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Bis(μ-carboxylatoethylphosphonato)bis-[aqua(2,2′-bipyridine)manganese(II)]

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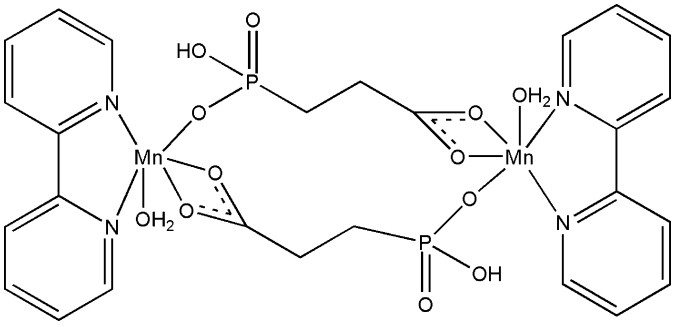
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.090; data-to-parameter ratio = 19.5.

The title compound, $[Mn_2(HO_3PCH_2CH_2COO)_2(C_8H_8N_2)_2(H_2O)_2]$, was obtained by hydrothermal synthesis. The manganese(II) ions are six-coordinate and are linked by two 2-carboxyethylphosphonate ligands, forming a centrosymmetric dimer. The Mn ions adopts a distorted octahedral coordination geometry. The dimers are further linked by O—H···O hydrogen bonds and π–π stacking interactions [centroid–centroid distance 4.2754 (4) Å].

Related literature

For related literature, see: Clearfield (1998); Cheetham *et al.* (1999); Stock *et al.* (2000); Serpaggi & Férey (1999); Ying & Mao *et al.* (2004); Ying *et al.* (2007). For the isostructural Zn(II) complex, see: Ying *et al.* (2006).



Experimental

Crystal data

$[Mn_2(C_5H_5O_5P)_2(C_8H_8N_2)_2(H_2O)_2]$
M_r = 762.36
Orthorhombic, *Pbca*
a = 8.7553 (13) Å
b = 18.060 (3) Å
c = 20.682 (3) Å
V = 3270.3 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.94 mm^{-1}
T = 293 (2) K
0.32 × 0.30 × 0.26 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.754, T_{max} = 0.796
23111 measured reflections
4057 independent reflections
2893 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.090
S = 0.99
4057 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6B···O4^{i}	0.93	2.13	2.6813 (18)	117
O1—H1B···O3^{ii}	0.82	1.73	2.5385 (19)	167

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: OM2188).

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supporting information

Acta Cryst. (2008). E**64**, m166 [https://doi.org/10.1107/S1600536807065142]

Bis(*μ*-carboxylatoethylphosphonato)bis[aqua(2,2′-bipyridine)manganese(II)]

Shao-Ming Ying, Yun Chen, Qiu-Yan Luo, Ya-Ping Xv and Dong-Sheng Liu

S1. Comment

In recent years, metal phosphonates have been a rapid expansion research field due to their potential application in the area of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry (Clearfield 1998). Many metal phosphonates have been reported (Cheetham *et al.*, 1999; Stock *et al.*, 2000; Serpaggi & Férey, 1999; Ying & Mao, 2004; Ying *et al.*, 2006). Metal phosphonates can exhibit various kinds of structures. We report here the crystal structure of a new manganese(II) carboxyalkylphosphonate complex synthesized by the hydrothermal method.

The asymmetric unit of the title compound contains one manganese(II) ion, one doubly deprotonated 2-carboxyethylphosphonic acid ligand, one 2,2′-bipyridine and one coordinated water molecule. The manganese(II) ion is six-coordinated by one phosphonate oxygen atom, one water molecule, two carboxylate oxygen atoms and two N atoms from a 2,2′-bipyridine molecule. The Mn—O distances range from 2.0646 (12) to 2.3161 (14) Å and the Mn—N distances are 2.2437 (16) and 2.2890 (16) Å. Two manganese(II) ions are linked by two 2-carboxyethylphosphonic acid ligands forming a dimer (Fig. 1). The dimers are further interlinked by O—H···O hydrogen bonds and *π*-*π* stacking interactions to form a three-dimensional supermolecular structure (Fig. 2). The compound is isostructural with a zinc(II) complex which has been reported recently (Ying *et al.*, 2007).

S2. Experimental

A mixture of manganese(II) acetate (0.5 mmol, 0.120 g), 2-carboxyethylphosphonic acid (0.5 mmol, 0.076 g), and 2,2′-bipyridine (0.5 mmol, 0.079 g) in 10 ml of distilled water was sealed in an autoclave equipped with a Teflon liner (20 ml) and then heated at 150°C for 3 days. Crystals of the title compound were obtained.

S3. Refinement

All hydrogen atoms were geometrically positioned with C—H = 0.93–0.98 Å, O—H = 0.82 Å, and refined in the riding-model approximation, with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(O).

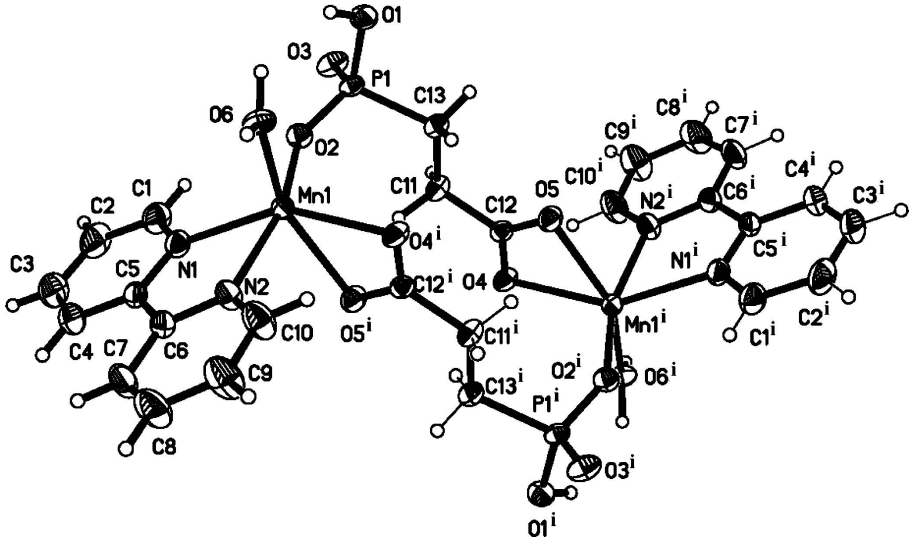

Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) 2 - *x*, -*y*, 1 - *z*.

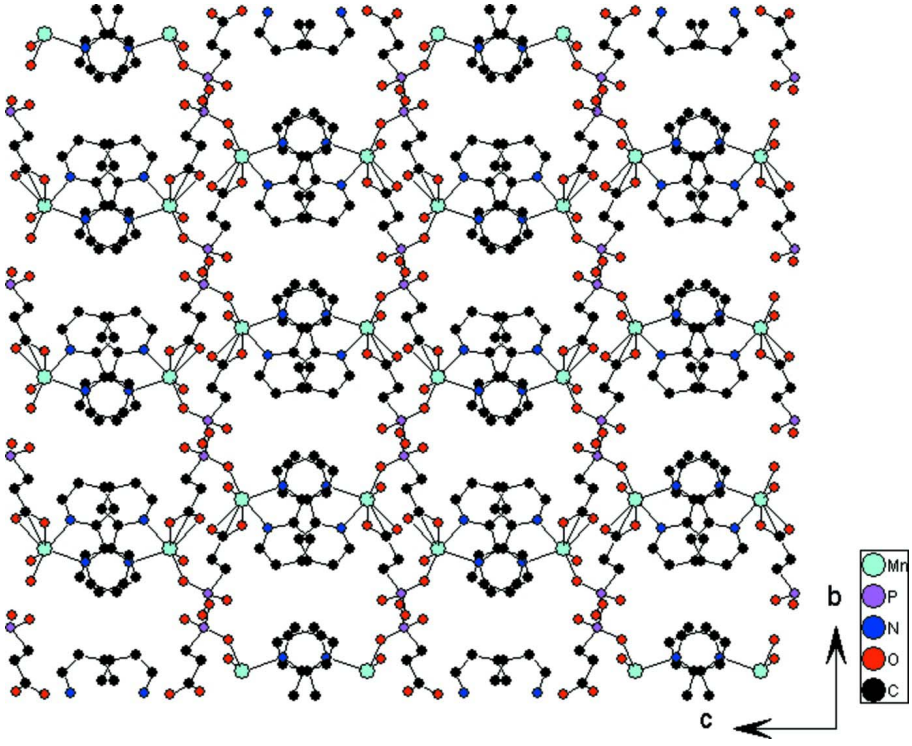

Figure 2

Packing diagram of the title compound viewed along the *a* axis. Hydrogen atoms are omitted for clarity.

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Crystal data

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Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 8.7553$ (13) Å
$b = 18.060$ (3) Å
$c = 20.682$ (3) Å
$V = 3270.3$ (8) Å^3
$Z = 4$
$F(000) = 1560$
$D_x = 1.548$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5461 reflections
$\theta = 2.5$–$28.2°$
$\mu = 0.94$ mm^{-1}
$T = 293$ K
Block, colourless
0.32 × 0.30 × 0.26 mm

Data collection

Bruker APEX area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min} = 0.754$, $T_{max} = 0.796$
23111 measured reflections
4057 independent reflections
2893 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.0°$
$h = -11 \rightarrow 11$
$k = -24 \rightarrow 24$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.090$
$S = 0.99$
4057 reflections
208 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.67540 (3)	0.073021 (14)	0.408219 (13)	0.02994 (10)
P1	0.84779 (5)	0.19961 (2)	0.50438 (2)	0.03026 (12)
N1	0.70029 (19)	0.11228 (9)	0.30583 (8)	0.0409 (4)
N2	0.5539 (2)	−0.01013 (9)	0.34242 (7)	0.0427 (4)
O1	0.71646 (15)	0.22186 (7)	0.55235 (6)	0.0417 (3)

H1B	0.6353	0.2240	0.5327	0.062*
O2	0.78629 (14)	0.16537 (7)	0.44369 (6)	0.0364 (3)
O3	0.94774 (14)	0.26603 (7)	0.49251 (7)	0.0441 (3)
O4	1.29300 (14)	0.01457 (7)	0.51674 (6)	0.0378 (3)
O5	1.11488 (16)	0.00513 (7)	0.59060 (6)	0.0419 (3)
O6	0.45857 (14)	0.10698 (7)	0.44337 (6)	0.0415 (3)
H6A	0.4491	0.1514	0.4658	0.050*
H6B	0.3731	0.0775	0.4363	0.050*
C1	0.7756 (3)	0.17412 (12)	0.29085 (11)	0.0538 (6)
H1A	0.8182	0.2023	0.3239	0.065*
C2	0.7923 (3)	0.19769 (14)	0.22728 (12)	0.0667 (7)
H2A	0.8457	0.2408	0.2177	0.080*
C3	0.7284 (3)	0.15608 (16)	0.17906 (12)	0.0703 (8)
H3A	0.7376	0.1709	0.1362	0.084*
C4	0.6509 (3)	0.09242 (14)	0.19413 (11)	0.0600 (7)
H4A	0.6078	0.0636	0.1616	0.072*
C5	0.6375 (2)	0.07146 (11)	0.25805 (9)	0.0402 (5)
C6	0.5559 (2)	0.00356 (11)	0.27852 (9)	0.0412 (5)
C7	0.4850 (3)	−0.04431 (14)	0.23502 (10)	0.0582 (6)
H7A	0.4878	−0.0345	0.1909	0.070*
C8	0.4116 (3)	−0.10562 (16)	0.25773 (12)	0.0758 (8)
H8A	0.3634	−0.1377	0.2291	0.091*
C9	0.4089 (3)	−0.12002 (14)	0.32312 (12)	0.0773 (9)
H9A	0.3599	−0.1616	0.3396	0.093*
C10	0.4818 (3)	−0.07028 (12)	0.36322 (11)	0.0632 (7)
H10A	0.4803	−0.0794	0.4075	0.076*
C11	1.0934 (2)	0.10444 (10)	0.51376 (9)	0.0380 (4)
H11A	1.0651	0.0930	0.4695	0.046*
H11B	1.1671	0.1445	0.5123	0.046*
C12	1.1699 (2)	0.03742 (10)	0.54257 (9)	0.0314 (4)
C13	0.9522 (2)	0.13154 (10)	0.54921 (9)	0.0393 (4)
H13A	0.9828	0.1526	0.5904	0.047*
H13B	0.8860	0.0897	0.5580	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.03305 (17)	0.02699 (15)	0.02977 (16)	0.00015 (11)	−0.00014 (11)	0.00075 (11)
P1	0.0241 (2)	0.0261 (2)	0.0406 (3)	0.00079 (18)	−0.0006 (2)	−0.00313 (19)
N1	0.0446 (10)	0.0396 (9)	0.0386 (9)	0.0034 (7)	0.0020 (8)	0.0085 (7)
N2	0.0506 (11)	0.0449 (10)	0.0325 (9)	−0.0091 (8)	−0.0030 (8)	0.0000 (7)
O1	0.0308 (7)	0.0512 (8)	0.0430 (8)	0.0083 (6)	0.0008 (6)	−0.0065 (6)
O2	0.0366 (7)	0.0329 (7)	0.0396 (7)	−0.0046 (5)	−0.0019 (6)	−0.0030 (6)
O3	0.0311 (7)	0.0292 (7)	0.0719 (10)	−0.0051 (5)	−0.0002 (7)	−0.0057 (6)
O4	0.0338 (7)	0.0338 (7)	0.0457 (8)	0.0075 (6)	0.0078 (6)	0.0066 (6)
O5	0.0443 (8)	0.0411 (8)	0.0403 (8)	0.0082 (6)	0.0105 (7)	0.0098 (6)
O6	0.0337 (7)	0.0318 (7)	0.0591 (8)	−0.0018 (6)	0.0060 (6)	−0.0074 (6)
C1	0.0614 (15)	0.0473 (13)	0.0527 (13)	−0.0027 (11)	0.0044 (12)	0.0119 (11)

C2	0.0764 (19)	0.0570 (15)	0.0667 (17)	0.0022 (13)	0.0152 (14)	0.0280 (13)
C3	0.092 (2)	0.0752 (18)	0.0435 (13)	0.0132 (15)	0.0154 (14)	0.0201 (13)
C4	0.0825 (19)	0.0638 (15)	0.0337 (11)	0.0127 (13)	0.0043 (11)	0.0085 (11)
C5	0.0437 (11)	0.0464 (11)	0.0305 (10)	0.0134 (9)	0.0009 (8)	0.0031 (9)
C6	0.0420 (12)	0.0462 (11)	0.0354 (10)	0.0080 (9)	−0.0041 (9)	−0.0008 (9)
C7	0.0699 (16)	0.0699 (15)	0.0348 (12)	−0.0029 (13)	−0.0109 (11)	−0.0052 (11)
C8	0.092 (2)	0.0759 (18)	0.0590 (16)	−0.0260 (17)	−0.0192 (16)	−0.0155 (14)
C9	0.102 (2)	0.0702 (17)	0.0596 (16)	−0.0440 (17)	−0.0095 (16)	−0.0037 (13)
C10	0.0830 (18)	0.0629 (15)	0.0437 (12)	−0.0296 (14)	−0.0059 (12)	0.0006 (11)
C11	0.0330 (10)	0.0335 (10)	0.0475 (11)	0.0045 (8)	0.0011 (9)	0.0085 (8)
C12	0.0310 (10)	0.0264 (9)	0.0367 (10)	−0.0005 (7)	−0.0034 (8)	−0.0027 (8)
C13	0.0378 (11)	0.0378 (10)	0.0422 (11)	0.0106 (8)	0.0002 (9)	0.0008 (8)

Geometric parameters (Å, º)

Mn1—O2	2.0646 (12)	C1—H1A	0.9300
Mn1—O6	2.1233 (13)	C2—C3	1.368 (4)
Mn1—O4^{i}	2.2334 (13)	C2—H2A	0.9300
Mn1—N1	2.2437 (16)	C3—C4	1.371 (4)
Mn1—N2	2.2890 (16)	C3—H3A	0.9300
Mn1—O5^{i}	2.3161 (14)	C4—C5	1.380 (3)
Mn1—C12^{i}	2.6170 (18)	C4—H4A	0.9300
P1—O2	1.4993 (13)	C5—C6	1.481 (3)
P1—O3	1.5050 (13)	C6—C7	1.394 (3)
P1—O1	1.5710 (13)	C7—C8	1.364 (3)
P1—C13	1.7909 (18)	C7—H7A	0.9300
N1—C1	1.334 (2)	C8—C9	1.377 (3)
N1—C5	1.350 (3)	C8—H8A	0.9300
N2—C10	1.328 (2)	C9—C10	1.379 (3)
N2—C6	1.345 (2)	C9—H9A	0.9300
O1—H1B	0.8200	C10—H10A	0.9300
O4—C12	1.272 (2)	C11—C12	1.506 (2)
O4—Mn1^{i}	2.2334 (13)	C11—C13	1.518 (2)
O5—C12	1.248 (2)	C11—H11A	0.9700
O5—Mn1^{i}	2.3161 (14)	C11—H11B	0.9700
O6—H6A	0.9300	C12—Mn1^{i}	2.6170 (18)
O6—H6B	0.9300	C13—H13A	0.9700
C1—C2	1.390 (3)	C13—H13B	0.9700
O2—Mn1—O6	93.75 (5)	C3—C2—H2A	120.7
O2—Mn1—O4^{i}	105.49 (5)	C1—C2—H2A	120.7
O6—Mn1—O4^{i}	94.44 (5)	C2—C3—C4	119.8 (2)
O2—Mn1—N1	91.97 (6)	C2—C3—H3A	120.1
O6—Mn1—N1	108.58 (6)	C4—C3—H3A	120.1
O4^{i}—Mn1—N1	150.19 (5)	C3—C4—C5	119.3 (2)
O2—Mn1—N2	163.71 (5)	C3—C4—H4A	120.3
O6—Mn1—N2	88.71 (6)	C5—C4—H4A	120.3
O4^{i}—Mn1—N2	90.35 (6)	N1—C5—C4	121.1 (2)

N1—Mn1—N2	72.02 (6)	N1—C5—C6	116.05 (16)
O2—Mn1—O5^{i}	96.64 (5)	C4—C5—C6	122.8 (2)
O6—Mn1—O5^{i}	151.79 (5)	N2—C6—C7	120.96 (19)
O4^{i}—Mn1—O5^{i}	57.51 (4)	N2—C6—C5	116.09 (17)
N1—Mn1—O5^{i}	97.21 (5)	C7—C6—C5	122.95 (18)
N2—Mn1—O5^{i}	88.57 (6)	C8—C7—C6	119.4 (2)
O2—Mn1—C12^{i}	103.54 (5)	C8—C7—H7A	120.3
O6—Mn1—C12^{i}	123.35 (6)	C6—C7—H7A	120.3
O4^{i}—Mn1—C12^{i}	29.05 (5)	C7—C8—C9	120.0 (2)
N1—Mn1—C12^{i}	123.89 (6)	C7—C8—H8A	120.0
N2—Mn1—C12^{i}	88.38 (6)	C9—C8—H8A	120.0
O5^{i}—Mn1—C12^{i}	28.49 (5)	C8—C9—C10	117.4 (2)
O2—P1—O3	113.64 (8)	C8—C9—H9A	121.3
O2—P1—O1	111.80 (8)	C10—C9—H9A	121.3
O3—P1—O1	108.95 (8)	N2—C10—C9	123.9 (2)
O2—P1—C13	109.49 (8)	N2—C10—H10A	118.0
O3—P1—C13	109.55 (9)	C9—C10—H10A	118.0
O1—P1—C13	102.85 (8)	C12—C11—C13	115.46 (16)
C1—N1—C5	119.24 (18)	C12—C11—H11A	108.4
C1—N1—Mn1	122.14 (15)	C13—C11—H11A	108.4
C5—N1—Mn1	118.61 (13)	C12—C11—H11B	108.4
C10—N2—C6	118.37 (18)	C13—C11—H11B	108.4
C10—N2—Mn1	124.41 (14)	H11A—C11—H11B	107.5
C6—N2—Mn1	117.22 (13)	O5—C12—O4	120.64 (17)
P1—O1—H1B	109.5	O5—C12—C11	121.25 (16)
P1—O2—Mn1	143.09 (8)	O4—C12—C11	118.11 (16)
C12—O4—Mn1^{i}	92.45 (11)	O5—C12—Mn1^{i}	62.24 (10)
C12—O5—Mn1^{i}	89.27 (11)	O4—C12—Mn1^{i}	58.50 (9)
Mn1—O6—H6A	120.0	C11—C12—Mn1^{i}	175.17 (13)
Mn1—O6—H6B	120.0	C11—C13—P1	112.77 (13)
H6A—O6—H6B	120.0	C11—C13—H13A	109.0
N1—C1—C2	121.9 (2)	P1—C13—H13A	109.0
N1—C1—H1A	119.1	C11—C13—H13B	109.0
C2—C1—H1A	119.1	P1—C13—H13B	109.0
C3—C2—C1	118.6 (2)	H13A—C13—H13B	107.8

Symmetry code: (i) −*x*+2, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*B*···O4^{ii}	0.93	2.13	2.6813 (18)	117
O1—H1*B*···O3^{iii}	0.82	1.73	2.5385 (19)	167

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