Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diaquabis[5-(1*H*-tetrazol-5-ylamino-κN^4)tetrazolato-κN^1]manganese(II) dihydrate

Jiao-Min Lin, Yang-Fan Guan 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

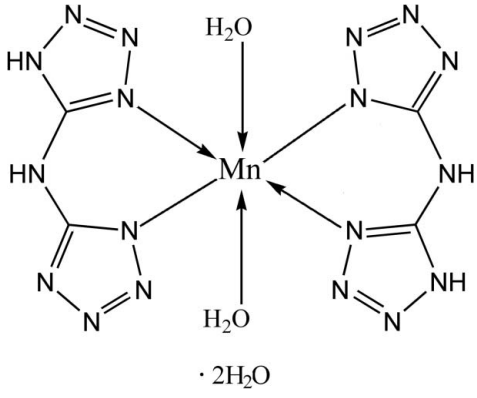
Received 23 October 2007; accepted 8 November 2007

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(N–C) = 0.004 Å; R factor = 0.052; wR factor = 0.145; data-to-parameter ratio = 12.8.

The title compound, $[Mn(C_2H_2N_9)_2(H_2O)_2]\cdot 2H_2O$, has been prepared under hydrothermal conditions. The Mn^{II} atom, lying on an inversion center, is coordinated in an octahedral geometry defined by four N atoms from two di-1*H*-tetrazol-5-ylaminate ligands in the equatorial plane and two water molecules in the axial positions. The complex molecules are linked into a three-dimensional network through O—H···N, N—H···O and N—H···N hydrogen bonds.

Related literature

For a related copper(II) complex of bistetrazolylimine, see: Friedrich *et al.* (2005).



Experimental

Crystal data

$[Mn(C_2H_2N_9)_2(H_2O)_2]\cdot 2H_2O$
M_r = 431.26
Orthorhombic, *Pbca*
a = 14.8048 (12) Å
b = 6.8674 (6) Å
c = 15.1623 (12) Å
V = 1541.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 296 (2) K
0.24 × 0.19 × 0.12 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.798, T_{max} = 0.891
23612 measured reflections
1764 independent reflections
1148 reflections with $I > 2\sigma(I)$
R_{int} = 0.084

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.145
S = 1.03
1764 reflections
138 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.191 (3)	Mn1—N6	2.304 (3)
Mn1—N1	2.199 (3)		
O1^i—Mn1—N1	87.37 (10)	O1—Mn1—N6	87.10 (11)
O1—Mn1—N1	92.63 (10)	N1—Mn1—N6	78.00 (9)
O1^i—Mn1—N6	92.90 (10)	N1^i—Mn1—N6	102.00 (9)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N9—H2···N3^{ii}	0.86	1.96	2.803 (4)	166
N5—H1···O2	0.86	1.87	2.716 (4)	169
O1—H3···N4^{iii}	0.82	1.97	2.782 (4)	172
O1—H4···N8^{iv}	0.79 (5)	2.33 (6)	3.072 (4)	157 (6)
O2—H5···N2^{v}	0.82 (5)	2.21 (5)	2.859 (5)	136 (4)
O2—H5···N7^{vi}	0.82 (5)	2.62 (5)	3.280 (4)	139 (4)
O2—H6···N7^{vii}	0.85 (6)	2.39 (7)	3.140 (4)	148 (5)
O2—H6···N2^{ii}	0.85 (6)	2.39 (6)	2.885 (4)	118 (5)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

We acknowledge financial support from the National Natural Science Foundation of China (grant No. 206710214) and the Science and Technology Program Foundation of Guangzhou, China (grant No. 2007 J1-co381).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2096).

References

Bruker (2001). *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Friedrich, M., Gólvez-Ruiz, J. C., Klapötke, T. M., Mayer, P., Weber, R. & Weigand, J. J. (2005). *Inorg. Chem.* **44**, 8044–8052.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E**63**, m3017 [**doi:10.1107/S1600536807057091**]

Diaquabis[5-(1*H*-tetrazol-5-ylamino-κN^4)tetrazolato-κN^1]manganese(II) dihydrate

J.-M. Lin, Y.-F. Guan and W. Dong

Comment

The metal complexes of bistetrazolylimine, containing nine electron-donating nitrogen atoms, have not been aroused sufficient attention (Friedrich *et al.*, 2005). The bistetrazolylimine and its deprotonated anions can show a number of different coordinating or bridging modes. The title complex consists of a Mn^{II} atom lying on an inversion center, two bistetrazolylimine ligands, two coordinated water molecules and two free water molecules (Table 1; Fig. 1). The ligand acts as chelating bidentate and the Mn^{II} atom is coordinated by four N atoms from two ligands and two water molecules in an octahedral geometry with the axial O—Mn—O bond angle of 180.0 (1)°. A three-dimensional network is constructed through O—H···N, N—H···O and N—H···N hydrogen bonds between the water molecules and the ligands (Table 2; Fig. 2).

Experimental

A mixture of manganese chlorate tetrahydrate (0.02 g, 0.1 mmol), bistetrazolylimine (0.031 g, 0.2 mmol) and water (20 ml) was heated in a 25 ml Teflon-lined autoclave at 433 K for 3 d, followed by slowly cooling to room temperature. The resulting mixture was filtered and washed with 95% methanol, and colorless crystals were collected and dried in air. Analysis, calculated for $C_4H_{12}MnN_{18}O_4$: C 11.13, H 2.78, N 58.46%; found: C 10.96, H 2.93, N 58.21%.

Refinement

H atoms bound to the ligand were positioned geometrically and refined as riding, with N—H = 0.86Å and U_{iso}(H) = 1.2U_{eq}(N). H atoms belonging to water molecules were located in a difference Fourier map. One H atom (H3) attached to the water molecule O1 was fixed with U_{iso}(H) = 1.5U_{eq}(O) and the other H atoms were refined isotropically. The highest residual electron density was found 0.95 Å from O1 and the deepest hole 0.23Å from Mn1.

Figures

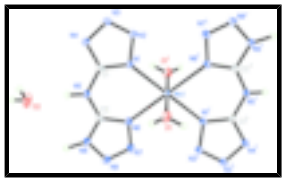


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) −*x* + 1, −*y*, −*z* + 1.]

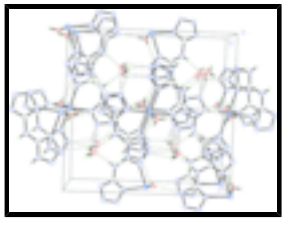


Fig. 2. The packing diagram of the title compound, showing a three-dimensional network connected by O—H···N, N—H···O and N—H···N hydrogen bonds (dashed lines).

Diaquabis[5-(1*H*-tetrazol-5-ylamino-κN^4)tetrazolato- κN^1]manganese(II) dihydrate

Crystal data

$[Mn(C_2H_2N_9)_2(H_2O)_2]\cdot 2H_2O$	F_{000} = 876.0
M_r = 431.26	D_x = 1.858 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 2291 reflections
a = 14.8048 (12) Å	θ = 2.7–27.5º
b = 6.8674 (6) Å	μ = 0.92 mm^{-1}
c = 15.1623 (12) Å	*T* = 296 (2) K
V = 1541.6 (2) Å^3	Block, colorless
Z = 4	0.24 × 0.19 × 0.12 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1764 independent reflections
Radiation source: fine-focus sealed tube	1148 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.084
T = 296(2) K	θ_{max} = 27.5º
φ and ω scans	θ_{min} = 2.7º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	*h* = −19→19
T_{min} = 0.798, T_{max} = 0.891	*k* = −8→8
23612 measured reflections	*l* = −19→19

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
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 0.1407P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.145	$(\Delta/\sigma)_{max} < 0.001$
S = 1.03	$\Delta\rho_{max}$ = 1.54 e Å^{-3}
1764 reflections	$\Delta\rho_{min}$ = −0.47 e Å^{-3}
138 parameters	Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0043 (13)
Secondary atom site location: difference Fourier map	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.5000	0.0000	0.5000	0.0220 (3)
N9	0.77109 (17)	0.0326 (4)	0.62014 (18)	0.0267 (7)
H2	0.8085	0.0652	0.6610	0.032*
N1	0.48570 (17)	0.0800 (4)	0.63974 (17)	0.0242 (7)
N5	0.63655 (18)	0.1039 (5)	0.69756 (17)	0.0288 (7)
H1	0.6677	0.1492	0.7408	0.035*
N3	0.41468 (18)	0.1035 (5)	0.76371 (18)	0.0295 (7)
N4	0.50344 (17)	0.1154 (5)	0.78366 (17)	0.0272 (7)
N8	0.79321 (19)	−0.0362 (4)	0.53957 (19)	0.0294 (7)
N2	0.40356 (18)	0.0821 (5)	0.67952 (18)	0.0310 (7)
N7	0.71908 (19)	−0.0692 (5)	0.49821 (18)	0.0297 (7)
N6	0.64677 (19)	−0.0217 (4)	0.54967 (17)	0.0253 (7)
C1	0.5441 (2)	0.0999 (5)	0.7061 (2)	0.0221 (7)
C2	0.6814 (2)	0.0412 (5)	0.6255 (2)	0.0244 (8)
O1	0.5313 (2)	0.2997 (4)	0.46099 (17)	0.0382 (7)
H3	0.5228	0.3125	0.4079	0.057*
H4	0.567 (4)	0.369 (8)	0.483 (3)	0.08 (2)*
O2	0.7346 (2)	0.2913 (5)	0.8230 (2)	0.0491 (9)
H6	0.769 (4)	0.248 (10)	0.864 (4)	0.11 (2)*
H5	0.707 (3)	0.377 (8)	0.850 (3)	0.070 (18)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0181 (4)	0.0321 (5)	0.0157 (4)	−0.0019 (3)	−0.0014 (3)	−0.0011 (3)
N9	0.0181 (15)	0.0419 (18)	0.0200 (13)	0.0020 (12)	−0.0032 (11)	−0.0026 (13)
N1	0.0159 (14)	0.0381 (17)	0.0186 (14)	−0.0006 (12)	0.0016 (10)	−0.0031 (13)
N5	0.0165 (14)	0.0505 (19)	0.0194 (13)	−0.0011 (13)	−0.0022 (11)	−0.0084 (14)
N3	0.0188 (15)	0.0464 (19)	0.0233 (14)	−0.0027 (14)	0.0026 (11)	−0.0016 (13)
N4	0.0191 (14)	0.043 (2)	0.0196 (13)	−0.0023 (12)	0.0009 (11)	−0.0036 (13)
N8	0.0221 (16)	0.043 (2)	0.0228 (15)	0.0016 (13)	0.0018 (12)	−0.0010 (13)
N2	0.0171 (15)	0.054 (2)	0.0224 (15)	−0.0028 (14)	0.0028 (11)	−0.0041 (14)
N7	0.0195 (15)	0.0431 (18)	0.0265 (15)	0.0040 (14)	−0.0003 (11)	−0.0043 (13)
N6	0.0193 (15)	0.0369 (18)	0.0197 (14)	0.0018 (12)	−0.0008 (11)	−0.0033 (12)
C1	0.0196 (17)	0.0283 (19)	0.0185 (16)	−0.0040 (14)	0.0013 (12)	0.0017 (14)
C2	0.0169 (16)	0.033 (2)	0.0230 (17)	0.0000 (14)	−0.0005 (13)	−0.0002 (14)
O1	0.0504 (18)	0.0390 (17)	0.0252 (13)	−0.0111 (14)	−0.0087 (14)	0.0034 (12)
O2	0.0460 (18)	0.056 (2)	0.0454 (18)	0.0218 (16)	−0.0190 (14)	−0.0193 (15)

Geometric parameters (Å, °)

Mn1—O1^{i}	2.191 (3)	N5—C1	1.376 (4)
Mn1—O1	2.191 (3)	N5—H1	0.8600
Mn1—N1	2.199 (3)	N3—N2	1.295 (4)

Mn1—N1^{i}	2.199 (3)	N3—N4	1.351 (4)
Mn1—N6	2.304 (3)	N4—C1	1.325 (4)
Mn1—N6^{i}	2.304 (3)	N8—N7	1.284 (4)
N9—C2	1.332 (4)	N7—N6	1.364 (4)
N9—N8	1.350 (4)	N6—C2	1.330 (4)
N9—H2	0.8600	O1—H3	0.8200
N1—C1	1.334 (4)	O1—H4	0.79 (5)
N1—N2	1.357 (4)	O2—H6	0.85 (6)
N5—C2	1.349 (4)	O2—H5	0.82 (5)
O1^{i}—Mn1—O1	180.00 (13)	C2—N5—C1	124.0 (3)
O1^{i}—Mn1—N1	87.37 (10)	C2—N5—H1	118.0
O1—Mn1—N1	92.63 (10)	C1—N5—H1	118.0
O1^{i}—Mn1—N1^{i}	92.63 (10)	N2—N3—N4	110.6 (3)
O1—Mn1—N1^{i}	87.37 (10)	C1—N4—N3	103.8 (3)
N1—Mn1—N1^{i}	180.0	N7—N8—N9	107.2 (3)
O1^{i}—Mn1—N6	92.90 (10)	N3—N2—N1	109.0 (2)
O1—Mn1—N6	87.10 (11)	N8—N7—N6	110.4 (3)
N1—Mn1—N6	78.00 (9)	C2—N6—N7	105.6 (3)
N1^{i}—Mn1—N6	102.00 (9)	C2—N6—Mn1	128.6 (2)
O1^{i}—Mn1—N6^{i}	87.10 (11)	N7—N6—Mn1	124.65 (19)
O1—Mn1—N6^{i}	92.90 (10)	N4—C1—N1	112.6 (3)
N1—Mn1—N6^{i}	102.00 (9)	N4—C1—N5	122.3 (3)
N1^{i}—Mn1—N6^{i}	78.00 (9)	N1—C1—N5	125.2 (3)
N6—Mn1—N6^{i}	180.0	N6—C2—N9	108.5 (3)
C2—N9—N8	108.2 (3)	N6—C2—N5	127.9 (3)
C2—N9—H2	125.9	N9—C2—N5	123.6 (3)
N8—N9—H2	125.9	Mn1—O1—H3	109.5
C1—N1—N2	104.1 (2)	Mn1—O1—H4	127 (4)
C1—N1—Mn1	133.7 (2)	H3—O1—H4	116.8
N2—N1—Mn1	121.14 (19)	H6—O2—H5	101 (5)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N9—H2···N3^{ii}	0.86	1.96	2.803 (4)	166
N5—H1···O2	0.86	1.87	2.716 (4)	169
O1—H3···N4^{iii}	0.82	1.97	2.782 (4)	172
O1—H4···N8^{iv}	0.79 (5)	2.33 (6)	3.072 (4)	157 (6)
O2—H5···N2^{v}	0.82 (5)	2.21 (5)	2.859 (5)	136 (4)
O2—H5···N7^{vi}	0.82 (5)	2.62 (5)	3.280 (4)	139 (4)
O2—H6···N7^{vii}	0.85 (6)	2.39 (7)	3.140 (4)	148 (5)
O2—H6···N2^{ii}	0.85 (6)	2.39 (6)	2.885 (4)	118 (5)

Symmetry codes: (ii) *x*+1/2, *y*, −*z*+3/2; (iii) *x*, −*y*+1/2, *z*−1/2; (iv) −*x*+3/2, *y*+1/2, *z*; (v) −*x*+1, *y*+1/2, −*z*+3/2; (vi) *x*, −*y*+1/2, *z*+1/2; (vii) −*x*+3/2, −*y*, *z*+1/2.

Fig. 1

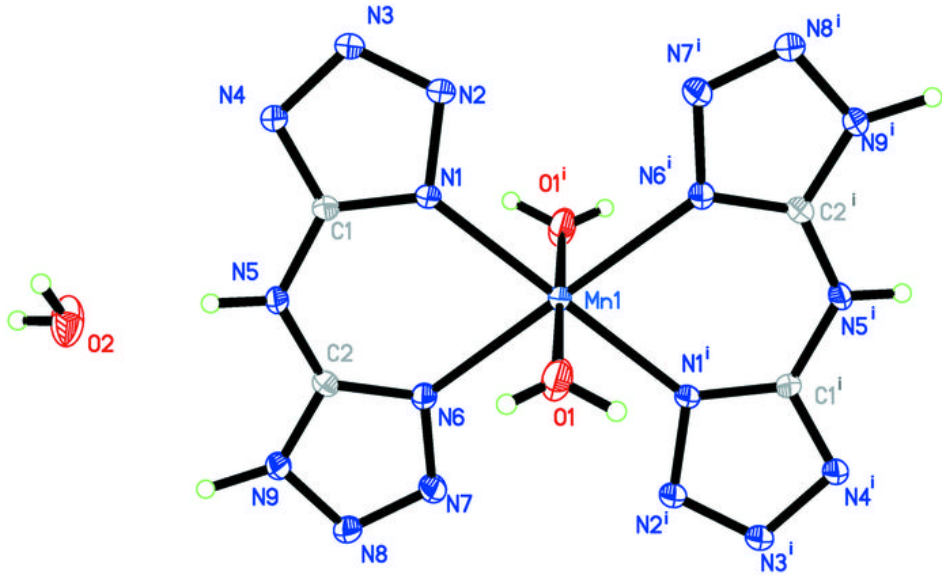

N3
N4
N2
N1
C1
N5
C2
N6
N9
N7
N8
O2
O1i
Mn1
O1
N7i
N8i
N6i
N9i
C2i
N5i
N1i
C1i
N4i
N2i
N3i

Fig. 2