is slightly rotated out of the phenyl-ring plane, with a O(2)—N(2)—C(14)—C(15) torsion angle of 16.4 (7)°.

Comment

As part of our continued interest in the synthesis of benzothiazolo[3,2-*a*]quinolinium salts (Cox *et al.*, 1982; Alegría *et al.*, 1993), we investigated the reaction of the anion of sodium 2-(1,3-benzothiazolyl)ethanonitrile with α,2-dibromo-5-nitrotoluene to give 2-(1,3-benzothiazolyl)-2-(2-bromo-5-nitrobenzyl)ethanonitrile. The title compound, (I), was unexpectedly obtained as a by-