

4-(1*H*-Tetrazol-5-yl)benzoic acid monohydrate

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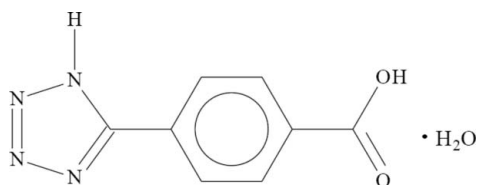
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.038; wR factor = 0.095; data-to-parameter ratio = 10.6.

The asymmetric unit of the title compound, $\text{C}_8\text{H}_6\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$, consists of one 4-(1*H*-tetrazol-5-yl)benzoic acid molecule and one water molecule. Hydrogen-bonding and π - π stacking (centroid-centroid distance between tetrazole and benzene rings = 3.78 Å) interactions link the molecules into a three-dimensional network.

Related literature

For general background, see: James *et al.* (2003); Kitagawa & Matsuda (2007); Maspoeh *et al.* (2007); Pan *et al.* (2006); Li *et al.* (2007). For related tetrazole ligands, see: Demko *et al.* (2001).



Experimental

Crystal data

$\text{C}_8\text{H}_6\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$
 $M_r = 208.18$
 Monoclinic, $P2_1/n$
 $a = 4.914$ (2) Å
 $b = 5.219$ (2) Å
 $c = 34.720$ (13) Å
 $\beta = 91.00$ (3)°

$V = 890.4$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 293$ (2) K
 $0.20 \times 0.10 \times 0.10$ mm

Data collection

Rigaku AFC-7R diffractometer
 Absorption correction: ψ scan
 (*Psi* in *WinAFC Diffractometer Control Software*; Rigaku 2002)
 $T_{\min} = 0.927$, $T_{\max} = 1.000$
 (expected range = 0.917–0.988)
 3386 measured reflections

1576 independent reflections
 1270 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 3 standard reflections
 every 200 reflections
 intensity decay: 0.3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.01$
 1576 reflections
 148 parameters
 4 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.17$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1}-\text{H1} \cdots \text{O2}^{\text{i}}$	0.877 (10)	1.744 (10)	2.620 (2)	176 (3)
$\text{O1W}-\text{H1WA} \cdots \text{N2}^{\text{ii}}$	0.858 (10)	2.234 (16)	2.957 (2)	142 (2)
$\text{O1W}-\text{H1WB} \cdots \text{N3}^{\text{iii}}$	0.859 (10)	2.046 (10)	2.903 (2)	175 (2)

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

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 2002); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2513).

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supplementary materials

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4-(1*H*-Tetrazol-5-yl)benzoic acid monohydrate

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Comment

The current interest in crystal engineering of metal-organic coordination polymers (MOCs) stems not only from their intriguing variety of architectures and topologies but also from their characteristic physical and/or chemical properties, including ferroelectricity, luminescence, magnetism, nonlinear optics, and gas storage, (James, *et al.* 2003; Kitagawa, *et al.* 2007; Maspoeh, *et al.* 2007; Pan, *et al.* 2006; Li, *et al.* 2007). Multifunctional organic ligands are necessary for constructing such frameworks. Tetrazoles are versatile ligands due to their many potential donor atoms. They can be synthesized easily by the reaction of a cyano group with NaN_3 in the presence of ZnBr_2 (Lewis acid) as a catalyst and water under reflux or hydrothermal reaction conditions (Demko, *et al.* 2001). Here, we report the synthesis and crystal structure of a new tetrazole $[\text{C}_8\text{H}_6\text{N}_4\text{O}_2]\cdot\text{H}_2\text{O}$ (I).

The asymmetric unit of (I), consists of one crystallographically independent 4-5*H*-tetrazolyl-benzenecarboxylate molecule and one lattice water molecule (Figure 1). The molecular skeleton of I is essentially planar and the dihedral angle between the tetrazole and benzene rings is 0.16° . Two adjacent 4-5*H*-tetrazolyl-benzenecarboxylate molecules are linked to form a centrosymmetric dimer through $\text{O1}—\text{H1}\cdots\text{O2}$ hydrogen bonds. These dimers are bridged by lattice water molecules through $\text{O1W}—\text{H1WA}\cdots\text{N2}$ and $\text{O1W}—\text{H1WB}\cdots\text{N3}$ hydrogen bonds to form a two-dimensional layer along the $[0\ 1\ 0]$ and $[7\ 0\ 1]$ directions, (Figure 2). The layers are organized further by π - π stacking interactions between the tetrazole and benzene rings to form a three-dimensional framework. The two rings involved in the π - π stacking interactions are nearly parallel to each other, with a dihedral angle of 0.15° between them. The $\text{Cg1}\cdots\text{Cg2}^i$ distance is $3.78\ \text{\AA}$ where Cg1 and Cg2 are the centroids of the $\text{C1}\cdots\text{C6}$ and $\text{C8/N1}\cdots\text{N4}$ rings respectively ($i = x-1, y, z$).

Experimental

A mixture of zinc bromide (225 mg, 1.0 mmol), Na(4-cba) (4-Hcba = 4-cyanobenzoic acid) (65 mg, 1.0 mmol) and NaN_3 (65 mg, 1.0 mmol) in 10 ml water were transferred into a Teflon-line stainless steel autoclave and heated to 413 K for 3 days, then cooled to room temperature at the rate of 1 K/h. The resulting solid powder was acidified with HCl (2*M*) to give the target product. Crystals were obtained by slow evaporation of the resulting solution.

Refinement

The H atoms bound to O1W, O1 and N1 were located in a difference Fourier synthesis and refined with isotropic displacement parameters and the O(N)—H distances restrained to a target value of $0.86(1)\ \text{\AA}$, and with $U_{\text{iso}}(\text{H})$ of O1W being $1.2U_{\text{eq}}(\text{O1W})$. The remaining aromatic H atoms were positioned geometrically and refined using a riding model with $d(\text{C}-\text{H}) = 0.93\ \text{\AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$.

Figures

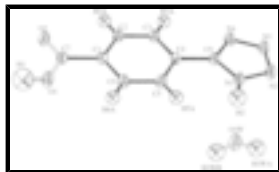


Fig. 1. The molecular structure of I, with 30% probability displacement ellipsoids.

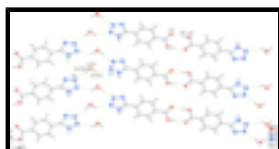


Fig. 2. Packing of (I) into two-dimensional layers linked by O—H...N and O—H...O hydrogen bonds (green dashed lines).

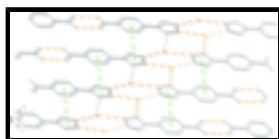


Fig. 3. A three-dimensional framework for (I) linked by the π - π stacking interactions (green dashed lines). Hydrogen bonds are shown as yellow dashed lines.

4-(1H-Tetrazol-5-yl)benzoic acid monohydrate

Crystal data

$C_8H_6N_4O_2 \cdot H_2O$

$M_r = 208.18$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 4.914$ (2) Å

$b = 5.219$ (2) Å

$c = 34.720$ (13) Å

$\beta = 91.00$ (3)°

$V = 890.4$ (6) Å³

$Z = 4$

$F_{000} = 432$

$D_x = 1.553$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 20 reflections

$\theta = 12$ – 30°

$\mu = 0.12$ mm⁻¹

$T = 293$ (2) K

Block, colorless

$0.20 \times 0.10 \times 0.10$ mm

Data collection

Rigaku AFC-7R
diffractometer

Radiation source: rotating-anode generator

Monochromator: graphite

$T = 293$ (2) K

ω - 2θ scans

Absorption correction: ψ scan

(Psi in *WinAFC Diffractometer Control Software*;
Rigaku 2002)

$T_{\min} = 0.928$, $T_{\max} = 1.000$

3386 measured reflections

1576 independent reflections

1270 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 3.5^\circ$

$h = -1 \rightarrow 5$

$k = -6 \rightarrow 6$

$l = -41 \rightarrow 41$

3 standard reflections

every 200 reflections

intensity decay: 0.3%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.095$	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.366P]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
1576 reflections	$(\Delta/\sigma)_{\max} < 0.001$
148 parameters	$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$
4 restraints	$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1W	1.3075 (3)	1.2115 (3)	0.22404 (4)	0.0510 (4)
H1WA	1.400 (4)	1.292 (4)	0.2414 (5)	0.061*
H1WB	1.175 (3)	1.304 (4)	0.2153 (6)	0.061*
O1	0.6331 (3)	1.1354 (3)	0.04240 (4)	0.0456 (4)
H1	0.509 (4)	1.157 (6)	0.0242 (6)	0.100*
O2	0.7482 (3)	0.7840 (3)	0.00986 (3)	0.0453 (4)
N1	1.6033 (3)	0.8366 (3)	0.18939 (4)	0.0363 (4)
H2	1.514 (4)	0.965 (3)	0.1990 (6)	0.068*
N2	1.8032 (3)	0.7255 (3)	0.21010 (4)	0.0429 (4)
N3	1.8788 (3)	0.5272 (3)	0.19041 (4)	0.0439 (4)
N4	1.7318 (3)	0.5062 (3)	0.15713 (4)	0.0396 (4)
C1	0.9801 (3)	0.8752 (3)	0.06869 (4)	0.0301 (4)
C2	1.1494 (4)	0.6629 (3)	0.06537 (5)	0.0345 (4)
H2A	1.1350	0.5576	0.0438	0.041*
C3	1.3393 (4)	0.6083 (3)	0.09416 (5)	0.0338 (4)
H3A	1.4531	0.4669	0.0918	0.041*

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C4	1.3602 (3)	0.7647 (3)	0.12651 (4)	0.0289 (4)
C5	1.1923 (4)	0.9778 (3)	0.12961 (5)	0.0340 (4)
H5A	1.2076	1.0839	0.1511	0.041*
C6	1.0034 (3)	1.0320 (3)	0.10098 (5)	0.0332 (4)
H6A	0.8908	1.1742	0.1033	0.040*
C7	0.7755 (3)	0.9317 (3)	0.03801 (5)	0.0319 (4)
C8	1.5608 (3)	0.7022 (3)	0.15704 (4)	0.0297 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1W	0.0586 (9)	0.0478 (9)	0.0459 (8)	0.0216 (7)	-0.0217 (6)	-0.0168 (6)
O1	0.0509 (8)	0.0439 (8)	0.0414 (7)	0.0187 (7)	-0.0173 (6)	-0.0079 (6)
O2	0.0510 (8)	0.0496 (8)	0.0348 (7)	0.0147 (7)	-0.0156 (6)	-0.0130 (6)
N1	0.0399 (9)	0.0372 (9)	0.0313 (8)	0.0110 (7)	-0.0114 (6)	-0.0040 (6)
N2	0.0458 (9)	0.0444 (9)	0.0380 (8)	0.0125 (8)	-0.0152 (7)	-0.0023 (7)
N3	0.0463 (9)	0.0443 (9)	0.0407 (8)	0.0143 (8)	-0.0138 (7)	-0.0013 (7)
N4	0.0430 (9)	0.0381 (9)	0.0374 (8)	0.0117 (7)	-0.0102 (7)	-0.0024 (7)
C1	0.0313 (9)	0.0303 (9)	0.0286 (8)	0.0010 (7)	-0.0027 (7)	-0.0002 (7)
C2	0.0396 (10)	0.0334 (10)	0.0302 (9)	0.0043 (8)	-0.0055 (7)	-0.0071 (7)
C3	0.0350 (9)	0.0318 (9)	0.0346 (9)	0.0077 (8)	-0.0052 (7)	-0.0029 (7)
C4	0.0289 (8)	0.0300 (9)	0.0277 (8)	0.0008 (7)	-0.0035 (7)	0.0016 (7)
C5	0.0399 (10)	0.0323 (9)	0.0294 (9)	0.0050 (8)	-0.0070 (7)	-0.0064 (7)
C6	0.0360 (9)	0.0297 (9)	0.0337 (9)	0.0080 (8)	-0.0052 (7)	-0.0027 (7)
C7	0.0333 (9)	0.0326 (9)	0.0296 (9)	0.0035 (8)	-0.0031 (7)	-0.0011 (7)
C8	0.0322 (9)	0.0285 (9)	0.0284 (8)	0.0020 (8)	-0.0029 (7)	0.0010 (7)

Geometric parameters (\AA , $^\circ$)

O1W—H1WA	0.858 (10)	C1—C2	1.392 (2)
O1W—H1WB	0.859 (10)	C1—C7	1.482 (2)
O1—C7	1.283 (2)	C2—C3	1.385 (2)
O1—H1	0.877 (10)	C2—H2A	0.9300
O2—C7	1.250 (2)	C3—C4	1.391 (2)
N1—C8	1.337 (2)	C3—H3A	0.9300
N1—N2	1.339 (2)	C4—C5	1.390 (2)
N1—H2	0.872 (10)	C4—C8	1.471 (2)
N2—N3	1.298 (2)	C5—C6	1.378 (2)
N3—N4	1.356 (2)	C5—H5A	0.9300
N4—C8	1.324 (2)	C6—H6A	0.9300
C1—C6	1.391 (2)		
H1WA—O1W—H1WB	111 (2)	C4—C3—H3A	120.0
C7—O1—H1	113 (2)	C5—C4—C3	119.78 (15)
C8—N1—N2	109.02 (14)	C5—C4—C8	120.84 (15)
C8—N1—H2	130.9 (16)	C3—C4—C8	119.38 (15)
N2—N1—H2	119.7 (15)	C6—C5—C4	120.14 (15)
N3—N2—N1	106.08 (14)	C6—C5—H5A	119.9
N2—N3—N4	111.08 (14)	C4—C5—H5A	119.9

C8—N4—N3	105.55 (14)	C5—C6—C1	120.35 (16)
C6—C1—C2	119.63 (15)	C5—C6—H6A	119.8
C6—C1—C7	120.49 (15)	C1—C6—H6A	119.8
C2—C1—C7	119.88 (15)	O2—C7—O1	123.55 (15)
C3—C2—C1	120.02 (16)	O2—C7—C1	120.08 (15)
C3—C2—H2A	120.0	O1—C7—C1	116.37 (14)
C1—C2—H2A	120.0	N4—C8—N1	108.27 (14)
C2—C3—C4	120.08 (16)	N4—C8—C4	126.17 (15)
C2—C3—H3A	120.0	N1—C8—C4	125.55 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots O2 ⁱ	0.877 (10)	1.744 (10)	2.620 (2)	176 (3)
O1W—H1WA \cdots N2 ⁱⁱ	0.858 (10)	2.234 (16)	2.957 (2)	142 (2)
O1W—H1WB \cdots N3 ⁱⁱⁱ	0.859 (10)	2.046 (10)	2.903 (2)	175 (2)

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $-x+7/2, y+1/2, -z+1/2$; (iii) $x-1, y+1, z$.

Fig. 1

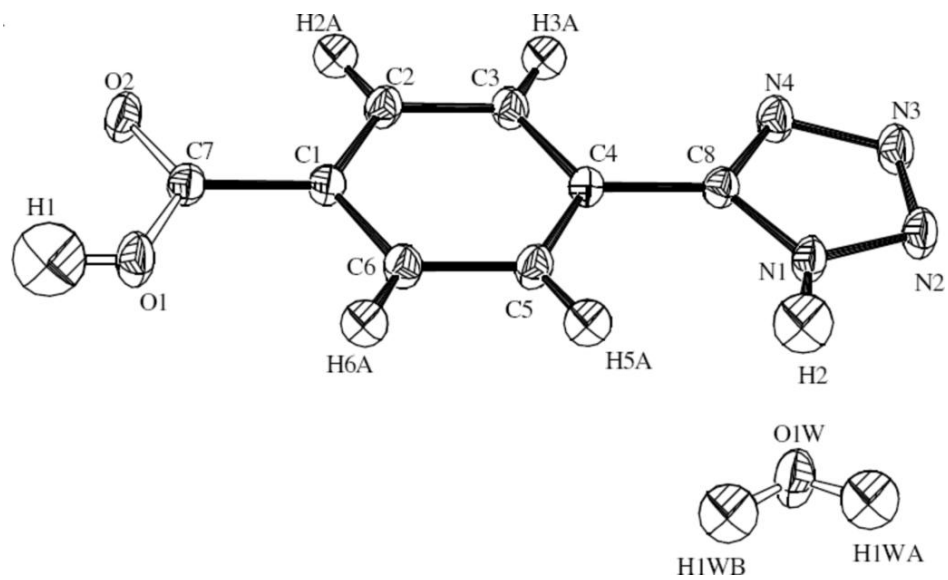


Fig. 2

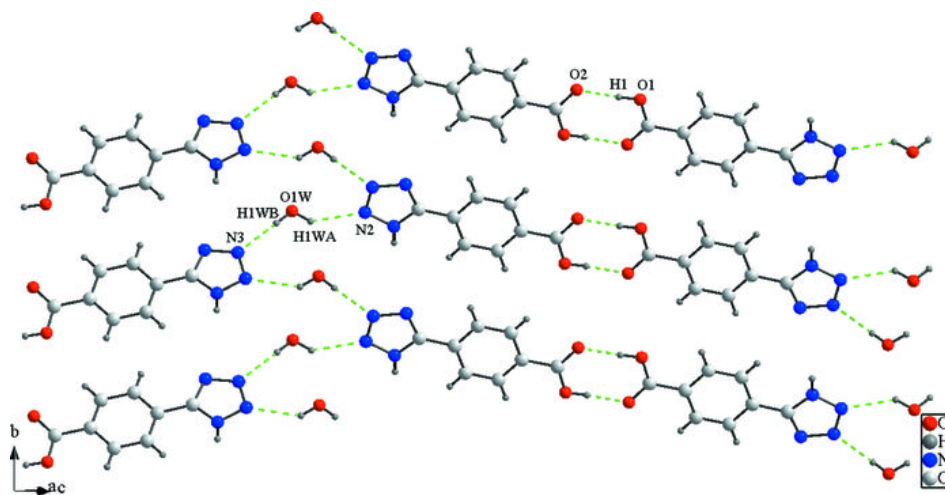


Fig. 3

