Tris(1H-benzimidazol-2-ylmethyl)-amine–solvent adducts

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The tris(1H-benzimidazol-2-ylmethyl)amine (ntb) molecule crystallizes in different solvent systems, resulting in two kinds of adduct, namely the monohydrate, $C_{24}H_{21}N_7 \cdot H_2O$ or ntb·H_2O, (I), and the acetonitrile–methanol–water (1/0.5/1.5) solvate, $C_{24}H_{21}N_7 \cdot C_2H_3N \cdot 0.5CH_4O \cdot 1.5H_2O$ or ntb·$1.5H_2O$·0.5MeOH·MeCN, (II). In both cases, ntb adopts a tripodal mode to form hydrogen bonds with a solvent water molecule via two N—H···O and one O—H···N hydrogen bond. In (I), the ntb·H_2O adduct is further assembled into a two-dimensional network by N—H···N and O—H···N hydrogen bonds, while in (II), a double-stranded one-dimensional chain structure is assembled via N—H···O and O—H···O hydrogen bonds, with the acetonitrile molecules located inside the cavities of the chain structure.

Comment

The tripodal compound tris(2-benzimidazolylmethyl)amine (ntb) is a versatile ligand which possesses three imine N atoms and three amine NH groups. The three imine N atoms can act as coordination donors to form various metal complexes (Moon et al., 2002; Su, Kang, Mu et al., 1998), while the three amine NH groups are potential hydrogen-bond donors (Su, Kang, Liu et al., 1998; Su et al., 2000). Since the three benzimidazolyl (Bim) arms can rotate freely about the methylene (–CH2–) groups and the three imine N atoms can also behave as hydrogen-bond acceptors, ntb is a good candidate for formation of hydrogen-bonded adducts via specific steric intermolecular recognition. We have been interested in the assembly of supramolecular aggregates with ntb-related compounds and report here two kinds of ntb·solvent adducts formed via multiple hydrogen bonds. The adduct ntb·H_2O, (I), has been reported previously (Zhou et al., 1999), but the structure was not fully determined or refined as no allowance was made for any of the H atoms in the structure. We have

redetermined the structure and located all the H atoms. The crystal structural analyses of the adducts (I) and ntb·MeCN·0.5MeOH·1.5H_2O, (II), revealed that the recognition of water molecules by ntb is specific in both adducts, but the extension of the hydrogen bonds is different, depending on the inclusion of different solvent molecules.

ntb

(I) ntb·H_2O

(II) ntb·MeCN·0.5MeOH·1.5H_2O
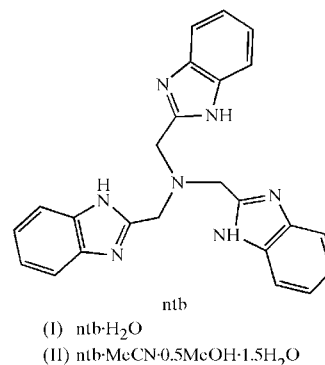
Our structure determination of (I) shows that all imine and amine groups of the ntb molecules and the water molecules are involved in hydrogen-bond formation (Table 1). The ntb molecule adopts a tripodal mode, with two NH groups and one imine N atom directed towards the water molecule, which is held by forming two D···A-type N—H···O and one A···D-type N···H—O hydrogen bond, as shown in Fig. 1. Such a hydrogen-bonding environment is specific for recognition of the water molecule because of its tetrahedral hydrogen-bonding geometry. The remaining H atom of the water molecule forms an O—H···N hydrogen bond with one 'outside' imine N atom belonging to a neighbouring ntb molecule. In addition, one more imine N atom and one NH group of a neighbouring ntb molecule form N—H···N hydrogen bonds, resulting in a two-dimensional network parallel to (10$\bar{1}$), as depicted in Fig. 2.

Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

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Figure 2
A view of the hydrogen-bonded two-dimensional network in (I) in the (10$\bar{1}$) plane. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (iii) $-x + 1$, $-y$, $-z + 1$; (iv) $-x + 1$, $-y + 1$, $-z + 1$.]
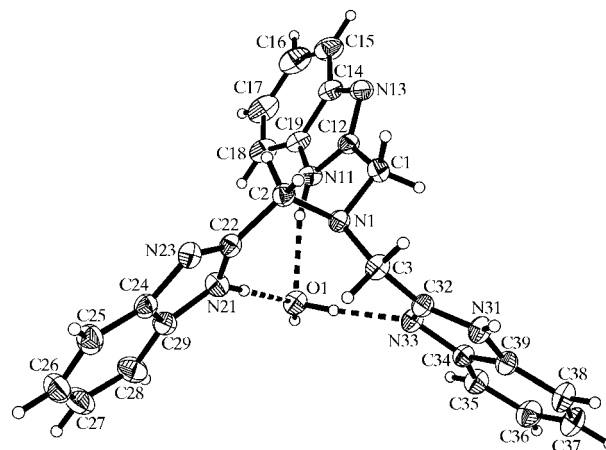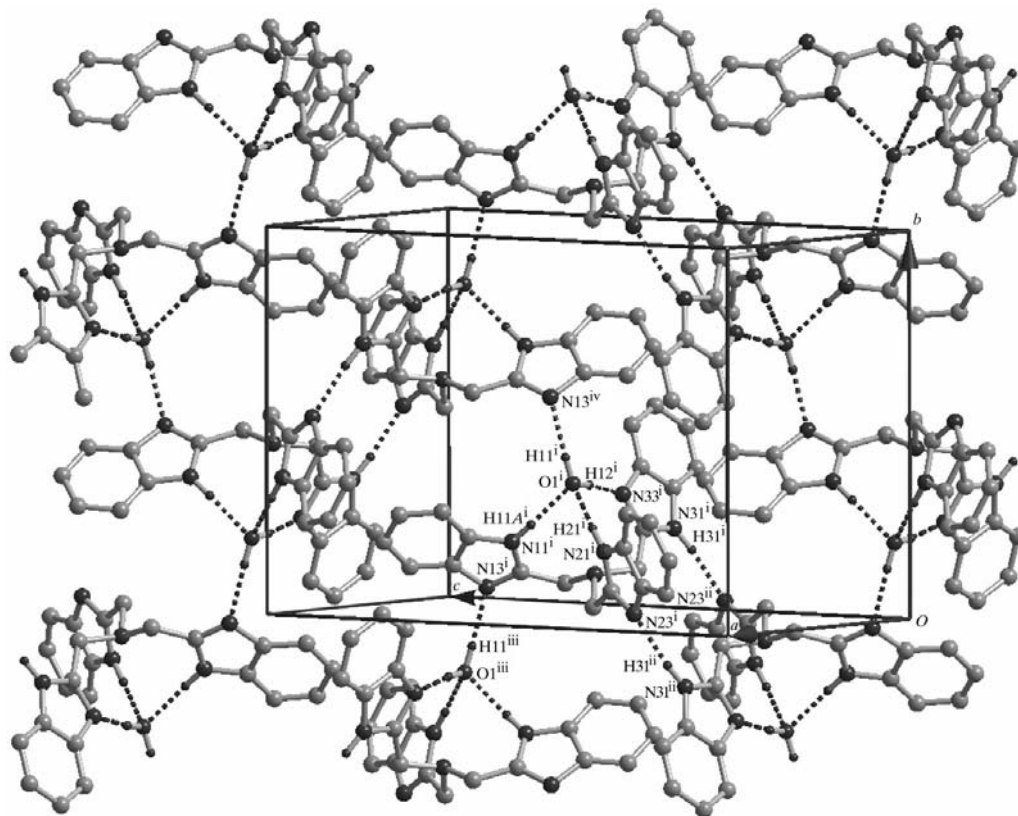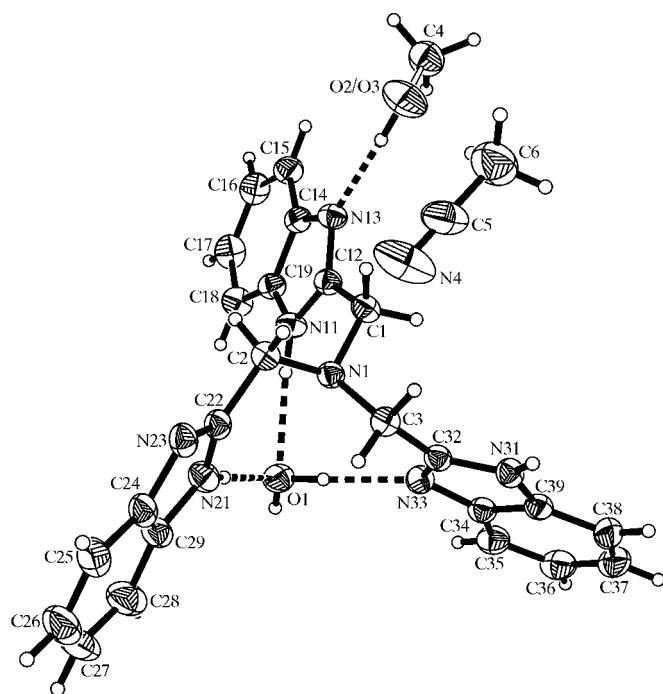

Figure 3
A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. Atoms O2 and O3 were constrained to share the same site.

When ntb crystallized in a hydrated MeOH/MeCN solution, adduct (II) was obtained. In this compound, all imine and amine groups of the ntb molecules are involved in hydrogen bonding (Table 2). Our structure determination shows that the water molecule is recognized by ntb in exactly the same way as in (I) (details are given in Table 2). As in (I), there are two $D \cdots A$-type N—H$\cdots$O and one $A \cdots D$-type N$\cdots$H—O hydrogen bond, as shown in Fig. 3. The ntb molecule takes on the same tripodal conformation in both (I) and (II), with one imine N atom and two NH groups pointing 'inside', and leaving two imine N atoms and one NH group directed 'outside' of the ntb·H$_2$O moiety.

The analysis of (II) was slightly complicated by disorder. The methanol molecule (O3/C4 in Fig. 3) lies adjacent to an inversion centre, with the methyl C atom at such a short intermolecular distance [2.298 (7) Å from C4 at $(2 - x, -y, -z)$] that it can be present with an occupancy of no more than 0.5. Occupancy refinement showed unequivocally that while methanol atom C4 is only present with 0.5 occupancy, the O-atom site has unit occupancy, implying that this site (labelled as O2 and O3 in Fig. 3) must contain a 0.5-occupancy water molecule (O2) as well as the 0.5-occupancy methanol atom O3.

One of the two outside imine N atom forms an N$\cdots$H—O hydrogen bond with the 0.5-occupancy methanol/water site (Fig. 3). Water molecule O1 forms its fourth O—H$\cdots$O
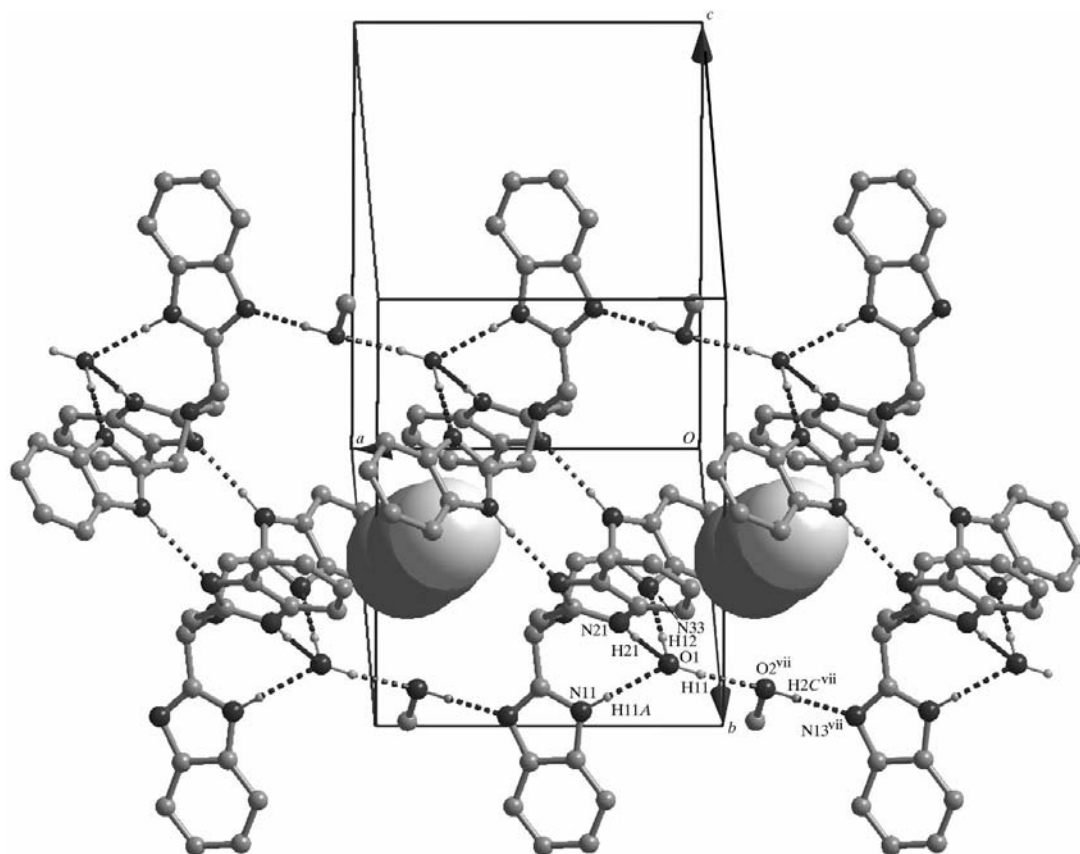
Figure 4
The hydrogen-bonded chain structure in (II), viewed along the *a* axis. Dashed lines indicate hydrogen bonds and guest acetonitrile molecules are shown in space-filling mode. [Symmetry code: (vii) $x - 1, y, z$.]

hydrogen bond with a neighbouring 0.5-occupancy methanol/ water site, thus generating a one-dimensional ntb··H$_2$O···MeOH/H$_2$O···ntb·H$_2$O···MeOH/H$_2$O chain, as depicted in Fig. 4. Since there remains one outside imine N atom and one outside NH group for each ntb molecule, two such one-dimensional chains are connected by the formation of N—H···N hydrogen bonds, resulting in a double-stranded chain along the *a* axis (Fig. 4). The acetonitrile molecules are located inside the cavities of such double-stranded chains, with only van der Waals contacts to the hydrogen-bonded chains.

The difference between (I) and (II) is that there is in (II) an additional site, equally occupied by methanol and water O = atoms, which disrupts the direct hydrogen bonding of the 'enclosed' water molecule to a neighbouring ntb molecule as in (I).

Experimental

Ntb was prepared from the condensation reaction between nitrilo-triacetate and 1,2-diaminobenzene in diethylene glycol (yield 85%). Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation from a 98% methanol solution at room temperature. Single crystals of (II) were obtained by slow evaporation from a 98% methanol/acetonitrile solution at room temperature.

Compound (I)

Crystal data

C$_{24}$H$_{21}$N$_7$·H$_2$O	$D_x = 1.261$ Mg m^{-3}
$M_r = 425.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 7855
$a = 9.9731$ (6) Å	reflections
$b = 12.3273$ (7) Å	$\theta = 4.2–26.3°$
$c = 18.2323$ (11) Å	$\mu = 0.08$ mm^{-1}
$\beta = 91.508$ (1)°	$T = 293$ (2) K
$V = 2240.7$ (2) Å^3	Block, colourless
$Z = 4$	$0.28 \times 0.2 \times 0.18$ mm

Data collection

Bruker SMART 1K CCD	6455 independent reflections
diffractometer	4526 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan	$\theta_{max} = 30.0°$
(*SADABS*; Sheldrick, 1996)	$h = -12 \rightarrow 14$
$T_{min} = 0.873$, $T_{max} = 1.000$	$k = -16 \rightarrow 17$
15554 measured reflections	$l = -24 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.115$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
6455 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}
310 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of	Extinction coefficient: 0.0042 (11)
independent and constrained	
refinement	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H11$A\cdots$O1	0.913 (14)	1.938 (14)	2.8380 (12)	168.2 (12)
N21—H21$\cdots$O1	0.973 (15)	1.886 (15)	2.8579 (12)	177.3 (13)
N31—H31$\cdots$N23^{v}	0.906 (13)	1.943 (13)	2.8406 (12)	170.4 (11)
O1—H11$\cdots$N13^{vi}	0.856 (15)	2.000 (16)	2.8410 (12)	167.0 (13)
O1—H12$\cdots$N33	0.924 (17)	1.903 (17)	2.8223 (12)	173.4 (13)

Symmetry codes: (v) $-x + 1, -y + 1, -z$; (vi) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Compound (II)

Crystal data

$C_{24}H_{21}N_7 \cdot C_2H_3N \cdot 0.5CH_4O \cdot 1.5H_2O$
$M_r = 491.58$
Triclinic, $P\bar{1}$
$a = 9.778$ (4) Å
$b = 9.995$ (2) Å
$c = 14.397$ (6) Å
$\alpha = 103.34$ (1)°
$\beta = 98.16$ (1)°
$\gamma = 102.34$ (1)°
$V = 1310.1$ (8) Å^3

$Z = 2$
$D_x = 1.246$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28
  reflections
$\theta = 4.6$–$12.6°$
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Block, colourless
$0.75 \times 0.65 \times 0.50$ mm

Data collection

Siemens $P4$ diffractometer
ω–2θ scans
Absorption correction: ψ scan
  (North et $al.$, 1968)
  $T_{min} = 0.885$, $T_{max} = 0.938$
5999 measured reflections
5066 independent reflections
3752 reflections with $I > 2\sigma(I)$

$R_{int} = 0.047$
$\theta_{max} = 26.0°$
$h = -1 \rightarrow 12$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections
  every 197 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.113$
$S = 1.01$
5066 reflections
358 parameters
H atoms treated by a mixture of
  independent and constrained
  refinement

$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2$
  $+ 0.303P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction: $SHELXL97$
Extinction coefficient: 0.106 (6)

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H11$A\cdots$O1	0.90 (2)	2.01 (2)	2.910 (2)	177 (2)
N21—H21$\cdots$O1	0.86 (2)	2.03 (2)	2.886 (2)	174.0 (18)
N31—H31$\cdots$N23^{iii}	0.91 (2)	1.91 (2)	2.826 (2)	176.3 (17)
O1—H11$\cdots$O2^{vii}/O3^{vii}	0.91 (2)	1.91 (3)	2.806 (2)	168 (2)
O1—H12$\cdots$N33	0.90 (2)	1.90 (2)	2.798 (2)	179 (2)
O2—H2$\cdots$N13	0.95 (3)	1.82 (3)	2.772 (2)	176 (3)

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

All H atoms, except those on O and N atoms involved in hydrogen-bond formation, were included as riding atoms, with C—H distances

of 0.93–0.97 Å and U_{iso}(H) values set at 1.5 (methyl H atoms) and 1.2 (other H atoms) times U_{eq}(C). The O- and N-bound H atoms were located in difference Fourier maps and refined with isotropic displacement parameters [for the OH group in (II), U_{iso}(H) = $1.5U_{eq}$(O)]. In (II) (as noted in the *Comment*), the methanol O atom was found to share a site with a water O atom. The site-occupancy refinement of the methyl C atom indicated an occupancy of 0.5, while that of the O atom was close to unity. The water (O2) and methanol (O3) O atoms were then assigned occupancies of 0.5 and constrained to lie at the same site. Only one H atom could be located at the O2/O3 site, and this was assigned unit occupancy. The missing 0.5-occupancy water H atom is presumably disordered. Difference maps showed that the H atoms of the methanol and acetonitrile methyl groups in (II) are diffuse, and these were allowed for as six H-atom sites with appropriate occupancy.

For (I), data collection: *SMART* (Siemens, 1993); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*. For (II), data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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