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4-Amino-3,5-dimethyl-4*H*1-,2,4-triazole–water (2/3)

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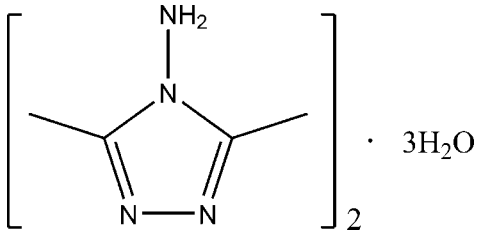
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.049; wR factor = 0.138; data-to-parameter ratio = 13.6.

The asymmetric unit of the title compound, $2C_4H_8N_4{\cdot}3H_2O$, contains two crystallographically independent 4-amino-3,5-dimethyl-1,2,4-triazole molecules and three water molecules. The structure exhibits N—H···O, O—H···N and O—H···O hydrogen bonds.

Related literature

For related structures, see: Wang *et al.* (2006); Zachara *et al.* 2004). For related literature, see: Beckmann & Brooker (2003); Bentiss *et al.* (1999); Collin *et al.* (2003); Curtis (2004).



Experimental

Crystal data

$2C_4H_8N_4{\cdot}3H_2O$
M_r = 278.34
Triclinic, $P\overline{1}$
a = 7.194 (4) Å
b = 8.680 (4) Å
c = 13.592 (7) Å
α = 72.332 (8)°
β = 84.993 (8)°
γ = 68.936 (7)°
V = 754.5 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.20 × 0.18 × 0.17 mm

Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.981, T_{max} = 0.984
5166 measured reflections
2904 independent reflections
2447 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.137
S = 1.03
2904 reflections
213 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4D···O1W	0.93 (2)	2.00 (2)	2.924 (3)	170.9 (18)
N4—H4E···O3W^{i}	0.88 (2)	2.21 (2)	3.078 (3)	168.3 (18)
N8—H8E···O2W^{ii}	0.93 (3)	2.23 (3)	3.104 (3)	156 (2)
O1W—H1WA···O2W^{iii}	0.84 (3)	1.95 (3)	2.793 (3)	173 (3)
O1W—H1WB···O3W^{iv}	0.92 (3)	1.93 (3)	2.810 (2)	160 (3)
O2W—H2WA···N2	0.87 (3)	2.02 (3)	2.885 (2)	171 (2)
O2W—H2WB···N5	0.90 (3)	1.93 (3)	2.816 (2)	168 (2)
O3W—H3WA···N1	0.88 (2)	1.92 (2)	2.787 (2)	168 (2)
O3W—H3WB···N6	0.89 (3)	1.93 (3)	2.827 (2)	176 (2)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: BT2782).

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supplementary materials

Acta Cryst. (2008). E**64**, o1893 [**doi:10.1107/S1600536808028146**]

4-Amino-3,5-dimethyl-4*H*1-,2,4-triazole-water (2/3)

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Comment

The derivatives of 4-amino-1,2,4-triazoles have considerable importance in medicinal chemistry, agricultural and industrial chemistry (Bentiss *et al.* 1999; Collin *et al.* 2003; Curtis *et al.* 2004). They have also been used as multidentate ligands in coordination chemistry (Beckmann *et al.* 2003). Here, we report a hydrated 4-amino-1,2,4-triazole $(mta)_2.3H_2O$ (mta = 4-amino-3,5-dimethyl-1,2,4-triazole).

The asymmetric unit of the title compound contains two crystallographically independent mta molecules and three water molecules. The C═N—N—C fragments of the tetrazine rings have the C═N distances of 1.299 (2), 1.300 (2) and 1.304 (2) Å, and the N—N distances of 1.392 (2) and 1.389 (2) Å. All other C—N distances are between 1.352 (2) and 1.362 (2) Å, which are considered to have part double-bond character. In the crystalline state, the mta and crystal water molecules are linked together by N—H···O, O—H···N and O—H···O hydrogen bonding.

Experimental

To a solution of mta (mta = 4-amino-3,5-dimethyl-1,2,4-triazole) (0.0228 g, 0.2 mmol) in CH_3OH (5 ml), an aqueous solution (5 ml) of $MnSO_4.H_2O$ (0.0169 g, 0.1 mmol) was added. The mixture was stirred for half an hour and filtered. The filtrate was allowed to evaporate slowly at room temperature. After several days, colorless block crystals were obtained in 5% yield (0.0007 g) based on mta.

Refinement

H atoms bonded to O and N atoms were located in a difference map and freely refined. Other H atoms were positioned geometrically and refined using a riding model with C—H = 0.96 Å and with U_{iso}(H) = 1.5U_{iso}(C).

Figures

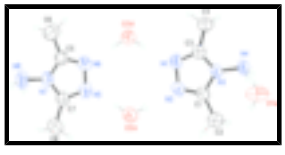

Fig. 1. The asymmetric unit of the title compound with 30% thermal ellipsoids.

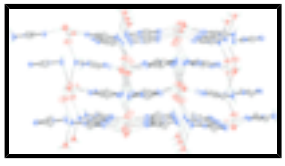

Fig. 2. The three-dimensional supramolecular network of the title compound. The H atoms bonded to C atoms are omitted for clarity.

4-Amino-3,5-dimethyl-4H-1,2,4-triazole–water (2/3)

Crystal data

$2C_4H_8N_4{\cdot}3H_2O$	$Z = 2$
$M_r = 278.34$	$F_{000} = 300$
Triclinic, $P\overline{1}$	$D_x = 1.225$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.194$ (4) Å	Cell parameters from 785 reflections
$b = 8.680$ (4) Å	$\theta = 2.4$–28.0º
$c = 13.592$ (7) Å	$\mu = 0.10$ mm^{-1}
$\alpha = 72.332$ (8)º	$T = 293$ (2) K
$\beta = 84.993$ (8)º	Block, colourless
$\gamma = 68.936$ (7)º	0.20 × 0.18 × 0.17 mm
$V = 754.5$ (6) Å^3	

Data collection

Bruker APEX CCD diffractometer	2904 independent reflections
Radiation source: fine-focus sealed tube	2447 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.014$
$T = 293(2)$ K	$\theta_{max} = 26.0$º
φ and ω scan	$\theta_{min} = 2.6$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$h = -8\rightarrow8$
$T_{min} = 0.981$, $T_{max} = 0.984$	$k = -10\rightarrow10$
5166 measured reflections	$l = -16\rightarrow12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.0952P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.137$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
2904 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
213 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.151 (12)
Secondary atom site location: difference Fourier map	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2307 (2)	0.21698 (19)	0.03818 (12)	0.0464 (4)
C2	0.2155 (3)	0.3435 (2)	0.09351 (15)	0.0675 (5)
H2A	0.2195	0.4487	0.0448	0.101*
H2B	0.3249	0.2973	0.1422	0.101*
H2C	0.0922	0.3666	0.1295	0.101*
C3	0.2508 (2)	−0.02273 (19)	0.01050 (12)	0.0450 (4)
C4	0.2584 (3)	−0.2021 (2)	0.02881 (14)	0.0574 (4)
H4A	0.2743	−0.2287	−0.0357	0.086*
H4B	0.1369	−0.2134	0.0596	0.086*
H4C	0.3691	−0.2805	0.0744	0.086*
C5	0.2491 (2)	0.3310 (2)	−0.54342 (13)	0.0518 (4)
C6	0.2507 (4)	0.2018 (3)	−0.59340 (17)	0.0790 (6)
H6A	0.2633	0.0947	−0.5416	0.119*
H6B	0.3612	0.1843	−0.6389	0.119*
H6C	0.1286	0.2421	−0.6324	0.119*
C7	0.2362 (2)	0.5735 (2)	−0.52294 (12)	0.0500 (4)
C8	0.2197 (3)	0.7564 (2)	−0.54624 (15)	0.0691 (5)
H8A	0.2259	0.7821	−0.4830	0.104*
H8B	0.0951	0.8304	−0.5817	0.104*
H8C	0.3274	0.7752	−0.5892	0.104*
N1	0.2638 (2)	0.08533 (18)	−0.07827 (10)	0.0528 (4)
N2	0.2508 (2)	0.23853 (17)	−0.06052 (10)	0.0533 (4)
N3	0.22893 (18)	0.05496 (15)	0.08561 (9)	0.0433 (3)
N4	0.2136 (3)	−0.02566 (19)	0.19138 (10)	0.0543 (4)
H4D	0.100 (3)	0.047 (3)	0.2139 (15)	0.071 (6)*
H4E	0.320 (3)	−0.030 (3)	0.2220 (15)	0.071 (6)*
N5	0.2546 (2)	0.46293 (18)	−0.43183 (10)	0.0568 (4)
N6	0.2637 (2)	0.30785 (18)	−0.44498 (11)	0.0579 (4)
N7	0.2326 (2)	0.49581 (17)	−0.59485 (9)	0.0511 (4)
N8	0.2096 (4)	0.5651 (3)	−0.70320 (12)	0.0790 (6)
H8D	0.105 (4)	0.659 (4)	−0.710 (2)	0.109 (10)*
H8E	0.325 (5)	0.589 (4)	−0.726 (2)	0.119 (10)*
O1W	−0.1595 (3)	0.1723 (3)	0.26863 (18)	0.1022 (7)

H1WA	−0.219 (5)	0.280 (4)	0.254 (2)	0.132 (12)*
H1WB	−0.248 (5)	0.128 (4)	0.254 (2)	0.131 (11)*
O2W	0.3524 (2)	0.47375 (18)	−0.23848 (12)	0.0706 (4)
H2WA	0.308 (4)	0.412 (3)	−0.186 (2)	0.090 (7)*
H2WB	0.308 (4)	0.466 (3)	−0.296 (2)	0.101 (8)*
O3W	0.3962 (2)	0.02300 (16)	−0.26616 (11)	0.0610 (4)
H3WA	0.341 (3)	0.055 (3)	−0.2121 (18)	0.079 (6)*
H3WB	0.349 (4)	0.114 (3)	−0.321 (2)	0.093 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0471 (8)	0.0429 (8)	0.0438 (8)	−0.0139 (6)	−0.0002 (6)	−0.0069 (6)
C2	0.0849 (13)	0.0529 (10)	0.0645 (11)	−0.0241 (9)	−0.0015 (10)	−0.0161 (9)
C3	0.0393 (7)	0.0485 (8)	0.0455 (8)	−0.0143 (6)	0.0017 (6)	−0.0128 (7)
C4	0.0574 (10)	0.0543 (10)	0.0636 (11)	−0.0213 (8)	0.0020 (8)	−0.0198 (8)
C5	0.0514 (9)	0.0550 (9)	0.0478 (9)	−0.0184 (7)	0.0075 (7)	−0.0152 (7)
C6	0.0942 (15)	0.0765 (13)	0.0778 (14)	−0.0334 (11)	0.0145 (11)	−0.0378 (11)
C7	0.0513 (9)	0.0539 (9)	0.0444 (9)	−0.0212 (7)	0.0050 (7)	−0.0115 (7)
C8	0.0833 (13)	0.0610 (11)	0.0660 (12)	−0.0345 (10)	0.0060 (10)	−0.0129 (9)
N1	0.0571 (8)	0.0584 (8)	0.0431 (7)	−0.0227 (6)	0.0055 (6)	−0.0134 (6)
N2	0.0589 (8)	0.0512 (8)	0.0455 (8)	−0.0221 (6)	0.0029 (6)	−0.0053 (6)
N3	0.0445 (7)	0.0430 (7)	0.0374 (7)	−0.0144 (5)	0.0013 (5)	−0.0060 (5)
N4	0.0632 (9)	0.0543 (8)	0.0378 (7)	−0.0206 (7)	0.0038 (7)	−0.0034 (6)
N5	0.0697 (9)	0.0578 (8)	0.0427 (8)	−0.0249 (7)	0.0031 (6)	−0.0119 (6)
N6	0.0709 (9)	0.0516 (8)	0.0467 (8)	−0.0213 (7)	0.0030 (6)	−0.0086 (6)
N7	0.0565 (8)	0.0584 (8)	0.0368 (7)	−0.0242 (6)	0.0045 (6)	−0.0080 (6)
N8	0.1082 (16)	0.0910 (14)	0.0374 (8)	−0.0448 (13)	0.0018 (9)	−0.0062 (8)
O1W	0.0737 (10)	0.0831 (12)	0.170 (2)	−0.0312 (9)	0.0195 (10)	−0.0655 (13)
O2W	0.1040 (11)	0.0668 (9)	0.0514 (8)	−0.0482 (8)	−0.0005 (7)	−0.0090 (6)
O3W	0.0781 (9)	0.0496 (7)	0.0488 (7)	−0.0161 (6)	0.0067 (6)	−0.0143 (6)

Geometric parameters (Å, °)

C1—N2	1.300 (2)	C7—N7	1.352 (2)
C1—N3	1.362 (2)	C7—C8	1.483 (2)
C1—C2	1.478 (2)	C8—H8A	0.9600
C2—H2A	0.9600	C8—H8B	0.9600
C2—H2B	0.9600	C8—H8C	0.9600
C2—H2C	0.9600	N1—N2	1.391 (2)
C3—N1	1.304 (2)	N3—N4	1.4091 (18)
C3—N3	1.355 (2)	N4—H4D	0.93 (2)
C3—C4	1.482 (2)	N4—H4E	0.88 (2)
C4—H4A	0.9600	N5—N6	1.389 (2)
C4—H4B	0.9600	N7—N8	1.411 (2)
C4—H4C	0.9600	N8—H8D	0.88 (3)
C5—N6	1.299 (2)	N8—H8E	0.93 (3)
C5—N7	1.354 (2)	O1W—H1WA	0.84 (3)
C5—C6	1.474 (3)	O1W—H1WB	0.92 (3)

C6—H6A	0.9600	O2W—H2WA	0.87 (3)
C6—H6B	0.9600	O2W—H2WB	0.90 (3)
C6—H6C	0.9600	O3W—H3WA	0.88 (2)
C7—N5	1.299 (2)	O3W—H3WB	0.89 (3)
N2—C1—N3	109.30 (14)	N5—C7—C8	126.38 (16)
N2—C1—C2	126.85 (15)	N7—C7—C8	124.62 (15)
N3—C1—C2	123.85 (15)	C7—C8—H8A	109.5
C1—C2—H2A	109.5	C7—C8—H8B	109.5
C1—C2—H2B	109.5	H8A—C8—H8B	109.5
H2A—C2—H2B	109.5	C7—C8—H8C	109.5
C1—C2—H2C	109.5	H8A—C8—H8C	109.5
H2A—C2—H2C	109.5	H8B—C8—H8C	109.5
H2B—C2—H2C	109.5	C3—N1—N2	107.78 (13)
N1—C3—N3	109.02 (14)	C1—N2—N1	107.36 (12)
N1—C3—C4	126.61 (15)	C3—N3—C1	106.55 (13)
N3—C3—C4	124.37 (14)	C3—N3—N4	124.23 (13)
C3—C4—H4A	109.5	C1—N3—N4	129.20 (13)
C3—C4—H4B	109.5	N3—N4—H4D	106.6 (12)
H4A—C4—H4B	109.5	N3—N4—H4E	105.8 (13)
C3—C4—H4C	109.5	H4D—N4—H4E	109.1 (17)
H4A—C4—H4C	109.5	C7—N5—N6	107.56 (14)
H4B—C4—H4C	109.5	C5—N6—N5	107.64 (13)
N6—C5—N7	108.89 (15)	C7—N7—C5	106.91 (14)
N6—C5—C6	126.70 (17)	C7—N7—N8	129.47 (15)
N7—C5—C6	124.41 (16)	C5—N7—N8	123.59 (15)
C5—C6—H6A	109.5	N7—N8—H8D	102.0 (18)
C5—C6—H6B	109.5	N7—N8—H8E	105.6 (17)
H6A—C6—H6B	109.5	H8D—N8—H8E	112 (3)
C5—C6—H6C	109.5	H1WA—O1W—H1WB	106 (3)
H6A—C6—H6C	109.5	H2WA—O2W—H2WB	107 (2)
H6B—C6—H6C	109.5	H3WA—O3W—H3WB	107 (2)
N5—C7—N7	109.00 (15)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4D···O1W	0.93 (2)	2.00 (2)	2.924 (3)	170.9 (18)
N4—H4E···O3W^{i}	0.88 (2)	2.21 (2)	3.078 (3)	168.3 (18)
N8—H8E···O2W^{ii}	0.93 (3)	2.23 (3)	3.104 (3)	156 (2)
O1W—H1WA···O2W^{iii}	0.84 (3)	1.95 (3)	2.793 (3)	173 (3)
O1W—H1WB···O3W^{iv}	0.92 (3)	1.93 (3)	2.810 (2)	160 (3)
O2W—H2WA···N2	0.87 (3)	2.02 (3)	2.885 (2)	171 (2)
O2W—H2WB···N5	0.90 (3)	1.93 (3)	2.816 (2)	168 (2)
O3W—H3WA···N1	0.88 (2)	1.92 (2)	2.787 (2)	168 (2)
O3W—H3WB···N6	0.89 (3)	1.93 (3)	2.827 (2)	176 (2)

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) −*x*+1, −*y*+1, −*z*−1; (iii) −*x*, −*y*+1, −*z*; (iv) −*x*, −*y*, −*z*.

Fig. 1

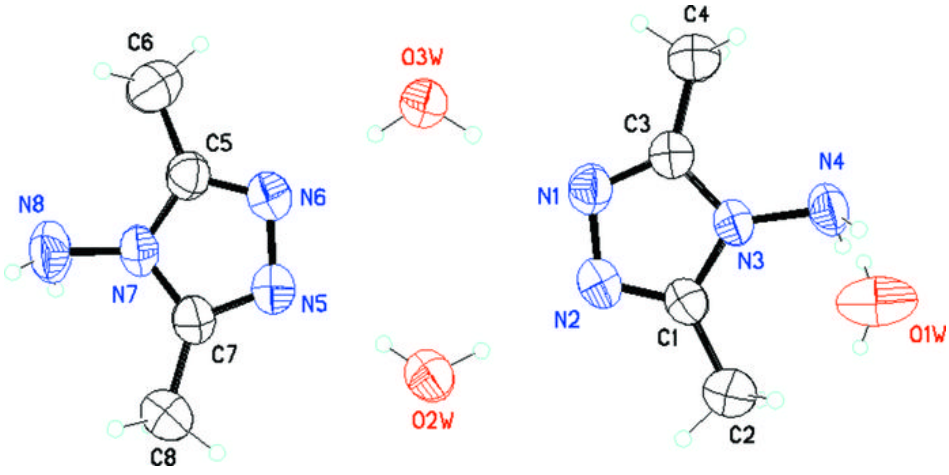

Fig. 2