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Aqua(4-bromobenzoato-κO)bis(1,10-phenanthroline-$\kappa^2 N,N'$)manganese(II) 4-bromobenzoate dihydrate

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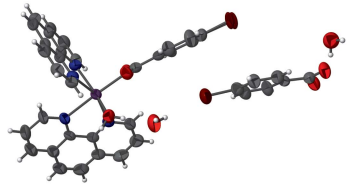
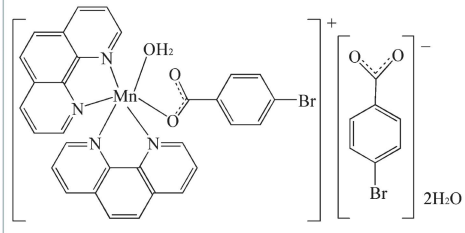
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $[Mn(C_7H_4BrO_2)(C_{12}H_8N_2)_2(H_2O)](C_7H_4BrO_2)\cdot 2H_2O$, consists of a monovalent $[Mn(C_7H_4BrO_2)(C_{12}H_8N_2)_2(H_2O)]^+$ complex cation, a 4-bromobenzoate anion and two lattice water molecules. In the complex cation, the Mn^{II} atom is coordinated by four N atoms from two bidentate chelating 1,10-phenanthroline (phen) ligands and two O atoms, one from a 4-bromobenzoate anion and the other from a coordinating water molecule. This completes an MnN_4O_2 coordination sphere with a distorted octahedral geometry. The Br atom of the bromobenzoato ligand is equally disordered over two sites. In the crystal, the complex cations are connected to each other *via* O—H···O, O—H···Br and C—H···O hydrogen bonds and π–π stacking interactions [closest separation = 3.492 (4) Å]. π–π contacts [closest separation = 3.771 (4) Å] also link the complex cations to both the coordinated and non-coordinating 4-bromobenzoate anions. Overall, these contacts generate a three-dimensional network structure.

3D view



Chemical scheme



Structure description

The structures $[Mn(phen)_2(H_2O)(C_7H_4FO_2)](C_7H_4FO_2)\cdot 2H_2O$, (Li *et al.*, 2011) and $[Mn_2(phen)_4(H_2O)(C_7H_4IO_2)](I)_2\cdot 2H_2O$ (Zhang, 2007) with Mn^{2+} cations and 1,10-phenanthroline (phen) ligands have been reported. We report here the synthesis and structure of the related complex aqua(4-bromobenzoato-κO)bis(1,10-phenanthroline-$\kappa^2 N,N'$)-manganese(II) 4-bromobenzoate dihydrate. The title complex is closely related to the compounds $[Mn(phen)_2(H_2O)(C_7H_4FO_2)](C_7H_4FO_2)\cdot 2H_2O$, (Li *et al.*, 2011) and $[Zn(H_2O)(phen)_2(C_7H_4BrO_2)](C_7H_4BrO_2)\cdot 2H_2O$, (Zhang *et al.*, 2010).

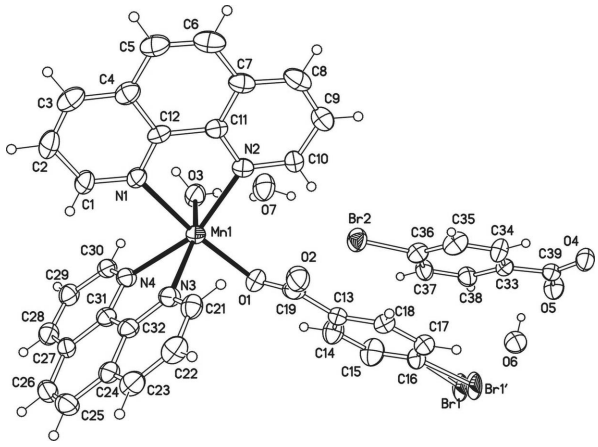


Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The title compound comprises an $[Mn(H_2O)(phen)_2(C_7H_4BrO_2)]^+$complex cation with the charge-balanced by a 4-bromobenzoate anion. Two lattice water molecules complete the asymmetric unit (Fig. 1). Within the cation, the Mn^{II} atom is coordinated by four N atoms from two bidentate chelating 1,10-phenanthroline (phen)ligands and two O atoms, one from a 4-bromobenzoate anion and the other from a coordinating water molecule. This completes an MnN_4O_2 coordination sphere with distorted octahedral geometry. The Mn—N bond lengths are in the range of 2.282 (5)–2.343 (5) Å with Mn—O bond lengths of 2.114 (5) and 2.128 (5) Å. The two crystallographically independent chelating phen ligands are almost perfectly planar (r.m.s. deviations = 0.018 and 0.032 Å, respectively). The dihedral angle between the mean planes of the phen ligands is 87.9 (1)°.

In the crystal, an extensive series of O—H···O, O—H···Br and C—H···O hydrogen bonds stabilize the structure (Table 1 and Fig. 2). In addition, inversion-related offset π–π contacts occur between adjacent N3,N4 phen ligands with $Cg6\cdots Cg6^{v}$ = 3.492 (4) and $Cg6\cdots Cg9^{v}$ = 3.689 (4) Å [symmetry code: (v) $1-x, -y, -z$; $Cg6$ and $Cg9$ are the centroids of the N4/C28–C31 and C24–C27/C21/C32 rings, respectively]. Furthermore

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3WA···O4^{i}	0.85	1.83	2.656 (7)	162
O3—H3WB···O7	0.85	1.85	2.696 (7)	179
O6—H6WA···O5	0.85	2.07	2.751 (8)	136
O6—H6WB···O5^{ii}	0.85	2.33	2.823 (7)	118
O6—H6WB···O7^{iii}	0.85	2.51	2.798 (9)	101
O7—H7WA···Br2	0.85	2.58	3.256 (6)	137
O7—H7WB···O6^{iii}	0.85	2.20	2.798 (9)	127
C21—H21A···O2	0.93	2.59	3.091 (9)	115
C28—H28A···O1^{iv}	0.93	2.57	3.402 (8)	149
C30—H30A···O3	0.93	2.53	3.107 (8)	121

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

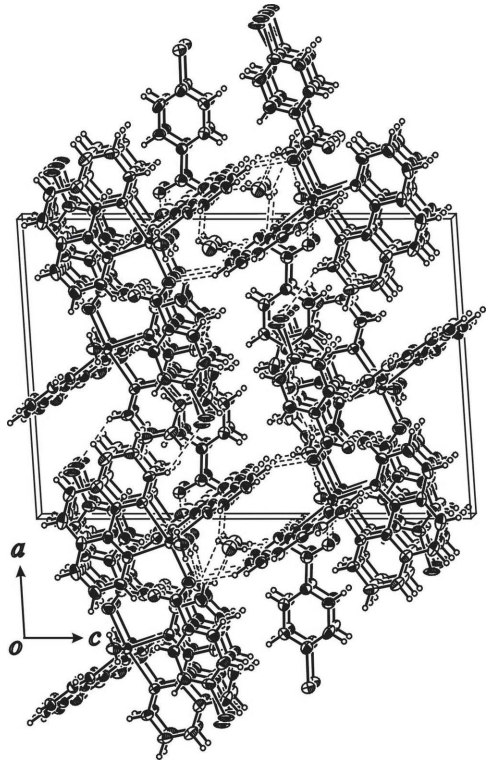


Figure 2
A packing diagram, viewed along the b axis. Dashed lines indicate hydrogen bonds.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Mn(C_7H_4BrO_2)(C_{12}H_8N_2)_2(H_2O)](C_7H_4BrO_2)\cdot 2H_2O$
M_r	869.42
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	14.193 (3), 11.912 (2), 21.253 (4)
β (°)	93.86 (3)
V (Å^3)	3584.9 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.65
Crystal size (mm)	0.49 × 0.40 × 0.35
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.289, 0.399
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26000, 5952, 3857
R_{int}	0.093
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.583
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.205, 1.13
No. of reflections	5952
No. of parameters	473
No. of restraints	6
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.66, −1.01

Computer programs: *RAPID-AUTO* (Rigaku, 1998), *CrystalStructure* (Rigaku/MSC, 2002), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

there are other significant π–π contacts $Cg4\cdots Cg8^{vi}$ =3.948 (4) Å and $Cg3\cdots Cg10^{vii}$ = 3.771 (4) Å between the aromatic rings of the other phen ligand and the benzene rings of both the coordinating and non-coordinating anions [symmetry codes: (vi) $\frac{3}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; (vii) $\frac{3}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z$; *Cg*3, *Cg*4, *Cg*8 and *Cg*10 are the centroids of the N1/C1–C4/C12, N2/C7–C11, C13–C18 and C33–C38 rings, respectively]. This extensive series of contacts combines to generate a three dimensional network structure.

Synthesis and crystallization

$MnCl_2\cdot 2H_2O$ (0.0811 g, 0.50 mmol) was dissolved in an appropriate amount of water, and then 1 *M* Na_2CO_3 solution was added. $MnCO_3$ was separated by filtration and was then washed five times with distilled water. The freshly prepared $MnCO_3$, 1,10-phenanthroline(phen)$\cdot H_2O$, 0.0493 g, 0.25 mmol) and 4-bromobenzoic acid (0.0516 g, 0.25 mmol), CH_3OH/H_2O (*v*/*v* = 1:2, 15 ml) were mixed and stirred for 2.0 h. Subsequently, the resulting suspension was heated in a 23 ml Teflon- lined stainless steel autoclave at 433 K for 5800 minutes. After the autoclave was cooled to room temperature over 2600 minutes, the solid was filtered off. The resulting filtrate was allowed to stand at room temperature, and slow evaporation over 1 month afforded yellow block-like single crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atom Br1 of the bromobenzoato ligand is equally disordered over two sites.

Acknowledgements

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full crystallographic data

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Aqua(4-bromobenzoato-κO)bis(1,10-phenanthroline-$\kappa^2 N,N'$)manganese(II) 4-bromobenzoate dihydrate

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Aqua(4-bromobenzoato-κO)bis(1,10-phenanthroline-$\kappa^2 N,N'$)manganese(II) 4-bromobenzoate dihydrate

Crystal data

$[Mn(C_7H_4BrO_2)(C_{12}H_8N_2)_2(H_2O)](C_7H_4BrO_2)\cdot 2H_2O$
M_r = 869.42
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 14.193 (3) Å
b = 11.912 (2) Å
c = 21.253 (4) Å
β = 93.86 (3)°
V = 3584.9 (12) Å^3
Z = 4
$F(000)$ = 1748
D_x = 1.611 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 14746 reflections
θ = 3.0–24.5°
μ = 2.65 mm^{-1}
T = 293 K
Block, yellow
0.49 × 0.40 × 0.35 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.289, T_{max} = 0.399
26000 measured reflections
5952 independent reflections
3857 reflections with $I > 2\sigma(I)$
R_{int} = 0.093
θ_{max} = 24.5°, θ_{min} = 3.0°
h = −16→16
k = −12→13
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.205
S = 1.13
5952 reflections
473 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
$w = 1/[\sigma^2(F_o^2) + (0.0898P)^2 + 6.5748P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −1.01 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0053 (6)

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.56915 (7)	0.11055 (8)	0.18912 (4)	0.0445 (3)	
N1	0.4353 (4)	0.1308 (4)	0.2469 (2)	0.0484 (13)	
N2	0.6170 (4)	0.1671 (5)	0.2888 (2)	0.0506 (13)	
N3	0.5305 (4)	−0.0764 (4)	0.1816 (2)	0.0487 (13)	
N4	0.4701 (4)	0.0841 (4)	0.0990 (2)	0.0449 (12)	
Br1	1.1551 (5)	0.0191 (13)	0.0874 (6)	0.0857 (12)	0.50
Br1′	1.1764 (5)	0.0103 (13)	0.0992 (6)	0.0857 (12)	0.50
Br2	0.93834 (5)	0.38650 (7)	0.10085 (4)	0.0712 (3)	
O1	0.7019 (3)	0.0811 (4)	0.1526 (2)	0.0626 (13)	
O2	0.7475 (4)	−0.0247 (5)	0.2351 (2)	0.0722 (14)	
O3	0.5724 (3)	0.2821 (4)	0.1613 (2)	0.0631 (12)	
H3WA	0.5294	0.3289	0.1687	0.076*	
H3WB	0.6186	0.3240	0.1534	0.076*	
O4	1.4147 (4)	0.4000 (5)	0.1686 (2)	0.0690 (14)	
O5	1.4133 (3)	0.4581 (5)	0.0697 (2)	0.0701 (14)	
O6	1.4030 (4)	0.4556 (5)	−0.0600 (3)	0.0849 (16)	
H6WA	1.3986	0.4925	−0.0261	0.102*	
H6WB	1.4264	0.5015	−0.0853	0.102*	
O7	0.7205 (4)	0.4136 (5)	0.1376 (3)	0.0854 (17)	
H7WA	0.7754	0.3885	0.1480	0.102*	
H7WB	0.7147	0.4419	0.1009	0.102*	
C1	0.3473 (5)	0.1152 (6)	0.2263 (3)	0.0599 (18)	
H1A	0.3350	0.0931	0.1846	0.072*	
C2	0.2707 (5)	0.1299 (7)	0.2636 (4)	0.072 (2)	
H2A	0.2092	0.1169	0.2472	0.086*	
C3	0.2883 (5)	0.1638 (6)	0.3245 (4)	0.069 (2)	
H3A	0.2385	0.1757	0.3499	0.082*	
C4	0.3804 (5)	0.1807 (6)	0.3485 (3)	0.0576 (17)	
C5	0.4046 (6)	0.2155 (7)	0.4125 (3)	0.069 (2)	
H5A	0.3571	0.2261	0.4400	0.082*	
C6	0.4940 (7)	0.2325 (7)	0.4325 (3)	0.074 (2)	
H6A	0.5078	0.2538	0.4742	0.088*	
C7	0.5697 (5)	0.2192 (6)	0.3921 (3)	0.0557 (17)	
C8	0.6649 (6)	0.2411 (6)	0.4104 (3)	0.071 (2)	
H8A	0.6819	0.2644	0.4514	0.085*	

C9	0.7325 (6)	0.2282 (7)	0.3684 (3)	0.072 (2)
H9A	0.7954	0.2441	0.3801	0.086*
C10	0.7060 (5)	0.1913 (7)	0.3082 (3)	0.0642 (19)
H10A	0.7526	0.1829	0.2798	0.077*
C11	0.5493 (5)	0.1832 (5)	0.3304 (3)	0.0463 (15)
C12	0.4530 (4)	0.1634 (5)	0.3078 (3)	0.0464 (15)
C13	0.8606 (5)	0.0191 (5)	0.1618 (3)	0.0489 (15)
C14	0.8805 (5)	0.0655 (7)	0.1047 (4)	0.067 (2)
H14A	0.8325	0.0988	0.0793	0.080*
C15	0.9710 (6)	0.0628 (8)	0.0853 (4)	0.078 (2)
H15A	0.9837	0.0934	0.0465	0.093*
C16	1.0420 (5)	0.0158 (6)	0.1224 (4)	0.0591 (18)
C17	1.0244 (5)	−0.0307 (6)	0.1787 (4)	0.0615 (19)
H17A	1.0733	−0.0632	0.2038	0.074*
C18	0.9340 (5)	−0.0297 (6)	0.1986 (3)	0.0519 (16)
H18A	0.9220	−0.0620	0.2371	0.062*
C19	0.7627 (5)	0.0248 (6)	0.1851 (3)	0.0571 (18)
C21	0.5591 (5)	−0.1556 (6)	0.2225 (3)	0.0543 (17)
H21A	0.5965	−0.1346	0.2582	0.065*
C22	0.5360 (5)	−0.2685 (6)	0.2146 (4)	0.0649 (19)
H22A	0.5569	−0.3210	0.2448	0.078*
C23	0.4827 (5)	−0.3015 (6)	0.1623 (4)	0.0620 (19)
H23A	0.4673	−0.3768	0.1562	0.074*
C24	0.4514 (4)	−0.2215 (6)	0.1179 (3)	0.0508 (16)
C25	0.3961 (5)	−0.2478 (7)	0.0603 (3)	0.0630 (19)
H25A	0.3812	−0.3222	0.0511	0.076*
C26	0.3658 (5)	−0.1671 (7)	0.0197 (3)	0.0620 (19)
H26A	0.3297	−0.1868	−0.0168	0.074*
C27	0.3875 (4)	−0.0527 (6)	0.0312 (3)	0.0500 (16)
C28	0.3580 (5)	0.0365 (7)	−0.0096 (3)	0.0597 (19)
H28A	0.3205	0.0217	−0.0462	0.072*
C29	0.3845 (5)	0.1437 (6)	0.0047 (3)	0.0561 (17)
H29A	0.3646	0.2025	−0.0217	0.067*
C30	0.4409 (4)	0.1644 (6)	0.0587 (3)	0.0495 (15)
H30A	0.4595	0.2379	0.0673	0.059*
C31	0.4436 (4)	−0.0226 (5)	0.0856 (3)	0.0441 (14)
C32	0.4752 (4)	−0.1087 (5)	0.1296 (3)	0.0465 (15)
C33	1.2670 (5)	0.4084 (5)	0.1103 (3)	0.0472 (15)
C34	1.2206 (5)	0.3675 (6)	0.1606 (3)	0.0594 (18)
H34A	1.2552	0.3462	0.1974	0.071*
C35	1.1240 (6)	0.3579 (7)	0.1569 (4)	0.070 (2)
H35A	1.0938	0.3285	0.1908	0.084*
C36	1.0719 (5)	0.3915 (6)	0.1036 (3)	0.0579 (17)
C37	1.1172 (5)	0.4316 (6)	0.0528 (3)	0.0599 (18)
H37A	1.0823	0.4527	0.0161	0.072*
C38	1.2146 (5)	0.4403 (6)	0.0564 (3)	0.0591 (18)
H38A	1.2450	0.4678	0.0222	0.071*
C39	1.3731 (5)	0.4228 (6)	0.1165 (3)	0.0524 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0424 (6)	0.0504 (6)	0.0409 (5)	0.0014 (4)	0.0039 (4)	−0.0048 (4)
N1	0.040 (3)	0.058 (3)	0.048 (3)	0.002 (2)	0.008 (2)	−0.003 (2)
N2	0.051 (3)	0.057 (3)	0.044 (3)	0.002 (3)	0.005 (2)	−0.009 (2)
N3	0.054 (3)	0.046 (3)	0.046 (3)	0.002 (3)	0.003 (2)	−0.003 (2)
N4	0.047 (3)	0.049 (3)	0.038 (3)	0.007 (2)	−0.001 (2)	0.000 (2)
Br1	0.020 (3)	0.134 (2)	0.103 (4)	−0.005 (3)	0.003 (2)	−0.019 (3)
Br1′	0.020 (3)	0.134 (2)	0.103 (4)	−0.005 (3)	0.003 (2)	−0.019 (3)
Br2	0.0485 (5)	0.0924 (7)	0.0734 (5)	−0.0039 (4)	0.0098 (4)	0.0010 (4)
O1	0.043 (3)	0.072 (3)	0.072 (3)	0.012 (2)	0.000 (2)	−0.006 (3)
O2	0.054 (3)	0.100 (4)	0.063 (3)	−0.005 (3)	0.009 (2)	−0.010 (3)
O3	0.050 (3)	0.051 (3)	0.089 (3)	0.000 (2)	0.004 (2)	0.000 (2)
O4	0.051 (3)	0.095 (4)	0.060 (3)	0.008 (3)	0.004 (2)	0.004 (3)
O5	0.053 (3)	0.095 (4)	0.064 (3)	−0.007 (3)	0.015 (2)	0.014 (3)
O6	0.0841 (18)	0.0868 (18)	0.0837 (18)	−0.0013 (10)	0.0060 (10)	−0.0003 (10)
O7	0.061 (3)	0.108 (5)	0.089 (4)	−0.010 (3)	0.011 (3)	0.009 (3)
C1	0.038 (4)	0.082 (5)	0.061 (4)	−0.006 (3)	0.014 (3)	−0.006 (3)
C2	0.042 (4)	0.080 (6)	0.095 (6)	−0.004 (4)	0.011 (4)	0.005 (4)
C3	0.063 (5)	0.068 (5)	0.079 (5)	0.007 (4)	0.035 (4)	0.005 (4)
C4	0.058 (4)	0.051 (4)	0.066 (4)	0.002 (3)	0.020 (3)	0.004 (3)
C5	0.083 (6)	0.068 (5)	0.058 (4)	0.002 (4)	0.029 (4)	−0.005 (4)
C6	0.105 (7)	0.067 (5)	0.050 (4)	−0.004 (5)	0.016 (4)	−0.009 (3)
C7	0.075 (5)	0.053 (4)	0.039 (3)	0.003 (4)	0.006 (3)	−0.003 (3)
C8	0.097 (6)	0.068 (5)	0.045 (4)	−0.002 (4)	−0.011 (4)	−0.010 (3)
C9	0.069 (5)	0.082 (6)	0.062 (4)	0.004 (4)	−0.013 (4)	−0.015 (4)
C10	0.042 (4)	0.087 (6)	0.063 (4)	0.002 (4)	−0.002 (3)	−0.023 (4)
C11	0.056 (4)	0.043 (4)	0.040 (3)	0.007 (3)	0.006 (3)	0.001 (3)
C12	0.051 (4)	0.045 (4)	0.044 (3)	0.007 (3)	0.015 (3)	−0.003 (3)
C13	0.051 (4)	0.044 (4)	0.052 (4)	0.000 (3)	0.001 (3)	−0.012 (3)
C14	0.058 (5)	0.076 (5)	0.066 (5)	0.005 (4)	0.003 (4)	0.015 (4)
C15	0.059 (5)	0.100 (6)	0.077 (5)	−0.010 (5)	0.025 (4)	0.018 (5)
C16	0.040 (4)	0.063 (5)	0.074 (5)	−0.003 (3)	0.001 (3)	−0.009 (4)
C17	0.053 (4)	0.055 (4)	0.075 (5)	0.009 (3)	−0.010 (4)	−0.013 (4)
C18	0.045 (4)	0.056 (4)	0.054 (4)	0.008 (3)	0.004 (3)	−0.006 (3)
C19	0.058 (4)	0.057 (4)	0.058 (4)	−0.006 (4)	0.010 (4)	−0.019 (3)
C21	0.045 (4)	0.068 (5)	0.050 (4)	0.001 (3)	0.008 (3)	0.006 (3)
C22	0.059 (5)	0.058 (5)	0.079 (5)	0.005 (4)	0.014 (4)	0.016 (4)
C23	0.054 (4)	0.046 (4)	0.088 (5)	−0.001 (3)	0.020 (4)	0.006 (4)
C24	0.041 (3)	0.055 (4)	0.057 (4)	−0.003 (3)	0.013 (3)	−0.007 (3)
C25	0.061 (5)	0.061 (5)	0.068 (5)	−0.013 (4)	0.015 (4)	−0.015 (4)
C26	0.046 (4)	0.085 (6)	0.056 (4)	−0.011 (4)	0.007 (3)	−0.020 (4)
C27	0.038 (3)	0.067 (5)	0.045 (3)	−0.001 (3)	0.004 (3)	−0.011 (3)
C28	0.050 (4)	0.089 (6)	0.040 (3)	0.004 (4)	0.004 (3)	−0.006 (3)
C29	0.051 (4)	0.071 (5)	0.045 (4)	0.012 (4)	−0.003 (3)	0.004 (3)
C30	0.049 (4)	0.053 (4)	0.046 (3)	0.008 (3)	−0.002 (3)	−0.005 (3)
C31	0.045 (4)	0.050 (4)	0.038 (3)	−0.002 (3)	0.011 (3)	−0.002 (3)

C32	0.044 (4)	0.053 (4)	0.044 (3)	0.000 (3)	0.013 (3)	−0.004 (3)
C33	0.047 (4)	0.045 (4)	0.050 (4)	0.004 (3)	0.006 (3)	−0.002 (3)
C34	0.043 (4)	0.072 (5)	0.064 (4)	0.007 (3)	0.006 (3)	0.018 (3)
C35	0.071 (5)	0.076 (5)	0.066 (5)	−0.001 (4)	0.033 (4)	0.016 (4)
C36	0.058 (4)	0.060 (4)	0.057 (4)	0.001 (3)	0.014 (3)	0.007 (3)
C37	0.052 (4)	0.079 (5)	0.048 (4)	0.000 (4)	−0.004 (3)	0.003 (3)
C38	0.057 (4)	0.071 (5)	0.050 (4)	−0.003 (4)	0.003 (3)	−0.001 (3)
C39	0.050 (4)	0.049 (4)	0.059 (4)	−0.001 (3)	0.003 (3)	−0.007 (3)

Geometric parameters (Å, º)

Mn1—O1	2.114 (5)	C10—H10A	0.9300
Mn1—O3	2.128 (5)	C11—C12	1.438 (9)
Mn1—N2	2.282 (5)	C13—C14	1.380 (9)
Mn1—N3	2.297 (5)	C13—C18	1.387 (9)
Mn1—N4	2.320 (5)	C13—C19	1.508 (9)
Mn1—N1	2.343 (5)	C14—C15	1.376 (11)
N1—C1	1.310 (8)	C14—H14A	0.9300
N1—C12	1.358 (7)	C15—C16	1.357 (11)
N2—C10	1.334 (8)	C15—H15A	0.9300
N2—C11	1.363 (7)	C16—C17	1.358 (10)
N3—C21	1.328 (8)	C17—C18	1.379 (10)
N3—C32	1.367 (8)	C17—H17A	0.9300
N4—C30	1.331 (8)	C18—H18A	0.9300
N4—C31	1.351 (8)	C21—C22	1.392 (10)
Br1—C16	1.814 (13)	C21—H21A	0.9300
Br1′—C16	2.003 (12)	C22—C23	1.360 (10)
Br2—C36	1.894 (7)	C22—H22A	0.9300
O1—C19	1.261 (8)	C23—C24	1.393 (10)
O2—C19	1.246 (8)	C23—H23A	0.9300
O3—H3WA	0.8500	C24—C32	1.404 (9)
O3—H3WB	0.8501	C24—C25	1.443 (9)
O4—C39	1.250 (8)	C25—C26	1.343 (10)
O5—C39	1.253 (8)	C25—H25A	0.9300
O6—H6WA	0.8500	C26—C27	1.415 (10)
O6—H6WB	0.8499	C26—H26A	0.9300
O7—H7WA	0.8500	C27—C31	1.404 (9)
O7—H7WB	0.8499	C27—C28	1.417 (10)
C1—C2	1.398 (10)	C28—C29	1.359 (10)
C1—H1A	0.9300	C28—H28A	0.9300
C2—C3	1.363 (11)	C29—C30	1.376 (9)
C2—H2A	0.9300	C29—H29A	0.9300
C3—C4	1.385 (10)	C30—H30A	0.9300
C3—H3A	0.9300	C31—C32	1.439 (9)
C4—C12	1.404 (8)	C33—C38	1.375 (9)
C4—C5	1.442 (10)	C33—C34	1.382 (9)
C5—C6	1.326 (11)	C33—C39	1.513 (9)
C5—H5A	0.9300	C34—C35	1.372 (10)

C6—C7	1.429 (10)	C34—H34A	0.9300
C6—H6A	0.9300	C35—C36	1.371 (10)
C7—C11	1.392 (8)	C35—H35A	0.9300
C7—C8	1.404 (10)	C36—C37	1.378 (10)
C8—C9	1.363 (11)	C37—C38	1.384 (10)
C8—H8A	0.9300	C37—H37A	0.9300
C9—C10	1.380 (9)	C38—H38A	0.9300
C9—H9A	0.9300		

O1—Mn1—O3	91.20 (19)	C16—C15—C14	120.4 (7)
O1—Mn1—N2	99.94 (19)	C16—C15—H15A	119.8
O3—Mn1—N2	87.91 (19)	C14—C15—H15A	119.8
O1—Mn1—N3	91.62 (19)	C15—C16—C17	120.5 (7)
O3—Mn1—N3	157.11 (18)	C15—C16—Br1	113.3 (7)
N2—Mn1—N3	113.92 (19)	C17—C16—Br1	126.2 (7)
O1—Mn1—N4	100.37 (18)	C15—C16—Br1′	123.5 (7)
O3—Mn1—N4	85.67 (18)	C17—C16—Br1′	116.0 (6)
N2—Mn1—N4	158.80 (18)	Br1—C16—Br1′	10.4 (7)
N3—Mn1—N4	71.48 (18)	C16—C17—C18	119.8 (7)
O1—Mn1—N1	169.49 (19)	C16—C17—H17A	120.1
O3—Mn1—N1	94.60 (18)	C18—C17—H17A	120.1
N2—Mn1—N1	71.58 (19)	C17—C18—C13	120.7 (6)
N3—Mn1—N1	86.44 (18)	C17—C18—H18A	119.7
N4—Mn1—N1	88.82 (18)	C13—C18—H18A	119.7
C1—N1—C12	118.1 (5)	O2—C19—O1	124.6 (7)
C1—N1—Mn1	126.8 (4)	O2—C19—C13	118.3 (7)
C12—N1—Mn1	115.1 (4)	O1—C19—C13	117.1 (6)
C10—N2—C11	117.6 (5)	N3—C21—C22	123.3 (7)
C10—N2—Mn1	124.6 (4)	N3—C21—H21A	118.4
C11—N2—Mn1	117.7 (4)	C22—C21—H21A	118.4
C21—N3—C32	117.5 (6)	C23—C22—C21	119.4 (7)
C21—N3—Mn1	125.6 (5)	C23—C22—H22A	120.3
C32—N3—Mn1	116.8 (4)	C21—C22—H22A	120.3
C30—N4—C31	118.0 (5)	C22—C23—C24	119.4 (7)
C30—N4—Mn1	125.4 (4)	C22—C23—H23A	120.3
C31—N4—Mn1	116.5 (4)	C24—C23—H23A	120.3
C19—O1—Mn1	118.7 (4)	C23—C24—C32	118.2 (6)
Mn1—O3—H3WA	123.4	C23—C24—C25	123.8 (7)
Mn1—O3—H3WB	130.6	C32—C24—C25	117.9 (6)
H3WA—O3—H3WB	103.0	C26—C25—C24	121.5 (7)
H6WA—O6—H6WB	105.0	C26—C25—H25A	119.3
H7WA—O7—H7WB	114.2	C24—C25—H25A	119.3
N1—C1—C2	123.6 (7)	C25—C26—C27	121.4 (6)
N1—C1—H1A	118.2	C25—C26—H26A	119.3
C2—C1—H1A	118.2	C27—C26—H26A	119.3
C3—C2—C1	118.4 (7)	C31—C27—C26	119.5 (6)
C3—C2—H2A	120.8	C31—C27—C28	116.1 (6)
C1—C2—H2A	120.8	C26—C27—C28	124.3 (6)

C2—C3—C4	120.0 (6)	C29—C28—C27	120.1 (6)
C2—C3—H3A	120.0	C29—C28—H28A	120.0
C4—C3—H3A	120.0	C27—C28—H28A	120.0
C3—C4—C12	117.8 (6)	C28—C29—C30	119.4 (7)
C3—C4—C5	123.2 (6)	C28—C29—H29A	120.3
C12—C4—C5	119.0 (7)	C30—C29—H29A	120.3
C6—C5—C4	120.5 (7)	N4—C30—C29	123.1 (7)
C6—C5—H5A	119.7	N4—C30—H30A	118.4
C4—C5—H5A	119.7	C29—C30—H30A	118.4
C5—C6—C7	122.2 (7)	N4—C31—C27	123.2 (6)
C5—C6—H6A	118.9	N4—C31—C32	117.6 (5)
C7—C6—H6A	118.9	C27—C31—C32	119.2 (6)
C11—C7—C8	116.9 (6)	N3—C32—C24	122.1 (6)
C11—C7—C6	118.9 (7)	N3—C32—C31	117.5 (6)
C8—C7—C6	124.2 (6)	C24—C32—C31	120.4 (6)
C9—C8—C7	120.3 (6)	C38—C33—C34	118.9 (6)
C9—C8—H8A	119.8	C38—C33—C39	121.4 (6)
C7—C8—H8A	119.8	C34—C33—C39	119.7 (6)
C8—C9—C10	118.9 (7)	C35—C34—C33	120.8 (7)
C8—C9—H9A	120.6	C35—C34—H34A	119.6
C10—C9—H9A	120.6	C33—C34—H34A	119.6
N2—C10—C9	123.3 (7)	C36—C35—C34	120.2 (6)
N2—C10—H10A	118.4	C36—C35—H35A	119.9
C9—C10—H10A	118.4	C34—C35—H35A	119.9
N2—C11—C7	123.0 (6)	C35—C36—C37	119.7 (7)
N2—C11—C12	117.1 (5)	C35—C36—Br2	119.9 (5)
C7—C11—C12	119.9 (6)	C37—C36—Br2	120.4 (6)
N1—C12—C4	122.1 (6)	C36—C37—C38	119.9 (7)
N1—C12—C11	118.4 (5)	C36—C37—H37A	120.1
C4—C12—C11	119.4 (6)	C38—C37—H37A	120.1
C14—C13—C18	118.2 (6)	C33—C38—C37	120.5 (6)
C14—C13—C19	121.2 (6)	C33—C38—H38A	119.7
C18—C13—C19	120.5 (6)	C37—C38—H38A	119.7
C15—C14—C13	120.4 (7)	O4—C39—O5	124.4 (6)
C15—C14—H14A	119.8	O4—C39—C33	117.5 (6)
C13—C14—H14A	119.8	O5—C39—C33	118.2 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*WA*···O4^{i}	0.85	1.83	2.656 (7)	162
O3—H3*WB*···O7	0.85	1.85	2.696 (7)	179
O6—H6*WA*···O5	0.85	2.07	2.751 (8)	136
O6—H6*WB*···O5^{ii}	0.85	2.33	2.823 (7)	118
O6—H6*WB*···O7^{iii}	0.85	2.51	2.798 (9)	101
O7—H7*WA*···Br2	0.85	2.58	3.256 (6)	137
O7—H7*WB*···O6^{iii}	0.85	2.20	2.798 (9)	127
C21—H21*A*···O2	0.93	2.59	3.091 (9)	115

C28—H28*A*···O1^{iv}	0.93	2.57	3.402 (8)	149
C30—H30*A*···O3	0.93	2.53	3.107 (8)	121

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