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A 1:1 adduct of hexamethylenetetramine and 4-hydroxy-3-methoxybenzaldehyde

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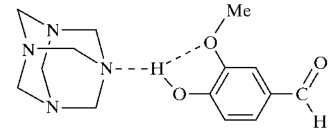
In the title complex, $C_6H_{12}N_4{\cdot}C_8H_8O_3$, the hexamethylenetetramine molecule accepts a single intermolecular O—H···N hydrogen bond from the hydroxy group of the 4-hydroxy-3-methoxybenzaldehyde moiety. The non-centrosymmetric crystal structure is built from alternating molecular sheets of 4-hydroxy-3-methoxybenzaldehyde and hexamethylenetetramine molecules, and is stabilized by intermolecular O—H···N, C—H···O and C—H···π interactions.

Comment

Phenols usually crystallize with hexamethylenetetramine (HMT) to form O—H···N hydrogen-bonded adducts, in which HMT acts as a mono-, bis- or tris-acceptor of hydrogen bonds (Jordan & Mak, 1970; Mak *et al.*, 1977, 1978; Mahmoud & Wallwork, 1979; Coupar, Ferguson *et al.*, 1997; Coupar, Glidewell & Ferguson, 1997). In only a few examples has HMT been found to act as an N—H···O hydrogen-bond donor, *i.e.* in the adducts of HMT with 2,4-dinitrophenol–water and with 2,4,6-trinitrophenol; in these, the nitrophenol molecules transfer the hydroxy H atom to the HMT moiety, thus forming an ion pair (Usman *et al.*, 2001, 2002). This unusual behaviour of HMT in the solid state is due to these two nitrophenols being stronger acids compared with the other substituted phenols investigated. In order to confirm this behaviour of HMT in the solid state, we have selected a very weak acid, namely 4-hydroxy-3-methoxybenzaldehyde (HMBA), to co-crystallize with HMT.

As expected, the H-atom transfer process was not observed in the title adduct, (I). The bond lengths and angles in (I) have normal values (Allen *et al.*, 1987). The average values of the N—C bond lengths, and of the C—N—C and N—C—N bond angles in the HMT moiety are 1.470 (4) Å, 107.9 (2)° and 112.5 (2)°, respectively, and are comparable with those of uncomplexed HMT obtained by neutron diffraction at 130 K [average C—N 1.469 (2) Å, N—C—N 107.88 (9)° and C—N—C 112.58 (8)°; Kampermann *et al.*, 1994] or with those of HMT in the adduct with 1,1,1-tris(hydroxyphenyl)ethane [average C—N 1.467 (5) Å; Coupar, Ferguson *et al.*, 1997]. The bond lengths and angles within the HMBA moiety agree with those of free HMBA (Velavan *et al.*, 1995), with the maximum difference being a deviation of 0.015 Å in the length of the C13—O2 bond.



(I)

In the title adduct, the HMBA molecule is nearly planar, with the O2 atom of the carboxylic acid group deviating by 0.145 (3) Å from the plane of the HMBA ring. The four six-

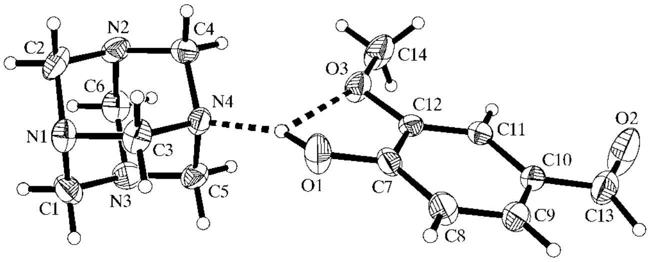


Figure 1
The structure of the title adduct showing 50% probability displacement ellipsoids and the atom-numbering scheme.

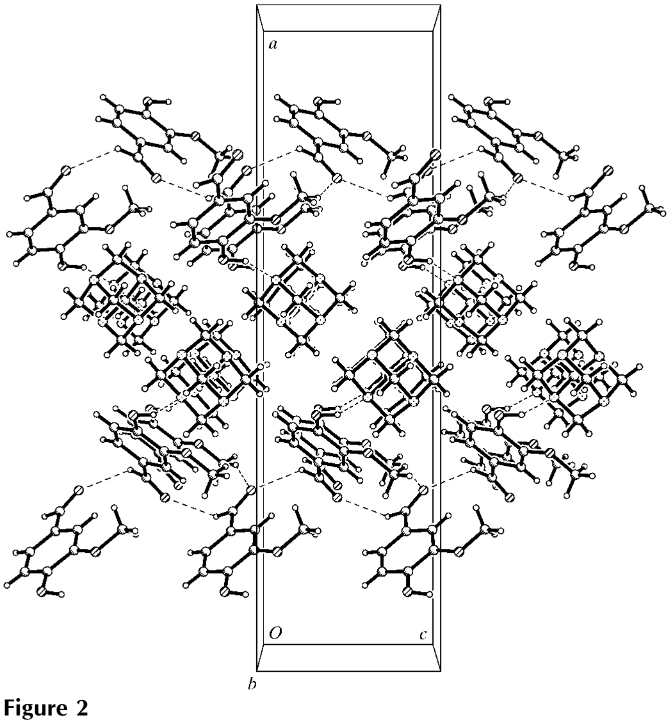


Figure 2
Packing diagram of the title adduct viewed down the *b* axis. The dashed lines denote the intermolecular hydrogen-bonding interactions.

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membered N—C—N—C—N—C rings of the HMT moiety adopt chair conformations, whose puckering parameters (Cremer & Pople, 1975) are listed in Table 3, and the absolute value of the mean deviation of all atoms from their mean-ring planes is 0.236 (3) Å.

In the title adduct, the two components are connected by an intermolecular O1—H1···N4 hydrogen bond, with the HMT moiety acting as a mono-acceptor and the HMBA molecule acting as a mono-donor in the conventional intermolecular hydrogen bond between the hydroxy group of the HMBA molecule and one of the amine N atoms of the HMT moiety, as was also observed in the HMT–phenol adducts studied previously (Wallwork, 1962; Mahmoud & Wallwork, 1979; Coupar, Ferguson *et al.*, 1997; Coupar, Glidewell & Ferguson, 1997). The N···O distance in the title adduct is slightly shorter than the average value (2.78 Å) found for O—H···N hydrogen bonds in other HMT–phenol adducts (Wallwork, 1962; Mahmoud & Wallwork, 1979; Coupar, Ferguson *et al.*, 1997; Coupar, Glidewell & Ferguson, 1997). Atom O1 actually facilitates a bifurcated hydrogen-bonding system, as it is also involved in an intramolecular O1—H1···O3 interaction which forms a closed five-membered H1—O1—C7—C12—O3 ring.

In the crystal structure of the title adduct, there are two intermolecular C—H···O interactions which link the HMBA moieties into molecular sheets that extend in the *b* and *c* directions. The HMT molecules are linked by O—H···N hydrogen-bonding interactions to these molecular sheets of HMBA and are alternately stacked along the *a* axis. Fig. 2 shows the packing diagram of the title adduct viewed down the *b* axis, and indicates the intermolecular interactions. Three intermolecular C—H···π interactions involving the centroid of the aromatic ring of the HMBA were also observed. All these interactions (see Table 2) stabilize the non-centrosymmetric packing in the title adduct.

Experimental

Hexamethylenetetramine (1.40 g, 10 mmol) and 4-hydroxy-3-methoxybenzaldehyde (1.52 g, 10 mmol) were thoroughly mixed and then dissolved in ethanol (50 ml) with the addition of a few drops of water. The resulting mixture was warmed until a clear solution was obtained. The solution was filtered and left to evaporate slowly in air. Yellow single crystals suitable for X-ray data collection were obtained from this solution after a few days (m.p. 352 K).

Crystal data

$C_6H_{12}N_4{\cdot}C_8H_8O_3$
$M_r = 292.34$
Orthorhombic, $Pca2_1$
$a = 27.1214$ (3) Å
$b = 7.1327$ (1) Å
$c = 7.4776$ (1) Å
$V = 1446.53$ (3) Å^3
$Z = 4$
$D_x = 1.342$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4976 reflections
$\theta = 2.9$–28.3°
$\mu = 0.10$ mm^{-1}
$T = 183$ (2) K
Block, colorless
0.32 × 0.24 × 0.12 mm

Table 1
Selected interatomic distances (Å).

O1—C7	1.349 (3)	O3—C12	1.372 (3)
O2—C13	1.218 (4)	O3—C14	1.426 (3)

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

Cg is the centroid of ring C7–C12.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3	1.01 (6)	2.30 (5)	2.703 (3)	102 (3)
O1—H1···N4	1.01 (6)	1.72 (5)	2.671 (3)	156 (4)
C13—H13···O2^{i}	1.05 (3)	2.40 (3)	3.019 (5)	117 (2)
C14—H14*A*···O2^{ii}	0.96	2.44	3.309 (4)	151
C3—H3B···*Cg*^{iii}	0.96	3.26	4.147 (3)	153
C14—H14C···*Cg*^{iv}	0.96	2.97	3.713 (3)	135

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

Table 3
Puckering parameters of the six-membered N—C—N—C—N—C ring of HMT.

Ring†	Q_2 (Å)	Q_3 (Å)	Q_T (Å)	θ (°)
A	0.007 (3)	0.578 (3)	0.578 (3)	0.0 (3)
B	0.008 (3)	−0.579 (3)	0.579 (3)	180.0 (3)
C	0.004 (3)	−0.577 (3)	0.577 (3)	178.3 (3)
D	0.007 (3)	0.577 (3)	0.577 (3)	0.0 (3)

† Rings *A*, *B*, *C* and *D* are defined by atoms N1/C1/N3/C5/N4/C3, N1/C1/N3/C6/N2/C2, N1/C2/N2/C4/N4/C3 and N2/C4/N4/C5/N3/C6, respectively.

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.970$, $T_{\max} = 0.989$
8042 measured reflections
1870 independent reflections
1441 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.077$
$\theta_{\max} = 28.3°$
$h = -35 \rightarrow 33$
$k = -7 \rightarrow 9$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.113$
$S = 0.94$
1870 reflections
200 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.030 (4)

The H atoms attached to atoms O1 and C13, which are involved in hydrogen bonds, were located in a difference Fourier map and were refined isotropically. After checking their presence in the difference map, the positions of all remaining H atoms were geometrically idealized and allowed to ride on their parent C atoms, with C—H distances in the range 0.93–0.97 Å. Due to the absence of any significant anomalous scatterers, the 1661 Friedel equivalents were merged before the final refinements. The choice of absolute structure was arbitrary.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1127). Services for accessing these data are described at the back of the journal.

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