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Tetraaquabis[5-(pyridin-3-yl)tetrazolido-κN^5]manganese(II) tetrahydrate

Chen Qi,[a] Xiang He,[a] Min Shao[b] and Ming-Xing Li[a]*

[a]Department of Chemistry, College of Science, Shanghai University, Shanghai, 200444, People's Republic of China, and [b]Laboratory for Microstructures, Shanghai University, Shanghai 200444, People's, Republic of China
Correspondence e-mail: mx_li@mail.shu.edu.cn

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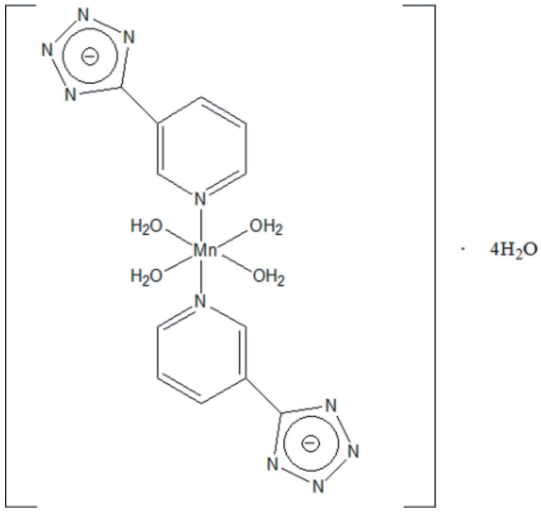
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.032; wR factor = 0.080; data-to-parameter ratio = 12.9.

The title compound, $[Mn(C_6H_4N_5)_2(H_2O)_4]\cdot 4H_2O$, was obtained by the solution reaction of $MnCl_2$ and 3-(2*H*-tetrazol-5-yl)pyridine. The Mn^{II} atom, located on an inversion center, shows a slightly distorted octahedral geometry and is coordinated by two pyridine N atoms from two 5-(pyridin-3-yl)tetrazolide ligands occupying *trans* positions and four water molecules. In the crystal, the mononuclear complex molecules and solvent water molecules are connected into a three-dimensional framework by O—H···N and O—H···O hydrogen bonds.

Related literature

For the synthesis and crystal structure of the isotypic zinc(II) complex $[Zn(C_6H_4N_5)_2(H_2O)_4]\cdot 4H_2O$, see: Mu *et al.* (2010).



Experimental

Crystal data

$[Mn(C_6H_4N_5)_2(H_2O)_4]\cdot 4H_2O$
M_r = 491.35
Triclinic, $P\overline{1}$
a = 8.137 (8) Å
b = 8.629 (8) Å
c = 8.761 (8) Å
α = 84.878 (10)°
β = 65.347 (8)°
γ = 72.571 (10)°
V = 533.0 (9) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.68 mm^{-1}
T = 293 K
0.15 × 0.10 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.922, T_{max} = 0.934
2785 measured reflections
1850 independent reflections
1712 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.080
S = 1.05
1850 reflections
143 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1B···O4^{i}	0.85	1.94	2.783 (3)	172
O1—H1A···N5^{ii}	0.85	1.91	2.731 (3)	163
O2—H2A···O3^{iii}	0.85	1.99	2.836 (3)	171
O2—H2B···O3^{iv}	0.85	1.96	2.800 (3)	169
O3—H3B···O4	0.85	1.96	2.803 (3)	171
O3—H3A···N2	0.85	1.96	2.797 (3)	170
O4—H4B···N3^{v}	0.85	2.03	2.878 (3)	177
O4—H4A···N4^{vi}	0.85	2.00	2.849 (3)	176

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

Data collection: *APEX2* (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: GK2497).

References

Bruker (2000). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Mu, Y.-Q., Zhao, J. & Li, C. (2010). *Acta Cryst.* E**66**, m1667.
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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2012). E**68**, m890 [https://doi.org/10.1107/S160053681202510X]

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Chen Qi, Xiang He, Min Shao and Ming-Xing Li

S1. Comment

3-(2*H*-Tetrazol-5-yl)pyridine (3-Ptz) is a multifunctional ligand which possesses five potential coordinate nitrogen atoms. Recently Mu *et al.* (2010) reported that hydrothermal reaction of $Zn(OAc)_2$ with 3-Ptz results in a mononuclear zinc complex $[Zn(C_6H_4N_5)_2(H_2O)_4].4H_2O$. We were able to prepare an analogues manganese(II) compound, $[Mn(C_6H_4N_5)_2(H_2O)_4].4H_2O$, by the solution reaction of $MnCl_2$ with 3-Ptz in a basic H_2O/ethanol solution. This compound is closely isostructural with the Zn complex reported by Mu *et al.* (2010)

S2. Experimental

A mixture of $MnCl_2$ (0.1 mmol), 3-Ptz (0.1 mmol), 1 ml NaOH solution (0.1 mol L^{-1}) was added into 10 ml H_2O/ethanol mixed solvent (1:1). After being stirred for twenty minutes, the mixture was filtered. The filtrate was left undisturbed for two days to give yellow block crystals with 35% yield based on 3-Ptz. Anal. calcd for $C_{12}H_{24}MnN_{10}O_8$ (%): C, 29.33; H, 4.92; N, 28.51. Found: C, 29.24; H, 4.83; N, 28.66. IR (KBr pellet, cm^{-1}): 3400*m*, 1613*m*, 1588*m*, 1464*m*, 1426s, 1372*m*, 1153s, 1019*m*, 787s, 750s, 696s, 642*m*, 463*m*.

S3. Refinement

All the H atoms were positioned geometrically (C—H = 0.93 Å, O—H = 0.85 Å), and allowed to ride on their parent atoms, with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5Ueq(O).

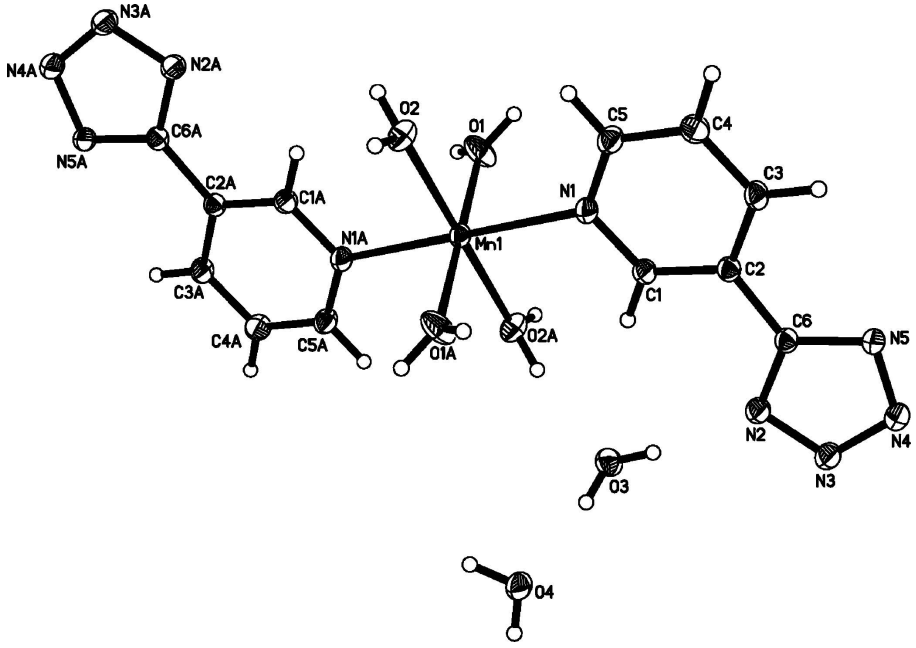

Figure 1

The asymmetric unit of the title complex. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (A) -*x*, -*y*, -*z*].

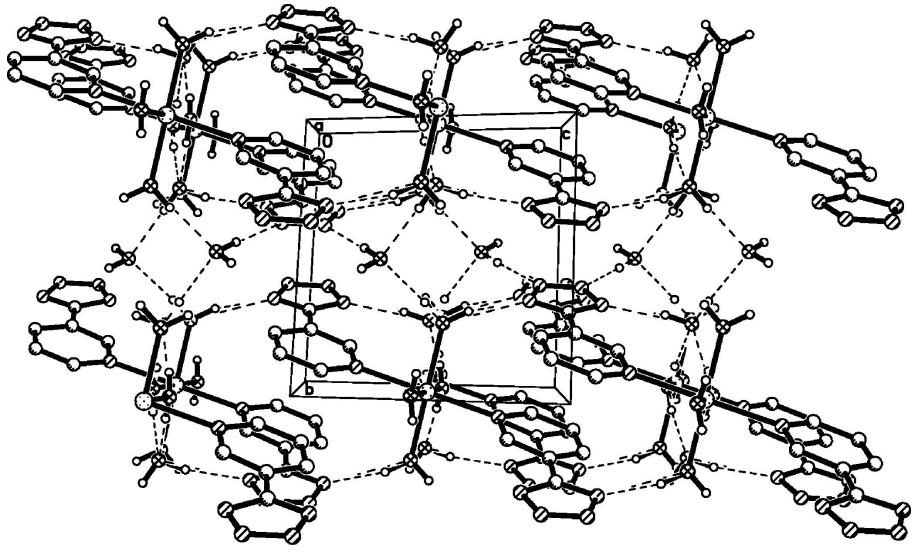

Figure 2

A crystal packing diagram of the title compound with hydrogen bonds shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

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Crystal data

$[Mn(C_6H_4N_5)_2(H_2O)_4]\cdot 4H_2O$
$M_r = 491.35$
Triclinic, $P\overline{1}$
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$b = 8.629$ (8) Å

c = 8.761 (8) Å
α = 84.878 (10)°
β = 65.347 (8)°
γ = 72.571 (10)°
V = 533.0 (9) Å^3
Z = 1
F(000) = 255
D_x = 1.531 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1565 reflections
θ = 2.5–27.3°
μ = 0.68 mm^{-1}
T = 293 K
Block, yellow
0.15 × 0.10 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.922, T_{max} = 0.934

2785 measured reflections
1850 independent reflections
1712 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.0°, θ_{min} = 2.5°
h = −7→9
k = −6→10
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.080
S = 1.05
1850 reflections
143 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.2064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.063 (6)

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	0.4972 (3)	0.8406 (3)	0.1955 (2)	0.0309 (5)
H1	0.3863	0.8330	0.2844	0.037*
C2	0.5378 (3)	0.7784 (2)	0.0396 (2)	0.0250 (4)
C3	0.7038 (3)	0.7881 (3)	−0.0919 (2)	0.0312 (4)
H3	0.7369	0.7485	−0.1993	0.037*
C4	0.8196 (3)	0.8579 (3)	−0.0606 (3)	0.0367 (5)
H4	0.9326	0.8647	−0.1468	0.044*

C5	0.7665 (3)	0.9175 (2)	0.0990 (3)	0.0313 (4)
H5	0.8457	0.9643	0.1180	0.038*
C6	0.4027 (3)	0.7086 (2)	0.0214 (2)	0.0253 (4)
Mn1	0.5000	1.0000	0.5000	0.02565 (17)
N1	0.6059 (2)	0.9108 (2)	0.22757 (19)	0.0291 (4)
N2	0.2536 (2)	0.6822 (2)	0.1516 (2)	0.0316 (4)
N3	0.1654 (2)	0.6214 (2)	0.0825 (2)	0.0345 (4)
N4	0.2572 (2)	0.6120 (2)	−0.0813 (2)	0.0335 (4)
N5	0.4088 (2)	0.6669 (2)	−0.12397 (19)	0.0293 (4)
O1	0.4248 (2)	1.25174 (18)	0.44974 (18)	0.0465 (4)
H1B	0.3486	1.3288	0.5213	0.056*
H1A	0.4587	1.2950	0.3548	0.056*
O2	0.79389 (19)	0.99831 (18)	0.44105 (18)	0.0364 (4)
H2A	0.8730	0.9173	0.4589	0.044*
H2B	0.8229	1.0820	0.4526	0.044*
O3	0.0823 (2)	0.75323 (18)	0.49811 (18)	0.0372 (4)
H3B	0.0942	0.6696	0.5562	0.045*
H3A	0.1346	0.7196	0.3958	0.045*
O4	0.1519 (2)	0.48719 (18)	0.69383 (17)	0.0359 (4)
H4B	0.0608	0.4519	0.7598	0.043*
H4A	0.1855	0.5271	0.7575	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0302 (10)	0.0403 (11)	0.0217 (10)	−0.0155 (9)	−0.0058 (8)	−0.0023 (8)
C2	0.0279 (10)	0.0230 (9)	0.0239 (10)	−0.0064 (8)	−0.0108 (8)	−0.0002 (7)
C3	0.0317 (10)	0.0378 (11)	0.0216 (10)	−0.0100 (9)	−0.0071 (8)	−0.0061 (8)
C4	0.0286 (10)	0.0506 (13)	0.0277 (11)	−0.0162 (10)	−0.0043 (8)	−0.0034 (9)
C5	0.0277 (10)	0.0374 (11)	0.0320 (11)	−0.0116 (8)	−0.0134 (8)	−0.0010 (9)
C6	0.0292 (10)	0.0226 (9)	0.0234 (10)	−0.0065 (8)	−0.0104 (8)	−0.0011 (7)
Mn1	0.0264 (2)	0.0299 (3)	0.0210 (2)	−0.00911 (17)	−0.00862 (17)	−0.00332 (16)
N1	0.0311 (9)	0.0351 (9)	0.0230 (8)	−0.0125 (7)	−0.0105 (7)	−0.0017 (7)
N2	0.0307 (9)	0.0386 (10)	0.0264 (9)	−0.0142 (7)	−0.0091 (7)	−0.0018 (7)
N3	0.0341 (9)	0.0405 (10)	0.0320 (9)	−0.0165 (8)	−0.0122 (7)	−0.0018 (8)
N4	0.0370 (9)	0.0370 (10)	0.0314 (9)	−0.0153 (8)	−0.0152 (8)	−0.0008 (7)
N5	0.0348 (9)	0.0320 (9)	0.0237 (9)	−0.0141 (7)	−0.0109 (7)	−0.0014 (7)
O1	0.0623 (10)	0.0321 (8)	0.0252 (8)	−0.0059 (7)	−0.0044 (7)	0.0003 (6)
O2	0.0302 (7)	0.0385 (8)	0.0429 (9)	−0.0084 (6)	−0.0166 (6)	−0.0071 (6)
O3	0.0407 (8)	0.0377 (8)	0.0292 (8)	−0.0113 (7)	−0.0100 (6)	−0.0011 (6)
O4	0.0401 (8)	0.0413 (8)	0.0273 (8)	−0.0177 (7)	−0.0094 (6)	−0.0044 (6)

Geometric parameters (Å, º)

C1—N1	1.337 (3)	Mn1—O2^{i}	2.222 (3)
C1—C2	1.382 (3)	Mn1—O2	2.222 (3)
C1—H1	0.9300	Mn1—N1	2.290 (3)
C2—C3	1.383 (3)	Mn1—N1^{i}	2.290 (3)

C2—C6	1.468 (3)	N2—N3	1.342 (2)
C3—C4	1.382 (3)	N3—N4	1.309 (3)
C3—H3	0.9300	N4—N5	1.349 (3)
C4—C5	1.377 (3)	O1—H1B	0.8500
C4—H4	0.9300	O1—H1A	0.8500
C5—N1	1.336 (3)	O2—H2A	0.8500
C5—H5	0.9300	O2—H2B	0.8501
C6—N5	1.331 (3)	O3—H3B	0.8500
C6—N2	1.338 (3)	O3—H3A	0.8501
Mn1—O1	2.132 (2)	O4—H4B	0.8500
Mn1—O1^{i}	2.132 (2)	O4—H4A	0.8501

N1—C1—C2	124.70 (17)	O1—Mn1—N1	95.02 (7)
N1—C1—H1	117.6	O1^{i}—Mn1—N1	84.98 (7)
C2—C1—H1	117.6	O2^{i}—Mn1—N1	92.50 (6)
C1—C2—C3	117.48 (18)	O2—Mn1—N1	87.50 (6)
C1—C2—C6	118.90 (17)	O1—Mn1—N1^{i}	84.98 (7)
C3—C2—C6	123.61 (18)	O1^{i}—Mn1—N1^{i}	95.02 (7)
C4—C3—C2	118.66 (19)	O2^{i}—Mn1—N1^{i}	87.50 (5)
C4—C3—H3	120.7	O2—Mn1—N1^{i}	92.50 (6)
C2—C3—H3	120.7	N1—Mn1—N1^{i}	179.999 (1)
C5—C4—C3	119.62 (19)	C5—N1—C1	116.74 (18)
C5—C4—H4	120.2	C5—N1—Mn1	127.06 (13)
C3—C4—H4	120.2	C1—N1—Mn1	116.17 (13)
N1—C5—C4	122.78 (19)	C6—N2—N3	104.94 (17)
N1—C5—H5	118.6	N4—N3—N2	109.54 (17)
C4—C5—H5	118.6	N3—N4—N5	109.28 (15)
N5—C6—N2	111.27 (17)	C6—N5—N4	104.97 (15)
N5—C6—C2	125.30 (17)	Mn1—O1—H1B	126.3
N2—C6—C2	123.42 (17)	Mn1—O1—H1A	127.6
O1—Mn1—O1^{i}	180.0	H1B—O1—H1A	106.1
O1—Mn1—O2^{i}	88.59 (7)	Mn1—O2—H2A	122.5
O1^{i}—Mn1—O2^{i}	91.41 (7)	Mn1—O2—H2B	123.2
O1—Mn1—O2	91.41 (7)	H2A—O2—H2B	106.1
O1^{i}—Mn1—O2	88.59 (7)	H3B—O3—H3A	106.7
O2^{i}—Mn1—O2	180.000 (1)	H4B—O4—H4A	105.2

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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