

Hexaaquamanganese(II) tetraaquabis(2-aminopyrazine- κN^4)manganese(II) disulfate dihydrate

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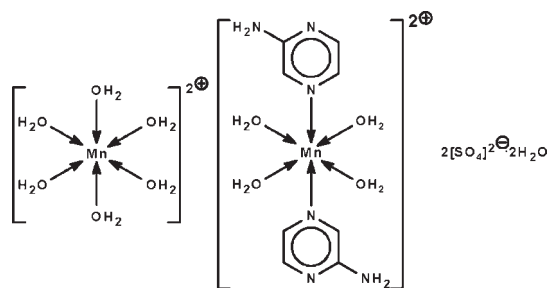
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.041; wR factor = 0.129; data-to-parameter ratio = 13.7.

The reaction of manganese(II) sulfate and 2-aminopyrazine affords the title salt, $[Mn(H_2O)_6][Mn(C_4H_5N_3)_2(H_2O)_4](SO_4)_2 \cdot 2H_2O$. The metal atoms in the tetraqua-coordinated and hexaaqua-coordinated cations lie on centers of inversion in octahedral geometries. The cations, anions and solvent water molecules are linked by $O-H \cdots O$, $N-H \cdots O$ and $O-H \cdots N$ hydrogen bonds into a three-dimensional network.

Related literature

For the isostructural cobalt(II) analog, see: Kang *et al.* (2009).



Experimental

Crystal data

$[Mn(H_2O)_6][Mn(C_4H_5N_3)_2(H_2O)_4](SO_4)_2 \cdot 2H_2O$
 $M_r = 708.43$
 Triclinic, $P\bar{1}$
 $a = 6.6242$ (3) Å
 $b = 8.4639$ (4) Å
 $c = 13.2719$ (8) Å
 $\alpha = 75.654$ (2)°
 $\beta = 78.364$ (2)°
 $\gamma = 78.834$ (2)°
 $V = 697.95$ (6) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.14$ mm⁻¹
 $T = 293$ K
 $0.38 \times 0.20 \times 0.18$ mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
 Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
 $T_{min} = 0.670$, $T_{max} = 0.821$
 6866 measured reflections
 3159 independent reflections
 2874 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.129$
 $S = 1.15$
 3159 reflections
 231 parameters
 14 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.74$ e Å⁻³
 $\Delta\rho_{min} = -0.40$ e Å⁻³

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1w—H1w1···O1	0.84 (1)	1.95 (2)	2.779 (3)	167 (4)
O1w—H1w2···N2 ⁱ	0.85 (1)	1.94 (1)	2.792 (3)	176 (5)
O2w—H2w1···O3	0.85 (1)	1.95 (1)	2.775 (3)	166 (4)
O2w—H2w2···O1 ⁱⁱ	0.85 (1)	1.92 (1)	2.770 (3)	172 (4)
O3w—H3w1···O2	0.85 (1)	1.90 (1)	2.744 (4)	170 (5)
O3w—H3w2···O6w	0.85 (1)	1.88 (1)	2.728 (4)	175 (4)
O4w—H4w1···O6w ⁱⁱⁱ	0.85 (1)	1.96 (2)	2.780 (4)	162 (5)
O4w—H4w2···O2 ⁱⁱⁱ	0.85 (1)	1.92 (2)	2.744 (4)	164 (5)
O5w—H5w1···O3 ^{iv}	0.84 (1)	2.00 (2)	2.813 (3)	159 (5)
O5w—H5w2···O4 ^v	0.85 (1)	1.88 (1)	2.726 (4)	177 (6)
O6w—H6w1···O3 ⁱ	0.85 (1)	1.95 (2)	2.783 (3)	167 (6)
O6w—H6w2···O4 ^{iv}	0.85 (1)	1.87 (1)	2.709 (4)	172 (6)
N3—H3n2···O1 ^{vi}	0.85 (1)	2.18 (1)	3.026 (4)	172 (5)

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalClear* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2658).

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supplementary materials

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Hexaaquamanganese(II) tetraaquabis(2-aminopyrazine- κN^4)manganese(II) disulfate dihydrate

L.-H. Huo, S. Gao and S. W. Ng

Experimental

To an aqueous solution of 3-aminopyrazine (0.19 g, 2 mmol) was added manganese(II) sulfate tetrahydrate (0.45 g, 2 mmol). Colorless crystals of the salt separated from the solution after a few days. CH&N elemental analysis. Calc. for $C_8H_{34}N_6O_{20}S_2Mn_2$: C 13.56, H 4.84, N 11.86%; found: C 13.52, H 4.80, N 11.85%.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.93 Å) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U(C)$. The amino and water H-atoms were located in a difference Fourier map, and were refined with a distance restraint of N—H = O—H = 0.85 ± 0.01 Å; their temperature factors were refined.

Figures

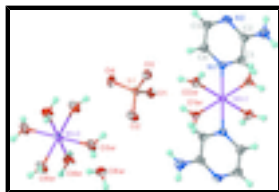


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $[Mn(H_2O)_6][Mn(H_2O)_4(C_4H_5N_3)_2]2[SO_4]2 \cdot 2H_2O$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

Hexaaquamanganese(II) tetraaquabis(2-aminopyrazine- κN^4)manganese(II) disulfate dihydrate

Crystal data

$[Mn(H_2O)_6][Mn(C_4H_5N_3)_2(H_2O)_4](SO_4)_2 \cdot 2H_2O$	$Z = 1$
$M_r = 708.43$	$F_{000} = 366$
Triclinic, $P\bar{1}$	$D_x = 1.685 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 6.6242 (3) \text{ \AA}$	Cell parameters from 6492 reflections
$b = 8.4639 (4) \text{ \AA}$	$\theta = 3.2\text{--}27.5^\circ$
$c = 13.2719 (8) \text{ \AA}$	$\mu = 1.14 \text{ mm}^{-1}$
$\alpha = 75.654 (2)^\circ$	$T = 293 \text{ K}$
$\beta = 78.364 (2)^\circ$	Prism, colorless
$\gamma = 78.834 (2)^\circ$	$0.38 \times 0.20 \times 0.18 \text{ mm}$
$V = 697.95 (6) \text{ \AA}^3$	

supplementary materials

Data collection

Rigaku R-Axis RAPID IP diffractometer	3159 independent reflections
Radiation source: fine-focus sealed tube	2874 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.025$
$T = 293$ K	$\theta_{\text{max}} = 27.5^\circ$
ω scans	$\theta_{\text{min}} = 3.2^\circ$
Absorption correction: Multi-scan (ABSCOR; Higashi, 1995)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.670$, $T_{\text{max}} = 0.821$	$k = -10 \rightarrow 10$
6866 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.129$	$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 1.1503P]$
$S = 1.15$	where $P = (F_o^2 + 2F_c^2)/3$
3159 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
231 parameters	$\Delta\rho_{\text{max}} = 0.74 \text{ e } \text{\AA}^{-3}$
14 restraints	$\Delta\rho_{\text{min}} = -0.40 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	1.0000	1.0000	0.5000	0.02349 (17)
Mn2	0.0000	0.5000	1.0000	0.02867 (18)
S1	0.47994 (10)	0.88750 (9)	0.80279 (5)	0.02457 (18)
O1	0.4091 (3)	0.9828 (3)	0.70435 (17)	0.0322 (5)
O2	0.5386 (4)	0.7129 (3)	0.7978 (2)	0.0444 (6)
O3	0.6644 (3)	0.9501 (3)	0.81657 (17)	0.0318 (5)
O4	0.3121 (4)	0.9084 (4)	0.89137 (19)	0.0441 (6)
O1W	0.7084 (4)	0.9110 (3)	0.53580 (19)	0.0335 (5)
O2W	1.0209 (4)	0.9617 (3)	0.66525 (17)	0.0345 (5)
O3W	0.2937 (4)	0.4732 (3)	0.8939 (2)	0.0471 (7)
O4W	-0.1480 (4)	0.4748 (3)	0.8707 (2)	0.0429 (6)
O5W	0.0400 (4)	0.2353 (3)	1.0577 (2)	0.0456 (6)
O6W	0.6189 (4)	0.2200 (3)	0.9081 (2)	0.0399 (6)
N1	0.8363 (4)	1.2689 (3)	0.4980 (2)	0.0301 (5)
N2	0.7098 (4)	1.6040 (3)	0.4930 (2)	0.0344 (6)

N3	0.7810 (6)	1.6587 (4)	0.3104 (3)	0.0482 (8)
C1	0.8414 (5)	1.3800 (4)	0.4078 (3)	0.0334 (7)
H1	0.8899	1.3447	0.3450	0.040*
C2	0.7760 (5)	1.5496 (4)	0.4039 (3)	0.0325 (6)
C3	0.7019 (5)	1.4892 (4)	0.5836 (3)	0.0376 (7)
H3	0.6532	1.5237	0.6466	0.045*
C4	0.7623 (5)	1.3238 (4)	0.5874 (3)	0.0348 (7)
H4	0.7522	1.2491	0.6521	0.042*
H1W1	0.614 (5)	0.948 (5)	0.581 (3)	0.048 (12)*
H1W2	0.715 (7)	0.817 (3)	0.521 (4)	0.053 (13)*
H2W1	0.919 (4)	0.972 (5)	0.714 (2)	0.028 (9)*
H2W2	1.135 (4)	0.967 (5)	0.683 (3)	0.044 (11)*
H3W1	0.357 (7)	0.556 (4)	0.866 (4)	0.066 (15)*
H3W2	0.391 (5)	0.392 (3)	0.901 (3)	0.039 (11)*
H4W1	-0.195 (8)	0.386 (4)	0.876 (4)	0.073 (17)*
H4W2	-0.247 (5)	0.554 (4)	0.859 (4)	0.063 (15)*
H5W1	0.126 (6)	0.160 (4)	1.089 (3)	0.059 (14)*
H5W2	-0.072 (5)	0.194 (7)	1.074 (5)	0.081 (18)*
H6W1	0.624 (9)	0.148 (5)	0.873 (4)	0.079 (18)*
H6W2	0.641 (9)	0.170 (6)	0.9698 (19)	0.072 (17)*
H3N1	0.831 (7)	1.629 (6)	0.252 (2)	0.062 (15)*
H3N2	0.738 (8)	1.7613 (19)	0.308 (4)	0.060 (14)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0217 (3)	0.0225 (3)	0.0255 (3)	-0.0022 (2)	-0.0054 (2)	-0.0034 (2)
Mn2	0.0218 (3)	0.0271 (3)	0.0341 (3)	-0.0032 (2)	-0.0067 (2)	0.0002 (2)
S1	0.0209 (3)	0.0257 (3)	0.0260 (3)	-0.0046 (3)	-0.0066 (2)	-0.0004 (3)
O1	0.0289 (11)	0.0353 (12)	0.0302 (11)	-0.0007 (9)	-0.0115 (9)	-0.0009 (9)
O2	0.0423 (14)	0.0252 (11)	0.0645 (17)	-0.0035 (10)	-0.0175 (12)	-0.0014 (11)
O3	0.0224 (10)	0.0385 (12)	0.0356 (11)	-0.0062 (9)	-0.0079 (8)	-0.0062 (9)
O4	0.0313 (12)	0.0672 (17)	0.0317 (12)	-0.0132 (12)	0.0012 (10)	-0.0078 (11)
O1W	0.0277 (11)	0.0325 (12)	0.0423 (13)	-0.0092 (9)	0.0038 (9)	-0.0157 (10)
O2W	0.0258 (11)	0.0521 (14)	0.0264 (10)	-0.0058 (10)	-0.0080 (9)	-0.0068 (10)
O3W	0.0281 (12)	0.0356 (14)	0.0671 (18)	-0.0064 (11)	0.0055 (12)	-0.0012 (12)
O4W	0.0395 (14)	0.0380 (14)	0.0542 (15)	-0.0039 (11)	-0.0212 (12)	-0.0059 (12)
O5W	0.0318 (13)	0.0320 (12)	0.0679 (17)	-0.0074 (10)	-0.0194 (12)	0.0096 (12)
O6W	0.0477 (14)	0.0317 (12)	0.0413 (14)	-0.0016 (11)	-0.0131 (11)	-0.0086 (10)
N1	0.0269 (12)	0.0226 (12)	0.0390 (14)	-0.0011 (10)	-0.0063 (10)	-0.0044 (10)
N2	0.0293 (13)	0.0255 (12)	0.0498 (16)	-0.0013 (10)	-0.0095 (12)	-0.0109 (11)
N3	0.063 (2)	0.0285 (15)	0.0451 (18)	0.0031 (15)	-0.0061 (16)	-0.0039 (13)
C1	0.0347 (16)	0.0256 (15)	0.0380 (16)	0.0001 (12)	-0.0061 (13)	-0.0069 (12)
C2	0.0289 (15)	0.0238 (14)	0.0435 (17)	-0.0014 (12)	-0.0071 (13)	-0.0060 (12)
C3	0.0337 (16)	0.0391 (18)	0.0425 (18)	0.0019 (14)	-0.0073 (14)	-0.0182 (14)
C4	0.0318 (16)	0.0335 (16)	0.0352 (16)	0.0037 (13)	-0.0075 (13)	-0.0051 (13)

supplementary materials

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

Mn1—O1W	2.131 (2)	O3W—H3W1	0.849 (10)
Mn1—O1W ⁱ	2.131 (2)	O3W—H3W2	0.849 (10)
Mn1—O2W ⁱ	2.165 (2)	O4W—H4W1	0.848 (10)
Mn1—O2W	2.165 (2)	O4W—H4W2	0.850 (10)
Mn1—N1	2.320 (2)	O5W—H5W1	0.849 (10)
Mn1—N1 ⁱ	2.320 (2)	O5W—H5W2	0.850 (10)
Mn2—O3W	2.168 (3)	O6W—H6W1	0.850 (10)
Mn2—O3W ⁱⁱ	2.168 (3)	O6W—H6W2	0.850 (10)
Mn2—O4W	2.212 (3)	N1—C1	1.325 (4)
Mn2—O4W ⁱⁱ	2.212 (3)	N1—C4	1.347 (4)
Mn2—O5W ⁱⁱ	2.163 (2)	N2—C2	1.337 (4)
Mn2—O5W	2.163 (2)	N2—C3	1.344 (5)
S1—O4	1.466 (2)	N3—C2	1.350 (5)
S1—O2	1.468 (3)	N3—H3N1	0.855 (10)
S1—O1	1.468 (2)	N3—H3N2	0.854 (10)
S1—O3	1.482 (2)	C1—C2	1.408 (4)
O1W—H1W1	0.844 (10)	C1—H1	0.9300
O1W—H1W2	0.851 (10)	C3—C4	1.371 (5)
O2W—H2W1	0.846 (10)	C3—H3	0.9300
O2W—H2W2	0.852 (10)	C4—H4	0.9300
O1W—Mn1—O1W ⁱ	180.000 (1)	Mn1—O1W—H1W1	118 (3)
O1W—Mn1—O2W ⁱ	87.90 (9)	Mn1—O1W—H1W2	114 (3)
O1W ⁱ —Mn1—O2W ⁱ	92.10 (9)	H1W1—O1W—H1W2	123 (4)
O1W—Mn1—O2W	92.10 (9)	Mn1—O2W—H2W1	125 (3)
O1W ⁱ —Mn1—O2W	87.90 (9)	Mn1—O2W—H2W2	120 (3)
O2W ⁱ —Mn1—O2W	180.000 (1)	H2W1—O2W—H2W2	112 (4)
O1W—Mn1—N1	91.71 (9)	Mn2—O3W—H3W1	120 (4)
O1W ⁱ —Mn1—N1	88.29 (9)	Mn2—O3W—H3W2	126 (3)
O2W ⁱ —Mn1—N1	89.32 (10)	H3W1—O3W—H3W2	104 (4)
O2W—Mn1—N1	90.68 (10)	Mn2—O4W—H4W1	119 (4)
O1W—Mn1—N1 ⁱ	88.29 (9)	Mn2—O4W—H4W2	110 (3)
O1W ⁱ —Mn1—N1 ⁱ	91.71 (9)	H4W1—O4W—H4W2	107 (5)
O2W ⁱ —Mn1—N1 ⁱ	90.68 (10)	Mn2—O5W—H5W1	139 (3)
O2W—Mn1—N1 ⁱ	89.32 (10)	Mn2—O5W—H5W2	115 (4)
N1—Mn1—N1 ⁱ	180.000 (1)	H5W1—O5W—H5W2	103 (5)
O5W ⁱⁱ —Mn2—O5W	180.000 (1)	H6W1—O6W—H6W2	108 (5)
O5W ⁱⁱ —Mn2—O3W	90.64 (10)	C1—N1—C4	117.4 (3)
O5W—Mn2—O3W	89.36 (10)	C1—N1—Mn1	119.9 (2)
O5W ⁱⁱ —Mn2—O3W ⁱⁱ	89.36 (10)	C4—N1—Mn1	121.9 (2)
O5W—Mn2—O3W ⁱⁱ	90.64 (10)	C2—N2—C3	116.8 (3)
O3W—Mn2—O3W ⁱⁱ	180.000 (1)	C2—N3—H3N1	122 (3)

O5W ⁱⁱ —Mn2—O4W	89.84 (10)	C2—N3—H3N2	121 (3)
O5W—Mn2—O4W	90.16 (10)	H3N1—N3—H3N2	117 (5)
O3W—Mn2—O4W	86.45 (11)	N1—C1—C2	122.2 (3)
O3W ⁱⁱ —Mn2—O4W	93.55 (11)	N1—C1—H1	118.9
O5W ⁱⁱ —Mn2—O4W ⁱⁱ	90.16 (10)	C2—C1—H1	118.9
O5W—Mn2—O4W ⁱⁱ	89.84 (10)	N2—C2—N3	119.4 (3)
O3W—Mn2—O4W ⁱⁱ	93.55 (11)	N2—C2—C1	120.2 (3)
O3W ⁱⁱ —Mn2—O4W ⁱⁱ	86.45 (11)	N3—C2—C1	120.4 (3)
O4W—Mn2—O4W ⁱⁱ	180.000 (1)	N2—C3—C4	123.1 (3)
O4—S1—O2	110.85 (17)	N2—C3—H3	118.4
O4—S1—O1	109.03 (14)	C4—C3—H3	118.4
O2—S1—O1	109.60 (15)	N1—C4—C3	120.3 (3)
O4—S1—O3	109.10 (14)	N1—C4—H4	119.9
O2—S1—O3	109.02 (14)	C3—C4—H4	119.9
O1—S1—O3	109.22 (13)		

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

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—H1w1 \cdots O1	0.84 (1)	1.95 (2)	2.779 (3)	167 (4)
O1w—H1w2 \cdots N2 ⁱⁱⁱ	0.85 (1)	1.94 (1)	2.792 (3)	176 (5)
O2w—H2w1 \cdots O3	0.85 (1)	1.95 (1)	2.775 (3)	166 (4)
O2w—H2w2 \cdots O1 ^{iv}	0.85 (1)	1.92 (1)	2.770 (3)	172 (4)
O3w—H3w1 \cdots O2	0.85 (1)	1.90 (1)	2.744 (4)	170 (5)
O3w—H3w2 \cdots O6w	0.85 (1)	1.88 (1)	2.728 (4)	175 (4)
O4w—H4w1 \cdots O6w ^v	0.85 (1)	1.96 (2)	2.780 (4)	162 (5)
O4w—H4w2 \cdots O2 ^v	0.85 (1)	1.92 (2)	2.744 (4)	164 (5)
O5w—H5w1 \cdots O3 ^{vi}	0.84 (1)	2.00 (2)	2.813 (3)	159 (5)
O5w—H5w2 \cdots O4 ⁱⁱ	0.85 (1)	1.88 (1)	2.726 (4)	177 (6)
O6w—H6w1 \cdots O3 ⁱⁱⁱ	0.85 (1)	1.95 (2)	2.783 (3)	167 (6)
O6w—H6w2 \cdots O4 ^{vi}	0.85 (1)	1.87 (1)	2.709 (4)	172 (6)
N3—H3n2 \cdots O1 ^{vii}	0.85 (1)	2.18 (1)	3.026 (4)	172 (5)

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

Fig. 1

