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Poly[butane-1,4-diammonium [tri-μ-oxalato-dimanganese(II)] hexahydrate]

Masaaki Sadakiyo,[a] Teppei Yamada[b] and Hiroshi Kitagawa[b]*

[a]International Institute for Carbon-Neutral Energy Research, Kyushu University, Moto-oka 744, Nishi-ku, Fukuoka 819-0395, Japan, and [b]Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan. *Correspondence e-mail: kitagawa@kuchem.kyoto-u.ac.jp

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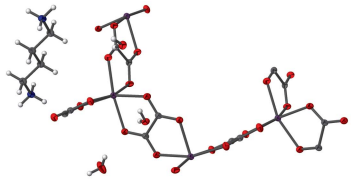
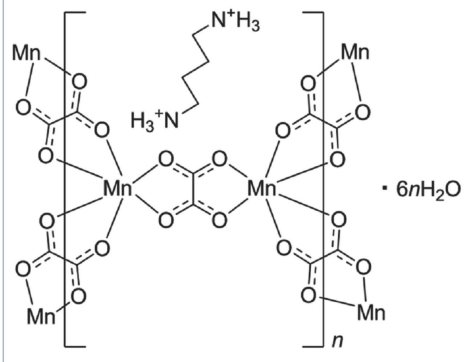
In the title coordination polymer, $\{(C_4H_{14}N_2)[Mn_2(C_2O_4)_3]\cdot 6H_2O\}_n$, the Mn^{II} ions are octahedrally coordinated by the oxalate ligands to form a two-dimensional honeycomb-like network. This anionic framework incorporates the centrosymmetric butane-1,4-diammonium ions as counter-cations. The two-dimensional network is slightly distorted as a result of the vertically incorporated cations. Three kinds of water molecules are located in an interlayer space, forming hydrogen bonds with the ammonium cations and the oxalate ligands of the framework.

3D view



Chemical scheme



Structure description

Oxalate-bridged infinite networks show various functionalities, such as ferromagnetism (Tamaki *et al.*, 1992), high proton conduction (Sadakiyo *et al.*, 2009) and selective adsorption properties (Sadakiyo *et al.*, 2011). In this study, the crystal structure of a new oxalato-bridged manganese(II) two-dimensional network is reported.

There is one crystallographically independent Mn atom in the asymmetric unit and the oxalate ligands form bridges between the Mn^{II} ions. O atoms of the oxalate ligands coordinate the Mn^{II} cations in a slightly distorted octahedral geometry, forming a honeycomb-like two-dimensional network of $[Mn_2(C_2O_4)_3]^{2-}$ units which in turn incorporate the butane-1,4-diammonium counter-cations, (Fig. 1). These cations lie on inversion centres located at the midpoint of the C4—C4^{iv} bond [symmetry code: (iv) $-x$, $-y+1$, $-z+2$]. The two-dimensional sheets are stacked to form a layered structure (Fig. 2). In the interlayer space, there are three independent water molecules (O3, O7 and O9) that form hydrogen bonds (Table 1) with both the ammonium substituents of the cation and the O atoms of the oxalate ligands (Fig. 3). The layer structure is distorted to accommodate the presence of the vertically incorporated cations, while other oxalate-

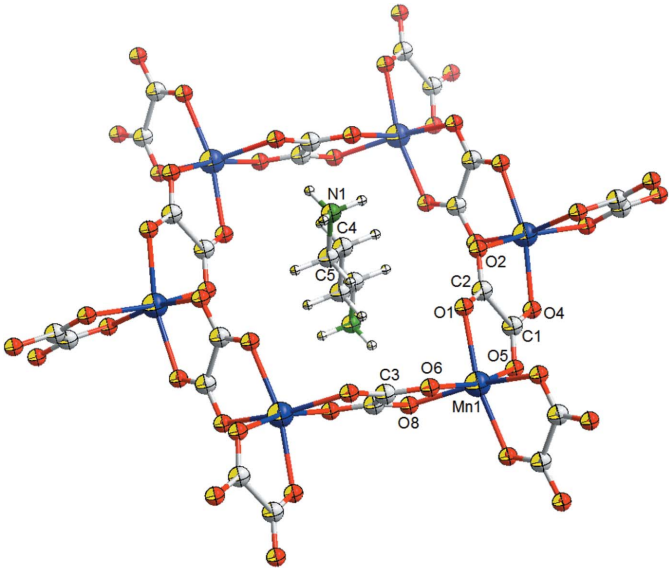


Figure 1
The sheet structure of $\{[Mn_2(C_2O_4)_3]^{2-}\}_n$, incorporating butane-1,4-diammonium cations, with displacement ellipsoids drawn at the 50% probability level.

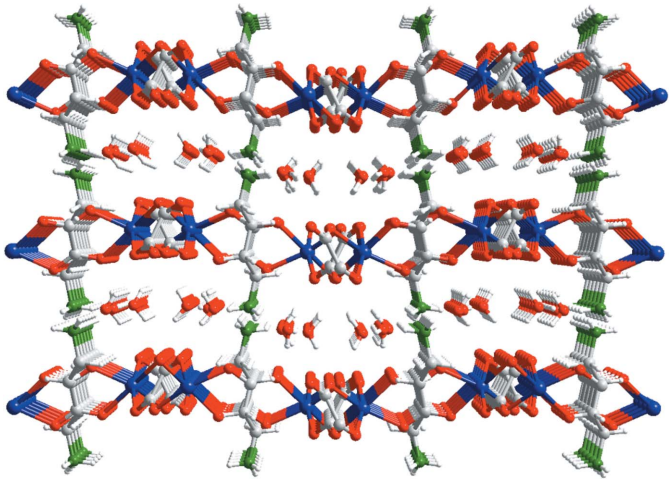


Figure 2
The layered structure of $(C_4N_2H_{14})[Mn_2(C_2O_4)_3]\cdot 6H_2O$.

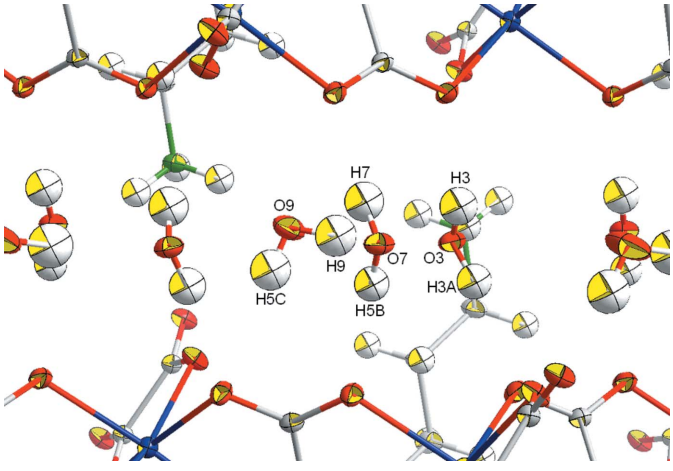


Figure 3
The water molecules included in the interlayer space, with displacement ellipsoids drawn at the 50% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O5	0.81 (2)	2.06 (2)	2.8196 (12)	157.3 (19)
O3—H3A···O2^{i}	0.82 (2)	2.01 (2)	2.8156 (12)	168.8 (19)
O7—H7···O4^{ii}	0.85 (2)	2.00 (2)	2.8392 (12)	169.6 (19)
O9—H9···O3^{iii}	0.84 (2)	2.02 (2)	2.8565 (15)	173 (2)
O7—H5B···O1	0.800 (19)	2.068 (19)	2.8603 (12)	171.1 (18)
O9—H5C···O6	0.79 (2)	2.08 (2)	2.8354 (14)	160 (2)
N1—H1···O3^{iv}	0.91	2.05	2.9349 (14)	165
N1—H1A···O7^{i}	0.91	1.99	2.8418 (14)	156
N1—H1B···O9^{i}	0.91	1.92	2.7868 (15)	157

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_4H_{14}N_2)[Mn_2(C_2O_4)_3]\cdot 6H_2O$
M_r	572.21
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	8.2623 (8), 16.1821 (15), 9.4702 (9)
β (°)	111.9172 (10)
V (Å^3)	1174.66 (19)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.16
Crystal size (mm)	0.15 × 0.15 × 0.05
Data collection	
Diffractometer	Bruker SMART APEX CCD detector
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.846, 0.944
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13965, 2975, 2789
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.684
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.056, 1.07
No. of reflections	2975
No. of parameters	170
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.55, −0.40

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SIR2002* (Burla *et al.* 2003), *SHELXL97* (Sheldrick 2008), *DIAMOND* (Brandenburg 1999) and *Yadokari-XG* (Kabuto *et al.* 2009).

bridged two-dimensional coordination polymers generally form a flat layer structure (Clemente-León *et al.*, 1997).

Synthesis and crystallization

A mixture of manganese (II) acetate tetrahydrate (10 mmol, 2451 mg), oxalic acid dihydrate (20 mmol, 2521 mg), 1,4-diaminobutane (10 mmol, 1.0 ml), and distilled water (550 mmol, 10 ml) was heated in a 50 ml Teflon-lined autoclave. The reaction temperature was controlled using a programmable oven. The mixture was kept at 403 K for 24 h. After that, it was cooled slowly to 298 K over 168 h. Colourless crystals were collected by filtration (several crystals were

stored in the mother liquid for structural analysis). After washing the samples with distilled water, the samples were dried under air (yield: 2324 mg, 81%). Elemental analysis calculated for $C_{10}H_{18}Mn_2N_2O_{14}$ (%): C 24.02, H 3.63, N 5.60; found: C 23.81, H 3.41, N 5.56.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$(C_4H_{14}N_2)[Mn_2(C_2O_4)_3]\cdot 6H_2O$
M_r = 572.21
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 8.2623 (8) Å
b = 16.1821 (15) Å
c = 9.4702 (9) Å
β = 111.9172 (10)°
V = 1174.66 (19) Å^3
Z = 2
$F(000)$ = 588
D_x = 1.618 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 9419 reflections
θ = 2.5–28.9°
μ = 1.16 mm^{-1}
T = 100 K
Platelet, colorless
0.15 × 0.15 × 0.05 mm

Data collection

Bruker SMART APEX CCD detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.846, T_{max} = 0.944
13965 measured reflections
2975 independent reflections
2789 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 29.1°, θ_{min} = 2.5°
h = −10→10
k = −21→21
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.056
S = 1.07
2975 reflections
170 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 0.5691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 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.

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}
Mn1	0.02869 (2)	0.169789 (10)	0.957930 (18)	0.01373 (6)
O1	−0.25273 (11)	0.17989 (5)	0.83745 (10)	0.01818 (17)
O2	0.04842 (10)	0.26513 (5)	1.12735 (9)	0.01710 (16)
O3	0.24744 (12)	0.17269 (6)	0.66258 (11)	0.02013 (18)
H3	0.197 (3)	0.2048 (13)	0.698 (2)	0.043 (5)*
H3A	0.335 (3)	0.1954 (12)	0.661 (2)	0.037 (5)*
O4	0.30602 (10)	0.19016 (5)	1.06540 (9)	0.01681 (16)
O5	0.00415 (10)	0.24760 (5)	0.76634 (9)	0.01656 (16)
O6	0.00269 (11)	0.08224 (5)	1.12066 (9)	0.01871 (17)
O7	−0.44146 (12)	0.09772 (6)	0.99547 (10)	0.01985 (17)
H7	−0.513 (2)	0.1308 (13)	1.012 (2)	0.041 (5)*
O8	0.04419 (11)	0.05226 (5)	0.85630 (9)	0.01841 (17)
C1	0.35089 (14)	0.23655 (7)	1.17931 (12)	0.0132 (2)
N1	0.19120 (13)	0.49595 (7)	0.76866 (11)	0.0181 (2)
H1	0.2093	0.5515	0.7721	0.027*
H1A	0.1648	0.4776	0.6718	0.027*
H1B	0.2895	0.4702	0.8319	0.027*
C2	−0.29846 (14)	0.22215 (7)	0.71826 (12)	0.0141 (2)
C3	−0.01213 (14)	0.00845 (7)	1.07678 (12)	0.0147 (2)
C4	0.07643 (16)	0.50957 (8)	0.97641 (13)	0.0188 (2)
H4	0.0947	0.5701	0.9786	0.023*
H4A	0.1837	0.4840	1.0498	0.023*
O9	−0.03534 (17)	0.11469 (9)	1.40088 (14)	0.0470 (4)
H9	0.052 (3)	0.1325 (15)	1.473 (2)	0.053 (6)*
C5	0.04384 (16)	0.47715 (8)	0.81809 (13)	0.0203 (2)
H5	0.0265	0.4166	0.8165	0.024*
H5A	−0.0644	0.5022	0.7452	0.024*
H5B	−0.391 (2)	0.1254 (11)	0.955 (2)	0.032 (4)*
H5C	−0.005 (3)	0.1135 (13)	1.331 (3)	0.051 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01273 (9)	0.01503 (9)	0.01310 (9)	−0.00011 (6)	0.00444 (7)	0.00001 (6)
O1	0.0135 (4)	0.0236 (4)	0.0177 (4)	−0.0004 (3)	0.0062 (3)	0.0064 (3)
O2	0.0117 (4)	0.0197 (4)	0.0190 (4)	0.0013 (3)	0.0047 (3)	−0.0040 (3)
O3	0.0168 (4)	0.0228 (4)	0.0246 (4)	−0.0020 (3)	0.0120 (4)	−0.0020 (3)
O4	0.0128 (4)	0.0211 (4)	0.0165 (4)	0.0007 (3)	0.0055 (3)	−0.0043 (3)
O5	0.0115 (4)	0.0205 (4)	0.0175 (4)	0.0000 (3)	0.0052 (3)	0.0028 (3)
O6	0.0275 (4)	0.0162 (4)	0.0151 (4)	−0.0003 (3)	0.0109 (3)	−0.0009 (3)

O7	0.0204 (4)	0.0204 (4)	0.0237 (4)	0.0017 (3)	0.0139 (4)	0.0027 (3)
O8	0.0248 (4)	0.0172 (4)	0.0171 (4)	−0.0003 (3)	0.0123 (3)	0.0004 (3)
C1	0.0125 (5)	0.0137 (5)	0.0147 (5)	0.0017 (4)	0.0065 (4)	0.0013 (4)
N1	0.0177 (5)	0.0237 (5)	0.0160 (4)	0.0014 (4)	0.0100 (4)	0.0010 (4)
C2	0.0133 (5)	0.0141 (5)	0.0164 (5)	−0.0009 (4)	0.0073 (4)	−0.0005 (4)
C3	0.0132 (5)	0.0185 (5)	0.0129 (5)	0.0008 (4)	0.0054 (4)	−0.0003 (4)
C4	0.0215 (6)	0.0221 (6)	0.0172 (5)	−0.0017 (4)	0.0123 (5)	−0.0007 (4)
O9	0.0439 (7)	0.0779 (9)	0.0282 (6)	−0.0362 (7)	0.0240 (5)	−0.0258 (6)
C5	0.0204 (6)	0.0257 (6)	0.0192 (5)	−0.0053 (5)	0.0122 (5)	−0.0027 (4)

Geometric parameters (Å, º)

Mn1—O5	2.1549 (8)	C1—C2^{i}	1.5638 (15)
Mn1—O8	2.1567 (8)	N1—C5	1.4897 (14)
Mn1—O4	2.1573 (8)	N1—H1	0.9100
Mn1—O6	2.1623 (8)	N1—H1A	0.9100
Mn1—O1	2.1805 (9)	N1—H1B	0.9100
Mn1—O2	2.1876 (8)	C2—O2^{ii}	1.2534 (13)
O1—C2	1.2513 (14)	C2—C1^{ii}	1.5638 (15)
O2—C2^{i}	1.2534 (14)	C3—O8^{iii}	1.2499 (14)
O3—H3	0.81 (2)	C3—C3^{iii}	1.564 (2)
O3—H3A	0.82 (2)	C4—C5	1.5147 (16)
O4—C1	1.2515 (13)	C4—C4^{iv}	1.520 (2)
O5—C1^{ii}	1.2528 (13)	C4—H4	0.9900
O6—C3	1.2552 (14)	C4—H4A	0.9900
O7—H7	0.85 (2)	O9—H9	0.84 (2)
O7—H5B	0.800 (19)	O9—H5C	0.79 (2)
O8—C3^{iii}	1.2499 (14)	C5—H5	0.9900
C1—O5^{i}	1.2528 (13)	C5—H5A	0.9900
O5—Mn1—O8	98.17 (3)	C5—N1—H1	109.5
O5—Mn1—O4	93.30 (3)	C5—N1—H1A	109.5
O8—Mn1—O4	96.65 (3)	H1—N1—H1A	109.5
O5—Mn1—O6	168.45 (3)	C5—N1—H1B	109.5
O8—Mn1—O6	77.20 (3)	H1—N1—H1B	109.5
O4—Mn1—O6	97.73 (3)	H1A—N1—H1B	109.5
O5—Mn1—O1	76.63 (3)	O1—C2—O2^{ii}	126.65 (10)
O8—Mn1—O1	93.55 (3)	O1—C2—C1^{ii}	116.56 (9)
O4—Mn1—O1	166.61 (3)	O2^{ii}—C2—C1^{ii}	116.79 (9)
O6—Mn1—O1	92.97 (3)	O8^{iii}—C3—O6	126.36 (10)
O5—Mn1—O2	99.40 (3)	O8^{iii}—C3—C3^{iii}	117.31 (12)
O8—Mn1—O2	161.54 (3)	O6—C3—C3^{iii}	116.33 (12)
O4—Mn1—O2	76.76 (3)	C5—C4—C4^{iv}	111.11 (13)
O6—Mn1—O2	86.53 (3)	C5—C4—H4	109.4
O1—Mn1—O2	95.96 (3)	C4^{iv}—C4—H4	109.4
C2—O1—Mn1	114.64 (7)	C5—C4—H4A	109.4
C2^{i}—O2—Mn1	113.54 (7)	C4^{iv}—C4—H4A	109.4
H3—O3—H3A	107.9 (19)	H4—C4—H4A	108.0

C1—O4—Mn1	114.78 (7)	H9—O9—H5C	104.1 (19)
C1^{ii}—O5—Mn1	115.33 (7)	N1—C5—C4	112.09 (10)
C3—O6—Mn1	114.25 (7)	N1—C5—H5	109.2
H7—O7—H5B	104.7 (19)	C4—C5—H5	109.2
C3^{iii}—O8—Mn1	114.07 (7)	N1—C5—H5A	109.2
O4—C1—O5^{i}	126.26 (10)	C4—C5—H5A	109.2
O4—C1—C2^{i}	116.99 (9)	H5—C5—H5A	107.9
O5^{i}—C1—C2^{i}	116.75 (9)		
O5—Mn1—O1—C2	1.12 (8)	O2—Mn1—O5—C1^{ii}	−93.12 (8)
O8—Mn1—O1—C2	−96.44 (8)	O5—Mn1—O6—C3	59.66 (19)
O4—Mn1—O1—C2	43.14 (17)	O8—Mn1—O6—C3	−7.78 (8)
O6—Mn1—O1—C2	−173.79 (8)	O4—Mn1—O6—C3	−102.89 (8)
O2—Mn1—O1—C2	99.40 (8)	O1—Mn1—O6—C3	85.19 (8)
O5—Mn1—O2—C2^{i}	−100.89 (8)	O2—Mn1—O6—C3	−179.01 (8)
O8—Mn1—O2—C2^{i}	61.08 (14)	O5—Mn1—O8—C3^{iii}	−161.48 (8)
O4—Mn1—O2—C2^{i}	−9.69 (8)	O4—Mn1—O8—C3^{iii}	104.20 (8)
O6—Mn1—O2—C2^{i}	89.09 (8)	O6—Mn1—O8—C3^{iii}	7.75 (8)
O1—Mn1—O2—C2^{i}	−178.27 (8)	O1—Mn1—O8—C3^{iii}	−84.50 (8)
O5—Mn1—O4—C1	106.38 (8)	O2—Mn1—O8—C3^{iii}	36.49 (15)
O8—Mn1—O4—C1	−154.99 (8)	Mn1—O4—C1—O5^{i}	174.36 (9)
O6—Mn1—O4—C1	−77.06 (8)	Mn1—O4—C1—C2^{i}	−4.78 (12)
O1—Mn1—O4—C1	65.67 (16)	Mn1—O1—C2—O2^{ii}	177.64 (9)
O2—Mn1—O4—C1	7.50 (8)	Mn1—O1—C2—C1^{ii}	−2.56 (12)
O8—Mn1—O5—C1^{ii}	92.56 (8)	Mn1—O6—C3—O8^{iii}	−173.20 (9)
O4—Mn1—O5—C1^{ii}	−170.24 (8)	Mn1—O6—C3—C3^{iii}	6.79 (15)
O6—Mn1—O5—C1^{ii}	27.1 (2)	C4^{iv}—C4—C5—N1	179.40 (12)
O1—Mn1—O5—C1^{ii}	0.83 (8)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O5	0.81 (2)	2.06 (2)	2.8196 (12)	157.3 (19)
O3—H3*A*···O2^{v}	0.82 (2)	2.01 (2)	2.8156 (12)	168.8 (19)
O7—H7···O4^{vi}	0.85 (2)	2.00 (2)	2.8392 (12)	169.6 (19)
O9—H9···O3^{vii}	0.84 (2)	2.02 (2)	2.8565 (15)	173 (2)
O7—H5*B*···O1	0.800 (19)	2.068 (19)	2.8603 (12)	171.1 (18)
O9—H5*C*···O6	0.79 (2)	2.08 (2)	2.8354 (14)	160 (2)
N1—H1···O3^{viii}	0.91	2.05	2.9349 (14)	165
N1—H1*A*···O7^{v}	0.91	1.99	2.8418 (14)	156
N1—H1*B*···O9^{v}	0.91	1.92	2.7868 (15)	157

Symmetry codes: (v) *x*+1/2, −*y*+1/2, *z*−1/2; (vi) *x*−1, *y*, *z*; (vii) *x*, *y*, *z*+1; (viii) −*x*+1/2, *y*+1/2, −*z*+3/2.