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Diaquabis[1-ethyl-6-fluoro-7-(4-methylpiperazin-4-ium-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylato-κ^2O^3,O^4]-manganese(II) benzene-1,4-dicarboxylate tetradecahydrate

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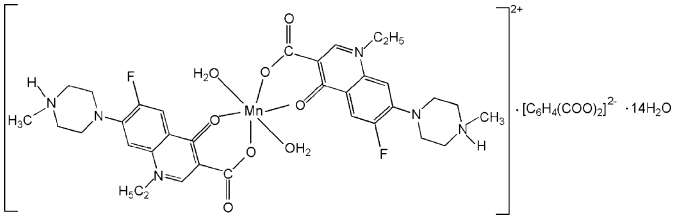
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.098; data-to-parameter ratio = 13.3.

In the title compound, $[Mn(C_{17}H_{20}FN_3O_3)_2(H_2O)_2]\cdot(C_8H_4O_4)\cdot14H_2O$, the Mn^{II} atom (site symmetry $\overline{1}$) exhibits a distorted MnO_6 octahedral geometry defined by two neutral bidentate *O*,*O*-bonded 1-ethyl-6-fluoro-7-(4-methylpiperazin-4-ium-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylate (Hpef) zwitterions and two water molecules. The charge-balancing benzene-1,4-dicarboxylate (1,4-bdc) anion is also centrosymmetric. An extensive network of O—H···O and O—H···N hydrogen bonds helps to establish the crystal packing.

Related literature

For the silver and cobalt complexes of the pef anion, see: Baenziger *et al.* (1986); An *et al.* (2007). For background literature on the medicinal uses of Hpef, see: Mizuki *et al.* (1996).



Experimental

Crystal data

$[Mn(C_{17}H_{20}FN_3O_3)_2(H_2O)_2]\cdot(C_8H_4O_4)\cdot14H_2O$
M_r = 1174.03
Triclinic, $P\overline{1}$
a = 11.147 (3) Å
b = 11.500 (3) Å
c = 11.832 (3) Å
α = 111.722 (4)°
β = 92.011 (4)°
γ = 102.066 (4)°
V = 1367.3 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 295 (2) K
0.34 × 0.26 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.894, T_{max} = 0.942
11720 measured reflections
5353 independent reflections
4645 reflections with $I > 2\sigma(I)$
R_{int} = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.098
S = 1.03
5353 reflections
402 parameters
25 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—O3	2.1261 (12)	Mn1—O4	2.2223 (15)
Mn1—O1	2.1569 (13)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H1*O*···O5	0.848 (9)	1.914 (10)	2.7565 (18)	173 (2)
N3—H3*N*···O1*W*^{i}	0.911 (10)	1.710 (10)	2.618 (2)	174 (2)
O1*W*—H1*W*1···O2^{ii}	0.841 (9)	1.813 (9)	2.644 (2)	169 (2)
O4—H2*O*···O6*W*^{iii}	0.853 (9)	1.983 (13)	2.787 (2)	156.7 (19)
O7*W*—H7*W*1···O6^{iv}	0.849 (9)	1.983 (9)	2.828 (2)	173 (2)
O7*W*—H7*W*2···O1^{v}	0.857 (9)	1.948 (10)	2.8013 (18)	174 (2)
O1*W*—H1*W*2···O7*W*^{iv}	0.840 (9)	1.825 (9)	2.662 (2)	175 (2)
O2*W*—H2*W*1···O6	0.846 (9)	1.923 (10)	2.764 (2)	172 (3)
O3*W*—H3*W*1···O5	0.851 (9)	1.954 (9)	2.797 (2)	171 (2)
O6*W*—H6*W*1···O2*W*^{vi}	0.857 (9)	1.932 (10)	2.785 (3)	174 (2)
O4*W*—H4*W*1···F1	0.853 (9)	2.287 (14)	2.976 (2)	138.1 (18)
O6*W*—H6*W*2···O6^{i}	0.855 (9)	2.126 (10)	2.972 (2)	170 (2)
O5*W*—H5*W*1···O2^{ii}	0.848 (9)	2.200 (12)	3.023 (3)	164 (2)
O2*W*—H2*W*2···O5*W*	0.849 (9)	2.065 (10)	2.912 (3)	175 (2)
O5*W*—H5*W*2···O4*W*	0.852 (9)	1.923 (10)	2.774 (3)	178 (3)
O4*W*—H4*W*2···O3*W*^{vi}	0.849 (9)	1.961 (11)	2.801 (3)	170 (2)
O3*W*—H3*W*2···O5*W*^{vii}	0.843 (9)	1.988 (12)	2.802 (3)	162 (2)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2468).

  doi:10.1107/S1600536807032072

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supplementary materials

Acta Cryst. (2007). E**63**, m2084-m2085 [**doi:10.1107/S1600536807032072**]

Diaquabis[1-ethyl-6-fluoro-7-(4-methylpiperazin-4-ium-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylato-κ^2O^3,O^4]manganese(II) benzene-1,4-dicarboxylate tetradecahydrate

Z. An, W. Qi and J. Huang

Comment

Pefloxacin (Hpef, $C_{17}H_{20}FN_3O_3$, 1-ethyl-6-fluoro-7-(4-methylpiperazin-1-yl)-4-oxo-quinoline-3-carboxylic acid) is member of a class of quinolones used to treat infections (Mizuki *et al.*, 1996). The silver(I) derivative of the pefloxacin (pef) anion has been reported (Baenziger *et al.*, 1986). The title manganese(II)-containing complex of Hper, (I), is reported here.

The structure of (I) is built up from Mn^{2+} cations (site symmetry $\bar{1}$) neutral Hpef ligands in their zwittrionic form (*i.e.* nominal proton transfer from the carboxylic acid group to a piperizine H atom), coordinated water molecules, a centrosymmetric 1,4-bdc anion and uncoordinated water molecules (Fig. 1). The manganese geometry is a slightly distorted octahedron (Table 1).

The components of (I) are linked by O—H···O and O—H···N hydrogen bonds involving all the potential donors, generating a three-dimensional supramolecular network (Table 2).

Experimental

A mixture of $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.061 g, 0.25 mmol), Hpef (0.17 g, 0.5 mmol), 1,4-benzenedicarboxylic acid (1,4-bdc, 0.04 g, 0.25 mmol) and water (12 ml) was stirred for 30 min in air. The mixture was then transferred to a 23 ml Teflon-lined hydrothermal bomb. The bomb was kept at 433 K for 72 h under autogenous pressure. Upon cooling, colorless prisms of (I) were obtained from the reaction mixture.

Refinement

The carbon-bound H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The H atoms on the N and water molecules were located in a difference map and refined with a distance restraint of N—H = 0.90 (1) Å, O—H = 0.85 (1) Å,and the constraint U_{iso}(H) = 1.5U_{eq}(N,*O*).

Figures

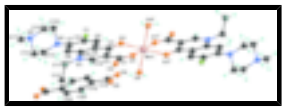


Fig. 1. The asymmetric unit of (I), show the Mn coordination, showing 50% displacement ellipsoids·(The uncoordinated water molecules are omitted for clarity). Symmetry code: (i) −*x*, −*y*, 1 − *z*. Yhe unlabelled atoms of the 1,4-bdc dianion are generated by the symmetry operation (1 − *x*, 1 − *y*, 2 − *z*).

Diaquabis[1-ethyl-6-fluoro-7-(4-methylpiperazin-4-ium-1-yl)-4-oxo-1,4- dihydroquinoline-3-carboxylato-κ^2O^3,O^4]manganese(II) benzene-1,4-dicarboxylate tetradecahydrate

Crystal data

$[Mn(C_{17}H_{20}FN_3O_3)_2(H_2O)_2](C_8H_4O_4)\cdot 14H_2O$	$Z = 1$
$M_r = 1174.03$	$F_{000} = 621$
Triclinic, $P\overline{1}$	$D_x = 1.426$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 11.147$ (3) Å	Cell parameters from 10985 reflections
$b = 11.500$ (3) Å	$\theta = 2.5$–26.0º
$c = 11.832$ (3) Å	$\mu = 0.34$ mm^{-1}
$\alpha = 111.722$ (4)º	$T = 295$ (2) K
$\beta = 92.011$ (4)º	Prism, colorless
$\gamma = 102.066$ (4)º	0.34 × 0.26 × 0.18 mm
$V = 1367.3$ (6) Å^3	

Data collection

Bruker SMART CCD diffractometer	5353 independent reflections
Radiation source: fine-focus sealed tube	4645 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.013$
$T = 295$(2) K	$\theta_{max} = 26.0$º
ω scans	$\theta_{min} = 2.5$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13\rightarrow13$
$T_{min} = 0.894$, $T_{max} = 0.942$	$k = -13\rightarrow14$
11720 measured reflections	$l = -14\rightarrow14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difmap and geom
$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.5532P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
5353 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
402 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
25 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.0000	0.0000	0.5000	0.03248 (11)
F1	0.46666 (10)	0.53125 (9)	0.63639 (11)	0.0466 (3)
O1	0.08828 (11)	−0.14497 (11)	0.51391 (13)	0.0442 (3)
O1W	0.0623 (2)	0.60894 (17)	0.6358 (2)	0.0861 (7)
O2	0.22468 (12)	−0.23558 (13)	0.56627 (17)	0.0632 (5)
O2W	0.14371 (15)	0.64240 (17)	0.92704 (17)	0.0661 (4)
O3	0.18601 (10)	0.10280 (11)	0.51526 (11)	0.0370 (3)
O3W	0.28264 (18)	0.06305 (16)	0.96455 (16)	0.0685 (5)
O4	0.01341 (12)	0.08480 (13)	0.70334 (12)	0.0460 (3)
O4W	0.54654 (17)	0.79875 (16)	0.82458 (17)	0.0690 (5)
O5	0.23622 (11)	0.22196 (11)	0.84581 (12)	0.0427 (3)
O5W	0.30062 (16)	0.81047 (17)	0.83005 (15)	0.0673 (4)
O6	0.18210 (11)	0.39621 (12)	0.84330 (13)	0.0475 (3)
O6W	0.91289 (15)	0.29089 (17)	0.83310 (16)	0.0660 (4)
O7W	0.91049 (14)	0.62388 (13)	0.39048 (14)	0.0551 (4)
N1	0.51219 (12)	0.07432 (13)	0.66259 (13)	0.0324 (3)
N2	0.69176 (12)	0.52516 (14)	0.72389 (13)	0.0353 (3)
N3	0.91188 (13)	0.72584 (14)	0.77586 (14)	0.0364 (3)
C1	0.19619 (15)	−0.14347 (15)	0.55046 (16)	0.0339 (4)
C2	0.29724 (14)	−0.02282 (15)	0.58101 (15)	0.0300 (3)
C3	0.28289 (14)	0.09020 (15)	0.56370 (14)	0.0283 (3)
C4	0.39132 (14)	0.19783 (15)	0.60438 (14)	0.0278 (3)
C5	0.38087 (14)	0.31463 (15)	0.59749 (15)	0.0314 (3)
H5A	0.3063	0.3221	0.5664	0.038*
C6	0.48032 (15)	0.41633 (15)	0.63654 (15)	0.0332 (4)
C7	0.59673 (14)	0.41172 (16)	0.68282 (14)	0.0315 (3)
C8	0.60684 (14)	0.29760 (16)	0.69184 (15)	0.0321 (3)
H8A	0.6819	0.2914	0.7232	0.039*
C9	0.50454 (14)	0.19059 (15)	0.65399 (14)	0.0288 (3)
C10	0.41142 (15)	−0.02378 (16)	0.62819 (15)	0.0329 (4)
H10A	0.4194	−0.0990	0.6370	0.039*
C11	0.62620 (16)	0.05826 (17)	0.71744 (17)	0.0382 (4)
H11A	0.6977	0.1031	0.6929	0.046*
H11B	0.6262	−0.0325	0.6864	0.046*
C12	0.6364 (2)	0.1097 (2)	0.85510 (18)	0.0512 (5)
H12A	0.6413	0.2006	0.8865	0.077*
H12B	0.7095	0.0945	0.8869	0.077*
H12C	0.5650	0.0668	0.8798	0.077*
C13	0.79810 (16)	0.53132 (17)	0.80351 (17)	0.0380 (4)
H13A	0.8515	0.4807	0.7553	0.046*
H13B	0.7705	0.4964	0.8638	0.046*
C14	0.86825 (16)	0.67091 (17)	0.86713 (16)	0.0391 (4)
H14A	0.8149	0.7205	0.9166	0.047*
H14B	0.9386	0.6767	0.9212	0.047*
C15	0.80610 (17)	0.71083 (18)	0.68622 (18)	0.0432 (4)

H15A	0.8371	0.7396	0.6231	0.052*
H15B	0.7515	0.7639	0.7279	0.052*
C16	0.73510 (17)	0.57148 (18)	0.62816 (17)	0.0434 (4)
H16A	0.6648	0.5633	0.5727	0.052*
H16B	0.7879	0.5192	0.5811	0.052*
C17	0.9810 (2)	0.86274 (19)	0.8371 (2)	0.0587 (6)
H17A	0.9272	0.9131	0.8826	0.088*
H17B	1.0105	0.8947	0.7763	0.088*
H17C	1.0498	0.8690	0.8918	0.088*
C18	0.25857 (15)	0.34060 (16)	0.86950 (s15)	0.0335 (4)
C19	0.38438 (14)	0.42305 (15)	0.93586 (14)	0.0311 (3)
C20	0.46415 (16)	0.37370 (17)	0.98691 (18)	0.0426 (4)
H20A	0.4412	0.2880	0.9783	0.051*
C21	0.57784 (16)	0.44940 (17)	1.05081 (19)	0.0434 (4)
H21A	0.6295	0.4141	1.0852	0.052*
H1W1	0.1161 (17)	0.6498 (18)	0.607 (2)	0.065*
H1W2	0.076 (2)	0.5375 (13)	0.629 (2)	0.065*
H2W1	0.161 (2)	0.5696 (12)	0.907 (2)	0.065*
H3W1	0.271 (2)	0.1053 (18)	0.9211 (17)	0.065*
H4W1	0.550 (2)	0.7200 (10)	0.7995 (19)	0.065*
H5W1	0.2664 (17)	0.787 (2)	0.7574 (12)	0.065*
H2W2	0.1932 (19)	0.6898 (17)	0.900 (2)	0.065*
H5W2	0.3756 (10)	0.805 (2)	0.8276 (19)	0.065*
H4W2	0.591 (2)	0.8406 (17)	0.8935 (13)	0.065*
H3W2	0.303 (2)	−0.0048 (15)	0.9206 (18)	0.065*
H1O	0.0850 (10)	0.1230 (19)	0.7420 (19)	0.065*
H3N	0.9643 (18)	0.682 (2)	0.7304 (19)	0.065*
H2O	−0.0366 (15)	0.1318 (19)	0.734 (2)	0.065*
H7W1	0.887 (2)	0.624 (2)	0.3214 (12)	0.065*
H7W2	0.9690 (16)	0.6912 (16)	0.4274 (17)	0.065*
H6W1	0.8902 (18)	0.311 (2)	0.9050 (12)	0.065*
H6W2	0.9887 (11)	0.330 (2)	0.8411 (19)	0.065*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.02475 (18)	0.02569 (18)	0.0422 (2)	−0.00318 (13)	−0.00723 (14)	0.01368 (15)
F1	0.0427 (6)	0.0294 (5)	0.0652 (7)	−0.0028 (4)	−0.0135 (5)	0.0234 (5)
O1	0.0340 (6)	0.0271 (6)	0.0653 (9)	−0.0040 (5)	−0.0115 (6)	0.0185 (6)
O1W	0.1294 (17)	0.0606 (11)	0.1088 (15)	0.0548 (11)	0.0819 (13)	0.0552 (11)
O2	0.0359 (7)	0.0407 (8)	0.1243 (14)	0.0035 (6)	0.0029 (8)	0.0481 (9)
O2W	0.0527 (9)	0.0580 (10)	0.0800 (12)	0.0161 (8)	0.0081 (8)	0.0166 (9)
O3	0.0257 (6)	0.0328 (6)	0.0523 (7)	−0.0024 (5)	−0.0070 (5)	0.0225 (6)
O3W	0.0795 (11)	0.0500 (9)	0.0772 (12)	0.0130 (8)	−0.0082 (9)	0.0290 (8)
O4	0.0378 (7)	0.0445 (7)	0.0446 (8)	0.0001 (6)	−0.0074 (6)	0.0110 (6)
O4W	0.0744 (11)	0.0449 (9)	0.0718 (11)	0.0043 (8)	−0.0024 (9)	0.0109 (8)
O5	0.0393 (7)	0.0338 (6)	0.0463 (7)	−0.0006 (5)	−0.0086 (5)	0.0122 (6)
O5W	0.0653 (10)	0.0660 (10)	0.0599 (10)	0.0114 (9)	−0.0115 (8)	0.0163 (8)

O6	0.0359 (7)	0.0423 (7)	0.0594 (8)	0.0026 (5)	−0.0121 (6)	0.0195 (6)
O6W	0.0509 (9)	0.0728 (11)	0.0716 (11)	0.0146 (8)	0.0112 (8)	0.0246 (9)
O7W	0.0614 (9)	0.0354 (7)	0.0620 (9)	−0.0024 (6)	−0.0176 (7)	0.0213 (7)
N1	0.0278 (7)	0.0320 (7)	0.0379 (8)	0.0044 (5)	0.0000 (5)	0.0158 (6)
N2	0.0293 (7)	0.0371 (8)	0.0362 (8)	−0.0074 (6)	−0.0069 (6)	0.0198 (6)
N3	0.0276 (7)	0.0309 (7)	0.0444 (8)	−0.0012 (6)	0.0038 (6)	0.0120 (6)
C1	0.0309 (8)	0.0268 (8)	0.0438 (10)	0.0025 (6)	0.0042 (7)	0.0157 (7)
C2	0.0276 (8)	0.0276 (8)	0.0328 (8)	0.0016 (6)	0.0027 (6)	0.0121 (7)
C3	0.0261 (7)	0.0276 (8)	0.0293 (8)	0.0006 (6)	0.0021 (6)	0.0120 (6)
C4	0.0251 (7)	0.0277 (8)	0.0288 (8)	0.0010 (6)	0.0006 (6)	0.0120 (6)
C5	0.0265 (8)	0.0323 (8)	0.0342 (8)	0.0008 (6)	−0.0040 (6)	0.0157 (7)
C6	0.0357 (9)	0.0270 (8)	0.0363 (9)	0.0003 (7)	−0.0027 (7)	0.0160 (7)
C7	0.0282 (8)	0.0325 (8)	0.0300 (8)	−0.0033 (6)	−0.0011 (6)	0.0138 (7)
C8	0.0240 (7)	0.0366 (9)	0.0342 (8)	0.0009 (6)	−0.0008 (6)	0.0158 (7)
C9	0.0273 (8)	0.0296 (8)	0.0292 (8)	0.0021 (6)	0.0019 (6)	0.0137 (6)
C10	0.0322 (8)	0.0297 (8)	0.0388 (9)	0.0051 (7)	0.0038 (7)	0.0168 (7)
C11	0.0314 (8)	0.0373 (9)	0.0473 (10)	0.0084 (7)	−0.0021 (7)	0.0187 (8)
C12	0.0513 (11)	0.0531 (12)	0.0483 (11)	0.0085 (9)	−0.0065 (9)	0.0220 (10)
C13	0.0311 (8)	0.0408 (9)	0.0410 (10)	−0.0034 (7)	−0.0049 (7)	0.0218 (8)
C14	0.0310 (8)	0.0426 (10)	0.0376 (9)	−0.0021 (7)	−0.0031 (7)	0.0153 (8)
C15	0.0372 (9)	0.0433 (10)	0.0513 (11)	−0.0016 (8)	−0.0008 (8)	0.0272 (9)
C16	0.0411 (10)	0.0461 (10)	0.0386 (10)	−0.0087 (8)	−0.0050 (8)	0.0227 (8)
C17	0.0507 (12)	0.0362 (10)	0.0724 (15)	−0.0085 (9)	−0.0010 (10)	0.0129 (10)
C18	0.0311 (8)	0.0363 (9)	0.0295 (8)	0.0024 (7)	0.0008 (6)	0.0118 (7)
C19	0.0279 (8)	0.0331 (8)	0.0289 (8)	0.0036 (6)	0.0020 (6)	0.0103 (7)
C20	0.0350 (9)	0.0318 (9)	0.0586 (12)	0.0017 (7)	−0.0048 (8)	0.0193 (8)
C21	0.0328 (9)	0.0392 (10)	0.0603 (12)	0.0035 (7)	−0.0081 (8)	0.0253 (9)

Geometric parameters (Å, °)

Mn1—O3	2.1261 (12)	C2—C10	1.376 (2)
Mn1—O3^{i}	2.1261 (12)	C2—C3	1.428 (2)
Mn1—O1	2.1569 (13)	C3—C4	1.455 (2)
Mn1—O1^{i}	2.1569 (13)	C4—C5	1.404 (2)
Mn1—O4^{i}	2.2223 (15)	C4—C9	1.404 (2)
Mn1—O4	2.2223 (15)	C5—C6	1.354 (2)
F1—C6	1.3621 (19)	C5—H5A	0.9300
O1—C1	1.258 (2)	C6—C7	1.410 (2)
O1W—H1W1	0.841 (9)	C7—C8	1.382 (2)
O1W—H1W2	0.840 (9)	C8—C9	1.409 (2)
O2—C1	1.241 (2)	C8—H8A	0.9300
O2W—H2W1	0.846 (9)	C10—H10A	0.9300
O2W—H2W2	0.849 (9)	C11—C12	1.504 (3)
O3—C3	1.2646 (19)	C11—H11A	0.9700
O3W—H3W1	0.851 (9)	C11—H11B	0.9700
O3W—H3W2	0.843 (9)	C12—H12A	0.9600
O4—H1O	0.848 (9)	C12—H12B	0.9600
O4—H2O	0.853 (9)	C12—H12C	0.9600

O4W—H4W1	0.853 (9)	C13—C14	1.515 (2)
O4W—H4W2	0.849 (9)	C13—H13A	0.9700
O5—C18	1.254 (2)	C13—H13B	0.9700
O5W—H5W1	0.848 (9)	C14—H14A	0.9700
O5W—H5W2	0.852 (9)	C14—H14B	0.9700
O6—C18	1.260 (2)	C15—C16	1.511 (2)
O6W—H6W1	0.857 (9)	C15—H15A	0.9700
O6W—H6W2	0.855 (9)	C15—H15B	0.9700
O7W—H7W1	0.849 (9)	C16—H16A	0.9700
O7W—H7W2	0.857 (9)	C16—H16B	0.9700
N1—C10	1.341 (2)	C17—H17A	0.9600
N1—C9	1.398 (2)	C17—H17B	0.9600
N1—C11	1.483 (2)	C17—H17C	0.9600
N2—C7	1.406 (2)	C18—C19	1.516 (2)
N2—C13	1.461 (2)	C19—C20	1.380 (2)
N2—C16	1.476 (2)	C19—C21^{ii}	1.385 (2)
N3—C17	1.485 (2)	C20—C21	1.386 (2)
N3—C14	1.488 (2)	C20—H20A	0.9300
N3—C15	1.496 (2)	C21—C19^{ii}	1.385 (2)
N3—H3N	0.911 (10)	C21—H21A	0.9300
C1—C2	1.507 (2)		
O3—Mn1—O3^{i}	180.0	C9—C8—H8A	119.7
O3—Mn1—O1	82.48 (5)	N1—C9—C4	117.96 (13)
O3^{i}—Mn1—O1	97.52 (5)	N1—C9—C8	121.74 (14)
O3—Mn1—O1^{i}	97.52 (5)	C4—C9—C8	120.29 (14)
O3^{i}—Mn1—O1^{i}	82.48 (5)	N1—C10—C2	125.66 (15)
O1—Mn1—O1^{i}	180.0	N1—C10—H10A	117.2
O3—Mn1—O4^{i}	91.74 (5)	C2—C10—H10A	117.2
O3^{i}—Mn1—O4^{i}	88.26 (5)	N1—C11—C12	111.96 (15)
O1—Mn1—O4^{i}	91.32 (5)	N1—C11—H11A	109.2
O1^{i}—Mn1—O4^{i}	88.68 (5)	C12—C11—H11A	109.2
O3—Mn1—O4	88.26 (5)	N1—C11—H11B	109.2
O3^{i}—Mn1—O4	91.74 (5)	C12—C11—H11B	109.2
O1—Mn1—O4	88.68 (5)	H11A—C11—H11B	107.9
O1^{i}—Mn1—O4	91.32 (5)	C11—C12—H12A	109.5
O4^{i}—Mn1—O4	180.0	C11—C12—H12B	109.5
C1—O1—Mn1	134.01 (10)	H12A—C12—H12B	109.5
H1W1—O1W—H1W2	112.1 (15)	C11—C12—H12C	109.5
H2W1—O2W—H2W2	109.9 (15)	H12A—C12—H12C	109.5
C3—O3—Mn1	128.61 (10)	H12B—C12—H12C	109.5
H3W1—O3W—H3W2	109.5 (15)	N2—C13—C14	108.54 (14)
Mn1—O4—H1O	116.7 (15)	N2—C13—H13A	110.0
Mn1—O4—H2O	116.2 (16)	C14—C13—H13A	110.0
H1O—O4—H2O	108.8 (14)	N2—C13—H13B	110.0
H4W1—O4W—H4W2	109.3 (14)	C14—C13—H13B	110.0
H5W1—O5W—H5W2	108.8 (14)	H13A—C13—H13B	108.4

H6W1—O6W—H6W2	107.5 (14)	N3—C14—C13	110.71 (14)
H7W1—O7W—H7W2	108.5 (14)	N3—C14—H14A	109.5
C10—N1—C9	119.52 (14)	C13—C14—H14A	109.5
C10—N1—C11	118.21 (14)	N3—C14—H14B	109.5
C9—N1—C11	122.10 (13)	C13—C14—H14B	109.5
C7—N2—C13	117.36 (13)	H14A—C14—H14B	108.1
C7—N2—C16	115.44 (13)	N3—C15—C16	110.30 (15)
C13—N2—C16	109.53 (13)	N3—C15—H15A	109.6
C17—N3—C14	111.28 (15)	C16—C15—H15A	109.6
C17—N3—C15	111.36 (15)	N3—C15—H15B	109.6
C14—N3—C15	110.75 (13)	C16—C15—H15B	109.6
C17—N3—H3N	107.0 (15)	H15A—C15—H15B	108.1
C14—N3—H3N	110.6 (15)	N2—C16—C15	110.04 (15)
C15—N3—H3N	105.7 (15)	N2—C16—H16A	109.7
O2—C1—O1	123.65 (15)	C15—C16—H16A	109.7
O2—C1—C2	117.11 (15)	N2—C16—H16B	109.7
O1—C1—C2	119.21 (14)	C15—C16—H16B	109.7
C10—C2—C3	118.45 (14)	H16A—C16—H16B	108.2
C10—C2—C1	116.66 (14)	N3—C17—H17A	109.5
C3—C2—C1	124.89 (14)	N3—C17—H17B	109.5
O3—C3—C2	125.65 (14)	H17A—C17—H17B	109.5
O3—C3—C4	118.56 (14)	N3—C17—H17C	109.5
C2—C3—C4	115.78 (14)	H17A—C17—H17C	109.5
C5—C4—C9	118.85 (14)	H17B—C17—H17C	109.5
C5—C4—C3	118.57 (14)	O5—C18—O6	124.04 (15)
C9—C4—C3	122.54 (14)	O5—C18—C19	118.20 (15)
C6—C5—C4	119.38 (15)	O6—C18—C19	117.75 (15)
C6—C5—H5A	120.3	C20—C19—C21^{ii}	117.87 (15)
C4—C5—H5A	120.3	C20—C19—C18	120.83 (15)
C5—C6—F1	118.66 (15)	C21^{ii}—C19—C18	121.29 (15)
C5—C6—C7	123.54 (15)	C19—C20—C21	121.25 (16)
F1—C6—C7	117.73 (14)	C19—C20—H20A	119.4
C8—C7—N2	124.55 (15)	C21—C20—H20A	119.4
C8—C7—C6	117.26 (14)	C19^{ii}—C21—C20	120.88 (17)
N2—C7—C6	118.06 (15)	C19^{ii}—C21—H21A	119.6
C7—C8—C9	120.62 (15)	C20—C21—H21A	119.6
C7—C8—H8A	119.7		
O3—Mn1—O1—C1	17.92 (17)	F1—C6—C7—N2	−1.0 (2)
O3^{i}—Mn1—O1—C1	−162.08 (17)	N2—C7—C8—C9	176.65 (15)
O1^{i}—Mn1—O1—C1	22 (19)	C6—C7—C8—C9	1.0 (2)
O4^{i}—Mn1—O1—C1	109.51 (17)	C10—N1—C9—C4	−2.6 (2)
O4—Mn1—O1—C1	−70.49 (17)	C11—N1—C9—C4	−177.88 (14)
O3^{i}—Mn1—O3—C3	149 (31)	C10—N1—C9—C8	178.36 (15)
O1—Mn1—O3—C3	−24.78 (14)	C11—N1—C9—C8	3.0 (2)
O1^{i}—Mn1—O3—C3	155.22 (14)	C5—C4—C9—N1	178.58 (14)
O4^{i}—Mn1—O3—C3	−115.88 (14)	C3—C4—C9—N1	0.8 (2)
O4—Mn1—O3—C3	64.12 (14)	C5—C4—C9—C8	−2.3 (2)

Mn1—O1—C1—O2	169.97 (15)	C3—C4—C9—C8	179.90 (15)
Mn1—O1—C1—C2	−8.1 (3)	C7—C8—C9—N1	−179.75 (15)
O2—C1—C2—C10	−2.4 (2)	C7—C8—C9—C4	1.2 (2)
O1—C1—C2—C10	175.82 (16)	C9—N1—C10—C2	1.5 (3)
O2—C1—C2—C3	177.16 (17)	C11—N1—C10—C2	177.01 (16)
O1—C1—C2—C3	−4.7 (3)	C3—C2—C10—N1	1.5 (3)
Mn1—O3—C3—C2	23.6 (2)	C1—C2—C10—N1	−178.98 (16)
Mn1—O3—C3—C4	−157.54 (11)	C10—N1—C11—C12	−93.51 (19)
C10—C2—C3—O3	175.89 (16)	C9—N1—C11—C12	81.9 (2)
C1—C2—C3—O3	−3.6 (3)	C7—N2—C13—C14	−162.98 (15)
C10—C2—C3—C4	−3.0 (2)	C16—N2—C13—C14	62.85 (19)
C1—C2—C3—C4	177.45 (15)	C17—N3—C14—C13	−179.95 (16)
O3—C3—C4—C5	5.2 (2)	C15—N3—C14—C13	55.6 (2)
C2—C3—C4—C5	−175.80 (14)	N2—C13—C14—N3	−59.88 (19)
O3—C3—C4—C9	−177.03 (15)	C17—N3—C15—C16	−178.28 (16)
C2—C3—C4—C9	2.0 (2)	C14—N3—C15—C16	−53.9 (2)
C9—C4—C5—C6	1.2 (2)	C7—N2—C16—C15	162.65 (15)
C3—C4—C5—C6	179.08 (15)	C13—N2—C16—C15	−62.2 (2)
C4—C5—C6—F1	−175.97 (14)	N3—C15—C16—N2	57.0 (2)
C4—C5—C6—C7	1.1 (3)	O5—C18—C19—C20	−10.7 (2)
C13—N2—C7—C8	−13.3 (2)	O6—C18—C19—C20	168.18 (17)
C16—N2—C7—C8	118.21 (19)	O5—C18—C19—C21^{ii}	170.47 (17)
C13—N2—C7—C6	162.27 (16)	O6—C18—C19—C21^{ii}	−10.7 (2)
C16—N2—C7—C6	−66.2 (2)	C21^{ii}—C19—C20—C21	0.8 (3)
C5—C6—C7—C8	−2.2 (3)	C18—C19—C20—C21	−178.11 (17)
F1—C6—C7—C8	174.87 (15)	C19—C20—C21—C19^{ii}	−0.8 (3)
C5—C6—C7—N2	−178.13 (16)		

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

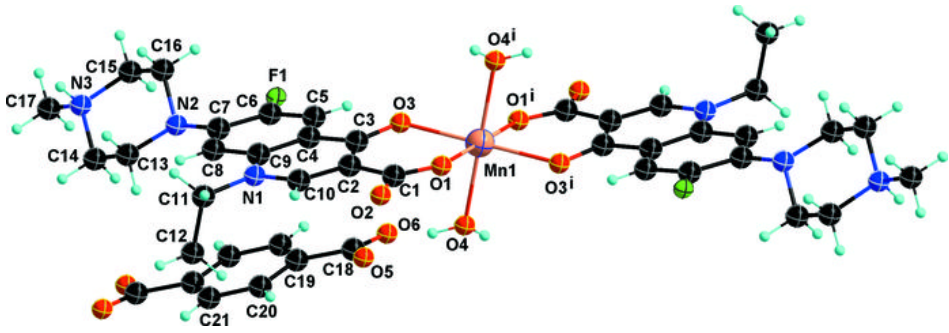
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1O···O5	0.848 (9)	1.914 (10)	2.7565 (18)	173 (2)
N3—H3N···O1W^{iii}	0.911 (10)	1.710 (10)	2.618 (2)	174 (2)
O1W—H1W1···O2^{iv}	0.841 (9)	1.813 (9)	2.644 (2)	169 (2)
O4—H2O···O6W^{v}	0.853 (9)	1.983 (13)	2.787 (2)	156.7 (19)
O7W—H7W1···O6^{vi}	0.849 (9)	1.983 (9)	2.828 (2)	173 (2)
O7W—H7W2···O1^{vii}	0.857 (9)	1.948 (10)	2.8013 (18)	174 (2)
O1W—H1W2···O7W^{vi}	0.840 (9)	1.825 (9)	2.662 (2)	175 (2)
O2W—H2W1···O6	0.846 (9)	1.923 (10)	2.764 (2)	172 (3)
O3W—H3W1···O5	0.851 (9)	1.954 (9)	2.797 (2)	171 (2)
O6W—H6W1···O2W^{ii}	0.857 (9)	1.932 (10)	2.785 (3)	174 (2)
O4W—H4W1···F1	0.853 (9)	2.287 (14)	2.976 (2)	138.1 (18)
O6W—H6W2···O6^{iii}	0.855 (9)	2.126 (10)	2.972 (2)	170 (2)
O5W—H5W1···O2^{iv}	0.848 (9)	2.200 (12)	3.023 (3)	164 (2)
O2W—H2W2···O5W	0.849 (9)	2.065 (10)	2.912 (3)	175 (2)

O5W—H5W2···O4W	0.852 (9)	1.923 (10)	2.774 (3)	178 (3)
O4W—H4W2···O3W^{ii}	0.849 (9)	1.961 (11)	2.801 (3)	170 (2)
O3W—H3W2···O5W^{viii}	0.843 (9)	1.988 (12)	2.802 (3)	162 (2)

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

Fig. 1


O4i
C16
C15
N3
C17
F1
N2
C7
C6
C5
O3
C3
O1i
C14
C13
C8
C9
C4
C2
C1
O1
Mn1
O3i
C11
N1
C10
O2
O6
C12
O4
C18
O5
C19
C20
C21