research communications

Crystal structure of tetraaquabis(pyrimidin-1-ium-4,6-diolato-κO^4)manganese(II)

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The Mn^{II} ion in the structure of the mononuclear title compound, $[Mn(C_4H_3N_2O_2)_2(H_2O)_4]$, is situated on an inversion center and is coordinated by two O atoms from two deprotonated 4,6-dihydroxypyrimidine ligands and by four O atoms from water molecules giving rise to a slightly distorted octahedral coordination sphere. The complex includes an intramolecular hydrogen bond between an aqua ligand and the non-protonated N ring atom. The extended structure is stabilized by intermolecular hydrogen bonds between aqua ligands, by hydrogen bonds between N and O atoms of the ligands of adjacent molecules, and by hydrogen bonds between aqua ligands and the non-coordinating O atom of an adjacent molecule.

1. Chemical context

H-tautomeric forms of 4,6-dihydroxypyrimidine (DHP) are known to exist and are associated with low disproportionation energies (Katrusiak & Katrusiak, 2003). Although crystal structures have been reported where cobalt(II) and nickel(II) are coordinated by the 4,6-dihydroxypyrimidine ligand through a ring nitrogen atom (Huang *et al.*, 2005; Wang *et al.*, 2006), prior to this report no complexes with ligation through a phenolate oxygen atom have been reported even though this mode of coordination does occur in complexes of 3,6-dihydroxypyridizine (Shennara *et al.*, 2015).
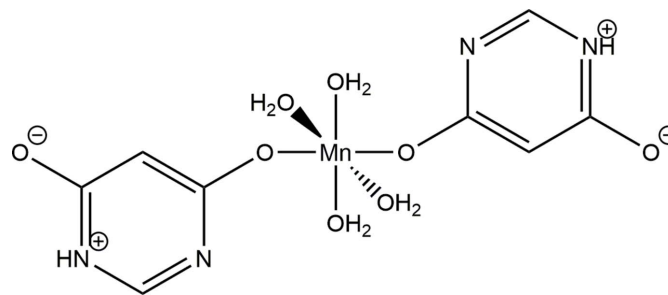
2. Structural commentary

Crystallographic analysis reveals that the title compound consists of a centrosymmetric mononuclear $[Mn(C_4H_3N_2O_2)_2(H_2O)_4]$ complex in which the Mn^{II} ion is in an O_6 environment that is close to octahedral. Two deprotonated 4,6-dihydroxypyrimidine ligands coordinate through the phenolate oxygen atom (O1) at axial positions, while four water molecules occupy the equatorial sites (Fig. 1). The bond lengths in the pyrimidine ligand are very similar to those found for the
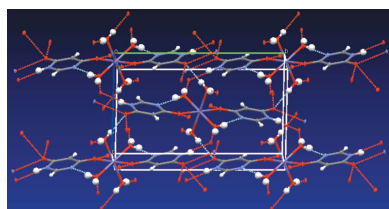
Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W1$\cdots$O2^{i}	0.80 (3)	2.03 (3)	2.8152 (14)	170 (2)
O1W—H1W2$\cdots$O1^{ii}	0.82 (3)	1.90 (3)	2.7127 (13)	176 (3)
O2W—H2W1$\cdots$N2	0.82 (3)	1.91 (3)	2.6929 (14)	159 (2)
O2W—H2W2$\cdots$O2^{iii}	0.84 (2)	1.85 (2)	2.6754 (13)	167 (2)
N1—H1$N\cdots$O2^{iv}	0.91 (2)	1.92 (2)	2.7966 (14)	162 (2)

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

Co and Ni complexes in which, however, ligation to the metal is through a nitrogen atom. For all three complexes, the structures indicate a zwitterionic form of the ligand resulting from transfer of a proton from the hydroxyl group to a ring nitrogen atom. Others have reported variability in the H-tautomeric forms of 4,6-dihydroxypyrimidine associated with low disproportionation energies (Katrusiak & Katrusiak, 2003). The structure of the complex includes an intramolecular hydrogen bond between an aqua ligand (O2W) and the non-protonated N^3 ring atom (N2) (Table 1).

3. Supramolecular features

Intermolecular hydrogen bonds between the aqua ligands of adjacent molecules are present. Hydrogen bonds also occur between the non-coordinating NH$^+$ and O$^-$ atoms of two DHP ligands in adjacent molecules and between an aqua ligand and the non-coordinating oxygen atom of an adjacent molecule (Table 1). This gives rise to a complex three-dimensional network, which is best analyzed in terms of graph-set theory (Etter *et al.*, 1990). There are four inter-
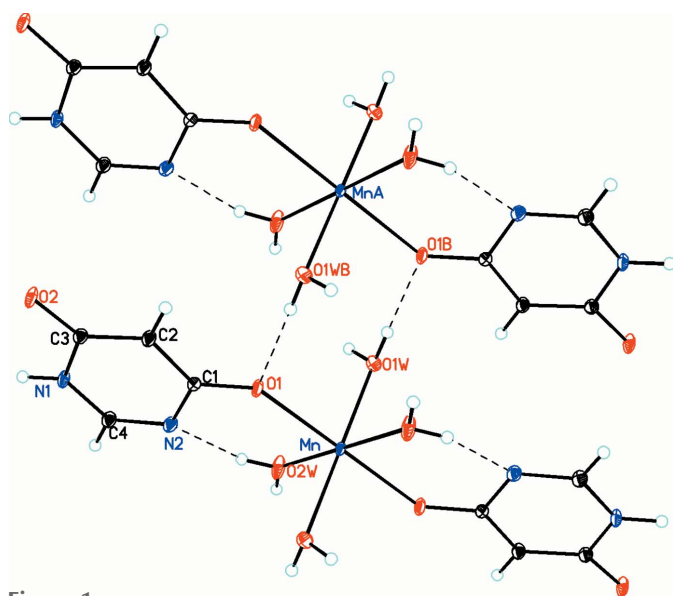
Figure 1
Diagram showing the complex and atom labeling, as well as the formation of {$C(4)[R_2^2(8)]$} chains in the *a*-axis direction linked by hydrogen bonds. Atomic displacement parameters are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.
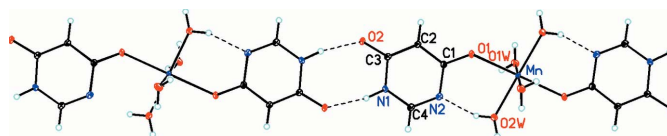
Figure 2
Diagram showing how the molecules link up into chains through the formation of $C(6)[R(6)R_2^2(8)]$ hydrogen bonds. Atomic displacement parameters are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.
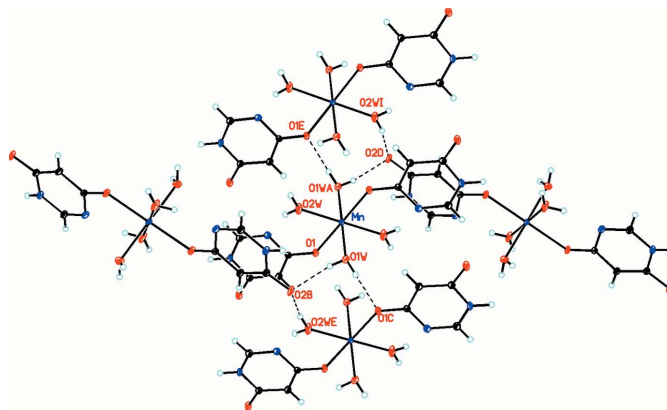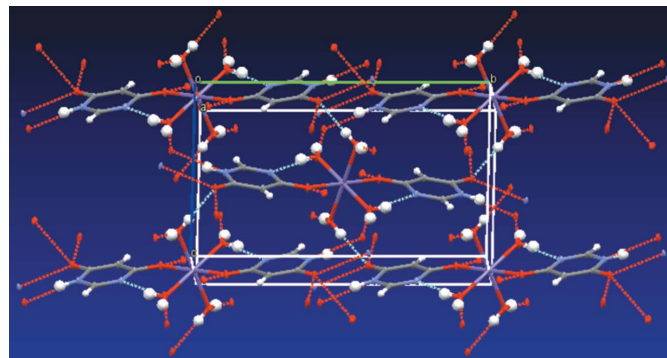

Figure 3
Diagram showing one of the two mutually perpendicular chains linked through the formation of $C(6)[R_3^2(8)]$ hydrogen bonds. Atomic displacement parameters are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

penetrating chains of hydrogen bonds. The first has a $C(4)[R_2^2(8)]$ motif and is shown in Fig. 1. The second has a $C(6)[R_1^1(6)R_2^2(8)]$ motif and is shown in Fig. 2. The chain depicted in Fig. 3 has a $C(6)[R_3^2(8)]$ motif and is duplicated in two mutually perpendicular directions, thus making up four chains altogether. The overall packing is shown in Fig. 4.

4. Database survey

A search in the Cambridge Structural Database (CSD version 5.37; Groom *et al.*, 2016) for structures of manganese of 4,6-dihydroxypyrimidines revealed that no such structures

Figure 4
Diagram showing how the four sets of chains linked by hydrogen bonds gives rise to the overall packing. Hydrogen bonds are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Mn(C_4H_3N_2O_2)_2(H_2O)_4]$
M_r	349.17
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, b, c (Å)	5.2156 (5), 14.0812 (14), 9.0595 (9)
β (°)	99.366 (2)
V (Å^3)	656.48 (11)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.05
Crystal size (mm)	$0.55 \times 0.41 \times 0.40$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.614, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2971, 1848, 1752
R_{int}	0.016
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.730
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.071, 1.10
No. of reflections	1848
No. of parameters	117
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.48, −0.32

Computer programs: *APEX2* (Bruker, 2005), *SAINT* (Bruker, 2002), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

exist, although there are twelve examples of manganese complexes of 2,4-dihydroxypyrimidine derivatives (CSD codes AMPTMN, AQAPAK, ICESEQ, IMEGAJ, JIRNUU, NOPSER, OFUDAU, QOSDOT, QOSNOD, RAGLAO, TAGVOM, and ZOGFOQ).

5. Synthesis and crystallization

0.5 mM aqueous solutions of the ligand and anhydrous $MnCl_2$, both purchased from Aldrich, were adjusted to pH 5.5 with NaOH/HCl and then mixed together in a 1:2 stoichiometry. The solutions were left to crystallize slowly at room temperature. Light-yellow crystals formed over two weeks. Room-temperature X-band EPR spectra of powdered crystals exhibited a single broad line centered at a g-value of near to 2.0 with a peak-to-peak line width of 660 G, the breadth of which indicates Mn$\cdots$Mn magnetic interactions, although not as strong as in the related maleic hydrazide (MH),

$Mn(MH)_2(H_2O)_4$, complex, for which a line width of 920 G was found (Shennara *et al.*, 2015). EPR spectra of aqueous solutions of the title complex had $g = 2.006$ and $A_{iso}(Mn) = 95.2$ G, similar to that of the $Mn(MH)_2$ complex

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically and refined as riding: C—H = 0.95 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. N—H and O—H hydrogen atoms were refined isotropically without restrictions on the bond lengths. Four reflections which were obvious outliers were omitted from the refinement (132, 163, 100, 011).

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supporting information

Crystal structure of tetraaquabis(pyrimidin-1-ium-4,6-diolato-κO^4)manganese(II)

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Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: SHELXT (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Tetraaquabis(pyrimidin-1-ium-4,6-diolato-κO^4)manganese(II)

Crystal data

[Mn(C$_4$H$_3$N$_2$O$_2$)$_2$(H$_2$O)$_4$]	$F(000) = 358$
$M_r = 349.17$	$D_x = 1.766$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.2156$ (5) Å	Cell parameters from 2512 reflections
$b = 14.0812$ (14) Å	$\theta = 2.7$–31.2°
$c = 9.0595$ (9) Å	$\mu = 1.05$ mm^{-1}
$\beta = 99.366$ (2)°	$T = 120$ K
$V = 656.48$ (11) Å^3	Block, yellow
$Z = 2$	$0.55 \times 0.41 \times 0.40$ mm

Data collection

Bruker APEXII CCD diffractometer	1848 independent reflections
ω scans	1752 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.016$
	$\theta_{max} = 31.2°$, $\theta_{min} = 2.9°$
$T_{min} = 0.614$, $T_{max} = 0.746$	$h = -7 \rightarrow 7$
2971 measured reflections	$k = -18 \rightarrow 18$
	$l = -3 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.027$	
$wR(F^2) = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.3858P]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
1848 reflections	$(\Delta/\sigma)_{max} < 0.001$
117 parameters	$\Delta\rho_{max} = 0.48$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.32$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Mn	0.500000	0.500000	0.500000	0.00759 (9)
O1	0.25688 (17)	0.38379 (6)	0.56407 (10)	0.01144 (18)
O2	−0.08946 (18)	0.07807 (6)	0.62265 (10)	0.01204 (18)
O1W	0.17104 (18)	0.54921 (7)	0.33556 (11)	0.01243 (18)
H1W1	0.114 (5)	0.5129 (16)	0.271 (3)	0.029 (6)*
H1W2	0.045 (5)	0.5682 (17)	0.370 (3)	0.040 (7)*
O2W	0.6010 (2)	0.40720 (7)	0.32982 (11)	0.0164 (2)
H2W1	0.562 (5)	0.3534 (18)	0.353 (3)	0.037 (6)*
H2W2	0.702 (5)	0.4026 (17)	0.267 (3)	0.035 (6)*
N1	0.2263 (2)	0.10486 (8)	0.48187 (11)	0.0094 (2)
H1N	0.219 (5)	0.0429 (18)	0.453 (3)	0.033 (6)*
N2	0.4089 (2)	0.25411 (8)	0.45266 (11)	0.0102 (2)
C1	0.2421 (2)	0.29415 (9)	0.54070 (13)	0.0084 (2)
C2	0.0651 (2)	0.23594 (9)	0.60057 (13)	0.0101 (2)
H2A	−0.049639	0.263207	0.660180	0.012*
C3	0.0573 (2)	0.13885 (9)	0.57302 (13)	0.0090 (2)
C4	0.3920 (2)	0.16342 (9)	0.42645 (13)	0.0102 (2)
H4A	0.503298	0.136653	0.364320	0.012*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn	0.00731 (13)	0.00453 (14)	0.01196 (13)	−0.00112 (8)	0.00470 (9)	−0.00066 (8)
O1	0.0118 (4)	0.0049 (4)	0.0192 (4)	−0.0018 (3)	0.0074 (3)	−0.0011 (3)
O2	0.0165 (4)	0.0057 (4)	0.0163 (4)	−0.0030 (3)	0.0097 (3)	−0.0001 (3)
O1W	0.0105 (4)	0.0099 (5)	0.0173 (4)	0.0014 (3)	0.0032 (3)	−0.0025 (3)
O2W	0.0242 (5)	0.0076 (5)	0.0219 (5)	−0.0037 (4)	0.0172 (4)	−0.0024 (3)
N1	0.0123 (5)	0.0051 (5)	0.0121 (4)	−0.0013 (3)	0.0058 (4)	−0.0019 (3)
N2	0.0096 (5)	0.0085 (5)	0.0134 (4)	−0.0014 (3)	0.0050 (4)	−0.0002 (4)
C1	0.0073 (5)	0.0070 (5)	0.0110 (4)	−0.0006 (4)	0.0018 (4)	0.0000 (4)
C2	0.0101 (5)	0.0074 (6)	0.0143 (5)	−0.0010 (4)	0.0063 (4)	−0.0002 (4)
C3	0.0091 (5)	0.0082 (6)	0.0106 (4)	−0.0007 (4)	0.0040 (4)	0.0002 (4)
C4	0.0108 (5)	0.0090 (6)	0.0118 (5)	−0.0009 (4)	0.0049 (4)	0.0007 (4)

Geometric parameters (Å, º)

Mn—O2W	2.1510 (10)	O2W—H2W2	0.84 (2)
Mn—O2W^i	2.1510 (10)	N1—C4	1.3491 (15)
Mn—O1W	2.1934 (10)	N1—C3	1.3871 (14)

Mn—O1W[i]	2.1935 (10)	N1—H1N	0.91 (2)
Mn—O1	2.2050 (9)	N2—C4	1.2993 (16)
Mn—O1[i]	2.2050 (9)	N2—C1	1.3917 (15)
O1—C1	1.2801 (15)	C1—C2	1.4074 (16)
O2—C3	1.2778 (14)	C2—C3	1.3892 (17)
O1W—H1W1	0.80 (3)	C2—H2A	0.9500
O1W—H1W2	0.82 (3)	C4—H4A	0.9500
O2W—H2W1	0.82 (3)		
O2W—Mn—O2W[i]	180.0	Mn—O2W—H2W1	106.3 (17)
O2W—Mn—O1W	87.76 (4)	Mn—O2W—H2W2	141.9 (16)
O2W[i]—Mn—O1W	92.24 (4)	H2W1—O2W—H2W2	108 (2)
O2W—Mn—O1W[i]	92.25 (4)	C4—N1—C3	121.20 (10)
O2W[i]—Mn—O1W[i]	87.75 (4)	C4—N1—H1N	118.5 (14)
O1W—Mn—O1W[i]	180.0	C3—N1—H1N	120.1 (15)
O2W—Mn—O1	87.49 (4)	C4—N2—C1	118.21 (10)
O2W[i]—Mn—O1	92.51 (4)	O1—C1—N2	117.88 (10)
O1W—Mn—O1	89.62 (4)	O1—C1—C2	122.43 (11)
O1W[i]—Mn—O1	90.38 (4)	N2—C1—C2	119.69 (11)
O2W—Mn—O1[i]	92.51 (4)	C3—C2—C1	120.38 (11)
O2W[i]—Mn—O1[i]	87.49 (4)	C3—C2—H2A	119.8
O1W—Mn—O1[i]	90.38 (4)	C1—C2—H2A	119.8
O1W[i]—Mn—O1[i]	89.62 (4)	O2—C3—N1	116.96 (11)
O1—Mn—O1[i]	180.0	O2—C3—C2	126.70 (11)
C1—O1—Mn	135.24 (8)	N1—C3—C2	116.34 (10)
Mn—O1W—H1W1	116.9 (17)	N2—C4—N1	124.15 (11)
Mn—O1W—H1W2	115.8 (18)	N2—C4—H4A	117.9
H1W1—O1W—H1W2	105 (2)	N1—C4—H4A	117.9
Mn—O1—C1—N2	−1.40 (18)	C4—N1—C3—O2	−178.77 (11)
Mn—O1—C1—C2	178.55 (9)	C4—N1—C3—C2	1.38 (17)
C4—N2—C1—O1	−178.88 (11)	C1—C2—C3—O2	178.56 (12)
C4—N2—C1—C2	1.17 (17)	C1—C2—C3—N1	−1.61 (17)
O1—C1—C2—C3	−179.55 (11)	C1—N2—C4—N1	−1.49 (18)
N2—C1—C2—C3	0.39 (18)	C3—N1—C4—N2	0.19 (19)

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H1*W*1···O2[ii]	0.80 (3)	2.03 (3)	2.8152 (14)	170 (2)
O1*W*—H1*W*2···O1[iii]	0.82 (3)	1.90 (3)	2.7127 (13)	176 (3)
O2*W*—H2*W*1···N2	0.82 (3)	1.91 (3)	2.6929 (14)	159 (2)
O2*W*—H2*W*2···O2[iv]	0.84 (2)	1.85 (2)	2.6754 (13)	167 (2)
N1—H1*N*···O2[v]	0.91 (2)	1.92 (2)	2.7966 (14)	162 (2)

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