

Diaquabis[5-(1*H*-tetrazol-5-ylamino- κ N⁴)-1*H*-tetrazolato- κ N¹]iron(II) dihydrate

Yang-Fan Guan, Dong-Yao Wang and Wen Dong*

School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, People's Republic of China

Correspondence e-mail: dw320@yahoo.com.cn

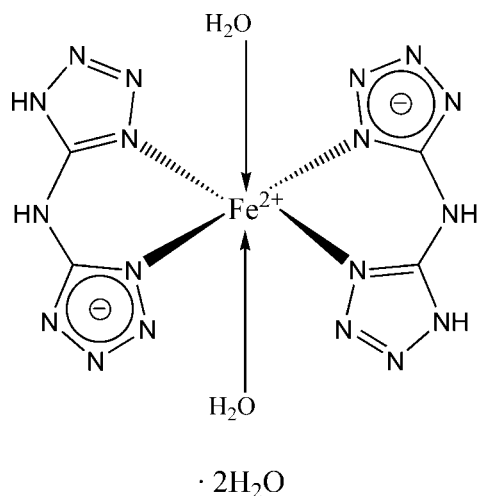
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{N}-\text{C}) = 0.002$ Å; R factor = 0.025; wR factor = 0.070; data-to-parameter ratio = 11.5.

The centrosymmetric title complex, $[\text{Fe}(\text{C}_2\text{H}_2\text{N}_9)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, has been prepared by an *in situ* [2+3] cycloaddition reaction of dicyanamide with sodium azide and ferrous sulfate, with heating and stirring. The Fe^{II} ion is coordinated by four N atoms from two 5-(1*H*-tetrazol-5-ylamino)-1*H*-tetrazolate ligands and two water molecules in axial positions in an octahedral geometry. The complex is linked into a three-dimensional network by $\text{O}-\text{H} \cdots \text{N}$, $\text{N}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds.

Related literature

Reports of related bistetrazolyimine complexes are rare; see, for example, the copper(II) complex (Friedrich *et al.*, 2005).



Experimental

Crystal data

 $[\text{Fe}(\text{C}_2\text{H}_2\text{N}_9)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 432.17$

 Monoclinic, $P2_1/c$
 $a = 7.6075$ (4) Å

 $b = 14.9759$ (7) Å

 $c = 6.8285$ (3) Å

 $\beta = 106.585$ (3)°

 $V = 745.60$ (6) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 1.08$ mm⁻¹
 $T = 296$ (2) K

 $0.23 \times 0.20 \times 0.13$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

 $T_{\text{min}} = 0.777$, $T_{\text{max}} = 0.868$

11556 measured reflections

1717 independent reflections

 1479 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.070$
 $S = 1.05$

1717 reflections

149 parameters

All H-atom parameters refined

 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N9}-\text{H3} \cdots \text{N3}^{\text{i}}$	0.87 (2)	1.93 (2)	2.797 (2)	172 (2)
$\text{O1}-\text{H1} \cdots \text{N4}^{\text{ii}}$	0.82 (3)	2.02 (3)	2.835 (2)	175 (3)
$\text{O1}-\text{H2} \cdots \text{N8}^{\text{iii}}$	0.77 (3)	2.20 (3)	2.958 (2)	171 (3)
$\text{N5}-\text{H4} \cdots \text{O2}^{\text{iv}}$	0.82 (2)	1.93 (2)	2.737 (2)	169.6 (19)
$\text{O2}-\text{H5} \cdots \text{N2}^{\text{v}}$	0.81 (3)	2.09 (3)	2.830 (2)	151 (2)
$\text{O2}-\text{H5} \cdots \text{N7}^{\text{v}}$	0.81 (3)	2.62 (3)	3.140 (2)	124 (2)
$\text{O2}-\text{H6} \cdots \text{N7}^{\text{vi}}$	0.81 (4)	2.43 (4)	3.169 (2)	153 (3)
$\text{O2}-\text{H6} \cdots \text{N2}^{\text{vi}}$	0.81 (4)	2.50 (4)	2.926 (2)	114 (3)

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

Data collection: *SMART* (Bruker, 2001–2005); cell refinement: *SAINT-Plus* (Bruker, 2001–2005); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001–2005); 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: AT2481).

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supplementary materials

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Y.-F. Guan, D.-Y. Wang and W. Dong

Comment

The complex of H₂BTA and its deprotonated anions have been not aroused sufficient attention (Friedrich *et al.*, 2005). The H₂BTA and its deprotonated anions can show hundreds of different coordinating or bridging modes. The title complex, (I), consists of a Fe(II) cation, two *HBTA*⁻ anion ligands, two coordinated water molecules and two solvent water molecules (Table 1 and Fig. 1). The *HBTA*⁻ ligand acts as a chelatingbidentate and the Fe^{II} cation is coordinated to four N atoms from two *HBTA*⁻ ligands and two water molecules to form an octahedral mononuclear complex with the axial O—Mn—O bond angle of 180°. The complex is constructed 3-D networks through O—H···N, N—H···O and N—H···N hydrogen bonds between water molecule and *HBTA*⁻ ligands (Fig. 2 and Fig. 3).

Experimental

A solution of Ferrosi Sulfate (0.0139 g, 0.05 mmol) and *L*-Ascorbic acid (0.009 g, 0.05 mmol) in 5 ml of water was slowly added to a 10 mL aqueous solution of *N,N*-bis(1(2)*H*-tetrazol-5-yl)-amine) (0.0078 g, 0.05 mmol). The mixture was stirred and refluxed for an hour. After cooling, the resulting mixture was filtered and colourless crystals were obtained by slow evaporation of the filtrate after two weeks. The colourless crystal were collected and dried in air. Elemental analysis, calculated (%) for C₄H₁₂Fe₁N₁₈O₄: C 11.11, H 2.78, N 58.31; found (%): C 10.95, H 3.09, N 58.98.

Refinement

All hydrogen atoms were found from difference Fourier mMaps and refined freely.

Figures

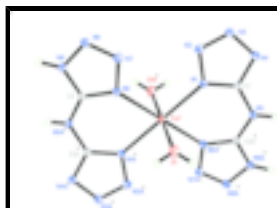


Fig. 1. The molecular structure of the complex, with atom labels and 30% probability displacement ellipsoids for non-H atoms. [Symmetry code: (i) $-x + 1, -y, -z$].

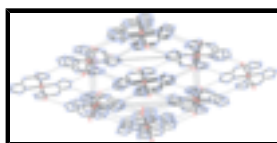


Fig. 2. The packing diagram of the complex, showing a three-dimensional network connected by O—H···N hydrogen bonds (dashed lines).

Diaquabis[5-(1*H*-tetrazol-5-ylamino- κ N⁴)-1*H*-tetrazolato- κ N¹]iron(II) dihydrate

Crystal data

[Fe(C ₄ H ₄ N ₁₈)(H ₂ O) ₂].2H ₂ O	$F_{000} = 440.0$
$M_r = 432.17$	$D_x = 1.925 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 7.6075 (4) \text{ \AA}$	Cell parameters from 1716 reflections
$b = 14.9759 (7) \text{ \AA}$	$\theta = 1.0\text{--}27.5^\circ$
$c = 6.8285 (3) \text{ \AA}$	$\mu = 1.08 \text{ mm}^{-1}$
$\beta = 106.585 (3)^\circ$	$T = 296 (2) \text{ K}$
$V = 745.60 (6) \text{ \AA}^3$	Block, colourless
$Z = 2$	$0.23 \times 0.20 \times 0.13 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	1717 independent reflections
Radiation source: fine-focus sealed tube	1479 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.030$
$T = 296(2) \text{ K}$	$\theta_{\text{max}} = 27.5^\circ$
phi and ω scans	$\theta_{\text{min}} = 2.7^\circ$
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.777$, $T_{\text{max}} = 0.868$	$k = -19 \rightarrow 19$
11556 measured reflections	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.306P]$
$wR(F^2) = 0.070$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} = 0.032$
1717 reflections	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
149 parameters	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL, $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.005 (1)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.5000	0.0000	0.0000	0.01676 (12)
N9	0.25250 (19)	0.26170 (9)	-0.0636 (2)	0.0211 (3)
N1	0.78512 (18)	0.01838 (9)	0.1552 (2)	0.0199 (3)
N8	0.41760 (19)	0.28148 (9)	0.0682 (2)	0.0230 (3)
N6	0.39630 (18)	0.13691 (9)	0.0282 (2)	0.0194 (3)
N3	1.04020 (19)	0.08854 (9)	0.2765 (2)	0.0248 (3)
C1	0.9229 (2)	-0.03919 (10)	0.2181 (2)	0.0170 (3)
C2	0.2411 (2)	0.17333 (10)	-0.0869 (2)	0.0178 (3)
N5	0.90614 (19)	-0.13073 (9)	0.2088 (2)	0.0229 (3)
N2	0.8654 (2)	0.09916 (9)	0.1938 (2)	0.0260 (3)
N7	0.50155 (19)	0.20714 (9)	0.1231 (2)	0.0233 (3)
N4	1.08411 (19)	0.00108 (9)	0.2944 (2)	0.0216 (3)
O2	0.1478 (2)	0.76781 (11)	0.4968 (2)	0.0372 (4)
O1	0.4408 (2)	-0.04110 (10)	0.2711 (2)	0.0309 (3)
H3	0.177 (3)	0.3046 (16)	-0.117 (4)	0.045 (7)*
H1	0.340 (4)	-0.0296 (19)	0.286 (4)	0.061 (9)*
H2	0.478 (4)	-0.085 (2)	0.325 (4)	0.064 (9)*
H4	0.987 (3)	-0.1610 (14)	0.285 (3)	0.026 (5)*
H5	0.184 (4)	0.7216 (19)	0.460 (4)	0.049 (7)*
H6	0.232 (5)	0.792 (2)	0.579 (6)	0.099 (13)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.01274 (18)	0.01342 (18)	0.02238 (19)	0.00098 (11)	0.00220 (12)	0.00022 (12)
N9	0.0173 (7)	0.0133 (7)	0.0301 (7)	0.0021 (5)	0.0026 (6)	-0.0012 (6)
N1	0.0159 (7)	0.0133 (6)	0.0284 (7)	-0.0001 (5)	0.0028 (6)	-0.0013 (5)
N8	0.0168 (7)	0.0176 (7)	0.0326 (8)	-0.0005 (5)	0.0036 (6)	-0.0047 (6)
N6	0.0162 (6)	0.0152 (6)	0.0248 (7)	0.0007 (5)	0.0026 (5)	-0.0015 (5)
N3	0.0185 (7)	0.0174 (7)	0.0361 (8)	-0.0021 (6)	0.0039 (6)	-0.0017 (6)
C1	0.0156 (7)	0.0159 (8)	0.0185 (7)	-0.0003 (6)	0.0034 (6)	-0.0005 (6)
C2	0.0170 (7)	0.0142 (7)	0.0226 (8)	0.0009 (6)	0.0064 (6)	-0.0004 (6)

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N5	0.0173 (7)	0.0133 (7)	0.0314 (8)	0.0028 (6)	-0.0039 (6)	0.0013 (6)
N2	0.0202 (7)	0.0143 (7)	0.0395 (8)	-0.0019 (5)	0.0021 (6)	-0.0019 (6)
N7	0.0188 (7)	0.0179 (7)	0.0309 (8)	-0.0001 (6)	0.0034 (6)	-0.0048 (6)
N4	0.0158 (7)	0.0170 (7)	0.0305 (8)	-0.0014 (5)	0.0043 (6)	-0.0019 (5)
O2	0.0345 (8)	0.0302 (8)	0.0384 (8)	0.0128 (6)	-0.0031 (6)	-0.0103 (6)
O1	0.0277 (7)	0.0345 (8)	0.0333 (7)	0.0107 (6)	0.0134 (6)	0.0124 (6)

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

Fe1—O1	2.1174 (14)	N6—N7	1.3680 (18)
Fe1—O1 ⁱ	2.1174 (14)	N3—N2	1.298 (2)
Fe1—N1	2.1427 (13)	N3—N4	1.3487 (19)
Fe1—N1 ⁱ	2.1427 (13)	C1—N4	1.332 (2)
Fe1—N6	2.2248 (13)	C1—N5	1.377 (2)
Fe1—N6 ⁱ	2.2248 (13)	C2—N5 ⁱ	1.350 (2)
N9—C2	1.333 (2)	N5—C2 ⁱ	1.350 (2)
N9—N8	1.3528 (19)	N5—H4	0.82 (2)
N9—H3	0.87 (2)	O2—H5	0.81 (3)
N1—C1	1.330 (2)	O2—H6	0.81 (4)
N1—N2	1.3469 (19)	O1—H1	0.82 (3)
N8—N7	1.2849 (19)	O1—H2	0.77 (3)
N6—C2	1.334 (2)		
O1—Fe1—O1 ⁱ	180.00 (12)	N7—N8—N9	107.11 (13)
O1—Fe1—N1	92.45 (6)	C2—N6—N7	105.34 (12)
O1 ⁱ —Fe1—N1	87.55 (6)	C2—N6—Fe1	127.02 (11)
O1—Fe1—N1 ⁱ	87.55 (6)	N7—N6—Fe1	125.14 (10)
O1 ⁱ —Fe1—N1 ⁱ	92.45 (6)	N2—N3—N4	110.80 (13)
N1—Fe1—N1 ⁱ	180.00 (12)	N1—C1—N4	112.68 (14)
O1—Fe1—N6	91.33 (5)	N1—C1—N5	125.20 (14)
O1 ⁱ —Fe1—N6	88.67 (5)	N4—C1—N5	122.12 (14)
N1—Fe1—N6	99.95 (5)	N9—C2—N6	108.63 (14)
N1 ⁱ —Fe1—N6	80.05 (5)	N9—C2—N5 ⁱ	123.85 (14)
O1—Fe1—N6 ⁱ	88.67 (5)	N6—C2—N5 ⁱ	127.52 (15)
O1 ⁱ —Fe1—N6 ⁱ	91.33 (5)	C2 ⁱ —N5—C1	123.28 (14)
N1—Fe1—N6 ⁱ	80.05 (5)	C2 ⁱ —N5—H4	117.9 (14)
N1 ⁱ —Fe1—N6 ⁱ	99.95 (5)	C1—N5—H4	118.8 (14)
N6—Fe1—N6 ⁱ	180.00 (9)	N3—N2—N1	109.04 (13)
C2—N9—N8	108.25 (13)	N8—N7—N6	110.67 (13)
C2—N9—H3	132.3 (16)	C1—N4—N3	103.16 (13)
N8—N9—H3	119.5 (16)	H5—O2—H6	109 (3)
C1—N1—N2	104.33 (12)	Fe1—O1—H1	119 (2)
C1—N1—Fe1	132.04 (11)	Fe1—O1—H2	122 (2)
N2—N1—Fe1	123.41 (10)	H1—O1—H2	111 (3)

Symmetry codes: (i) $-x+1, -y, -z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N9—H3···N3 ⁱⁱ	0.87 (2)	1.93 (2)	2.797 (2)	172 (2)
O1—H1···N4 ⁱⁱⁱ	0.82 (3)	2.02 (3)	2.835 (2)	175 (3)
O1—H2···N8 ^{iv}	0.77 (3)	2.20 (3)	2.958 (2)	171 (3)
N5—H4···O2 ^v	0.82 (2)	1.93 (2)	2.737 (2)	169.6 (19)
O2—H5···N2 ^{vi}	0.81 (3)	2.09 (3)	2.830 (2)	151 (2)
O2—H5···N7 ^{vi}	0.81 (3)	2.62 (3)	3.140 (2)	124 (2)
O2—H6···N7 ^{vii}	0.81 (4)	2.43 (4)	3.169 (2)	153 (3)
O2—H6···N2 ^{vii}	0.81 (4)	2.50 (4)	2.926 (2)	114 (3)

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

Fig. 1

i

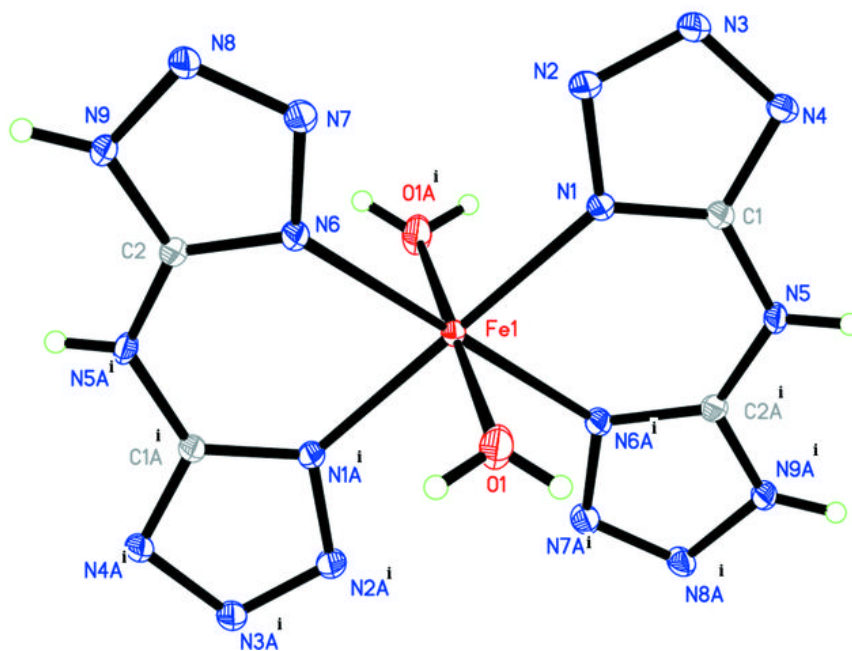


Fig. 2

