Hexamethylenetetramine–4-nitro-catechol–water (1/2/1)

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In the title adduct, 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane–4-nitrobenzene-1,2-diol–water (1/2/1), $C_6H_{12}N_4 \cdot 2C_6H_5NO_4 \cdot H_2O$, the hexamethylenetetramine molecule acts as an acceptor of intermolecular O—H⋯N hydrogen-bonding interactions from the water molecule and the hydroxy groups of one of the two symmetry-independent 4-nitrocatechol molecules. The structure is built from molecular layers which are stabilized by three intermolecular O—H⋯O, two intermolecular O—H⋯N and four intermolecular C—H⋯O hydrogen bonds. The layers are further interconnected by one additional intermolecular O—H⋯N and two intermolecular C—H⋯O hydrogen bonds.

Comment

Interactions between phenols and amines play an important role in biological systems (Blow, 1976). Phenol–amine adducts are also widely used for the study of hydrogen bonding, since the two components are generally linked by intermolecular hydrogen bonds of the O—H⋯O, O—H⋯N or N—H⋯O types, and these adducts are among the most robust and versatile synthons in crystal engineering (Fan *et al.*, 1994; Desiraju, 1995). Following on from our interest in the hydrogen bonds mentioned above, we have recently investigated the crystal structures of the adducts of phenols or organic acids with several amines, such as bipyridine (Chantrapromma *et al.*, 2002a), N,N-dimethlylethylenediamine (Chantrapromma *et al.*, 2002c), piperazine (Usman *et al.*, 2002b), quinuclidine (Chantrapromma *et al.*, 2002d), diazabicyclo[2.2.2]octane (Chantrapromma *et al.*, 2002b) and hexamethylenetetramine (Usman *et al.*, 2001). In these adducts, we have found that the behaviour of the amines in the solid state, whether as a hydrogen-bond donor or as a hydrogen-bond acceptor, is related to this process, which strongly depends on

the acidity of the phenol or organic acid counterpart; the basicity of the amine does not play any significant role in the H-atom transfer process. In order to evaluate the H-atom transfer process and the hydrogen-bonding properties of phenol–amine adducts in the solid state, we have now focused on the adduct of hexamethylenetetramine (HMT), a strong base, with 4-nitrocatechol, which is a relatively weak acid. The crystal structure of HMT–4-nitrocatechol–water (1/2/1), (I), determined at 213 K, is reported.

(I)
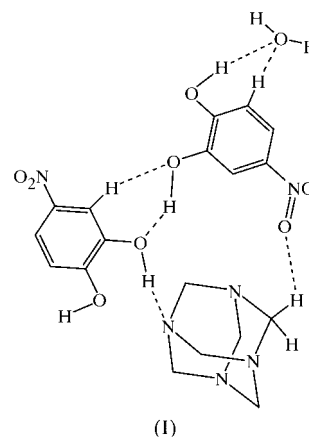
The asymmetric unit of (I) contains one HMT molecule, two independent 4-nitrocatechol molecules and one water molecule. As expected, the H-atom transfer process was not observed, because 4-nitrocatechol is a relatively weak acid, even though HMT is a strong base. All bond lengths and angles (Table 1) have normal values (Allen *et al.*, 1987). The geometric parameters for the HMT molecule are comparable with those of uncomplexed HMT obtained from neutron diffraction at 130 K (Kampermann *et al.*, 1994), and with those of HMT in the adducts HMT–1,1,1-tris(hydroxyphenyl)ethane (Coupar *et al.*, 1997) and HMT–4-hydroxy-3-methoxybenzaldehyde (Usman *et al.*, 2002a). Along with the unambiguous location and refinement of all H atoms in the structure, the present determination shows the HMT molecule to be unprotonated.

The bond lengths and angles within the two symmetry-independent 4-nitrocatechol molecules are comparable and both molecules are nearly planar. The planes of the nitro groups are slightly twisted about the C—N bonds, so that the O3/O4/N5/C10 and O7/O8/N6/C16 planes make angles of 2.40 (8) and 1.90 (8)° with their respective aromatic ring planes.

Within the asymmetric unit (Fig. 1), the two symmetry-independent 4-nitrocatechol molecules are interconnected by intermolecular C9—H9⋯O6 and O6—H1O6⋯O2 hydrogen bonds (Table 2), and then linked to the water molecule via O5—H1O5⋯O1W and C18—H18⋯O1W hydrogen-bonding interactions and to the HMT molecule via O2—H1O2⋯N1 and C4—H4B⋯O7 hydrogen bonds. In the crystal packing, these hydrogen-bonding interactions, together with O1W—H1W1⋯O3^i, C12—H12⋯O8^{vi} and O1—H1O1⋯N4^{iii} hydrogen bonds [symmetry codes: (i) $1-x, -y, -1-z$; (iii)
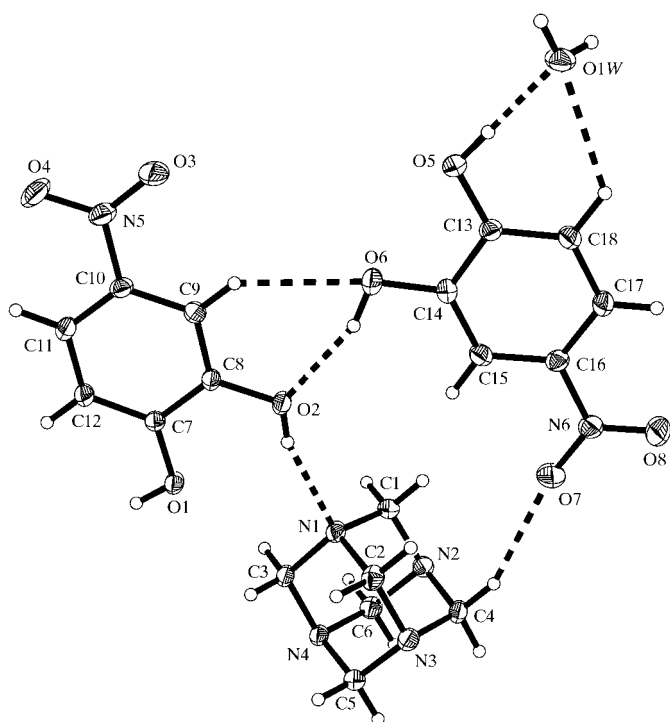
organic compounds

Figure 1
The structure of the title adduct, showing 50% probability displacement ellipsoids and the atom-numbering scheme. The dashed lines denote the hydrogen-bonding interactions within the asymmetric unit.

$2 - x$, $-y$, $1 - z$; (vi) $1 + x$, $y - 1$, z], generate molecular layers which lie perpendicular to the ab plane (Fig. 2). One molecular layer contains six different hydrogen-bonded ring patterns (Bernstein *et al.*, 1995), namely those linking the water molecule to a single 4-nitrocatechol molecule [$R_2^1(6)$], the two symmetry-independent 4-nitrocatechol molecules [$R_2^2(6)$], the two symmetry-independent 4-nitrocatechol mol-
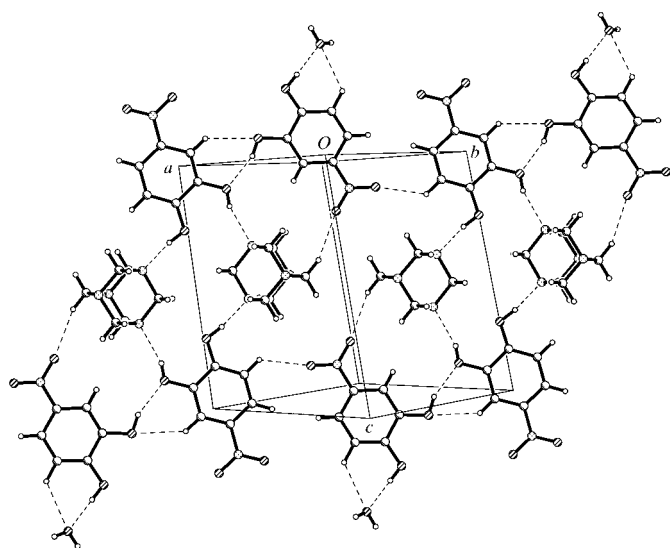

Figure 2
Packing diagram of the title adduct, viewed down the b axis, showing the molecular layer. The dashed lines denote the hydrogen-bonding interactions.

ecules to a HMT molecule [$R_3^3(14)$], two symmetry-related 4-nitrocatechol molecules to two symmetry-related HMT molecules [$R_4^4(18)$], four symmetry-related 4-nitrocatechol molecules to two symmetry-related HMT molecules [$R_6^6(26)$], and two symmetry-related water molecules to two symmetry-related 4-nitrocatechol molecules [$R_4^4(28)$]. The molecular layers are stacked, one above the other, along the b direction and are interconnected by an O1W—H2W1$\cdots$N2^{ii} hydrogen bond [symmetry code: (ii) $1 - x$, $1 - y$, $-z$] between the water molecule and a HMT molecule. The HMT molecule also interacts with two 4-nitrocatechol molecules in two adjacent molecular layers *via* C1—H1$B\cdots$O4^{iv} and C2—H2$A\cdots$O5^v interactions [symmetry codes: (iv) $2 - x$, $-y$, $-z$; (v) $1 - x$, $-y$, $-z$].

Experimental

The title adduct was prepared by thoroughly mixing HMT (1.4 g, 10 mmol) and 4-nitrocatechol (3.10 g, 20 mmol). The mixture was then dissolved in acetone (50 ml) with the addition of water (2 ml). The resulting mixture was warmed until all the solid had dissolved. The solution was then filtered and the filtrate left to evaporate slowly in air. Yellow single crystals suitable for X-ray diffraction analysis were obtained after a few days (m.p. 418 K).

Crystal data

$C_6H_{12}N_4\cdot 2C_6H_5NO_4\cdot H_2O$	$Z = 2$
$M_r = 468.43$	$D_x = 1.536$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.3520 (5)$ Å	Cell parameters from 4255
$b = 9.7671 (5)$ Å	reflections
$c = 11.8264 (6)$ Å	$\theta = 2.5–28.3°$
$\alpha = 99.489 (1)°$	$\mu = 0.13$ mm^{-1}
$\beta = 107.504 (1)°$	$T = 213 (2)$ K
$\gamma = 91.441 (1)°$	Slab, yellow
$V = 1012.9 (1)$ Å^3	$0.36 \times 0.20 \times 0.12$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	4761 independent reflections
	4136 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.011$
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.3°$
$T_{min} = 0.956$, $T_{max} = 0.985$	$h = -12 \rightarrow 5$
6443 measured reflections	$k = -13 \rightarrow 12$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.3743P]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
4761 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
394 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected interatomic distances (Å).

N1—C3	1.4748 (15)	N3—C4	1.4648 (17)
N1—C1	1.4768 (17)	N3—C5	1.4650 (16)
N1—C2	1.4873 (17)	N3—C2	1.4715 (17)
N2—C6	1.4739 (16)	N4—C6	1.4820 (18)
N2—C1	1.4768 (16)	N4—C3	1.4837 (16)
N2—C4	1.4889 (18)	N4—C5	1.4908 (17)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1W1\cdots O3^i$	0.83 (2)	2.11 (2)	2.940 (2)	178 (2)
$O1W-H2W1\cdots N2^{ii}$	0.83 (3)	2.02 (3)	2.840 (2)	172 (2)
$O1-H1O1\cdots N4^{iii}$	0.90 (2)	1.80 (2)	2.684 (2)	171 (2)
$O2-H1O2\cdots N1$	0.82 (2)	2.09 (2)	2.877 (2)	161 (2)
$O5-H1O5\cdots O1W$	0.85 (2)	1.81 (2)	2.654 (2)	177 (2)
$O6-H1O6\cdots O2$	0.90 (2)	1.99 (2)	2.847 (2)	160 (2)
$C1-H1B\cdots O4^{iv}$	0.96 (2)	2.58 (2)	3.417 (2)	146 (2)
$C2-H2A\cdots O5^v$	0.98 (2)	2.47 (2)	3.433 (2)	166 (2)
$C4-H4B\cdots O7$	0.97 (2)	2.45 (2)	3.370 (2)	158 (2)
$C9-H9\cdots O6$	0.95 (2)	2.49 (2)	3.244 (2)	136 (2)
$C12-H12\cdots O8^{vi}$	0.98 (2)	2.47 (2)	3.158 (2)	127 (2)
$C18-H18\cdots O1W$	1.06 (1)	2.50 (2)	3.235 (2)	126 (1)

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

All H atoms were refined; C—H distances were in the range 0.929 (18)–1.060 (13) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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