metal-organic compounds

(Croconato-κ²O,O′)bis(1,10-phenanthroline-κ²N,N′)manganese(II)

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The title complex, $[Mn(C_5O_5)(C_{12}H_8N_2)_2]$, lies across a crystallographic twofold axis which passes through the Mn atom and bisects the croconate ligand. The two 1,10-phenanthroline (phen) ligands are arranged in a propeller manner and the local molecular geometry of the MnN_4O_2 unit is severely distorted octahedral. This may be interpreted as a structural perturbation of the MnN_4 square by the croconate ligand. In the crystal structure, the dipole moments of the molecules are arranged alternately along the $+b$ and $-b$ directions. All the phen ligands are involved in π stacking interactions, alternately along the [110] and [$\bar{1}$10] directions. The alternate spacings between the neighbouring phen planes in the one-dimensional π stacks are 3.361 (2) and 3.526 (2) Å.

Related literature

For related literature, see: Chen *et al.* (2005, 2007); Coronado *et al.* (2007); Maji *et al.* (2003); Sletten *et al.* (1998); Wang *et al.* (2002).
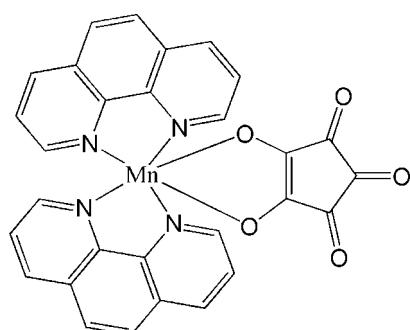
Experimental

Crystal data

$[Mn(C_5O_5)(C_{12}H_8N_2)_2]$	$V = 2341.30$ (16) Å³
$M_r = 555.40$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.9185$ (6) Å	$\mu = 0.62$ mm⁻¹
$b = 10.3749$ (4) Å	$T = 120$ (2) K
$c = 16.0859$ (6) Å	$0.44 \times 0.33 \times 0.22$ mm
$\beta = 109.885$ (1)°	

Data collection

Siemens SMART 1K CCD area-detector diffractometer	16256 measured reflections
	3356 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	3214 reflections with $I > 2\sigma(I)$
$T_{min} = 0.617$, $T_{max} = 0.746$ (expected range = 0.722–0.873)	$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	210 parameters
$wR(F^2) = 0.081$	All H-atom parameters refined
$S = 1.06$	$\Delta\rho_{max} = 0.50$ e Å⁻³
3356 reflections	$\Delta\rho_{min} = -0.22$ e Å⁻³

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* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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supporting information

(Croconato-*κ²O,O′*)bis(1,10-phenanthroline-*κ²N,N′*)manganese(II)

Hong-Feng Chen, Hong-Yu Chen, Xia Chen, Andrei S. Batsanov and Qi Fang

S1. Comment

The croconate $C_5O_5^{2-}$ anion has attracted increasing attention in recent years because this polydentate ligand gave rise to a variety of interesting complexes (Coronado *et al.*, 2007; Chen *et al.*, 2005; Maji *et al.*, 2003; Wang *et al.*, 2002; Sletten *et al.*, 1998). Typically, the $C_5O_5^{2-}$ anion can serve as a terminal bidentate ligand and a bridging ligand utilizing more than two O atoms for coordination. By comparison, the coordination chemistry of the neutral 1,10-phenanthroline bidentate ligand has been well studied.

Recently, we reported three mixed-ligand complexes [M(phen)$_2$(C$_5$O$_5$)] (M=Co, Ni, Cu) (Chen *et al.*, 2007), which have both croconate and 1,10-phenanthroline ligands. In this study, we report a new member of this family: [Mn(phen)$_2$(C$_5$O$_5$)] which is isostructural to [Cu(phen)$_2$(C$_5$O$_5$)].

[Mn(phen)$_2$(C$_5$O$_5$)] shows following common features with other three known [M(phen)$_2$(C$_5$O$_5$)] complexes: the molecule lies across twofold axis which is along the direction of the molecular dipole moment. Around the molecular axis, two phen ligands are arranged in a chiral propeller manner. The C—O bond lengths involving coordinated O atoms are longer than those of other C—O bonds.

The mean M—N bond lengths in [M(phen)$_2$(C$_5$O$_5$)] series are 2.2515 (9), 2.124 (2), 2.080 (3), and 2.065 (2) Å for the Mn, Co, Ni, and Cu complexes respectively, showing monotonous shortening with increasing the atomic number. The M—O lengths in [M(phen)$_2$(C$_5$O$_5$)] are 2.2163 (8), 2.120 (2), 2.098 (3), and 2.303 (2) Å for the Mn, Co, Ni, and Cu complexes respectively, showing a similar shortening tendency except for Cu complex which has the longest M—O length.

The molecular conformation of [Mn(phen)$_2$(C$_5$O$_5$)] is close to [Cu(phen)$_2$(C$_5$O$_5$)] while different from [Co(phen)$_2$(C$_5$O$_5$)] and [Ni(phen)$_2$(C$_5$O$_5$)]. The dihedral angles between the two phen planes for the Mn, Co, Ni, and Cu complexes are 46.5 (1), 85.7 (1), 86.0 (1), and 40.7 (1)°, respectively. In fact, the local polyhedral CoN$_4$O$_2$ and NiN$_4$O$_2$ in [M(phen)$_2$(C$_5$O$_5$)] is close to the octahedral while MnN$_4$O$_2$ and CuN$_4$O$_2$ in their complexes is severely distorted from the octahedral. We can suppose that the Mn(II)(Cu(II)) ion intially combines two phen ligands forming a MnN$_4$ (CuN$_4$) square, and then this square is distorted by adding the croconato ligand. This supposition may be supported by the relatively longest Mn—O and Cu—O bond length mentioned above in these complexes.

As shown in Fig.2, the dipole moments of [Mn(phen)$_2$(C$_5$O$_5$)] molecules are arranged alternatively along +b and-b directions. All phen ligands are parallel packed with the π-stacks being alternatively along the [110] and [-110] directions. The spacings between the neighboring phen planes in this kind of 1-D π-stacks are 3.361 (2) and 3.526 (2) Å (alternatively spaced).

Both in the molecular view and in the crystal view, four [M(phen)$_2$(C$_5$O$_5$)] members can be classified into two groups: the octahedral and *Pbcn* symmetric isostructural pair of [Co(phen)$_2$(C$_5$O$_5$)] and [Ni(phen)$_2$(C$_5$O$_5$)]; the non-octahedral and *C*2/*c* symmetric isostructural pair of [Mn(phen)$_2$(C$_5$O$_5$)] and [Cu(phen)$_2$(C$_5$O$_5$)]. The similarity between Mn and Cu complexes here may be related to the fact that the d-shell is half-filled for Mn(II) and almost full-filled for Cu(II) ions.

S2. Experimental

[$K_2(C_5O_5)$] (0.10 g) and $MnCl_2.4H_2O$ (0.09 g) were dissolved in mixed solvent of water (15 ml) and dimethylformamide (10 ml). Then 1,10-phenanthroline (0.15 g) was added. The mixture was heated to 340–350 K under continuous stirring for 20 min and then filtered. The green prisms crystals were obtained by slow evaporation at 313 K.

S3. Refinement

All the H atoms were located in a difference Fourier map and refined in the isotropic approximation.
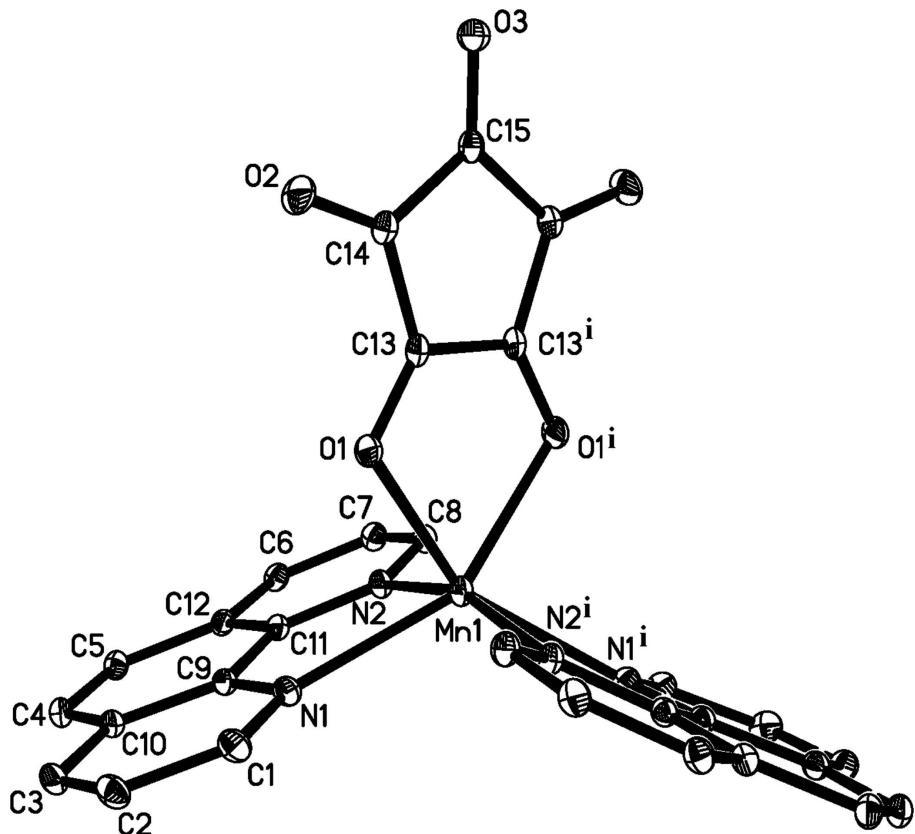
Figure 1

The molecular structure of [$Mn(phen)_2(C_5O_5)$]. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted. [symmetry code: (i) -x, y, -z + 1/2.]
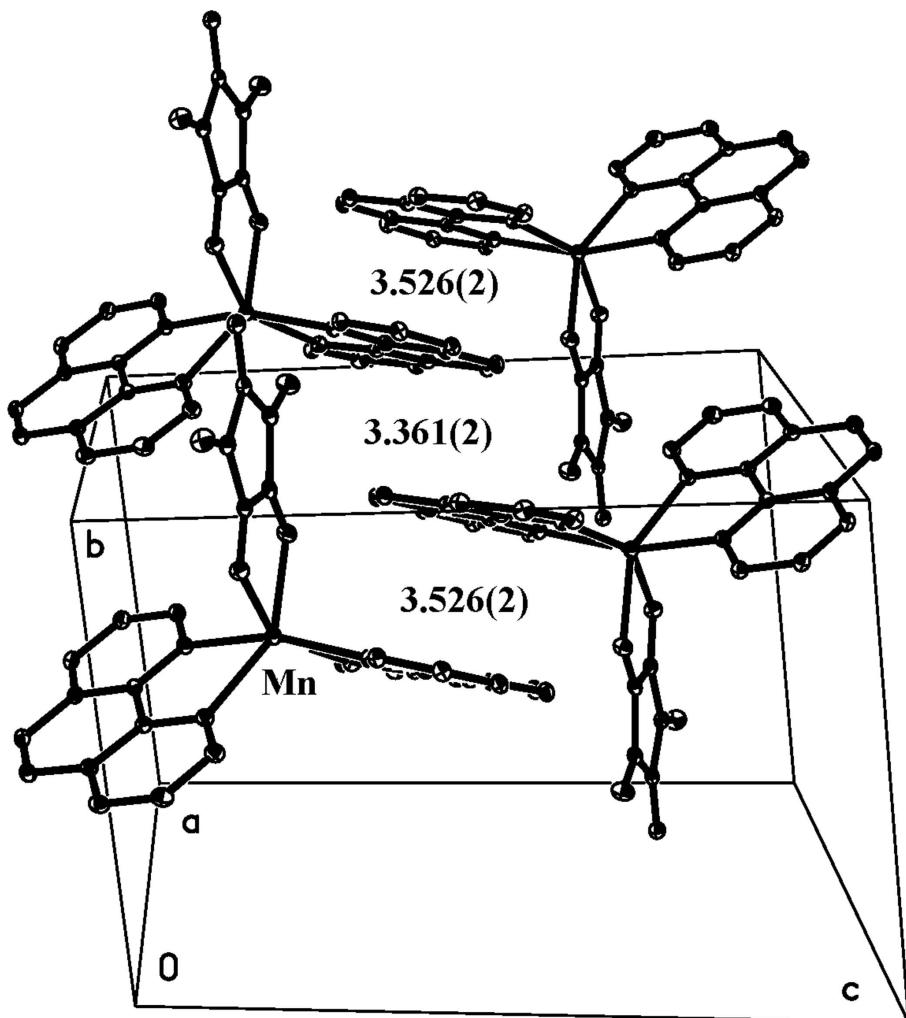
Figure 2

A packing plot of [Mn(phen)₂(C₅O₅)].

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Crystal data
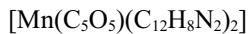
[Mn(C₅O₅)(C₁₂H₈N₂)₂]	$F(000) = 1132$
$M_r = 555.40$	$D_x = 1.576$ Mg m⁻³
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 6761 reflections
$a = 14.9185\ (6)$ Å	$\theta = 2.4$–30.0°
$b = 10.3749\ (4)$ Å	$\mu = 0.62$ mm⁻¹
$c = 16.0859\ (6)$ Å	$T = 120$ K
$\beta = 109.885\ (1)°$	Parallelepiped, green
$V = 2341.30\ (16)$ Å³	$0.44 \times 0.33 \times 0.22$ mm
$Z = 4$	

Data collection

Siemens SMART 1K CCD area-detector diffractometer	16256 measured reflections
Radiation source: fine-focus sealed tube	3356 independent reflections
Graphite monochromator	3214 reflections with $I > 2\sigma(I)$
Detector resolution: 8 pixels mm^{-1}	$R_{int} = 0.020$
φ and ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan	$h = -20 \rightarrow 20$
(*SADABS*; Bruker, 2006)	$k = -14 \rightarrow 14$
$T_{min} = 0.617$, $T_{max} = 0.746$	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.026$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.081$	All H-atom parameters refined
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 1.5339P]$
3356 reflections	where $P = (F_o^2 + 2F_c^2)/3$
210 parameters	$(\Delta/\sigma)_{max} = 0.001$
0 restraints	$\Delta\rho_{max} = 0.50$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.22$ 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	0.5000	0.26400 (2)	0.2500	0.01622 (7)
O1	0.59885 (5)	0.43062 (7)	0.28042 (5)	0.02103 (16)
O2	0.67021 (6)	0.70377 (9)	0.30364 (6)	0.02748 (18)
O3	0.5000	0.87022 (11)	0.2500	0.0219 (2)
N1	0.62594 (6)	0.15684 (8)	0.34684 (6)	0.01795 (16)
N2	0.46304 (6)	0.23245 (8)	0.37113 (6)	0.01674 (17)
C1	0.70739 (7)	0.12417 (11)	0.33554 (7)	0.0215 (2)
H1	0.7115 (10)	0.1353 (15)	0.2787 (10)	0.025 (4)*
C2	0.78638 (8)	0.07591 (11)	0.40428 (8)	0.0236 (2)
H2	0.8456 (12)	0.0555 (17)	0.3931 (11)	0.035 (4)*
C3	0.78032 (7)	0.05937 (10)	0.48675 (8)	0.0216 (2)
H3	0.8314 (10)	0.0290 (15)	0.5356 (10)	0.023 (3)*
C10	0.69459 (7)	0.09129 (10)	0.50113 (7)	0.01780 (18)
C9	0.61971 (7)	0.14089 (9)	0.42867 (6)	0.01610 (18)
C11	0.53204 (6)	0.17845 (9)	0.44123 (6)	0.01574 (18)
C12	0.52078 (7)	0.15896 (10)	0.52374 (6)	0.01709 (18)

C5	0.59808 (7)	0.10556 (10)	0.59570 (7)	0.01991 (19)
H5	0.5877 (11)	0.0922 (15)	0.6492 (11)	0.030 (4)*
C4	0.68188 (7)	0.07441 (10)	0.58486 (7)	0.02041 (19)
H4	0.7324 (11)	0.0420 (15)	0.6319 (10)	0.023 (3)*
C6	0.43206 (7)	0.19283 (10)	0.53119 (7)	0.01892 (19)
H6	0.4204 (11)	0.1750 (15)	0.5844 (11)	0.027 (4)*
C7	0.36277 (8)	0.24697 (10)	0.45998 (7)	0.0194 (2)
H7	0.3036 (12)	0.2722 (14)	0.4624 (11)	0.025 (4)*
C8	0.38134 (7)	0.26697 (10)	0.38121 (7)	0.01831 (19)
H8	0.3372 (10)	0.3074 (14)	0.3314 (10)	0.020 (3)*
C13	0.55136 (6)	0.53447 (10)	0.26577 (6)	0.01663 (18)
C14	0.58663 (7)	0.66724 (10)	0.27693 (6)	0.01791 (18)
C15	0.5000	0.75179 (14)	0.2500	0.0172 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01278 (11)	0.02053 (12)	0.01434 (11)	0.000	0.00330 (8)	0.000
O1	0.0128 (3)	0.0224 (4)	0.0243 (4)	0.0014 (3)	0.0017 (3)	−0.0019 (3)
O2	0.0147 (3)	0.0294 (4)	0.0350 (4)	−0.0044 (3)	0.0041 (3)	−0.0040 (3)
O3	0.0248 (5)	0.0215 (5)	0.0198 (5)	0.000	0.0083 (4)	0.000
N1	0.0156 (4)	0.0193 (4)	0.0190 (4)	0.0014 (3)	0.0061 (3)	0.0006 (3)
N2	0.0132 (4)	0.0201 (4)	0.0156 (4)	0.0011 (3)	0.0031 (3)	0.0006 (3)
C1	0.0192 (5)	0.0234 (5)	0.0236 (5)	0.0032 (4)	0.0094 (4)	0.0018 (4)
C2	0.0167 (4)	0.0249 (5)	0.0301 (5)	0.0047 (4)	0.0090 (4)	0.0017 (4)
C3	0.0147 (4)	0.0218 (5)	0.0256 (5)	0.0033 (3)	0.0034 (4)	0.0011 (4)
C10	0.0144 (4)	0.0173 (4)	0.0193 (4)	0.0003 (3)	0.0025 (3)	−0.0004 (3)
C9	0.0136 (4)	0.0160 (4)	0.0175 (4)	−0.0001 (3)	0.0037 (3)	−0.0007 (3)
C11	0.0130 (4)	0.0167 (4)	0.0160 (4)	−0.0004 (3)	0.0030 (3)	−0.0010 (3)
C12	0.0155 (4)	0.0186 (4)	0.0155 (4)	−0.0010 (3)	0.0032 (3)	−0.0021 (3)
C5	0.0198 (4)	0.0228 (5)	0.0147 (4)	0.0001 (4)	0.0027 (3)	−0.0005 (3)
C4	0.0174 (4)	0.0219 (5)	0.0176 (4)	0.0012 (3)	0.0003 (3)	0.0003 (3)
C6	0.0179 (4)	0.0228 (5)	0.0161 (4)	−0.0019 (4)	0.0060 (3)	−0.0030 (4)
C7	0.0150 (4)	0.0239 (5)	0.0196 (5)	0.0005 (3)	0.0064 (4)	−0.0022 (3)
C8	0.0138 (4)	0.0220 (5)	0.0181 (5)	0.0012 (3)	0.0040 (3)	0.0002 (3)
C13	0.0119 (4)	0.0230 (4)	0.0134 (4)	−0.0001 (3)	0.0023 (3)	−0.0011 (3)
C14	0.0139 (4)	0.0232 (5)	0.0157 (4)	−0.0009 (3)	0.0040 (3)	−0.0018 (3)
C15	0.0150 (6)	0.0234 (6)	0.0130 (6)	0.000	0.0046 (5)	0.000

Geometric parameters (Å, º)

Mn1—O1	2.2163 (8)	C10—C9	1.4091 (13)
Mn1—O1i	2.2163 (8)	C10—C4	1.4333 (15)
Mn1—N2	2.2222 (9)	C9—C11	1.4433 (13)
Mn1—N2i	2.2222 (9)	C11—C12	1.4080 (13)
Mn1—N1i	2.2807 (9)	C12—C6	1.4134 (13)
Mn1—N1	2.2807 (9)	C12—C5	1.4383 (13)
O1—C13	1.2668 (12)	C5—C4	1.3587 (15)

O2—C14	1.2323 (12)	C5—H5	0.934 (17)
O3—C15	1.2287 (18)	C4—H4	0.931 (15)
N1—C1	1.3322 (13)	C6—C7	1.3750 (15)
N1—C9	1.3607 (13)	C6—H6	0.947 (16)
N2—C8	1.3321 (13)	C7—C8	1.4015 (15)
N2—C11	1.3621 (12)	C7—H7	0.934 (17)
C1—C2	1.4055 (15)	C8—H8	0.945 (14)
C1—H1	0.944 (16)	C13—C13ⁱ	1.4412 (18)
C2—C3	1.3709 (16)	C13—C14	1.4637 (14)
C2—H2	0.982 (17)	C14—C15	1.4989 (13)
C3—C10	1.4143 (14)	C15—C14ⁱ	1.4989 (13)
C3—H3	0.943 (15)		
O1—Mn1—O1ⁱ	77.48 (4)	N1—C9—C10	123.29 (9)
O1—Mn1—N2	105.44 (3)	N1—C9—C11	117.77 (8)
O1ⁱ—Mn1—N2	87.91 (3)	C10—C9—C11	118.94 (9)
O1—Mn1—N2ⁱ	87.91 (3)	N2—C11—C12	122.72 (9)
O1ⁱ—Mn1—N2ⁱ	105.44 (3)	N2—C11—C9	117.44 (9)
N2—Mn1—N2ⁱ	163.06 (5)	C12—C11—C9	119.84 (8)
O1—Mn1—N1ⁱ	149.62 (3)	C11—C12—C6	117.37 (9)
O1ⁱ—Mn1—N1ⁱ	84.13 (3)	C11—C12—C5	119.60 (9)
N2—Mn1—N1ⁱ	97.74 (3)	C6—C12—C5	123.03 (9)
N2ⁱ—Mn1—N1ⁱ	73.85 (3)	C4—C5—C12	120.61 (9)
O1—Mn1—N1	84.13 (3)	C4—C5—H5	122.0 (10)
O1ⁱ—Mn1—N1	149.62 (3)	C12—C5—H5	117.3 (10)
N2—Mn1—N1	73.85 (3)	C5—C4—C10	120.87 (9)
N2ⁱ—Mn1—N1	97.74 (3)	C5—C4—H4	120.5 (9)
N1ⁱ—Mn1—N1	121.66 (5)	C10—C4—H4	118.6 (9)
C13—O1—Mn1	109.53 (6)	C7—C6—C12	119.42 (9)
C1—N1—C9	117.82 (9)	C7—C6—H6	121.0 (9)
C1—N1—Mn1	127.48 (7)	C12—C6—H6	119.5 (9)
C9—N1—Mn1	114.11 (6)	C6—C7—C8	119.34 (10)
C8—N2—C11	118.35 (9)	C6—C7—H7	122.2 (10)
C8—N2—Mn1	125.26 (7)	C8—C7—H7	118.5 (10)
C11—N2—Mn1	116.32 (7)	N2—C8—C7	122.73 (10)
N1—C1—C2	122.87 (10)	N2—C8—H8	114.7 (9)
N1—C1—H1	117.6 (9)	C7—C8—H8	122.5 (9)
C2—C1—H1	119.5 (9)	O1—C13—C13ⁱ	121.73 (5)
C3—C2—C1	119.50 (10)	O1—C13—C14	128.51 (8)
C3—C2—H2	120.6 (10)	C13ⁱ—C13—C14	109.76 (5)
C1—C2—H2	119.9 (10)	O2—C14—C13	127.67 (10)
C2—C3—C10	119.33 (9)	O2—C14—C15	126.27 (10)
C2—C3—H3	123.1 (9)	C13—C14—C15	106.06 (8)
C10—C3—H3	117.5 (9)	O3—C15—C14ⁱ	125.82 (6)
C9—C10—C3	117.18 (9)	O3—C15—C14	125.82 (6)

| C9—C10—C4 | 120.06 (9) | C14^i—C15—C14 | 108.36 (12) |
| C3—C10—C4 | 122.76 (9) | | |

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