metal-organic compounds

Diaquabis(tetrazolo[1,5-a]pyridine-8-carboxylato-$\kappa^2 N^1$,O)manganese(II) dihydrate

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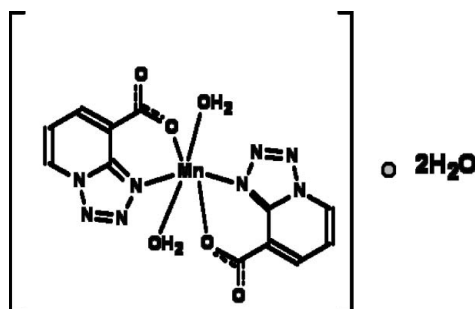Correspondence e-mail: jiande-zhao@163.com

In the title compound, $[\mathrm{Mn(C_6H_3N_4O_2)_2(H_2O)_2}]\cdot 2\mathrm{H_2O}$, the $\mathrm{Mn^{II}}$ atom is located on a twofold rotation axis and is octahedrally coordinated by the N and O atoms of the chelating tetrazolo[1,5-a]pyridine-8-carboxylate anions and the O atoms of two water molecules. Hydrogen bonds of the O—H⋯O and O—H⋯N types lead to the formation of layers parallel to (100).

Related literature

For background to coordination compounds, see: Kulynych & Shimizu (2002); Liu *et al.* (2001); Xue & Liu (2009).

Experimental

Crystal data

$[\mathrm{Mn(C_6H_3N_4O_2)_2(H_2O)_2}]\cdot 2\mathrm{H_2O}$
$M_r = 453.25$
Orthorhombic, $Pnna$
$a = 19.041$ (4) Å
$b = 11.694$ (2) Å
$c = 7.5371$ (15) Å
$V = 1678.3$ (6) Å³
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.85$ mm^{-1}
$T = 293$ K
$0.5 \times 0.5 \times 0.5$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.60$, $T_{max} = 0.662$
16422 measured reflections
1925 independent reflections
1755 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$
$S = 1.20$
1925 reflections
132 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H11⋯O2^i	0.85	1.93	2.7644 (17)	166
O1W—H12⋯O2W^{ii}	0.85	1.91	2.7538 (19)	171
O2W—H21⋯O1	0.89	1.95	2.8287 (18)	172
O2W—H22⋯N2^{iii}	0.76	2.25	3.003 (2)	169

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

Data collection: *SCXmini* (Rigaku, 2006); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2463).

References

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supporting information

Diaquabis(tetrazolo[1,5-*a*]pyridine-8-carboxylato-*κ²N¹*,O)manganese(II) dihydrate

Jian-De Zhao

S1. Comment

Coordination complexes have attracted great attention in recent years. (Kulynych & Shimizu, 2002). Polydentate ligand have some heteroatom can coordinated to metal in different ways, and can form Hydrogen bonds between to give supermolecule net(Liu *et al.*, 2001). The tetrazolo(1,5-*a*)pyridine-8-carboxylate have multi-coordinated position and may behavs as a polydentate ligand. The related maganese structure with two water molecules as solvent has been recently reported (Xue & Liu, 2009).

In the title compound, the manganese atom is located on a two fold axis and octahedrally coordinated by two water molecules and two bidentate N,O tetrazolo(1,5-*a*)pyridine-8-carboxylate,(Fig. 1).

Each tetrazolo(1,5-*a*) pyridine-8-carboxylate chelates to one manganese atom. One type of water coordinates to the manganese atom whereas the other acts as lattice water. A two dimensional supramolecular network parallel to the (1 0 0) plane, is formed by the hydrogen bond interactions between the water molecules and the nitrogen of the tetrazolo(1,5-*a*)pyridine-8-carboxylate ligands (Table 1, Fig. 2).
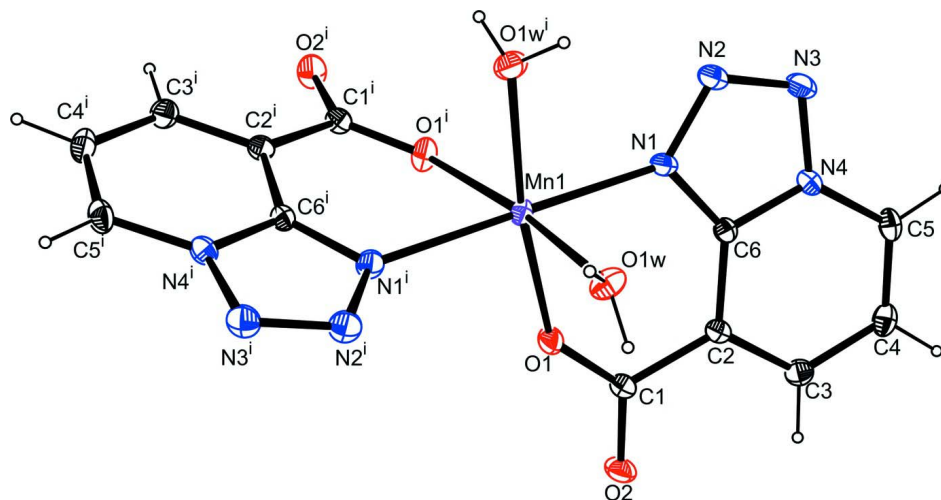
The structure is closely related to the dihydrate complex (Xue & Liu, 2009), the only difference being the occurence of two solvate water molecules in the previous structure.

S2. Experimental

A mixture of manganeset(II)nitrate and sodium azide (1 mmol), 2-chloronicotinic acid(0.5 mmol), in 10 ml of water was sealed in a Teflon-lined stainless-steel Parr bomb that was heated at 363 K for 48 h. Red crystals of the title complex were collected after the bomb was allowed to cool to room temperature.Yield 20% based on manganese(II). Caution: Azides may be explosive. Although we have met no problems in this work, only a small amount of them should be prepared and handled with great caution.

S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O-H= 0.85 (1)Å and H···H= 1.39 (2)Å) with $U_{iso}(H) = 1.5U_{eq}(O)$. In the last stage of refinement they were treated as riding on their parent O atoms.

Figure 1

A view of the title compound showing the coordination of Mn atom with the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level. H atoms and the solvate water molecule have been omitted for clarity. [Symmetry codes: (i) -x+1/2, -y, z]
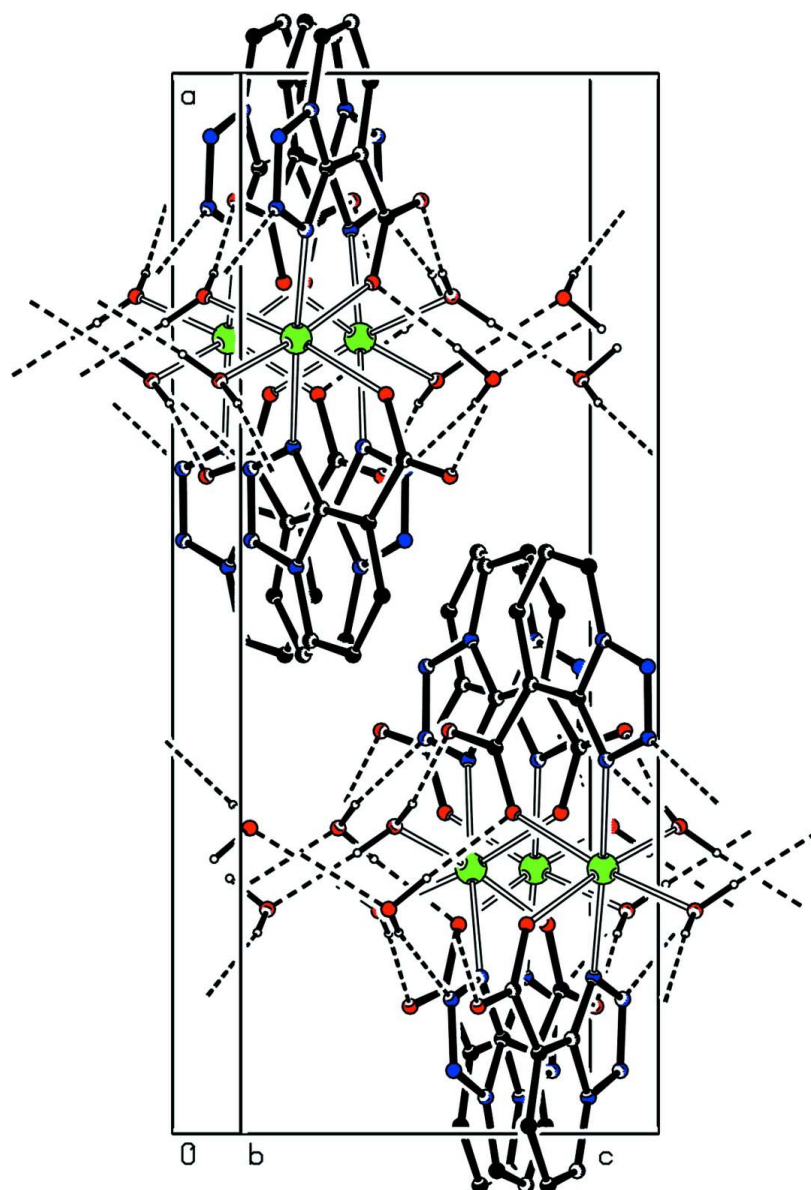
Figure 2
Partial packing view showing the formation of layers parallel to the (1 0 0) plane. H atoms not involved in hydrogen bondings have been omitted for clarity. H bonds are shown as dashed lines.

Diaquabis(tetrazolo[1,5-*a*]pyridine-8-carboxylato- *κ²N¹,O*)manganese(II) dihydrate

Crystal data

[Mn(C$_6$H$_3$N$_4$O$_2$)$_2$(H$_2$O)$_2$]·2H$_2$O	$F(000) = 924$
$M_r = 453.25$	$D_x = 1.794$ Mg m^{-3}
Orthorhombic, *Pnna*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2a 2bc	Cell parameters from 15650 reflections
$a = 19.041$ (4) Å	$\theta = 3.2–27.9°$
$b = 11.694$ (2) Å	$\mu = 0.85$ mm^{-1}
$c = 7.5371$ (15) Å	$T = 293$ K
$V = 1678.3$ (6) Å^3	Block, yellow
$Z = 4$	$0.5 \times 0.5 \times 0.5$ mm

Data collection

Rigaku SCXmini diffractometer	16422 measured reflections
Radiation source: fine-focus sealed tube	1925 independent reflections
Graphite monochromator	1755 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.029$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
	$h = -24 \rightarrow 24$
$T_{min} = 0.60$, $T_{max} = 0.662$	$k = -15 \rightarrow 15$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.032$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.081$	
$S = 1.20$	H-atom parameters constrained
1925 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.6168P]$
132 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.26$ e Å⁻³
	$\Delta\rho_{min} = -0.34$ e Å⁻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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Mn1	0.2500	0.0000	0.86700 (4)	0.01925 (12)
O1	0.19724 (6)	0.09901 (10)	0.66846 (16)	0.0263 (3)
O1W	0.21023 (6)	0.11467 (10)	1.06874 (17)	0.0294 (3)
H11	0.1888	0.1746	1.0359	0.044*
H12	0.2351	0.1270	1.1599	0.044*
O2	0.12016 (6)	0.21215 (10)	0.53402 (17)	0.0306 (3)
N1	0.14757 (7)	−0.09265 (11)	0.85974 (18)	0.0233 (3)
N2	0.12692 (8)	−0.18779 (12)	0.9450 (2)	0.0279 (3)
N3	0.05962 (8)	−0.20081 (12)	0.9411 (2)	0.0285 (3)
N4	0.03454 (7)	−0.10924 (11)	0.84998 (17)	0.0212 (3)
C1	0.13563 (9)	0.13028 (13)	0.6301 (2)	0.0201 (3)
C2	0.07619 (8)	0.05909 (13)	0.7039 (2)	0.0194 (3)
C3	0.00732 (9)	0.08539 (14)	0.6756 (2)	0.0244 (3)
H3	−0.0036	0.1528	0.6161	0.029*
C4	−0.04836 (9)	0.01396 (14)	0.7335 (2)	0.0276 (4)
H4	−0.0946	0.0355	0.7122	0.033*

C5	−0.03481 (9)	−0.08466 (15)	0.8190 (2)	0.0261 (4)	
H5	−0.0706	−0.1336	0.8551	0.031*	
C6	0.08933 (8)	−0.04294 (13)	0.7994 (2)	0.0185 (3)	
O2W	0.28824 (7)	0.12927 (11)	0.37555 (17)	0.0354 (3)	
H21	0.2590	0.1132	0.4635	0.053*	
H22	0.3103	0.1791	0.4079	0.053*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01548 (18)	0.02138 (19)	0.02089 (19)	0.00086 (12)	0.000	0.000
O1	0.0199 (6)	0.0302 (6)	0.0287 (6)	−0.0007 (5)	−0.0003 (5)	0.0108 (5)
O1W	0.0325 (7)	0.0280 (6)	0.0277 (6)	0.0091 (5)	−0.0033 (5)	−0.0048 (5)
O2	0.0297 (6)	0.0260 (6)	0.0362 (7)	−0.0035 (5)	−0.0053 (6)	0.0141 (5)
N1	0.0222 (7)	0.0181 (6)	0.0295 (7)	−0.0005 (5)	−0.0016 (5)	0.0066 (5)
N2	0.0295 (7)	0.0215 (7)	0.0326 (8)	−0.0017 (6)	0.0003 (6)	0.0083 (6)
N3	0.0312 (8)	0.0219 (7)	0.0324 (8)	−0.0038 (6)	0.0002 (6)	0.0079 (6)
N4	0.0215 (7)	0.0194 (6)	0.0226 (7)	−0.0044 (5)	0.0011 (5)	0.0018 (5)
C1	0.0230 (8)	0.0190 (7)	0.0185 (7)	−0.0021 (6)	−0.0002 (6)	0.0016 (6)
C2	0.0224 (8)	0.0175 (7)	0.0183 (7)	−0.0011 (6)	0.0004 (6)	0.0007 (6)
C3	0.0248 (8)	0.0245 (8)	0.0239 (8)	0.0018 (6)	−0.0025 (6)	0.0016 (6)
C4	0.0171 (7)	0.0369 (9)	0.0289 (9)	0.0015 (7)	−0.0009 (7)	−0.0018 (7)
C5	0.0178 (8)	0.0326 (9)	0.0279 (8)	−0.0068 (7)	0.0027 (7)	−0.0021 (7)
C6	0.0177 (7)	0.0187 (7)	0.0190 (7)	−0.0023 (6)	0.0001 (6)	−0.0003 (6)
O2W	0.0383 (8)	0.0386 (7)	0.0293 (7)	−0.0081 (6)	0.0032 (5)	−0.0043 (5)

Geometric parameters (Å, º)

Mn1—O1	2.1422 (12)	N3—N4	1.3588 (19)
Mn1—O1i	2.1422 (12)	N4—C6	1.3546 (19)
Mn1—O1W	2.1642 (12)	N4—C5	1.372 (2)
Mn1—O1Wi	2.1642 (12)	C1—C2	1.511 (2)
Mn1—N1	2.2317 (14)	C2—C3	1.364 (2)
Mn1—N1i	2.2317 (14)	C2—C6	1.416 (2)
O1—C1	1.262 (2)	C3—C4	1.418 (2)
O1W—H11	0.8477	C3—H3	0.9300
O1W—H12	0.8471	C4—C5	1.346 (2)
O2—C1	1.2362 (19)	C4—H4	0.9300
N1—C6	1.332 (2)	C5—H5	0.9300
N1—N2	1.3438 (19)	O2W—H21	0.8853
N2—N3	1.291 (2)	O2W—H22	0.7585
O1—Mn1—O1i	91.38 (7)	N2—N3—N4	105.51 (12)
O1—Mn1—O1W	89.53 (5)	C6—N4—N3	108.82 (13)
O1i—Mn1—O1W	171.80 (5)	C6—N4—C5	125.01 (14)
O1—Mn1—O1Wi	171.80 (5)	N3—N4—C5	126.13 (14)
O1i—Mn1—O1Wi	89.53 (5)	O2—C1—O1	125.44 (15)
O1W—Mn1—O1Wi	90.73 (7)	O2—C1—C2	117.64 (14)

O1—Mn1—N1	80.53 (5)	O1—C1—C2	116.89 (13)
O1ⁱ—Mn1—N1	97.49 (5)	C3—C2—C6	116.08 (14)
O1W—Mn1—N1	90.70 (5)	C3—C2—C1	122.57 (14)
O1Wⁱ—Mn1—N1	91.27 (5)	C6—C2—C1	121.27 (14)
O1—Mn1—N1ⁱ	97.49 (5)	C2—C3—C4	122.53 (15)
O1ⁱ—Mn1—N1ⁱ	80.53 (5)	C2—C3—H3	118.7
O1W—Mn1—N1ⁱ	91.27 (5)	C4—C3—H3	118.7
O1Wⁱ—Mn1—N1ⁱ	90.70 (5)	C5—C4—C3	120.56 (16)
N1—Mn1—N1ⁱ	177.19 (7)	C5—C4—H4	119.7
C1—O1—Mn1	138.78 (10)	C3—C4—H4	119.7
Mn1—O1W—H11	118.4	C4—C5—N4	116.47 (15)
Mn1—O1W—H12	118.7	C4—C5—H5	121.8
H11—O1W—H12	111.4	N4—C5—H5	121.8
C6—N1—N2	106.31 (13)	N1—C6—N4	107.18 (13)
C6—N1—Mn1	121.61 (10)	N1—C6—C2	133.50 (14)
N2—N1—Mn1	130.24 (11)	N4—C6—C2	119.29 (14)
N3—N2—N1	112.16 (13)	H21—O2W—H22	105.7

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H11···O2ⁱⁱ	0.85	1.93	2.7644 (17)	166
O1*W*—H12···O2*W*ⁱⁱⁱ	0.85	1.91	2.7538 (19)	171
O2*W*—H21···O1	0.89	1.95	2.8287 (18)	172
O2*W*—H22···N2ⁱᵛ	0.76	2.25	3.003 (2)	169

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