Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tetraaquabis[(4-oxo-4*H*-pyridin-1-yl)-acetato]manganese(II)

Zhu-Yan Zhang,[a,b] Shan Gao,[b]* Li-Hua Huo[b] and Jing-Gui Zhao[b]

[a]School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]School of Pharmaceutical Science, Harbin Medical University, Harbin 150086, People's Republic of China
Correspondence e-mail: shangao67@yahoo.com

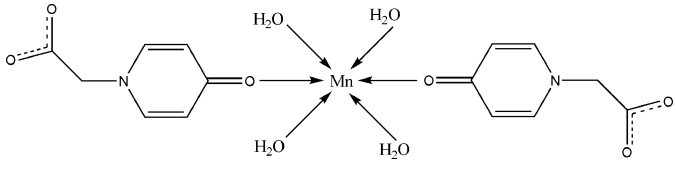
Received 20 April 2007; accepted 24 April 2007

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.027; wR factor = 0.071; data-to-parameter ratio = 14.6.

In the title centrosymmetric mononuclear Mn^{II} complex, $[Mn(C_7H_6NO_3)_2(H_2O)_4]$, the Mn^{II} ion, which lies on an inversion centre, has an octahedral geometry and is six-coordinated by two carbonyl O atoms from two (4-oxo-4*H*-pyridin-1-yl)acetate (4-OPA$^-$) anions and four water molecules. The mononuclear units are linked into a two-dimensional network parallel to the $(01\bar{1})$ plane by O—H···O intermolecular hydrogen bonds. Adjacent networks are cross-linked *via* weak π–π stacking interactions between pyridine rings, with a centroid–centroid distance of 3.758 (3) Å

Related literature

For general background, see: Edwards *et al.* (1977). Complexes with 4-OPA$^-$ exist as either mononuclear with the ligands as counter-anions (Gao *et al.*, 2004; Zhang *et al.*, 2004*a*,*b*; Zhao *et al.*, 2004; Zhang *et al.*, 2005) or as polymers with the metal ions bridged by the 4-OPA$^-$ ligands (Zhang *et al.*, 2006).



Experimental

Crystal data

$[Mn(C_7H_6NO_3)_2(H_2O)_4]$
M_r = 431.26
Triclinic, $P\bar{1}$
a = 5.4191 (11) Å
b = 9.0498 (18) Å
c = 10.044 (2) Å
α = 108.16 (3)°
β = 99.32 (3)°
γ = 103.38 (3)°
V = 440.5 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 295 (2) K
0.36 × 0.28 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.760, T_{max} = 0.868
4337 measured reflections
1981 independent reflections
1844 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.071
S = 1.08
1981 reflections
136 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O2^{i}	0.85 (1)	1.82 (1)	2.6674 (17)	178 (2)
O1W—H1W2···O1^{ii}	0.85 (1)	1.87 (1)	2.7208 (17)	177 (2)
O2W—H2W1···O1^{iii}	0.85 (1)	1.81 (1)	2.6557 (17)	173 (2)
O2W—H2W2···O3^{iv}	0.84 (1)	1.93 (1)	2.7677 (17)	169 (2)

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

We thank the Heilongjiang Province Natural Science Foundation (No. B200501), the Scientific Fund for Remarkable Teachers of Heilongjiang Province (No. 1054 G036), Heilongjiang University, and Harbin Medical University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2374).

References

Edwards, M. L., Bambury, R. E. & Ritter, H. W. (1977). *J. Med. Chem.* **20**, 560–563.
Gao, S., Zhang, Z.-Y., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2004). *Acta Cryst.* E**60**, m444–m446.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Zhang, Z.-Y., Gao, S., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2005). *Acta Cryst.* E**61**, m85–m86.
Zhang, Z.-Y., Gao, S., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2006). *Chin. J. Inorg. Chem.* **22**, 905–908.
Zhang, Z.-Y., Gao, S., Huo, L.-H., Zhao, H., Zhao, J.-G. & Ng, S. W. (2004*a*). *Acta Cryst.* E**60**, m544–m545.
Zhang, Z.-Y., Gao, S., Huo, L.-H., Zhao, H., Zhao, J.-G. & Ng, S. W. (2004*b*). *Acta Cryst.* E**60**, m676–m678.
Zhao, J.-G., Zhang, Z.-Y., Huo, L.-H. & Gao, S. (2004). *Acta Cryst.* E**60**, m1987–m1988.

  doi:10.1107/S1600536807020533

supplementary materials

Acta Cryst. (2007). E**63**, m1514 [**doi:10.1107/S1600536807020533**]

Tetraaquabis[(4-oxo-4*H*-pyridin-1-yl)acetato]manganese(II)

Z.-Y. Zhang, S. Gao, L.-H. Huo and J.-G. Zhao

Comment

(4-Oxo-4*H*-pyrindin-1-yl)acetic acid (4-OPA$^-$), an important medical intermediate (Edwards *et al.*, 1977), is a potential multidentate ligand with versatile binding ability. Recent studies in our laboratory have demontrated that the complexes containing 4-OPA$^-$ ligands exhibit two type structures: mononuclear in which the 4-OPA$^-$ ligands exist as counter anions (Gao *et al.*, 2004; Zhang *et al.*, 2004*a*,b; Zhao *et al.*, 2004; Zhang *et al.*, 2005) and polymer with the adjacent metal ions bridged by carbonyl and carboxylate groups of 4-OPA$^-$ ligand (Zhang *et al.*, 2006).

As illustrated in Fig. 1, the title complex has a mononuclear structure, in which the (4-oxo-4*H*-pyridin-1-yl)acetate ligands are coordinated to the Mn^{II} atom through the carbonyl O atoms in a monodentate fashion. The Mn^{II} atom is located on an inversion center and is coordinated by two carbonyl O atoms and four water molecules, forming an octahedral coordination geometry. The Mn—$O_{carbonyl}$ bond distance is 2.1960 (11) Å, and the Mn—O_w distances are 2.1557 (14) and 2.1952 (12) Å.

The planes of the carboxylate group (O1/O2/C1/C2) and pyridine ring (N1/C3—C7) form a dihedral angle of 67.27 (9)°. The C—O bond lengths [O1—C1 = 1.2566 (18) Å and O2—C1 = 1.2366 (19) Å] suggest delocalization of π-electron density over the carboxylate group.

The coordinated water molecules form intermolecular O—H···O hydrogen bonds with uncoordinated carboxylate groups of adjacent molecules, connecting the mononuclear units into a two-dimensional network parallel to the (0 1 $\bar{1}$) plane. The O···O distances of the hydrogen bonds lie in the range 2.6557 (17)-2.7677 (17) Å and the O—H···O angles range from 169.5 (19) to 178 (2)° (Table 1). The adjacent networks are cross-linked via weak π-π stacking interactions between the pyridine rings of the molecules at (x, y, z) and (1-x, 1-y, -z), with a centroid···centroid distance of 3.758 (3) Å (Fig. 2).

Experimental

The title complex was prepared by the addition of $MnCl_2.4H_2O$ (3.96 g, 20 mmol) to a solution of (4-oxo-4*H*-pyridin-1-yl)acetic acid (5.84 g, 40 mmol) in H_2O-DMF (1:1 v/v), and the pH was adjusted to 7 with 0.2 M NaOH solution. Colourless single crystals of (I) were obtained from the filtered solution, after slow evaporation at room temperature for a week. Analysis calculated for $C_{14}H_{20}MnN_2O_{10}$: C 38.99, H 4.67, N 6.49%; found: C 38.77, H 4.54, N 6.66%.

Refinement

H atoms of water molecules were located in Fourier difference maps and refined with the restraints O—H = 0.85 (1) Å and H···H = 1.39 (1) Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$. C-bound H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and were included in the refinement in the riding-model approximation.

Figures

Fig. 1. A view of complex (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (i) 1-x, 1-y, 1-z.

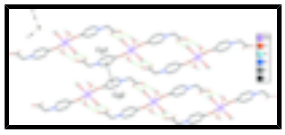


Fig. 2. The three-dimensional network of (I), viewed along the *a* axis. Dashed lines indicate O–H···O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted. Cg1 and Cg2 represent the centroids of adjacent pyridine rings, as defined in the comment.

Tetraaquabis[(4-oxo-4*H*-pyridin-1-yl)acetato]manganese(II)

Crystal data

$[Mn(C_7H_6NO_3)_2(H_2O)_4]$	$Z = 1$
$M_r = 431.26$	$F_{000} = 223$
Triclinic, $P\overline{1}$	$D_x = 1.626$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 5.4191$ (11) Å	Cell parameters from 4131 reflections
$b = 9.0498$ (18) Å	$\theta = 3.9$–$27.5°$
$c = 10.044$ (2) Å	$\mu = 0.81$ mm^{-1}
$\alpha = 108.16$ (3)°	$T = 295$ (2) K
$\beta = 99.32$ (3)°	Prism, colourless
$\gamma = 103.38$ (3)°	0.36 × 0.28 × 0.18 mm
$V = 440.5$ (2) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	1981 independent reflections
Radiation source: fine-focus sealed tube	1844 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.014$
Detector resolution: 10.000 pixels mm^{-1}	$\theta_{max} = 27.5°$
$T = 295(2)$ K	$\theta_{min} = 3.9°$
ω scans	$h = -6 \rightarrow 7$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -11 \rightarrow 11$
$T_{min} = 0.760$, $T_{max} = 0.868$	$l = -13 \rightarrow 13$
4337 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.1219P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
1981 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}
136 parameters	Extinction correction: none
6 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.5000	0.5000	0.5000	0.02410 (10)
O1W	0.7476 (2)	0.74902 (12)	0.58032 (12)	0.0342 (2)
H1W1	0.693 (3)	0.8273 (18)	0.624 (2)	0.051*
H1W2	0.894 (3)	0.789 (2)	0.566 (2)	0.051*
O1	0.2242 (2)	−0.11738 (13)	−0.45608 (12)	0.0373 (3)
O2W	0.79418 (19)	0.41863 (13)	0.61161 (11)	0.0320 (2)
H2W1	0.775 (3)	0.3193 (12)	0.5618 (19)	0.048*
H2W2	0.955 (2)	0.4702 (19)	0.634 (2)	0.048*
O2	0.5889 (2)	−0.00381 (14)	−0.27545 (12)	0.0402 (3)
O3	0.66629 (19)	0.44717 (13)	0.31126 (10)	0.0324 (2)
N1	0.3688 (2)	0.22273 (14)	−0.12628 (12)	0.0257 (2)
C1	0.3723 (3)	−0.00777 (17)	−0.34111 (14)	0.0272 (3)
C2	0.2691 (3)	0.13736 (17)	−0.28357 (14)	0.0298 (3)
H2A	0.3194	0.2135	−0.3313	0.036*
H2B	0.0790	0.0990	−0.3076	0.036*
C3	0.2162 (3)	0.20104 (18)	−0.03597 (15)	0.0303 (3)
H3	0.0439	0.1340	−0.0750	0.036*
C4	0.3070 (3)	0.27423 (19)	0.11032 (16)	0.0317 (3)
H4	0.1955	0.2578	0.1691	0.038*
C5	0.5707 (3)	0.37566 (17)	0.17470 (15)	0.0256 (3)
C6	0.7223 (3)	0.39426 (18)	0.07528 (15)	0.0309 (3)
H6	0.8961	0.4594	0.1103	0.037*
C7	0.6192 (3)	0.31899 (18)	−0.07022 (16)	0.0309 (3)
H7	0.7240	0.3343	−0.1325	0.037*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01991 (15)	0.02699 (16)	0.01976 (15)	0.00453 (11)	0.00473 (11)	0.00294 (11)
O1W	0.0286 (5)	0.0281 (5)	0.0383 (6)	0.0039 (4)	0.0135 (5)	0.0030 (4)
O1	0.0295 (5)	0.0329 (5)	0.0332 (5)	0.0051 (4)	0.0037 (4)	−0.0046 (4)
O2W	0.0236 (5)	0.0325 (5)	0.0299 (5)	0.0075 (4)	0.0013 (4)	0.0014 (4)
O2	0.0326 (6)	0.0417 (6)	0.0354 (6)	0.0156 (5)	0.0009 (5)	0.0001 (5)
O3	0.0234 (5)	0.0426 (6)	0.0204 (5)	0.0052 (4)	0.0042 (4)	0.0009 (4)
N1	0.0252 (5)	0.0257 (5)	0.0205 (5)	0.0067 (4)	0.0022 (4)	0.0030 (4)

C1	0.0269 (7)	0.0278 (7)	0.0230 (6)	0.0051 (5)	0.0079 (5)	0.0055 (5)
C2	0.0329 (7)	0.0300 (7)	0.0200 (6)	0.0100 (6)	0.0002 (5)	0.0034 (5)
C3	0.0210 (6)	0.0340 (7)	0.0276 (7)	0.0033 (5)	0.0023 (5)	0.0058 (6)
C4	0.0237 (6)	0.0397 (8)	0.0259 (7)	0.0038 (6)	0.0069 (5)	0.0080 (6)
C5	0.0228 (6)	0.0277 (6)	0.0223 (6)	0.0083 (5)	0.0045 (5)	0.0039 (5)
C6	0.0217 (6)	0.0342 (7)	0.0256 (7)	0.0006 (5)	0.0053 (5)	0.0020 (6)
C7	0.0269 (7)	0.0340 (7)	0.0262 (7)	0.0036 (5)	0.0095 (6)	0.0061 (6)

Geometric parameters (Å, °)

Mn1—O1W	2.1557 (14)	O2W—H2W2	0.845 (9)
Mn1—O2W	2.1952 (12)	N1—C7	1.3481 (19)
Mn1—O3	2.1960 (11)	N1—C3	1.3506 (19)
O1—C1	1.2566 (18)	N1—C2	1.4677 (17)
O2—C1	1.2366 (19)	C1—C2	1.531 (2)
O3—C5	1.2767 (17)	C2—H2A	0.97
C3—C4	1.359 (2)	C2—H2B	0.97
C6—C7	1.360 (2)	C3—H3	0.93
Mn1—O1W^{i}	2.1557 (14)	C4—C5	1.423 (2)
Mn1—O2W^{i}	2.1952 (12)	C4—H4	0.93
Mn1—O3^{i}	2.1960 (11)	C5—C6	1.417 (2)
O1W—H1W1	0.853 (9)	C6—H6	0.93
O1W—H1W2	0.848 (9)	C7—H7	0.93
O2W—H2W1	0.854 (9)		
O1W—Mn1—O2W	93.31 (5)	C3—N1—C2	120.87 (12)
O1W—Mn1—O2W^{i}	86.69 (5)	O2—C1—O1	127.28 (14)
O1W—Mn1—O3	89.68 (5)	O2—C1—C2	118.63 (12)
O2W—Mn1—O3	89.39 (4)	O1—C1—C2	114.04 (13)
O1W—Mn1—O3^{i}	90.32 (5)	N1—C2—H2A	109.0
O2W—Mn1—O3^{i}	90.61 (4)	C1—C2—H2A	109.0
N1—C2—C1	112.72 (12)	N1—C2—H2B	109.0
O1W^{i}—Mn1—O1W	180	C1—C2—H2B	109.0
O1W^{i}—Mn1—O2W	86.69 (5)	H2A—C2—H2B	107.8
O1W^{i}—Mn1—O2W^{i}	93.31 (5)	N1—C3—C4	121.97 (13)
O2W—Mn1—O2W^{i}	180	N1—C3—H3	119.0
O1W^{i}—Mn1—O3	90.32 (5)	C4—C3—H3	119.0
O2W^{i}—Mn1—O3	90.61 (4)	C3—C4—C5	120.86 (13)
O1W^{i}—Mn1—O3^{i}	89.68 (5)	C3—C4—H4	119.6
O2W^{i}—Mn1—O3^{i}	89.39 (4)	C5—C4—H4	119.6
O3—Mn1—O3^{i}	180.0	O3—C5—C6	121.59 (12)
Mn1—O1W—H1W1	121.0 (13)	O3—C5—C4	123.50 (13)
Mn1—O1W—H1W2	130.2 (12)	C6—C5—C4	114.91 (12)
H1W1—O1W—H1W2	108.3 (13)	C7—C6—C5	121.46 (13)
Mn1—O2W—H2W1	108.5 (13)	C7—C6—H6	119.3
Mn1—O2W—H2W2	120.6 (14)	C5—C6—H6	119.3
H2W1—O2W—H2W2	107.7 (13)	N1—C7—C6	121.54 (13)

C5—O3—Mn1	134.77 (9)	N1—C7—H7	119.2
C7—N1—C3	119.26 (12)	C6—C7—H7	119.2
C7—N1—C2	119.81 (12)		
O1W^{i}—Mn1—O3—C5	47.96 (14)	N1—C3—C4—C5	−1.0 (2)
O1W—Mn1—O3—C5	−132.04 (14)	Mn1—O3—C5—C6	164.14 (11)
O2W—Mn1—O3—C5	134.65 (14)	Mn1—O3—C5—C4	−15.0 (2)
O2W^{i}—Mn1—O3—C5	−45.35 (14)	C3—C4—C5—O3	−179.92 (14)
C7—N1—C2—C1	74.23 (17)	C3—C4—C5—C6	0.9 (2)
C3—N1—C2—C1	−103.03 (15)	O3—C5—C6—C7	−179.46 (14)
O2—C1—C2—N1	−28.52 (19)	C4—C5—C6—C7	−0.3 (2)
O1—C1—C2—N1	153.79 (13)	C3—N1—C7—C6	0.3 (2)
C7—N1—C3—C4	0.4 (2)	C2—N1—C7—C6	−177.01 (14)
C2—N1—C3—C4	177.64 (14)	C5—C6—C7—N1	−0.3 (2)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1W1···O2^{ii}	0.85 (1)	1.82 (1)	2.6674 (17)	178 (2)
O1W—H1W2···O1^{iii}	0.85 (1)	1.87 (1)	2.7208 (17)	177 (2)
O2W—H2W1···O1^{iv}	0.85 (1)	1.81 (1)	2.6557 (17)	173 (2)
O2W—H2W2···O3^{v}	0.84 (1)	1.93 (1)	2.7677 (17)	169 (2)

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

Fig. 1

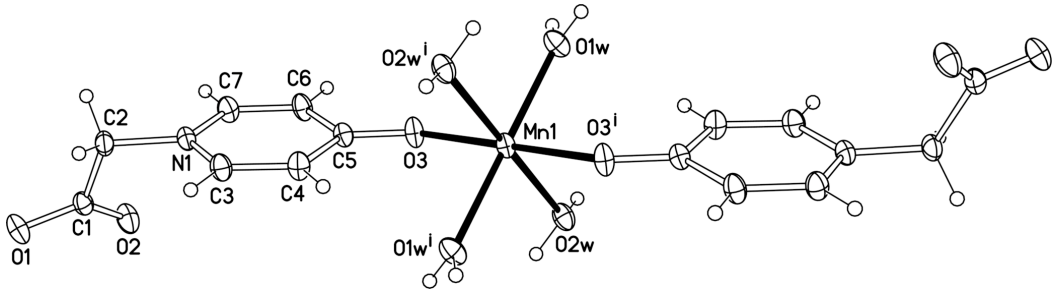


Fig. 2