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Hexaaquamanganese(II) bis[5-(4-nitrophenyl)tetrazolate]

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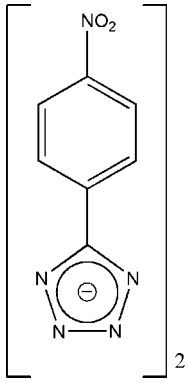
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.100; data-to-parameter ratio = 15.8.

The title compound, $[Mn(H_2O)_6](C_7H_4N_5O_2)_2$, was obtained by the *in situ* hydrothermal reaction of $MnCl_2$ with 4-nitrobenzonitrile in the presence of NaN_3. The Mn atoms are located on inversion centres. The structure comprises hydrogen-bonded sheets of deprotonated 5-(4-nitrophenyl)tetrazole anions and hexaaquamanganese(II) cations.

Related literature

For the chemistry of tetrazole, see: Arp *et al.* (2000); Dunica *et al.* (1991); Wang *et al.* (2005); Wittenberger & Donner (1993).



$[Mn(H_2O)_6]^{2+}$

Experimental

Crystal data

$[Mn(H_2O)_6](C_7H_4N_5O_2)_2$
M_r = 543.34
Monoclinic, $P2_1/c$
a = 7.954 (7) Å
b = 10.317 (8) Å
c = 13.537 (11) Å
β = 97.157 (16)°
V = 1102.2 (15) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.67 mm^{-1}
T = 293 (2) K
0.35 × 0.19 × 0.19 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.837, T_{max} = 1.000
(expected range = 0.736–0.880)
10660 measured reflections
2520 independent reflections
2221 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.100
S = 1.08
2520 reflections
160 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···N3^{i}	0.86	1.98	2.825 (2)	166
O3—H3B···N1^{ii}	0.81	2.02	2.819 (3)	170
O4—H4A···O2^{iii}	0.80	2.24	3.000 (3)	158
O4—H4B···O1^{iv}	0.79	2.07	2.822 (3)	159
O5—H5A···N2^{v}	0.86	1.96	2.789 (3)	161
O5—H5B···N4^{vi}	0.82	1.96	2.777 (3)	170

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

This work was supported by a Start-up Grant from Southeast University to Professor Ren-Gen Xiong.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2527).

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supplementary materials

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Hexaaquamanganese(II) bis[5-(4-nitrophenyl)tetrazolate]

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Comment

The tetrazole functional group has found a wide range of applications in coordination chemistry as ligands, in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group, and in materials science as high density energy materials (Wang *et al.*,2005; Dunica *et al.*, 1991; Wittenberger *et al.*, 1993). We report here the crystal structure of the title compound, hexa-aqua-manganese(II) bis-5-(4-nitrophenyl)tetrazolate.

The bond distances and angles of tetrazole ring are comparable to those found in other tetrazole-containing compounds (Wang *et al.*, 2005; Arp *et al.*, 2000). The Mn^{2+} ions are octahedronally coordinated by six water molecules. For the four of the six water molecules, each of them donates one hydrogen bond; For the other two water molecules, each of them donates two hydrogen bonds. As shown in Fig. 2, the anion and aqua-cations are contacted by H-bonds between O atoms from the coordinated water molecules and the N atoms from tetrazole groups or O atoms from nitro groups.

Experimental

A mixture of 4-nitrobenzonitrile (30 mg, 0.2 mmol), NaN_3 (26 mg, 0.4 mmol), $MnCl_2?4H_2O$(59.3 mg, 0.3 mmol) ethanol (1 ml) and a few drops of water sealed in a glass tube was maintained at 120 °C. Pale-yellow block crystals suitable for X-ray analysis were obtained after 3 days.

Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C, O atoms to which they are bonded, with U_{iso}(H) = 1.2Ueq(C) or U_{iso}(H) = 1.5Ueq(O). The structure shows a pseudo-A centring, but refinement in space group C2/m results in disorder of the water molecules and significantly worse figures of merit.

Figures

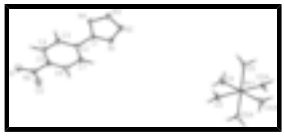

Fig. 1. A view of the asymmetric unit time-of-flight he title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level. Atoms labelled with suffix A are generated by the symmetry operator $-x + 1, -y, -z + 2$.

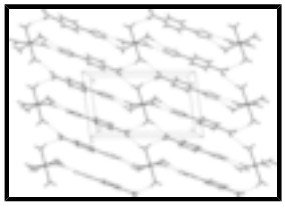

Fig. 2. The crystal packing of the title compound viewed along the *b* axis. The dashed lines show O—H···N,*O*—H···O Hydrogen bonds presented in Table 2.

Hexaaquamanganese(II) bis[5-(4-nitrophenyl)tetrazolate]

Crystal data

$[Mn(H_2O)_6](C_7H_4N_5O_2)_2$	$F_{000} = 558$
$M_r = 543.34$	$D_x = 1.637$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2744 reflections
$a = 7.954$ (7) Å	$\theta = 3.0$–27.5º
$b = 10.317$ (8) Å	$\mu = 0.67$ mm^{-1}
$c = 13.537$ (11) Å	$T = 293$ (2) K
$\beta = 97.157$ (16)º	Block, yellow
$V = 1102.2$ (15) Å^3	0.35 × 0.19 × 0.19 mm
$Z = 2$	

Data collection

Rigaku Mercury2 (2x2 bin mode) diffractometer	2221 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.028$
Monochromator: graphite	$\theta_{max} = 27.5$º
$T = 293$(2) K	$\theta_{min} = 3.0$º
ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	$k = -13 \rightarrow 13$
$T_{min} = 0.837$, $T_{max} = 1.000$	$l = -17 \rightarrow 17$
10660 measured reflections	Standard reflections: ?
2520 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.2401P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
2520 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Mn1	0.5000	0.0000	1.0000	0.03147 (14)
C1	0.6929 (2)	0.99094 (13)	0.58668 (13)	0.0292 (3)
C2	0.7548 (2)	0.99156 (14)	0.48888 (12)	0.0291 (3)
C3	0.7496 (2)	1.10551 (16)	0.43314 (12)	0.0384 (4)
H3	0.7045	1.1805	0.4575	0.046*
C4	0.8109 (2)	1.10797 (18)	0.34188 (13)	0.0412 (4)
H4	0.8075	1.1837	0.3044	0.049*
C5	0.8771 (2)	0.99548 (15)	0.30807 (13)	0.0356 (4)
C6	0.8825 (2)	0.88029 (18)	0.36036 (13)	0.0410 (4)
H6	0.9265	0.8056	0.3350	0.049*
C7	0.8207 (2)	0.87909 (17)	0.45139 (13)	0.0382 (4)
H7	0.8231	0.8026	0.4879	0.046*
N1	0.68587 (19)	0.88555 (13)	0.64346 (10)	0.0369 (3)
N2	0.6243 (2)	0.92766 (15)	0.72523 (11)	0.0403 (3)
N3	0.5957 (2)	1.05356 (15)	0.71783 (11)	0.0407 (3)
N4	0.6378 (2)	1.09577 (13)	0.63085 (10)	0.0379 (3)
N5	0.9448 (2)	0.99757 (15)	0.21236 (12)	0.0438 (4)
O1	0.9327 (2)	1.09802 (15)	0.16354 (10)	0.0587 (4)
O2	1.0104 (2)	0.89956 (17)	0.18422 (12)	0.0674 (5)
O3	0.40897 (18)	0.12248 (12)	0.87429 (8)	0.0444 (3)
H3A	0.4620	0.1146	0.8226	0.067*
H3B	0.3742	0.1959	0.8741	0.067*
O4	0.76411 (19)	0.04297 (18)	0.97221 (10)	0.0613 (4)
H4A	0.8060	0.0456	0.9213	0.092*
H4B	0.8321	0.0589	1.0179	0.092*
O5	0.50240 (19)	0.15689 (12)	1.10283 (9)	0.0491 (4)
H5A	0.4586	0.1494	1.1575	0.074*
H5B	0.5529	0.2268	1.1089	0.074*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

Mn1	0.0456 (2)	0.0249 (2)	0.0255 (2)	0.00061 (13)	0.01037 (15)	−0.00051 (11)
C1	0.0320 (7)	0.0256 (7)	0.0312 (8)	−0.0010 (6)	0.0091 (6)	0.0005 (5)
C2	0.0302 (8)	0.0303 (8)	0.0280 (8)	−0.0028 (6)	0.0078 (6)	−0.0005 (5)
C3	0.0516 (10)	0.0296 (8)	0.0357 (8)	0.0016 (7)	0.0128 (7)	0.0011 (7)
C4	0.0540 (11)	0.0374 (9)	0.0340 (8)	−0.0028 (8)	0.0123 (8)	0.0048 (7)
C5	0.0358 (8)	0.0438 (10)	0.0286 (8)	−0.0049 (7)	0.0097 (7)	−0.0006 (6)
C6	0.0478 (10)	0.0386 (9)	0.0398 (9)	0.0060 (8)	0.0178 (8)	−0.0021 (7)
C7	0.0462 (9)	0.0311 (8)	0.0403 (9)	0.0036 (7)	0.0171 (7)	0.0032 (7)
N1	0.0502 (8)	0.0283 (7)	0.0354 (7)	0.0000 (6)	0.0181 (6)	0.0015 (6)
N2	0.0539 (9)	0.0344 (7)	0.0362 (7)	−0.0010 (6)	0.0201 (7)	0.0008 (6)
N3	0.0580 (9)	0.0329 (8)	0.0348 (7)	0.0022 (7)	0.0197 (7)	−0.0005 (6)
N4	0.0538 (9)	0.0285 (7)	0.0348 (7)	0.0027 (6)	0.0187 (6)	0.0007 (6)
N5	0.0432 (8)	0.0585 (11)	0.0316 (8)	−0.0076 (7)	0.0127 (7)	−0.0011 (6)
O1	0.0856 (11)	0.0572 (9)	0.0361 (7)	−0.0196 (8)	0.0189 (7)	0.0041 (6)
O2	0.0802 (11)	0.0769 (11)	0.0526 (8)	0.0189 (9)	0.0384 (8)	0.0027 (8)
O3	0.0717 (9)	0.0328 (6)	0.0318 (6)	0.0164 (6)	0.0184 (6)	0.0065 (5)
O4	0.0510 (8)	0.1000 (12)	0.0361 (7)	−0.0124 (8)	0.0177 (6)	−0.0016 (8)
O5	0.0874 (10)	0.0281 (6)	0.0373 (7)	−0.0124 (6)	0.0294 (7)	−0.0083 (5)

Geometric parameters (Å, °)

Mn1—O5	2.1334 (17)	C5—N5	1.464 (2)
Mn1—O5^{i}	2.1334 (17)	C6—C7	1.382 (2)
Mn1—O3^{i}	2.1702 (17)	C6—H6	0.9300
Mn1—O3	2.1702 (17)	C7—H7	0.9300
Mn1—O4^{i}	2.225 (2)	N1—N2	1.338 (2)
Mn1—O4	2.225 (2)	N2—N3	1.320 (3)
C1—N4	1.336 (2)	N3—N4	1.336 (2)
C1—N1	1.337 (2)	N5—O2	1.221 (2)
C1—C2	1.469 (2)	N5—O1	1.226 (2)
C2—C7	1.395 (2)	O3—H3A	0.8644
C2—C3	1.395 (2)	O3—H3B	0.8067
C3—C4	1.384 (2)	O4—H4A	0.8020
C3—H3	0.9300	O4—H4B	0.7867
C4—C5	1.376 (3)	O5—H5A	0.8599
C4—H4	0.9300	O5—H5B	0.8245
C5—C6	1.381 (3)		
O5—Mn1—O5^{i}	180.0	C3—C4—H4	120.9
O5—Mn1—O3^{i}	87.43 (8)	C4—C5—C6	122.95 (17)
O5^{i}—Mn1—O3^{i}	92.57 (8)	C4—C5—N5	118.70 (15)
O5—Mn1—O3	92.57 (8)	C6—C5—N5	118.35 (15)
O5^{i}—Mn1—O3	87.43 (8)	C5—C6—C7	118.21 (16)
O3^{i}—Mn1—O3	180.0	C5—C6—H6	120.9
O5—Mn1—O4^{i}	88.44 (6)	C7—C6—H6	120.9
O5^{i}—Mn1—O4^{i}	91.56 (6)	C6—C7—C2	120.55 (16)
O3^{i}—Mn1—O4^{i}	88.92 (7)	C6—C7—H7	119.7

O3—Mn1—O4^{i}	91.08 (7)	C2—C7—H7	119.7
O5—Mn1—O4	91.56 (6)	C1—N1—N2	104.92 (14)
O5^{i}—Mn1—O4	88.44 (6)	N3—N2—N1	109.52 (13)
O3^{i}—Mn1—O4	91.08 (7)	N2—N3—N4	109.13 (12)
O3—Mn1—O4	88.92 (7)	C1—N4—N3	105.23 (14)
O4^{i}—Mn1—O4	180.00 (7)	O2—N5—O1	122.65 (18)
N4—C1—N1	111.20 (16)	O2—N5—C5	118.88 (15)
N4—C1—C2	124.43 (13)	O1—N5—C5	118.47 (16)
N1—C1—C2	124.36 (14)	Mn1—O3—H3A	115.5
C7—C2—C3	119.45 (16)	Mn1—O3—H3B	129.1
C7—C2—C1	120.52 (14)	H3A—O3—H3B	106.7
C3—C2—C1	120.03 (14)	Mn1—O4—H4A	130.8
C4—C3—C2	120.55 (16)	Mn1—O4—H4B	118.6
C4—C3—H3	119.7	H4A—O4—H4B	110.5
C2—C3—H3	119.7	Mn1—O5—H5A	121.5
C5—C4—C3	118.27 (16)	Mn1—O5—H5B	133.8
C5—C4—H4	120.9	H5A—O5—H5B	103.8

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···N3^{ii}	0.86	1.98	2.825 (2)	166
O3—H3B···N1^{iii}	0.81	2.02	2.819 (3)	170
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O5—H5A···N2^{vi}	0.86	1.96	2.789 (3)	161
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Symmetry codes: (ii) *x*, *y*−1, *z*; (iii) −*x*+1, *y*−1/2, −*z*+3/2; (iv) −*x*+2, −*y*+1, −*z*+1; (v) *x*, *y*−1, *z*+1; (vi) −*x*+1, −*y*+1, −*z*+2; (vii) *x*, −*y*+3/2, *z*+1/2.

Fig. 1

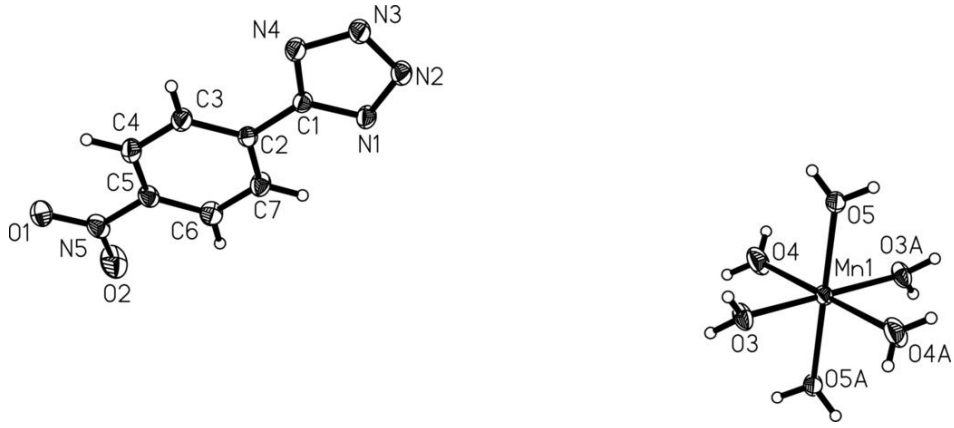

Fig. 2