

Diaquabis[5-(pyrimidin-2-yl)tetrazolato]-manganese(II)

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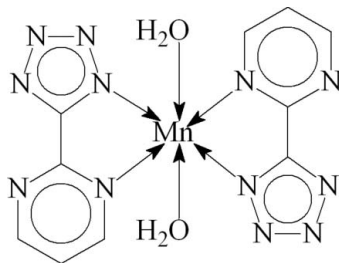
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.029; wR factor = 0.076; data-to-parameter ratio = 14.2.

The title complex, $[\text{Mn}(\text{C}_5\text{H}_3\text{N}_6)_2(\text{H}_2\text{O})_2]$, possesses a crystallographically imposed center of symmetry occupied by an Mn^{II} ion, which is coordinated by four N atoms from two 5-(pyrimidin-2-yl)tetrazolate ligands [$\text{Mn}-\text{N} = 2.2066$ (13) and 2.2731 (15) Å] and two water molecules [$\text{Mn}-\text{O} = 2.1868$ (14) Å] in a distorted octahedral geometry. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds link the complexes into two-dimensional sheets parallel to the bc plane.

Related literature

The synthesis of 2-(1*H*-tetrazol-5-yl)pyrimidine was described by Demko & Sharpless (2001); for the crystal structures of related complexes, see: Wang *et al.* (2003), Mo *et al.* (2004), Rodríguez *et al.* (2005), Luo *et al.* (2006), Peng *et al.* (2007).



Experimental

Crystal data

$[\text{Mn}(\text{C}_5\text{H}_3\text{N}_6)_2(\text{H}_2\text{O})_2]$	$b = 13.095$ (3) Å
$M_r = 385.24$	$c = 7.2958$ (15) Å
Monoclinic, $P2_1/c$	$\beta = 97.18$ (3)°
$a = 8.0084$ (16) Å	$V = 759.1$ (3) Å ³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.91$ mm⁻¹

$T = 293$ (2) K
 $0.16 \times 0.14 \times 0.02$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\text{min}} = 0.929$, $T_{\text{max}} = 1.000$
7203 measured reflections
1737 independent reflections
1431 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.076$
 $S = 1.03$
1737 reflections
122 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1W}-\text{H1WA}\cdots\text{N4}^i$	0.830 (9)	1.943 (10)	2.7673 (18)	172 (2)
$\text{O1W}-\text{H1WB}\cdots\text{N3}^ii$	0.844 (9)	1.978 (10)	2.8171 (17)	173 (2)

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT and SHELXTL (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); 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: CV2240).

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supplementary materials

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Diaquabis[5-(pyrimidin-2-yl)tetrazolato]manganese(II)

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Comment

5-Substituted 1*H*-tetrazole ligands are often used in metal-organic complexes. With N-heterocyclic substituents, most of metal complexes were structurally characterized, in which 2-position N-containing derivatives always give mono-nuclear complexes. Such as, diaquabis[5-(pyridyl-2-yl)tetrazolato]manganese(II), diaquabis[5-(pyridyl-2-yl)tetrazolato]copper(II), diaquabis[5-(pyridyl-2-yl)tetrazolato]zinc(II), diaquabis[5-(pyrazin-2-yl)tetrazolato]zinc(II) and diaquabis[5-(pyrazin-2-yl)tetrazolato]manganese(II) (Wang *et al.*, 2003; Mo *et al.*, 2004; Rodríguez *et al.*, 2005; Luo *et al.*, 2006; Peng *et al.*, 2007). Herein, 2-(1*H*-tetrazol-5-yl)pyrimidine (L) ligands were used to give a similar mono-nuclear Mn(II) complex, diaquabis[5-(pyrimidin-2-yl)tetrazolato]manganese(II) (I). With this ligand, two two-dimensional Co(II) and Fe(II) complexes were reported recently (Rodríguez *et al.*, 2005).

In the title complex (I), the central Mn(II) ion is located on an inversion center and coordinated by two deprotonated bidentate L ligands via one of the pyrimidinyl nitrogen and the tetrazole nitrogen in the 1-position and two water molecules with a transoid pseudo-octahedral geometry geometry (Fig. 1). The structure is similar to those of diaquabis[5-(pyridyl-2-yl)tetrazolato]manganese(II), diaquabis[5-(pyridyl-2-yl)tetrazolato]copper(II), diaquabis[5-(pyridyl-2-yl)tetrazolato]zinc(II), diaquabis[5-(pyrazin-2-yl)tetrazolato]zinc(II), diaquabis[5-(pyrazin-2-yl)tetrazolato]manganese(II) (Wang *et al.*, 2003; Mo *et al.*, 2004; Rodríguez *et al.*, 2005; Luo *et al.*, 2006; Peng *et al.*, 2007).

An interesting aspect of the structure is the way in which the mononuclear units are interlinked via hydrogen bonds into a two-dimensional network. As shown in Fig. 2, each coordinated water molecule of a mononuclear unit interlinks with the tetrazole rings from two neighboring mononuclear units through O—H \cdots N hydrogen bond, and each tetrazole ring forms two O—H \cdots N hydrogen bonds via the nitrogen atoms at 3- and 4-positions with also two adjacent molecules. Thus, each unit forms a total of eight hydrogen bonds with its four neighbors. The related hydrogen bond parameters are listed in the Table.

Experimental

The ligand, 2-(1*H*-tetrazol-5-yl)pyrimidine (L) was synthesized according to the literature method (Demko & Sharpless, 2001). A mixture of MnCl₂·4H₂O (40 mg, 0.2 mmol) and ligand L (60 mg, 0.4 mmol) in water (10 ml) was placed in a Teflon-lined stainless-steel Parr bomb that was heated at 393 K for 48 h. Colorless crystals were collected after the bomb allowed to cool to room temperature spontaneously. Yield, 40%.

Refinement

The C-bound H atoms were placed in calculated positions (C—H 0.93 Å) and treated in the subsequent refinement as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. Two H atoms of the water molecule were located in Fourier difference map and refined with bond restraints O—H = 0.84 (1) Å, and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$.

Figures

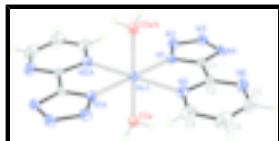


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level [symmetry code: (A) 1 - x, 2 - y, - z].

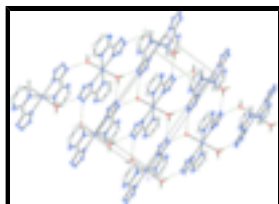


Fig. 2. Two-dimensional hydrogen-bonded network.

Diaquabis[5-(pyrimidin-2-yl)tetrazolato]manganese(II)

Crystal data

[Mn(C₅H₃N₆)₂(H₂O)₂]

$M_r = 385.24$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.0084$ (16) Å

$b = 13.095$ (3) Å

$c = 7.2958$ (15) Å

$\beta = 97.18$ (3)°

$V = 759.1$ (3) Å³

$Z = 2$

$F_{000} = 390$

$D_x = 1.685$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 5442 reflections

$\theta = 3.0$ – 27.5 °

$\mu = 0.91$ mm⁻¹

$T = 293$ (2) K

Block, colourless

$0.16 \times 0.14 \times 0.02$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 1998)

$T_{\min} = 0.929$, $T_{\max} = 1.000$

7203 measured reflections

1737 independent reflections

1431 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 27.5$ °

$\theta_{\min} = 3.0$ °

$h = -10 \rightarrow 10$

$k = -17 \rightarrow 16$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.1658P]$$

$$R[F^2 > 2\sigma(F^2)] = 0.029$$

$$wR(F^2) = 0.076$$

$$S = 1.03$$

1737 reflections

122 parameters

2 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL97,
 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.020 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.5000	1.0000	0.0000	0.03101 (14)
N1	0.54376 (17)	1.16630 (9)	-0.00415 (17)	0.0303 (3)
N2	0.65673 (19)	1.23355 (10)	-0.05190 (19)	0.0359 (3)
N3	0.5993 (2)	1.32610 (10)	-0.02615 (19)	0.0388 (4)
N4	0.4487 (2)	1.32100 (10)	0.03793 (19)	0.0368 (3)
N5	0.27899 (18)	1.07056 (10)	0.12166 (18)	0.0348 (3)
N6	0.1532 (2)	1.23123 (13)	0.1739 (2)	0.0466 (4)
C1	0.4187 (2)	1.22145 (11)	0.0503 (2)	0.0297 (3)
C2	0.2734 (2)	1.17322 (12)	0.1182 (2)	0.0320 (4)
C3	0.1543 (3)	1.02274 (16)	0.1923 (3)	0.0495 (5)
H3A	0.1547	0.9518	0.1987	0.059*
C4	0.0256 (3)	1.07621 (19)	0.2555 (3)	0.0618 (6)
H4A	-0.0606	1.0430	0.3060	0.074*
C5	0.0292 (3)	1.18049 (19)	0.2413 (3)	0.0578 (6)
H5A	-0.0586	1.2178	0.2803	0.069*
O1W	0.64119 (17)	0.99277 (8)	0.27633 (16)	0.0359 (3)
H1WA	0.623 (3)	0.9423 (12)	0.340 (3)	0.054*
H1WB	0.632 (3)	1.0442 (12)	0.344 (3)	0.054*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0393 (2)	0.01818 (19)	0.0371 (2)	-0.00146 (14)	0.01063 (15)	-0.00165 (12)
N1	0.0360 (8)	0.0227 (7)	0.0333 (7)	-0.0030 (5)	0.0083 (6)	0.0001 (5)
N2	0.0446 (9)	0.0262 (7)	0.0376 (7)	-0.0071 (6)	0.0081 (6)	0.0014 (5)
N3	0.0563 (10)	0.0219 (7)	0.0377 (8)	-0.0059 (6)	0.0042 (7)	0.0025 (5)
N4	0.0507 (9)	0.0219 (7)	0.0365 (8)	0.0035 (6)	0.0008 (6)	-0.0005 (5)
N5	0.0359 (8)	0.0335 (7)	0.0360 (7)	-0.0051 (6)	0.0086 (6)	-0.0034 (5)
N6	0.0388 (10)	0.0556 (10)	0.0456 (9)	0.0139 (7)	0.0056 (7)	-0.0070 (7)
C1	0.0385 (9)	0.0229 (8)	0.0268 (7)	0.0035 (6)	0.0007 (6)	-0.0017 (5)
C2	0.0338 (9)	0.0339 (9)	0.0276 (8)	0.0040 (7)	0.0011 (6)	-0.0044 (6)
C3	0.0447 (12)	0.0544 (12)	0.0511 (11)	-0.0160 (9)	0.0125 (9)	-0.0017 (8)
C4	0.0387 (13)	0.0904 (18)	0.0594 (13)	-0.0148 (11)	0.0181 (10)	-0.0052 (11)
C5	0.0347 (12)	0.0875 (17)	0.0521 (12)	0.0108 (11)	0.0093 (9)	-0.0123 (10)
O1W	0.0492 (8)	0.0222 (6)	0.0373 (7)	-0.0026 (5)	0.0095 (5)	0.0003 (4)

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

Mn1—O1W	2.1868 (14)	N5—C2	1.345 (2)
Mn1—O1W ⁱ	2.1868 (14)	N6—C2	1.329 (2)
Mn1—N1	2.2066 (13)	N6—C5	1.338 (3)
Mn1—N1 ⁱ	2.2066 (13)	C1—C2	1.464 (2)
Mn1—N5 ⁱ	2.2731 (15)	C3—C4	1.373 (3)
Mn1—N5	2.2731 (15)	C3—H3A	0.9300
N1—C1	1.335 (2)	C4—C5	1.370 (3)
N1—N2	1.3394 (18)	C4—H4A	0.9300
N2—N3	1.3181 (19)	C5—H5A	0.9300
N3—N4	1.349 (2)	O1W—H1WA	0.830 (9)
N4—C1	1.331 (2)	O1W—H1WB	0.844 (9)
N5—C3	1.335 (2)		
O1W—Mn1—O1W ⁱ	180.00 (5)	C3—N5—Mn1	128.04 (13)
O1W—Mn1—N1	89.47 (4)	C2—N5—Mn1	115.14 (11)
O1W ⁱ —Mn1—N1	90.53 (4)	C2—N6—C5	115.28 (18)
O1W—Mn1—N1 ⁱ	90.53 (4)	N4—C1—N1	111.16 (15)
O1W ⁱ —Mn1—N1 ⁱ	89.47 (4)	N4—C1—C2	127.15 (15)
N1—Mn1—N1 ⁱ	180.0	N1—C1—C2	121.67 (13)
O1W—Mn1—N5 ⁱ	90.24 (5)	N6—C2—N5	126.13 (16)
O1W ⁱ —Mn1—N5 ⁱ	89.76 (5)	N6—C2—C1	119.56 (15)
N1—Mn1—N5 ⁱ	105.25 (5)	N5—C2—C1	114.29 (14)
N1 ⁱ —Mn1—N5 ⁱ	74.75 (5)	N5—C3—C4	121.32 (19)
O1W—Mn1—N5	89.76 (5)	N5—C3—H3A	119.3
O1W ⁱ —Mn1—N5	90.24 (5)	C4—C3—H3A	119.3
N1—Mn1—N5	74.75 (5)	C5—C4—C3	117.3 (2)
N1 ⁱ —Mn1—N5	105.25 (5)	C5—C4—H4A	121.4

N5 ⁱ —Mn1—N5	180.0	C3—C4—H4A	121.4
C1—N1—N2	106.15 (13)	N6—C5—C4	123.15 (19)
C1—N1—Mn1	113.79 (10)	N6—C5—H5A	118.4
N2—N1—Mn1	140.00 (11)	C4—C5—H5A	118.4
N3—N2—N1	107.96 (14)	Mn1—O1W—H1WA	116.2 (15)
N2—N3—N4	110.30 (12)	Mn1—O1W—H1WB	115.5 (15)
C1—N4—N3	104.43 (13)	H1WA—O1W—H1WB	106 (2)
C3—N5—C2	116.81 (16)		
O1W—Mn1—N1—C1	-94.61 (11)	N3—N4—C1—C2	178.01 (14)
O1W ⁱ —Mn1—N1—C1	85.39 (11)	N2—N1—C1—N4	0.21 (17)
N5 ⁱ —Mn1—N1—C1	175.28 (10)	Mn1—N1—C1—N4	-177.47 (9)
N5—Mn1—N1—C1	-4.72 (10)	N2—N1—C1—C2	-178.20 (13)
O1W—Mn1—N1—N2	88.86 (16)	Mn1—N1—C1—C2	4.12 (18)
O1W ⁱ —Mn1—N1—N2	-91.14 (16)	C5—N6—C2—N5	1.0 (3)
N5 ⁱ —Mn1—N1—N2	-1.25 (16)	C5—N6—C2—C1	-177.15 (16)
N5—Mn1—N1—N2	178.75 (16)	C3—N5—C2—N6	-1.9 (2)
C1—N1—N2—N3	-0.03 (16)	Mn1—N5—C2—N6	176.97 (13)
Mn1—N1—N2—N3	176.67 (11)	C3—N5—C2—C1	176.30 (15)
N1—N2—N3—N4	-0.16 (18)	Mn1—N5—C2—C1	-4.78 (17)
N2—N3—N4—C1	0.28 (18)	N4—C1—C2—N6	0.7 (2)
O1W—Mn1—N5—C3	-86.51 (15)	N1—C1—C2—N6	178.89 (14)
O1W ⁱ —Mn1—N5—C3	93.49 (15)	N4—C1—C2—N5	-177.63 (14)
N1—Mn1—N5—C3	-176.02 (16)	N1—C1—C2—N5	0.5 (2)
N1 ⁱ —Mn1—N5—C3	3.98 (16)	C2—N5—C3—C4	1.0 (3)
O1W—Mn1—N5—C2	94.72 (11)	Mn1—N5—C3—C4	-177.80 (14)
O1W ⁱ —Mn1—N5—C2	-85.28 (11)	N5—C3—C4—C5	0.7 (3)
N1—Mn1—N5—C2	5.20 (11)	C2—N6—C5—C4	0.9 (3)
N1 ⁱ —Mn1—N5—C2	-174.80 (11)	C3—C4—C5—N6	-1.8 (3)
N3—N4—C1—N1	-0.30 (17)		

Symmetry codes: (i) $-x+1, -y+2, -z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<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>
O1W—H1WA \cdots N4 ⁱⁱ	0.830 (9)	1.943 (10)	2.7673 (18)	172 (2)
O1W—H1WB \cdots N3 ⁱⁱⁱ	0.844 (9)	1.978 (10)	2.8171 (17)	173 (2)

Symmetry codes: (ii) $-x+1, y-1/2, -z+1/2$; (iii) $x, -y+5/2, z+1/2$.

Fig. 1

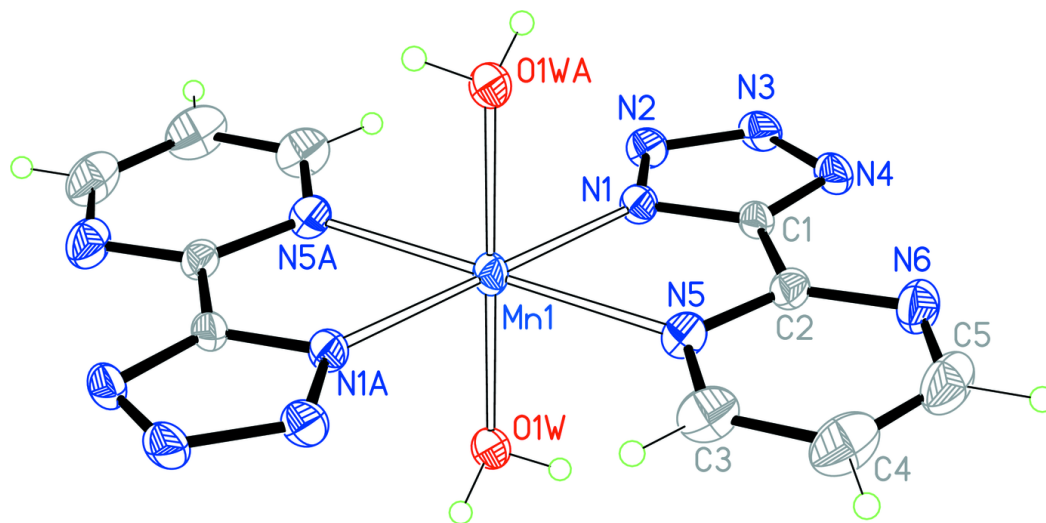


Fig. 2

