

Poly[[[(1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylato)manganese(II)]- μ_3 -4,4'-oxydibenzoato] monohydrate]

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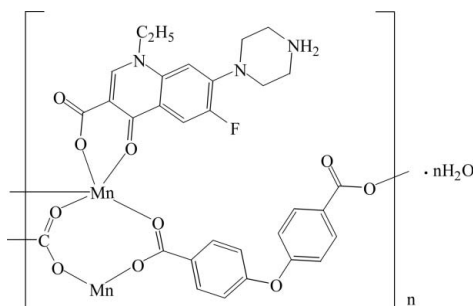
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.038; wR factor = 0.129; data-to-parameter ratio = 15.3.

In the title compound, $[\text{Mn}(\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_3)(\text{C}_{14}\text{H}_8\text{O}_5)\cdot\text{H}_2\text{O}]_n$, the unique Mn^{II} ion is coordinated by two O atoms from a chelating 1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylate ligand and three O atoms from three 4,4'-oxydibenzoate ligands, forming a distorted square-pyramidal coordination environment. In the crystal structure, centrosymmetric dinuclear manganese units are linked *via* 4,4'-oxydibenzoate ligands into one-dimensional chains; these chains are, in turn, connected *via* intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to form a two-dimensional supramolecular network. The O atom of the solvent water molecule is disordered over two sites with equal occupancies; the attached H atoms are common to both sites.

Related literature

For general background, see: Xiao *et al.* (2005). For a related structure, see: An *et al.* (2007).



Experimental

Crystal data

| | |
|---|-----------------------------------|
| $[\text{Mn}(\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_3)(\text{C}_{14}\text{H}_8\text{O}_5)]\cdot\text{H}_2\text{O}$ | $\gamma = 102.318$ (5)° |
| $M_r = 648.49$ | $V = 1390.1$ (10) Å ³ |
| Triclinic, $P\bar{1}$ | $Z = 2$ |
| $a = 10.208$ (5) Å | Mo $K\alpha$ radiation |
| $b = 11.915$ (5) Å | $\mu = 0.55$ mm ⁻¹ |
| $c = 13.202$ (5) Å | $T = 298$ (2) K |
| $\alpha = 100.751$ (5)° | $0.23 \times 0.20 \times 0.18$ mm |
| $\beta = 112.010$ (5)° | |

Data collection

| | |
|---|--|
| Bruker SMART APEX CCD area-detector diffractometer | 13533 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 6236 independent reflections |
| $T_{\min} = 0.885$, $T_{\max} = 0.908$ | 5434 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.031$ |

Refinement

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | 6 restraints |
| $wR(F^2) = 0.129$ | H-atom parameters constrained |
| $S = 1.05$ | $\Delta\rho_{\text{max}} = 0.55$ e Å ⁻³ |
| 6236 reflections | $\Delta\rho_{\text{min}} = -0.35$ e Å ⁻³ |
| 407 parameters | |

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O1}^w-\text{H2}\cdots\text{O3}^i$ | 1.16 | 2.40 | 3.359 (14) | 138 |
| $\text{O1}^w-\text{H2}\cdots\text{O4}^i$ | 1.16 | 1.87 | 2.874 (12) | 142 |
| $\text{N3}-\text{H3B}\cdots\text{O8}^i$ | 0.90 | 1.80 | 2.694 (3) | 169 |
| $\text{N3}-\text{H3C}\cdots\text{O4}^{ii}$ | 0.90 | 1.83 | 2.716 (3) | 169 |

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2564).

References

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supplementary materials

Acta Cryst. (2008). E64, m21 [doi:10.1107/S1600536807060825]

Poly[[[(1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylato)manganese(II)]- μ_3 -4,4'-oxydibenzoato] monohydrate]

J. Hong

Comment

Norfloxacin [1-Ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazin-1-yl)quinoline-3-carboxylic acid, Hcf] is a member of a class of quinolones that is used to treat infections (Xiao *et al.* 2005; An *et al.* 2007). As a part of our ongoing investigations in this field, we report here the crystal structure of the title compound. In the crystal structure of the title compound, the Mn atoms are coordinated by three oxygen atoms of one Hcf ligand, one 4,4'-oxydibenzoate ligand and one oxygen atom from one symmetry related 4,4'-oxydibenzoate within a distorted square-pyramidal geometry (Figure 1). In the crystal structure, dinuclear manganese units are linked *via* the 4,4'-oxydibenzoate anions into a one-dimensional chain running along [-2, -3, 2]. Finally, one-dimensional chains are connected with N—H \cdots O and O—H \cdots O hydrogen bonds to form a two-dimensional supramolecular network.

Experimental

The title compound was prepared by a hydrothermal method. A mixture of MnCl₂ (0.07 g 0.5 mmol), norfloxacin (0.16 g 0.5 mmol), 4,4'-oxy-bisbenzoic acid (0.13 g 0.5 mmol) and water (10 ml) was stirred for 20 min and then transferred to a 23 ml Teflon reactor. The reactor was kept at 433 K for 72 h under autogenous pressure. Single crystals of were obtained after cooling to room temperature.

Refinement

H atoms were placed in calculated positions with C—H = 0.93, 0.96 and 0.97 Å and N—H = 0.90 Å, and refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C, N, O)$. H atoms of water molecule were located in difference maps but were included as riding with O - H = 0.85 Å and $U_{iso}(H) = 1.5 U_{eq}(O)$. The O atom of the water molecule is disordered over two sites with the ratio of refined occupancies being 0.50 (2):0.50 (2). The H atoms of this water molecule are common to both sites.

Figures

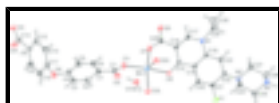


Fig. 1. Part of the crystal structure with labeling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: i = x - 1, y - 1, z; ii = -x + 2, -y + 1, -z + 1]. The disorder is not shown.

catena-Poly[[[(1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline- 3-carboxylato- $\kappa^2 O^3, O^4$)manganese(II)]- μ -4,4'-oxydibenzoato- $\kappa^3 O, O^1:O^1$] monohydrate]

Crystal data

[Mn(C₁₆H₁₈N₃O₃)(C₁₄H₈O₅)]·H₂O

Z = 2

supplementary materials

$M_r = 648.49$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 10.208$ (5) Å

$b = 11.915$ (5) Å

$c = 13.202$ (5) Å

$\alpha = 100.751$ (5)°

$\beta = 112.010$ (5)°

$\gamma = 102.318$ (5)°

$V = 1390.1$ (10) Å³

$F_{000} = 670$

$D_x = 1.549$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 13533 reflections

$\theta = 3.2$ – 27.5 °

$\mu = 0.55$ mm⁻¹

$T = 298$ (2) K

Block, colorless

$0.23 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.885$, $T_{\max} = 0.908$

13533 measured reflections

6236 independent reflections

5434 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 27.5$ °

$\theta_{\text{min}} = 3.2$ °

$h = -12 \rightarrow 13$

$k = -14 \rightarrow 15$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.129$

$S = 1.05$

6236 reflections

407 parameters

6 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0863P)^2 + 0.3678P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.55$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|---------------|--------------|----------------------------------|-----------|
| Mn1 | 0.87296 (3) | 0.44003 (2) | 0.32348 (2) | 0.02128 (10) | |
| C1 | 1.1128 (2) | 0.82195 (16) | 0.49788 (16) | 0.0247 (4) | |
| C2 | 1.1270 (2) | 0.90958 (17) | 0.59100 (16) | 0.0264 (4) | |
| H2A | 1.0997 | 0.8865 | 0.6456 | 0.032* | |
| C3 | 1.1812 (2) | 1.03007 (17) | 0.60306 (16) | 0.0273 (4) | |
| H3A | 1.1903 | 1.0879 | 0.6654 | 0.033* | |
| C4 | 1.2219 (2) | 1.06439 (16) | 0.52159 (17) | 0.0262 (4) | |
| C5 | 1.2094 (2) | 0.97946 (18) | 0.42831 (18) | 0.0314 (4) | |
| H5A | 1.2378 | 1.0029 | 0.3743 | 0.038* | |
| C6 | 1.1536 (2) | 0.85872 (17) | 0.41711 (18) | 0.0297 (4) | |
| H6A | 1.1432 | 0.8010 | 0.3541 | 0.036* | |
| C7 | 1.0531 (2) | 0.69147 (17) | 0.48503 (18) | 0.0264 (4) | |
| C8 | 1.4875 (2) | 1.36779 (17) | 0.38123 (17) | 0.0265 (4) | |
| C9 | 1.3520 (2) | 1.37948 (19) | 0.37526 (19) | 0.0323 (4) | |
| H9A | 1.3122 | 1.4316 | 0.3380 | 0.039* | |
| C10 | 1.2758 (2) | 1.31470 (19) | 0.42401 (19) | 0.0315 (4) | |
| H10A | 1.1860 | 1.3237 | 0.4205 | 0.038* | |
| C11 | 1.3354 (2) | 1.23664 (16) | 0.47793 (17) | 0.0280 (4) | |
| C12 | 1.4669 (2) | 1.21939 (18) | 0.48114 (18) | 0.0329 (4) | |
| H12A | 1.5031 | 1.1635 | 0.5143 | 0.039* | |
| C13 | 1.5432 (2) | 1.28651 (19) | 0.43436 (18) | 0.0303 (4) | |
| H13A | 1.6331 | 1.2773 | 0.4384 | 0.036* | |
| C14 | 1.5780 (2) | 1.44426 (18) | 0.33786 (18) | 0.0298 (4) | |
| C15 | 0.72279 (18) | 0.18861 (15) | 0.16263 (14) | 0.0198 (3) | |
| C16 | 0.84417 (19) | 0.18967 (15) | 0.13214 (15) | 0.0208 (3) | |
| C17 | 0.8599 (2) | 0.08327 (16) | 0.08805 (16) | 0.0247 (4) | |
| H17A | 0.9375 | 0.0866 | 0.0669 | 0.030* | |
| C18 | 0.65597 (18) | -0.03553 (15) | 0.10430 (14) | 0.0201 (3) | |
| C19 | 0.62933 (18) | 0.06987 (15) | 0.14683 (14) | 0.0195 (3) | |
| C20 | 0.51069 (19) | 0.06089 (16) | 0.17796 (15) | 0.0224 (3) | |
| H20A | 0.4918 | 0.1299 | 0.2068 | 0.027* | |
| C21 | 0.42376 (19) | -0.04923 (17) | 0.16565 (16) | 0.0239 (4) | |
| C22 | 0.44917 (19) | -0.15747 (15) | 0.12569 (15) | 0.0216 (3) | |
| C23 | 0.56632 (19) | -0.14844 (15) | 0.09490 (15) | 0.0208 (3) | |
| H23A | 0.5859 | -0.2178 | 0.0677 | 0.025* | |
| C24 | 0.3535 (2) | -0.28055 (17) | 0.22389 (17) | 0.0278 (4) | |
| H24A | 0.3440 | -0.2084 | 0.2647 | 0.033* | |
| H24B | 0.4467 | -0.2906 | 0.2713 | 0.033* | |
| C25 | 0.2255 (2) | -0.38815 (17) | 0.20169 (19) | 0.0303 (4) | |
| H25A | 0.2272 | -0.3970 | 0.2737 | 0.036* | |

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|------|--------------|---------------|--------------|-------------|----------|
| H25B | 0.1318 | -0.3765 | 0.1578 | 0.036* | |
| C26 | 0.2411 (2) | -0.48454 (17) | 0.02785 (17) | 0.0314 (4) | |
| H26A | 0.1473 | -0.4761 | -0.0203 | 0.038* | |
| H26B | 0.2525 | -0.5562 | -0.0121 | 0.038* | |
| C27 | 0.3680 (2) | -0.37514 (16) | 0.04987 (16) | 0.0271 (4) | |
| H27A | 0.4625 | -0.3864 | 0.0925 | 0.032* | |
| H27B | 0.3646 | -0.3653 | -0.0223 | 0.032* | |
| C28 | 0.95504 (19) | 0.30350 (15) | 0.14442 (16) | 0.0230 (4) | |
| C29 | 0.8106 (2) | -0.13254 (17) | 0.02814 (19) | 0.0298 (4) | |
| H29A | 0.8568 | -0.1147 | -0.0216 | 0.036* | |
| H29B | 0.7203 | -0.1998 | -0.0167 | 0.036* | |
| C30 | 0.9141 (3) | -0.1668 (2) | 0.1229 (2) | 0.0460 (6) | |
| H30A | 0.9362 | -0.2358 | 0.0915 | 0.069* | |
| H30B | 0.8681 | -0.1855 | 0.1718 | 0.069* | |
| H30C | 1.0044 | -0.1010 | 0.1665 | 0.069* | |
| F1 | 0.30490 (14) | -0.05557 (11) | 0.18978 (12) | 0.0368 (3) | |
| N1 | 0.77241 (17) | -0.02611 (13) | 0.07263 (14) | 0.0234 (3) | |
| N2 | 0.35453 (17) | -0.26761 (13) | 0.11516 (13) | 0.0232 (3) | |
| N3 | 0.23945 (18) | -0.49768 (14) | 0.13743 (14) | 0.0272 (3) | |
| H3B | 0.1626 | -0.5617 | 0.1228 | 0.033* | |
| H3C | 0.3240 | -0.5105 | 0.1802 | 0.033* | |
| O1 | 1.01455 (17) | 0.61842 (12) | 0.38860 (14) | 0.0356 (3) | |
| O2 | 1.04421 (16) | 0.66314 (13) | 0.56977 (14) | 0.0323 (3) | |
| O3 | 1.71509 (15) | 1.46076 (13) | 0.38222 (13) | 0.0342 (3) | |
| O4 | 1.51348 (18) | 1.48909 (17) | 0.26125 (17) | 0.0451 (4) | |
| O5 | 1.26452 (19) | 1.18672 (13) | 0.53831 (14) | 0.0360 (3) | |
| O6 | 0.69325 (14) | 0.28045 (11) | 0.19922 (12) | 0.0260 (3) | |
| O7 | 0.96748 (15) | 0.40179 (12) | 0.20826 (12) | 0.0291 (3) | |
| O8 | 1.03114 (17) | 0.29361 (12) | 0.08966 (14) | 0.0366 (4) | |
| O1W | 0.7413 (5) | 0.5678 (6) | 0.2066 (4) | 0.0338 (16) | 0.50 (2) |
| H1 | 0.8224 | 0.6189 | 0.2575 | 0.051* | |
| H2 | 0.6698 | 0.5411 | 0.2226 | 0.051* | |
| O1W' | 0.7286 (5) | 0.6219 (15) | 0.2009 (4) | 0.064 (3) | 0.50 (2) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Mn1 | 0.02024 (16) | 0.01816 (15) | 0.02471 (16) | 0.00072 (10) | 0.01335 (11) | 0.00295 (11) |
| C1 | 0.0233 (9) | 0.0223 (9) | 0.0277 (9) | 0.0064 (7) | 0.0100 (7) | 0.0088 (7) |
| C2 | 0.0276 (9) | 0.0303 (10) | 0.0235 (9) | 0.0084 (7) | 0.0120 (7) | 0.0111 (7) |
| C3 | 0.0333 (10) | 0.0251 (9) | 0.0217 (9) | 0.0085 (7) | 0.0113 (7) | 0.0047 (7) |
| C4 | 0.0290 (10) | 0.0202 (8) | 0.0281 (9) | 0.0054 (7) | 0.0120 (7) | 0.0074 (7) |
| C5 | 0.0406 (11) | 0.0261 (9) | 0.0300 (10) | 0.0049 (8) | 0.0209 (8) | 0.0080 (8) |
| C6 | 0.0356 (11) | 0.0235 (9) | 0.0302 (10) | 0.0053 (7) | 0.0184 (8) | 0.0039 (7) |
| C7 | 0.0199 (9) | 0.0237 (9) | 0.0373 (10) | 0.0071 (7) | 0.0136 (7) | 0.0098 (8) |
| C8 | 0.0223 (9) | 0.0252 (9) | 0.0318 (10) | 0.0059 (7) | 0.0130 (7) | 0.0071 (7) |
| C9 | 0.0314 (11) | 0.0360 (11) | 0.0426 (12) | 0.0168 (8) | 0.0214 (9) | 0.0214 (9) |
| C10 | 0.0287 (10) | 0.0331 (10) | 0.0395 (11) | 0.0105 (8) | 0.0193 (8) | 0.0149 (9) |

| | | | | | | |
|------|-------------|-------------|-------------|-------------|-------------|-------------|
| C11 | 0.0343 (10) | 0.0203 (8) | 0.0271 (9) | 0.0026 (7) | 0.0152 (8) | 0.0047 (7) |
| C12 | 0.0404 (11) | 0.0278 (10) | 0.0330 (10) | 0.0144 (8) | 0.0149 (9) | 0.0122 (8) |
| C13 | 0.0237 (9) | 0.0321 (10) | 0.0357 (11) | 0.0115 (7) | 0.0123 (8) | 0.0096 (8) |
| C14 | 0.0269 (10) | 0.0271 (9) | 0.0386 (11) | 0.0086 (7) | 0.0189 (8) | 0.0070 (8) |
| C15 | 0.0185 (8) | 0.0178 (8) | 0.0187 (8) | 0.0002 (6) | 0.0073 (6) | 0.0038 (6) |
| C16 | 0.0178 (8) | 0.0193 (8) | 0.0235 (8) | -0.0016 (6) | 0.0115 (6) | 0.0050 (6) |
| C17 | 0.0220 (9) | 0.0221 (8) | 0.0302 (9) | 0.0002 (6) | 0.0164 (7) | 0.0048 (7) |
| C18 | 0.0184 (8) | 0.0195 (8) | 0.0205 (8) | 0.0010 (6) | 0.0092 (6) | 0.0052 (6) |
| C19 | 0.0185 (8) | 0.0190 (8) | 0.0188 (8) | 0.0012 (6) | 0.0086 (6) | 0.0050 (6) |
| C20 | 0.0212 (9) | 0.0207 (8) | 0.0248 (8) | 0.0026 (6) | 0.0128 (7) | 0.0041 (7) |
| C21 | 0.0171 (8) | 0.0268 (9) | 0.0292 (9) | 0.0013 (6) | 0.0150 (7) | 0.0072 (7) |
| C22 | 0.0208 (8) | 0.0192 (8) | 0.0206 (8) | -0.0018 (6) | 0.0085 (6) | 0.0067 (6) |
| C23 | 0.0186 (8) | 0.0170 (8) | 0.0247 (8) | 0.0009 (6) | 0.0103 (6) | 0.0048 (6) |
| C24 | 0.0331 (10) | 0.0230 (9) | 0.0271 (9) | 0.0009 (7) | 0.0165 (8) | 0.0084 (7) |
| C25 | 0.0330 (11) | 0.0257 (9) | 0.0395 (11) | 0.0051 (8) | 0.0238 (9) | 0.0133 (8) |
| C26 | 0.0347 (11) | 0.0220 (9) | 0.0281 (10) | -0.0059 (7) | 0.0127 (8) | 0.0050 (7) |
| C27 | 0.0311 (10) | 0.0205 (8) | 0.0254 (9) | -0.0025 (7) | 0.0143 (7) | 0.0051 (7) |
| C28 | 0.0219 (9) | 0.0187 (8) | 0.0270 (9) | -0.0015 (6) | 0.0141 (7) | 0.0052 (7) |
| C29 | 0.0315 (10) | 0.0193 (8) | 0.0406 (11) | 0.0031 (7) | 0.0237 (8) | 0.0011 (7) |
| C30 | 0.0532 (15) | 0.0436 (13) | 0.0495 (14) | 0.0252 (11) | 0.0262 (12) | 0.0118 (11) |
| F1 | 0.0323 (7) | 0.0301 (6) | 0.0591 (8) | 0.0045 (5) | 0.0345 (6) | 0.0122 (6) |
| N1 | 0.0222 (7) | 0.0173 (7) | 0.0319 (8) | 0.0020 (5) | 0.0167 (6) | 0.0039 (6) |
| N2 | 0.0238 (8) | 0.0188 (7) | 0.0248 (8) | -0.0020 (5) | 0.0126 (6) | 0.0070 (6) |
| N3 | 0.0251 (8) | 0.0222 (7) | 0.0341 (9) | 0.0002 (6) | 0.0152 (7) | 0.0111 (6) |
| O1 | 0.0395 (8) | 0.0201 (6) | 0.0445 (9) | 0.0001 (6) | 0.0227 (7) | 0.0043 (6) |
| O2 | 0.0312 (7) | 0.0333 (7) | 0.0440 (8) | 0.0142 (6) | 0.0213 (6) | 0.0214 (6) |
| O3 | 0.0235 (7) | 0.0362 (8) | 0.0410 (8) | 0.0066 (6) | 0.0180 (6) | 0.0017 (6) |
| O4 | 0.0338 (9) | 0.0575 (10) | 0.0628 (11) | 0.0180 (7) | 0.0291 (8) | 0.0375 (9) |
| O5 | 0.0542 (10) | 0.0213 (7) | 0.0401 (8) | 0.0064 (6) | 0.0314 (7) | 0.0087 (6) |
| O6 | 0.0214 (6) | 0.0181 (6) | 0.0350 (7) | 0.0007 (5) | 0.0144 (5) | 0.0017 (5) |
| O7 | 0.0322 (7) | 0.0191 (6) | 0.0358 (8) | -0.0029 (5) | 0.0232 (6) | 0.0017 (5) |
| O8 | 0.0412 (9) | 0.0226 (7) | 0.0504 (9) | -0.0047 (6) | 0.0370 (7) | 0.0003 (6) |
| O1W | 0.0325 (17) | 0.036 (2) | 0.0339 (17) | 0.0081 (9) | 0.0168 (11) | 0.0111 (9) |
| O1W' | 0.051 (3) | 0.092 (8) | 0.057 (3) | 0.018 (3) | 0.028 (2) | 0.035 (3) |

Geometric parameters (Å, °)

| | | | |
|----------------------|-------------|----------|-----------|
| Mn1—O3 ⁱ | 2.0723 (16) | C18—C19 | 1.401 (2) |
| Mn1—O2 ⁱⁱ | 2.0997 (15) | C18—C23 | 1.411 (2) |
| Mn1—O1 | 2.1028 (16) | C19—C20 | 1.408 (2) |
| Mn1—O7 | 2.1170 (15) | C20—C21 | 1.360 (2) |
| Mn1—O6 | 2.1827 (14) | C20—H20A | 0.9300 |
| C1—C6 | 1.390 (3) | C21—F1 | 1.356 (2) |
| C1—C2 | 1.395 (3) | C21—C22 | 1.414 (3) |
| C1—C7 | 1.496 (3) | C22—C23 | 1.390 (3) |
| C2—C3 | 1.379 (3) | C22—N2 | 1.402 (2) |
| C2—H2A | 0.9300 | C23—H23A | 0.9300 |
| C3—C4 | 1.387 (3) | C24—N2 | 1.476 (2) |
| C3—H3A | 0.9300 | C24—C25 | 1.515 (3) |

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| | | | |
|---------------------------------------|-------------|-----------------------|-------------|
| C4—O5 | 1.378 (2) | C24—H24A | 0.9700 |
| C4—C5 | 1.385 (3) | C24—H24B | 0.9700 |
| C5—C6 | 1.387 (3) | C25—N3 | 1.483 (3) |
| C5—H5A | 0.9300 | C25—H25A | 0.9700 |
| C6—H6A | 0.9300 | C25—H25B | 0.9700 |
| C7—O2 | 1.256 (3) | C26—N3 | 1.490 (3) |
| C7—O1 | 1.264 (3) | C26—C27 | 1.523 (2) |
| C8—C9 | 1.393 (3) | C26—H26A | 0.9700 |
| C8—C13 | 1.394 (3) | C26—H26B | 0.9700 |
| C8—C14 | 1.498 (3) | C27—N2 | 1.468 (2) |
| C9—C10 | 1.386 (3) | C27—H27A | 0.9700 |
| C9—H9A | 0.9300 | C27—H27B | 0.9700 |
| C10—C11 | 1.380 (3) | C28—O8 | 1.252 (2) |
| C10—H10A | 0.9300 | C28—O7 | 1.259 (2) |
| C11—C12 | 1.387 (3) | C29—N1 | 1.487 (2) |
| C11—O5 | 1.392 (2) | C29—C30 | 1.494 (3) |
| C12—C13 | 1.381 (3) | C29—H29A | 0.9700 |
| C12—H12A | 0.9300 | C29—H29B | 0.9700 |
| C13—H13A | 0.9300 | C30—H30A | 0.9600 |
| C14—O3 | 1.251 (3) | C30—H30B | 0.9600 |
| C14—O4 | 1.263 (3) | C30—H30C | 0.9600 |
| C15—O6 | 1.255 (2) | N3—H3B | 0.9000 |
| C15—C16 | 1.437 (2) | N3—H3C | 0.9000 |
| C15—C19 | 1.456 (2) | O2—Mn1 ⁱⁱ | 2.0997 (15) |
| C16—C17 | 1.361 (3) | O3—Mn1 ⁱⁱⁱ | 2.0723 (16) |
| C16—C28 | 1.507 (2) | O1W—H1 | 0.8501 |
| C17—N1 | 1.344 (2) | O1W—H2 | 0.8500 |
| C17—H17A | 0.9300 | O1W'—H1 | 0.9823 |
| C18—N1 | 1.390 (2) | O1W'—H2 | 1.1648 |
| O3 ⁱ —Mn1—O2 ⁱⁱ | 94.25 (7) | C19—C20—H20A | 120.1 |
| O3 ⁱ —Mn1—O1 | 99.66 (7) | F1—C21—C20 | 118.42 (16) |
| O2 ⁱⁱ —Mn1—O1 | 110.98 (7) | F1—C21—C22 | 118.55 (15) |
| O3 ⁱ —Mn1—O7 | 159.82 (6) | C20—C21—C22 | 123.01 (16) |
| O2 ⁱⁱ —Mn1—O7 | 98.92 (6) | C23—C22—N2 | 123.11 (16) |
| O1—Mn1—O7 | 89.87 (6) | C23—C22—C21 | 117.17 (15) |
| O3 ⁱ —Mn1—O6 | 83.01 (6) | N2—C22—C21 | 119.69 (16) |
| O2 ⁱⁱ —Mn1—O6 | 90.64 (6) | C22—C23—C18 | 120.92 (16) |
| O1—Mn1—O6 | 157.82 (6) | C22—C23—H23A | 119.5 |
| O7—Mn1—O6 | 81.62 (6) | C18—C23—H23A | 119.5 |
| C6—C1—C2 | 118.53 (18) | N2—C24—C25 | 110.46 (16) |
| C6—C1—C7 | 121.02 (17) | N2—C24—H24A | 109.6 |
| C2—C1—C7 | 120.45 (18) | C25—C24—H24A | 109.6 |
| C3—C2—C1 | 120.77 (18) | N2—C24—H24B | 109.6 |
| C3—C2—H2A | 119.6 | C25—C24—H24B | 109.6 |
| C1—C2—H2A | 119.6 | H24A—C24—H24B | 108.1 |
| C2—C3—C4 | 119.57 (18) | N3—C25—C24 | 109.14 (16) |
| C2—C3—H3A | 120.2 | N3—C25—H25A | 109.9 |

| | | | |
|--------------|-------------|---------------------------|-------------|
| C4—C3—H3A | 120.2 | C24—C25—H25A | 109.9 |
| O5—C4—C5 | 124.49 (18) | N3—C25—H25B | 109.9 |
| O5—C4—C3 | 114.36 (17) | C24—C25—H25B | 109.9 |
| C5—C4—C3 | 121.01 (18) | H25A—C25—H25B | 108.3 |
| C4—C5—C6 | 118.62 (19) | N3—C26—C27 | 110.69 (15) |
| C4—C5—H5A | 120.7 | N3—C26—H26A | 109.5 |
| C6—C5—H5A | 120.7 | C27—C26—H26A | 109.5 |
| C5—C6—C1 | 121.51 (18) | N3—C26—H26B | 109.5 |
| C5—C6—H6A | 119.2 | C27—C26—H26B | 109.5 |
| C1—C6—H6A | 119.2 | H26A—C26—H26B | 108.1 |
| O2—C7—O1 | 125.27 (18) | N2—C27—C26 | 109.42 (16) |
| O2—C7—C1 | 117.92 (18) | N2—C27—H27A | 109.8 |
| O1—C7—C1 | 116.81 (18) | C26—C27—H27A | 109.8 |
| C9—C8—C13 | 118.67 (19) | N2—C27—H27B | 109.8 |
| C9—C8—C14 | 121.97 (18) | C26—C27—H27B | 109.8 |
| C13—C8—C14 | 119.29 (17) | H27A—C27—H27B | 108.2 |
| C10—C9—C8 | 121.04 (19) | O8—C28—O7 | 123.65 (15) |
| C10—C9—H9A | 119.5 | O8—C28—C16 | 116.83 (16) |
| C8—C9—H9A | 119.5 | O7—C28—C16 | 119.52 (16) |
| C11—C10—C9 | 118.86 (19) | N1—C29—C30 | 111.51 (17) |
| C11—C10—H10A | 120.6 | N1—C29—H29A | 109.3 |
| C9—C10—H10A | 120.6 | C30—C29—H29A | 109.3 |
| C10—C11—C12 | 121.40 (19) | N1—C29—H29B | 109.3 |
| C10—C11—O5 | 116.02 (19) | C30—C29—H29B | 109.3 |
| C12—C11—O5 | 122.25 (19) | H29A—C29—H29B | 108.0 |
| C13—C12—C11 | 119.01 (19) | C29—C30—H30A | 109.5 |
| C13—C12—H12A | 120.5 | C29—C30—H30B | 109.5 |
| C11—C12—H12A | 120.5 | H30A—C30—H30B | 109.5 |
| C12—C13—C8 | 120.93 (19) | C29—C30—H30C | 109.5 |
| C12—C13—H13A | 119.5 | H30A—C30—H30C | 109.5 |
| C8—C13—H13A | 119.5 | H30B—C30—H30C | 109.5 |
| O3—C14—O4 | 124.1 (2) | C17—N1—C18 | 119.41 (15) |
| O3—C14—C8 | 116.81 (19) | C17—N1—C29 | 117.84 (15) |
| O4—C14—C8 | 119.05 (18) | C18—N1—C29 | 122.66 (15) |
| O6—C15—C16 | 124.88 (15) | C22—N2—C27 | 115.72 (15) |
| O6—C15—C19 | 119.88 (16) | C22—N2—C24 | 114.10 (14) |
| C16—C15—C19 | 115.23 (15) | C27—N2—C24 | 111.64 (15) |
| C17—C16—C15 | 119.13 (15) | C25—N3—C26 | 110.69 (15) |
| C17—C16—C28 | 117.57 (16) | C25—N3—H3B | 109.5 |
| C15—C16—C28 | 123.30 (16) | C26—N3—H3B | 109.5 |
| N1—C17—C16 | 125.34 (17) | C25—N3—H3C | 109.5 |
| N1—C17—H17A | 117.3 | C26—N3—H3C | 109.5 |
| C16—C17—H17A | 117.3 | H3B—N3—H3C | 108.1 |
| N1—C18—C19 | 118.70 (15) | C7—O1—Mn1 | 127.16 (13) |
| N1—C18—C23 | 121.14 (16) | C7—O2—Mn1 ⁱⁱ | 139.01 (13) |
| C19—C18—C23 | 120.16 (16) | C14—O3—Mn1 ⁱⁱⁱ | 136.07 (15) |
| C18—C19—C20 | 118.98 (16) | C4—O5—C11 | 120.98 (16) |
| C18—C19—C15 | 122.11 (16) | C15—O6—Mn1 | 119.80 (11) |

supplementary materials

| | | | |
|--------------|-------------|-------------------------|-------------|
| C20—C19—C15 | 118.89 (16) | C28—O7—Mn1 | 131.03 (11) |
| C21—C20—C19 | 119.72 (17) | H1—O1W—H2 | 120.8 |
| C21—C20—H20A | 120.1 | H1—O1W ⁱ —H2 | 86.6 |

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

Hydrogen-bond geometry (Å, °)

| <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 ⁱ —H2 \cdots O3 ⁱ | 1.16 | 2.40 | 3.359 (14) | 138 |
| O1W ⁱ —H2 \cdots O4 ⁱ | 1.16 | 1.87 | 2.874 (12) | 142 |
| N3—H3B \cdots O8 ⁱ | 0.90 | 1.80 | 2.694 (3) | 169 |
| N3—H3C \cdots O4 ^{iv} | 0.90 | 1.83 | 2.716 (3) | 169 |

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

Fig. 1

