



Synthesis and crystal structure of a heterobimetallic nickel–manganese 12-metallacrown-4 methanol disolvate monohydrate compound

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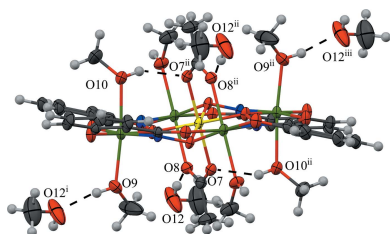
Keywords: nickel; manganese; heterobimetallic; metallacrown; crystal structure.**CCDC reference:** 2034558**Supporting information:** this article has supporting information at journals.iucr.org/e

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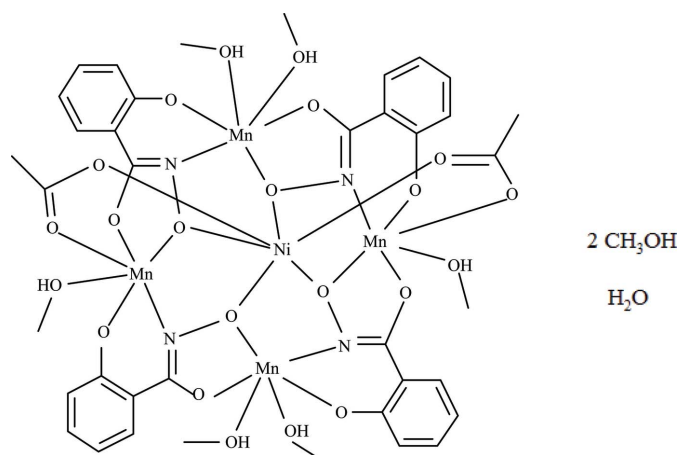
The synthesis and crystal structure of the title compound [systematic name: di- μ -acetato-tetrakis(μ_4 -*N*,2-dioxidobenzene-1-carboximidato)hexamethanol-tetramanganese(III)nickel(II) methanol disolvate monohydrate], $[\text{Mn}_4\text{Ni}(\text{C}_7\text{H}_4\text{NO}_3)_4(\text{C}_2\text{H}_3\text{O}_2)_2(\text{CH}_4\text{O})_6] \cdot 2\text{CH}_4\text{O} \cdot \text{H}_2\text{O}$ or $\text{Ni}(\text{OAc})_2[12\text{-MC}_{\text{Mn(III)N(shi)-4}}](\text{CH}_3\text{OH})_6 \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$, where MC is metallacrown, OAc^- is acetate, and shi^{3-} is salicylhydroximate, are reported. The macrocyclic metallacrown is positioned on an inversion center located on the Ni^{II} ion that resides in the central MC cavity. The macrocycle consists of an $\text{Mn}^{\text{III}}\text{-N-O}$ repeat unit that recurs four times to generate an overall square-shaped molecule. Both the Ni^{II} and Mn^{III} ions are six-coordinate with an octahedral geometry. In addition, the Mn^{III} ions possess an elongated Jahn–Teller distortion along the z -axis of the coordination environment. The interstitial water molecule is slightly offset from and disordered about an inversion center.

1. Chemical context

Since their recognition in 1989 by Pecoraro, metallacrowns (MC) have proven to be a versatile class of metallamacrocycles with applications such as single-molecule magnets, magnetorefrigerants and optical imaging agents (Mezei *et al.*, 2007; Nguyen & Pecoraro, 2017; Lutter *et al.*, 2018). The archetypal metallacrown consists of a cyclic metal–nitrogen–oxygen repeat unit that generates a central cavity that is capable of binding a metal ion. Initially, homometallic compounds were produced; however, heterobimetallic systems were soon generated that typically contained transition-metal ions in the ring metal position and either alkali or lanthanide ions captured in the central cavity of the MC (Pecoraro *et al.*, 1997; Mezei *et al.*, 2007). In addition, heterotrimetallic systems that bind both alkali and lanthanide ions have been reported since 2014 (Azar *et al.*, 2014). One area lacking is the use of two different transition-metal ions in an archetypal MC. While several examples of heterobimetallic 3d ‘collapsed’ metallacrowns, species without a central MC cavity and thus no central metal ion (Psomas *et al.*, 2001; Gole *et al.*, 2010), and inverse metallacrowns, species that bind a non-metal atom in the central MC cavity to the ring metal ions (Szyrwił *et al.*, 2013; Shiga *et al.*, 2014; Zhang *et al.*, 2014; Nesterova *et al.*, 2015), have been reported, only two heterobimetallic 3d archetypal 12-MC-4 compounds have been described to date. In 2014, Happ and Rentschler reported a $\text{Cu}^{\text{II}}(\text{DMF})_2\text{Cl}_2[12\text{-MC}_{\text{Fe(III)N(shi)-4}}](\text{DMF})_4 \cdot 2\text{DMF}$ compound



that contains Fe^{III} ions in the ring positions and a Cu^{II} ion captured in the central MC cavity (Happ & Rentschler, 2014). Recently we described the structure of $(\text{TMA})_2\{\text{Mn}(\text{OAc})_2[12\text{-MC}_{\text{Mn}(\text{III})\text{Cu}(\text{II})\text{N}(\text{shi})-4](\text{CH}_3\text{OH})\}_2 \cdot 2.90\text{CH}_3\text{OH}$ that consists of alternating Cu^{II} and Mn^{III} ions about the MC ring and an Mn^{II} ion bound to the central MC cavity (Lewis *et al.*, 2020). Herein we report a third heterobimetallic $3d$ archetypal 12-MC-4 compound: $\text{Ni}^{\text{II}}(\text{OAc})_2[12\text{-MC}_{\text{Mn}(\text{III})\text{N}(\text{shi})-4](\text{CH}_3\text{OH})_6 \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$, **1**, that contains ring Mn^{III} ions and a Ni^{II} ion captured in the central MC cavity. Future work will focus on the magnetic properties of the compound as the similar $\text{Mn}(\text{OAc})_2[12\text{-MC}_{\text{Mn}(\text{III})\text{N}(\text{shi})-4}]$ (Zaleski *et al.*, 2011) and $\{\text{Mn}(\text{OAc})_2[12\text{-MC}_{\text{Mn}(\text{III})\text{Cu}(\text{II})\text{N}(\text{shi})-4]\}^{2-}$ (Lewis *et al.*, 2020) systems behave as single-molecule magnets.



2. Structural commentary

The title metallacrown compound is positioned about an inversion center located on the Ni^{II} ion that resides in the central MC cavity (Fig. 1). The metallacrown macrocycle possesses an $\text{Mn}^{\text{III}}\text{-N-O}$ repeat unit that generates an approximately square molecule due to the fused five- and six-membered chelate rings of the shi^{3-} ligand that place the Mn^{III} ions 90° relative to each other. The oxime oxygen atoms of the shi^{3-} ligands generate the MC cavity and also bind the central Ni^{II} ion. Two acetate anions, which bind on opposite faces of the MC, tether the Ni^{II} ion to the MC by forming three atom bridges to two of the ring Mn^{III} ions. In addition to average bond lengths and bond-valence-sum (BVS) values (Table 1; Liu & Thorp, 1993), the oxidation state assignments of the Ni^{II} and Mn^{III} ions are supported by overall molecular charges, where one Ni^{II} and four Mn^{III} ions are counterbalanced by four shi^{3-} and two acetate anions.

The central Ni^{II} ion is six-coordinate with an octahedral geometry as verified by a SHAPE analysis (SHAPE 2.1; Llunell *et al.*, 2013; Pinsky & Avnir, 1998). Continuous shape measure (CSHM) values of less than 1.0 indicate only minor distortions from the ideal geometry (Cirera *et al.*, 2005); thus, the CSHM value of 0.164 for the octahedral geometry clearly defines the shape about the Ni^{II} ion (Table 2). The coordination environment is comprised of four oxime oxygen from four shi^{3-} ligands in the equatorial plane and two axial carboxylate

Table 1

Average bond length (\AA) and bond-valence-sum (BVS) values (v.u.) used to support assigned oxidation states of the nickel and manganese ions of **1**.

	Avg. bond length	BVS value	Assigned oxidation state
Ni1	2.021	2.34	2+
Mn1	2.031	3.06	3+
Mn2	2.026	3.06	3+

oxygen atoms of two acetate anions. As mentioned above, the acetate anions bind on opposite faces of the MC and connect the Ni^{II} ion to two Mn^{III} ions (Mn2). The acetate binding motif is different than the analogous homometallic $\text{Mn}^{\text{II}}(\text{OAc})_2[12\text{-MC}_{\text{Mn}(\text{III})\text{N}(\text{shi})-4](\text{DMF})_6 \cdot 2\text{DMF}$, where the acetate anions bind on the same face of the MC and the central Mn^{II} ion exhibits a geometry that is best described as a trigonal prism (Lah & Pecoraro, 1989).

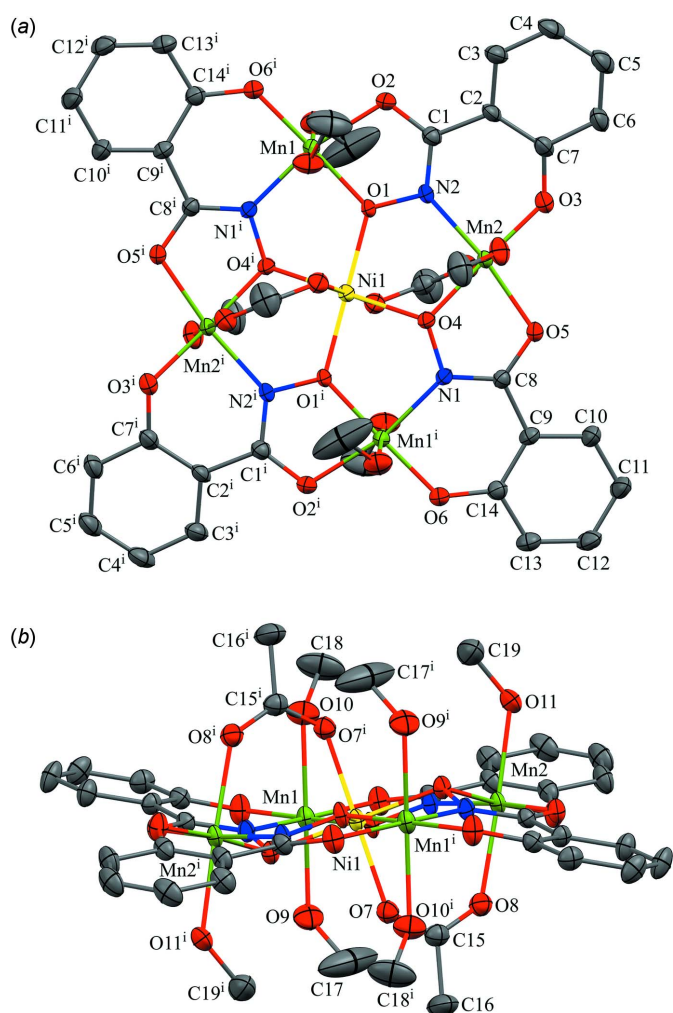


Figure 1

The molecular structure of the title compound, (a) top view with only the metal atoms and shi^{3-} ligands labeled for clarity and (b) side view with only the metal atoms and axial ligands labeled for clarity. The displacement ellipsoids are at the 50% probability level. For clarity, hydrogen atoms and solvent molecules have been omitted. [Color scheme: yellow— Ni^{II} , green— Mn^{III} , red—O, blue—N and gray—C; symmetry code: (i) $-x + 1, -y + 1, -z + 1$].

Table 2

Continuous Shapes Measures (CShM) values for the geometry about the six-coordinate central Ni^{II} and ring Mn^{III} ions of **1**.

Shape	Hexagon (D_{6h})	Pentagonal pyramid (C_{5v})	Octahedron (O_h)	Trigonal prism (D_{3h})	Johnson pentagonal pyramid (J2; C_{5v})
Ni1	31.656	29.242	0.164	16.201	32.416
Mn1	31.782	26.077	1.106	13.698	29.622
Mn2	31.099	26.575	0.821	15.377	29.523

The ring Mn^{III} ions (Mn1 and Mn2) are six-coordinate with a tetragonally distorted octahedral geometry (Table 2). The Jahn–Teller elongation, typical of a high-spin $3d^4$ ion, is located along the z -axis of each Mn^{III} ion. For both Mn1 and Mn2, the equatorial coordination environment is composed of *trans* chelate rings from two shi³⁻ ligands. A five-membered chelate ring is generated from an oxime oxygen atom and a carbonyl oxygen atom of one shi³⁻ ligand, and a six-membered chelate ring is produced by an oxime nitrogen atom and a phenolate oxygen atom of the second shi³⁻ ligand. For Mn1 the axial atoms are oxygen atoms from two methanol molecules, while for Mn2 the axial atoms are an oxygen atom from a methanol molecule and a carboxylate oxygen atom from an acetate anion.

In addition, solvent methanol and water molecules are located in the structure, and the methanol molecules form hydrogen bonds to the metallacrown. The water molecule associated with O13 is slightly offset from and disordered about an inversion center.

3. Supramolecular features

The coordinated and interstitial methanol molecules of **1** participate in several hydrogen bonds (Figs. 2 and 3, Table 3). The hydroxyl group of the methanol molecule associated with O9 and coordinated to Mn1 forms a hydrogen bond to an oxygen atom (O12) of an interstitial methanol molecule. In addition, the hydroxy group of another methanol molecule

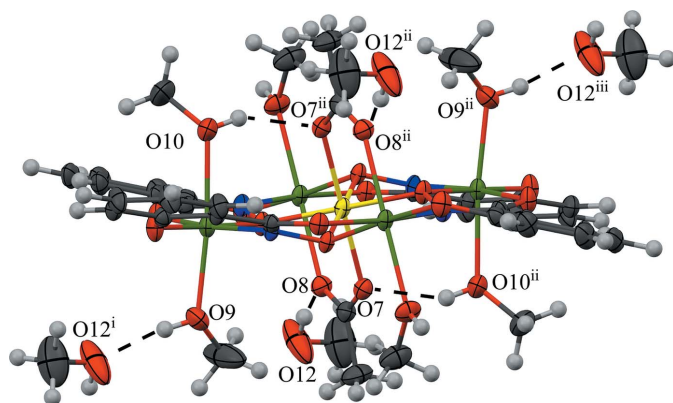


Figure 2

Intramolecular hydrogen bonding (dashed lines) between the coordinated methanol molecule (O10) and a carboxylate oxygen atom (O7) of the bridging acetate anion, and intermolecular hydrogen bonding (dashed lines) of the interstitial methanol molecule (O12) with a coordinated methanol molecule (O9) and a carboxylate oxygen atom (O8) of the bridging acetate anion. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x - 1, y, z$]

Table 3

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9–H9O \cdots O12 ⁱ	0.82 (2)	1.82 (2)	2.630 (4)	172 (4)
O10–H10O \cdots O7 ⁱⁱ	0.84 (2)	1.97 (3)	2.713 (3)	148 (4)
O11–H11O \cdots O5 ⁱⁱⁱ	0.83 (2)	1.95 (2)	2.778 (2)	178 (4)
O12–H12A \cdots O8	0.84	1.94	2.743 (3)	159

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

associated with O10 and coordinated to Mn1 forms an intramolecular hydrogen bond to a carboxylate oxygen atom (O7) of an acetate anion. Also the hydroxyl group of the interstitial methanol molecule associated with O12 forms a hydrogen bond to the other carboxylate oxygen atom (O8) of the acetate anion. Lastly, a one-dimensional chain of metallacrowns is mediated by the hydroxyl group of a methanol molecule associated with O11 and coordinated to Mn2 that forms a hydrogen bond to a carboxylate oxygen atom (O5) of a shi³⁻ ligand of a neighboring metallacrown. As a symmetry-equivalent hydrogen bond also occurs on the opposite side of the MC, a one-dimensional chain is established (Fig. 3). The connection between the neighboring MCs, the hydrogen bonds between the MC and the interstitial methanol molecules, and pure van der Waals forces contribute to the overall packing of **1**.

4. Database survey

A survey of the Cambridge Structural Database (CSD version 5.41, update May 2020, Groom *et al.*, 2016) reveals that there are three other heterobimetallic manganese-nickel MC

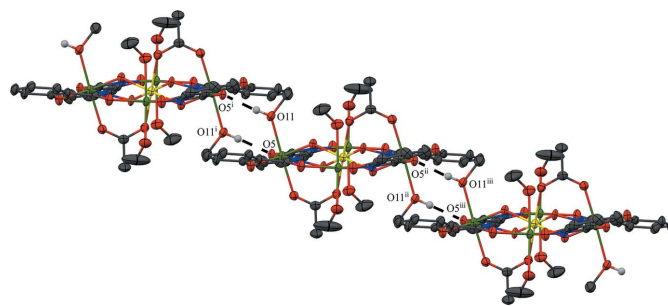


Figure 3

Intermolecular hydrogen bonding (dashed lines) between the carboxylate oxygen atom (O5) of a shi³⁻ ligand and a coordinated methanol molecule (O11) of a neighboring metallacrown that then generates a one-dimensional chain. For clarity only the hydrogen atoms involved in the interactions have been included. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y - 1, z$]

compounds. The first reported manganese-nickel MC is a ‘collapsed’ metallacrown as it does not contain a central cavity. The structure has an *M*–*N*–*O* repeat unit but two of the oxime oxygen atoms bind to ring metal ions across the potential central cavity, thus collapsing the cavity and preventing the binding of a central metal ion. The compound [12-MC_{Ni(II)Mn(III)N(Shi)2(pko)2-4}](OAc)₂ (QOCXAH; Psomas *et al.*, 2001), where pko[−] is 2,2′-dipyridylketonoximate, contains both Mn^{III} and Ni^{II} ions in the MC ring positions with the metals arranged in an alternating pattern. The two other compounds can both be considered dimers of inverse 9-MC-3 systems, where each MC binds a μ₃-O in the central cavity instead of a metal ion. In both compounds, two inverse 9-MC-3 units, each based on an Mn^{III}₂Ni^{II} core, are linked together to form a dimer. The main difference between the structures is the MC framework ligand: salicylaldehyde oxime (XIFGUQ; Szyrwiel *et al.*, 2013) or 5-chlorosalicylaldehyde oxime (LOKHIE; Zhang *et al.*, 2014). Thus, **1** represents the only manganese–nickel archetypal MC structure type as **1** contains a central metal ion.

5. Synthesis and crystallization

Manganese(II) acetate tetrahydrate (99+%), tetraethylammonium acetate tetrahydrate (99%), salicylhydroxamic acid (99%), nickel(II) acetate tetrahydrate (99.995%), *N,N*-dimethylformamide (DMF, Certified ACS grade) and methanol (ACS grade) were purchased from Acros Organics, Acros Organics, Alfa Aesar, Sigma–Aldrich, BDH Chemicals and Pharmco-AAPER, respectively. All reagents were used as received without further purification.

Tetraethylammonium acetate tetrahydrate (4 mmol, 1.0462 g) and salicylhydroxamic acid (2 mmol, 0.3063 g) were dissolved in 4 mL of DMF and 4 mL of methanol, resulting in a clear orange solution. In two separate vessels, nickel(II) acetate tetrahydrate (0.125 mmol, 0.0312 g) was dissolved in 4 mL of DMF and 4 mL of methanol resulting in a green–blue solution and manganese(II) acetate tetrahydrate (2 mmol, 0.4909 g) was dissolved in 4 mL of DMF and 4 mL of methanol resulting in a clear orange solution. The manganese(II) acetate solution was then added to the tetraethylammonium acetate/salicylhydroxamic acid solution resulting in a brown solution. The nickel(II) acetate was then immediately added and no color change was detected; however, the formation of a precipitate was observed. The mixture was then left to stir overnight and subsequently gravity filtered the next day. The filtrate was a dark orange–brown solution and no precipitate was recovered. Slow evaporation of the filtrate at room temperature afforded X-ray quality dark-brown block-shaped crystals after 16 weeks. A small fraction of crystals and mother liquor were separated for analysis by single crystal X-ray diffraction. The remaining crystals were washed with cold DMF and dried. The percent yield was 22% based on nickel(II) acetate tetrahydrate.

Table 4
Experimental details.

Crystal data	
Chemical formula	[Mn ₄ Ni(C ₇ H ₄ NO ₃) ₄ (C ₂ H ₃ O ₂) ₂ -(CH ₄ O) ₆] ₂ ·2CH ₄ O·H ₂ O
<i>M_r</i>	1271.35
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.3647 (7), 10.7781 (8), 11.8303 (8)
α , β , γ (°)	85.318 (3), 86.231 (3), 77.583 (3)
<i>V</i> (Å ³)	1284.78 (16)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	1.40
Crystal size (mm)	0.24 × 0.22 × 0.13
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan (SADABS2016/2; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.616, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13573, 7767, 6204
<i>R</i> _{int}	0.026
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.717
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.050, 0.137, 1.07
No. of reflections	7767
No. of parameters	355
No. of restraints	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	1.79, −1.02

Computer programs: APEX3 and SAINT (Bruker, 2018), SHELXS97 (Sheldrick, 2008), SHELXL2018/3 (Sheldrick, 2015), SHELXLE (Hübschle *et al.*, 2011), Mercury (Macrae *et al.*, 2020) and publCIF (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. An electron density region disordered around an inversion center was refined as a water molecule located slightly offset of the inversion center. The water hydrogen-atom positions were initially refined and O–H and H···H distances were restrained to 0.84 (2) and 1.36 (2) Å, respectively, and further restrained based on hydrogen-bonding considerations while a damping factor was applied. In the final refinement cycles the hydrogen atoms were constrained to ride on the oxygen carrier atom. The displacement parameters of the water O atom were restrained to be close to isotropic. For the methanol molecules, the O–H bond distance was also restrained to 0.84 (2) Å. The *U*_{iso} values for the O–H hydrogen atoms (water and methanol) were set to a multiple of the value of the carrying oxygen atom (1.5 times). All other hydrogen atoms were placed in calculated positions and refined as riding on their carrier atoms with C–H distances of 0.95 Å for *sp*² carbon atoms and 0.98 Å for methyl carbon atoms. The *U*_{iso} values for hydrogen atoms were set to a multiple of the value of the carrying carbon atom (1.2 times for *sp*²-hybridized carbon atoms or 1.5 times for methyl carbon atoms).

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supporting information

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Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINTE* (Bruker, 2018); data reduction: *SAINTE* (Bruker, 2018); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015), *SHELXL* (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Di- μ -acetato-tetrakis(μ_4 -*N*,2-dioxidobenzene-1-carboximidato)hexamethanoltetramanganese(III)nickel(II) methanol disolvate monohydrate

Crystal data

$[\text{Mn}_4\text{Ni}(\text{C}_7\text{H}_4\text{NO}_3)_4(\text{C}_2\text{H}_3\text{O}_2)_2(\text{CH}_4\text{O})_6] \cdot 2\text{CH}_4\text{O} \cdot \text{H}_2\text{O}$

$M_r = 1271.35$

Triclinic, $P\bar{1}$

$a = 10.3647$ (7) Å

$b = 10.7781$ (8) Å

$c = 11.8303$ (8) Å

$\alpha = 85.318$ (3)°

$\beta = 86.231$ (3)°

$\gamma = 77.583$ (3)°

$V = 1284.78$ (16) Å³

$Z = 1$

$F(000) = 652$

$D_x = 1.643$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9780 reflections

$\theta = 2.6\text{--}30.6^\circ$

$\mu = 1.40$ mm⁻¹

$T = 150$ K

Block, brown

$0.24 \times 0.22 \times 0.13$ mm

Data collection

Bruker AXS D8 Quest CMOS
diffractometer

Radiation source: fine focus sealed tube X-ray
source

Triumph curved graphite crystal
monochromator

Detector resolution: 10.4167 pixels mm⁻¹

ω and ϕ scans

Absorption correction: multi-scan
(*SADABS2016/2*; Krause *et al.*, 2015)

$T_{\min} = 0.616$, $T_{\max} = 0.746$

13573 measured reflections

7767 independent reflections

6204 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 30.6^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -14 \rightarrow 14$

$k = -15 \rightarrow 15$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.137$

$S = 1.07$

7767 reflections

355 parameters

9 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 1.2905P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.030$
 $\Delta\rho_{\max} = 1.79 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.02 \text{ e } \text{\AA}^{-3}$

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. A single electron density disordered around an inversion center was refined as a water molecule located slightly offset of the inversion center. The water H atom positions were initially refined and O-H and H...H distances were restrained to 0.84 (2) and 1.36 (2) Angstrom, respectively and further restrained based on hydrogen bonding considerations while a damping factor was applied. In the final refinement cycles the H atoms were constrained to ride on the oxygen carrier atom.

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)
Ni1	0.5000	0.5000	0.5000	0.01808 (10)	
Mn1	0.72582 (4)	0.43090 (3)	0.28526 (3)	0.01909 (10)	
Mn2	0.59489 (3)	0.76188 (3)	0.52263 (3)	0.01796 (9)	
O1	0.65814 (17)	0.52833 (15)	0.40892 (14)	0.0203 (3)	
O2	0.81297 (18)	0.57917 (17)	0.25092 (15)	0.0256 (4)	
O3	0.72951 (19)	0.85163 (17)	0.49693 (15)	0.0272 (4)	
O4	0.44721 (17)	0.67981 (15)	0.54628 (13)	0.0191 (3)	
O5	0.50532 (17)	0.84616 (15)	0.65760 (14)	0.0209 (3)	
O6	0.21353 (19)	0.66578 (18)	0.83693 (15)	0.0278 (4)	
O7	0.61523 (18)	0.44755 (16)	0.64128 (14)	0.0239 (3)	
O8	0.70764 (18)	0.61703 (17)	0.64174 (15)	0.0259 (4)	
O9	0.8980 (2)	0.3245 (2)	0.37362 (19)	0.0349 (4)	
H9O	0.964 (3)	0.307 (4)	0.331 (3)	0.052*	
O10	0.5606 (2)	0.5444 (2)	0.17778 (16)	0.0344 (4)	
H10O	0.498 (3)	0.576 (4)	0.222 (3)	0.052*	
O11	0.4808 (2)	0.90151 (17)	0.39868 (17)	0.0300 (4)	
H11O	0.486 (4)	0.977 (2)	0.384 (3)	0.045*	
O12	0.8752 (3)	0.7344 (5)	0.7432 (3)	0.0847 (13)	
H12A	0.8150	0.7177	0.7066	0.127*	
O13	1.015 (3)	0.4661 (18)	-0.003 (2)	0.156 (6)	0.5
H13A	0.9779	0.5158	0.0521	0.233*	0.5
H13B	0.9842	0.3968	0.0223	0.233*	0.5
N1	0.3884 (2)	0.69063 (18)	0.65720 (15)	0.0182 (4)	
N2	0.6789 (2)	0.65323 (18)	0.39992 (16)	0.0199 (4)	
C1	0.7675 (2)	0.6685 (2)	0.31880 (19)	0.0213 (4)	
C2	0.8140 (2)	0.7887 (2)	0.3086 (2)	0.0220 (4)	
C3	0.8848 (3)	0.8180 (2)	0.2086 (2)	0.0273 (5)	
H3	0.8979	0.7621	0.1488	0.033*	
C4	0.9360 (3)	0.9269 (3)	0.1955 (3)	0.0338 (6)	

H4	0.9836	0.9460	0.1272	0.041*
C5	0.9169 (3)	1.0079 (3)	0.2831 (3)	0.0342 (6)
H5	0.9525	1.0825	0.2747	0.041*
C6	0.8469 (3)	0.9817 (2)	0.3826 (2)	0.0301 (5)
H6	0.8353	1.0383	0.4417	0.036*
C7	0.7929 (2)	0.8724 (2)	0.3972 (2)	0.0232 (5)
C8	0.4211 (2)	0.7826 (2)	0.70775 (18)	0.0183 (4)
C9	0.3615 (2)	0.8147 (2)	0.82130 (18)	0.0203 (4)
C10	0.4022 (3)	0.9118 (3)	0.8729 (2)	0.0268 (5)
H10	0.4670	0.9525	0.8345	0.032*
C11	0.3501 (3)	0.9492 (3)	0.9781 (2)	0.0327 (6)
H11	0.3787	1.0151	1.0116	0.039*
C12	0.2558 (3)	0.8900 (3)	1.0346 (2)	0.0316 (6)
H12	0.2203	0.9151	1.1073	0.038*
C13	0.2134 (3)	0.7951 (3)	0.9856 (2)	0.0259 (5)
H13	0.1483	0.7557	1.0252	0.031*
C14	0.2643 (2)	0.7553 (2)	0.87871 (19)	0.0216 (4)
C15	0.6980 (3)	0.5059 (2)	0.6754 (2)	0.0258 (5)
C16	0.7891 (4)	0.4355 (3)	0.7642 (3)	0.0443 (8)
H16A	0.8066	0.3439	0.7540	0.066*
H16B	0.7475	0.4518	0.8399	0.066*
H16C	0.8726	0.4649	0.7565	0.066*
C17	0.9312 (5)	0.3374 (7)	0.4821 (4)	0.107 (3)
H17A	1.0278	0.3194	0.4855	0.129*
H17B	0.8951	0.2773	0.5352	0.129*
H17C	0.8945	0.4245	0.5030	0.129*
C18	0.5752 (4)	0.6311 (4)	0.0836 (3)	0.0627 (12)
H18A	0.6480	0.5919	0.0324	0.094*
H18B	0.5944	0.7086	0.1103	0.094*
H18C	0.4930	0.6529	0.0430	0.094*
C19	0.3701 (4)	0.8873 (3)	0.3386 (3)	0.0447 (8)
H19A	0.3931	0.8898	0.2569	0.067*
H19B	0.2946	0.9568	0.3545	0.067*
H19C	0.3468	0.8055	0.3633	0.067*
C20	0.8243 (6)	0.7872 (6)	0.8340 (5)	0.0872 (18)
H20A	0.7712	0.8719	0.8138	0.105*
H20B	0.8951	0.7951	0.8822	0.105*
H20C	0.7679	0.7347	0.8754	0.105*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0219 (2)	0.01533 (19)	0.01792 (18)	-0.00658 (15)	0.00285 (14)	-0.00226 (14)
Mn1	0.02230 (19)	0.01651 (17)	0.01929 (16)	-0.00688 (13)	0.00547 (12)	-0.00386 (12)
Mn2	0.02245 (18)	0.01363 (16)	0.01896 (16)	-0.00712 (13)	0.00365 (12)	-0.00290 (12)
O1	0.0270 (8)	0.0128 (7)	0.0225 (7)	-0.0092 (6)	0.0070 (6)	-0.0038 (6)
O2	0.0284 (9)	0.0234 (8)	0.0260 (8)	-0.0104 (7)	0.0107 (7)	-0.0053 (7)
O3	0.0324 (10)	0.0250 (8)	0.0282 (8)	-0.0149 (7)	0.0028 (7)	-0.0055 (7)

O4	0.0251 (8)	0.0171 (7)	0.0159 (7)	-0.0070 (6)	0.0043 (6)	-0.0030 (6)
O5	0.0260 (9)	0.0164 (7)	0.0218 (7)	-0.0078 (6)	0.0024 (6)	-0.0045 (6)
O6	0.0324 (10)	0.0275 (9)	0.0264 (8)	-0.0139 (8)	0.0112 (7)	-0.0094 (7)
O7	0.0271 (9)	0.0227 (8)	0.0223 (8)	-0.0066 (7)	0.0000 (7)	-0.0004 (6)
O8	0.0261 (9)	0.0262 (9)	0.0265 (8)	-0.0084 (7)	-0.0030 (7)	0.0003 (7)
O9	0.0228 (10)	0.0386 (11)	0.0400 (11)	0.0006 (8)	0.0007 (8)	-0.0037 (9)
O10	0.0312 (11)	0.0416 (11)	0.0267 (9)	-0.0048 (9)	0.0037 (8)	0.0075 (8)
O11	0.0385 (11)	0.0183 (8)	0.0342 (9)	-0.0087 (7)	-0.0071 (8)	0.0038 (7)
O12	0.0352 (14)	0.156 (4)	0.076 (2)	-0.0347 (19)	0.0118 (14)	-0.064 (2)
O13	0.170 (9)	0.188 (12)	0.099 (5)	-0.036 (9)	0.009 (6)	0.026 (9)
N1	0.0229 (9)	0.0162 (8)	0.0158 (8)	-0.0051 (7)	0.0033 (7)	-0.0037 (6)
N2	0.0247 (10)	0.0144 (8)	0.0224 (8)	-0.0090 (7)	0.0039 (7)	-0.0026 (7)
C1	0.0225 (11)	0.0198 (10)	0.0216 (10)	-0.0061 (8)	0.0018 (8)	0.0010 (8)
C2	0.0194 (11)	0.0181 (10)	0.0292 (11)	-0.0081 (8)	0.0040 (9)	0.0018 (9)
C3	0.0238 (12)	0.0255 (11)	0.0316 (12)	-0.0070 (9)	0.0073 (9)	0.0009 (10)
C4	0.0276 (13)	0.0286 (13)	0.0435 (15)	-0.0095 (11)	0.0084 (11)	0.0089 (11)
C5	0.0299 (14)	0.0229 (12)	0.0506 (16)	-0.0116 (10)	0.0051 (12)	0.0034 (11)
C6	0.0309 (14)	0.0200 (11)	0.0418 (14)	-0.0117 (10)	0.0027 (11)	-0.0021 (10)
C7	0.0179 (11)	0.0193 (10)	0.0326 (12)	-0.0053 (8)	0.0003 (9)	0.0001 (9)
C8	0.0186 (10)	0.0170 (9)	0.0188 (9)	-0.0031 (8)	0.0005 (8)	-0.0019 (8)
C9	0.0216 (11)	0.0224 (10)	0.0164 (9)	-0.0032 (8)	0.0014 (8)	-0.0043 (8)
C10	0.0273 (12)	0.0303 (12)	0.0251 (11)	-0.0091 (10)	0.0031 (9)	-0.0110 (10)
C11	0.0294 (13)	0.0437 (15)	0.0297 (12)	-0.0135 (12)	0.0040 (10)	-0.0200 (11)
C12	0.0279 (13)	0.0466 (16)	0.0219 (11)	-0.0090 (12)	0.0045 (9)	-0.0132 (11)
C13	0.0253 (12)	0.0313 (12)	0.0197 (10)	-0.0039 (10)	0.0035 (9)	-0.0031 (9)
C14	0.0217 (11)	0.0211 (10)	0.0212 (10)	-0.0033 (8)	0.0010 (8)	-0.0018 (8)
C15	0.0257 (12)	0.0288 (12)	0.0213 (10)	-0.0024 (10)	-0.0002 (9)	-0.0020 (9)
C16	0.0485 (19)	0.0448 (17)	0.0405 (16)	-0.0108 (14)	-0.0223 (14)	0.0105 (14)
C17	0.070 (3)	0.176 (6)	0.044 (2)	0.061 (4)	-0.022 (2)	-0.035 (3)
C18	0.051 (2)	0.073 (3)	0.051 (2)	-0.0006 (19)	0.0063 (17)	0.033 (2)
C19	0.058 (2)	0.0368 (16)	0.0437 (17)	-0.0176 (15)	-0.0181 (15)	0.0064 (13)
C20	0.092 (4)	0.097 (4)	0.088 (4)	-0.048 (3)	0.031 (3)	-0.047 (3)

Geometric parameters (Å, °)

Ni1—O1	1.9673 (16)	N2—C1	1.309 (3)
Ni1—O1 ⁱ	1.9673 (16)	C1—C2	1.470 (3)
Ni1—O4 ⁱ	2.0082 (15)	C2—C3	1.401 (3)
Ni1—O4	2.0082 (15)	C2—C7	1.414 (4)
Ni1—O7	2.0874 (17)	C3—C4	1.382 (4)
Ni1—O7 ⁱ	2.0874 (17)	C3—H3	0.9500
Mn1—O6 ⁱ	1.8480 (17)	C4—C5	1.387 (4)
Mn1—O1	1.8799 (16)	C4—H4	0.9500
Mn1—N1 ⁱ	1.9990 (19)	C5—C6	1.383 (4)
Mn1—O2	2.0003 (18)	C5—H5	0.9500
Mn1—O9	2.182 (2)	C6—C7	1.404 (3)
Mn1—O10	2.275 (2)	C6—H6	0.9500
Mn2—O3	1.8578 (18)	C8—C9	1.477 (3)

Mn2—O4	1.9208 (17)	C9—C10	1.405 (3)
Mn2—N2	1.9772 (19)	C9—C14	1.415 (3)
Mn2—O5	1.9789 (17)	C10—C11	1.380 (3)
Mn2—O8	2.2048 (18)	C10—H10	0.9500
Mn2—O11	2.2170 (18)	C11—C12	1.386 (4)
O1—N2	1.403 (2)	C11—H11	0.9500
O2—C1	1.294 (3)	C12—C13	1.378 (4)
O3—C7	1.339 (3)	C12—H12	0.9500
O4—N1	1.413 (2)	C13—C14	1.402 (3)
O5—C8	1.306 (3)	C13—H13	0.9500
O6—C14	1.335 (3)	C15—C16	1.504 (4)
O6—Mn1 ⁱ	1.8480 (17)	C16—H16A	0.9800
O7—C15	1.270 (3)	C16—H16B	0.9800
O8—C15	1.254 (3)	C16—H16C	0.9800
O9—C17	1.377 (5)	C17—H17A	0.9800
O9—H9O	0.820 (19)	C17—H17B	0.9800
O10—C18	1.416 (4)	C17—H17C	0.9800
O10—H10O	0.838 (18)	C18—H18A	0.9800
O11—C19	1.431 (4)	C18—H18B	0.9800
O11—H11O	0.834 (18)	C18—H18C	0.9800
O12—C20	1.285 (5)	C19—H19A	0.9800
O12—H12A	0.8400	C19—H19B	0.9800
O13—H13A	0.8912	C19—H19C	0.9800
O13—H13B	0.8940	C20—H20A	0.9800
N1—C8	1.313 (3)	C20—H20B	0.9800
N1—Mn1 ⁱ	1.9991 (19)	C20—H20C	0.9800
O1—Ni1—O1 ⁱ	180.0	O2—C1—C2	121.6 (2)
O1—Ni1—O4 ⁱ	85.54 (6)	N2—C1—C2	118.0 (2)
O1 ⁱ —Ni1—O4 ⁱ	94.46 (6)	C3—C2—C7	119.7 (2)
O1—Ni1—O4	94.46 (6)	C3—C2—C1	118.1 (2)
O1 ⁱ —Ni1—O4	85.54 (6)	C7—C2—C1	122.2 (2)
O4 ⁱ —Ni1—O4	180.0	C4—C3—C2	121.0 (3)
O1—Ni1—O7	89.30 (7)	C4—C3—H3	119.5
O1 ⁱ —Ni1—O7	90.70 (7)	C2—C3—H3	119.5
O4 ⁱ —Ni1—O7	89.35 (7)	C3—C4—C5	119.2 (3)
O4—Ni1—O7	90.65 (7)	C3—C4—H4	120.4
O1—Ni1—O7 ⁱ	90.70 (7)	C5—C4—H4	120.4
O1 ⁱ —Ni1—O7 ⁱ	89.30 (7)	C6—C5—C4	121.0 (2)
O4 ⁱ —Ni1—O7 ⁱ	90.65 (7)	C6—C5—H5	119.5
O4—Ni1—O7 ⁱ	89.35 (7)	C4—C5—H5	119.5
O7—Ni1—O7 ⁱ	180.0	C5—C6—C7	120.7 (3)
O6 ⁱ —Mn1—O1	177.99 (8)	C5—C6—H6	119.7
O6 ⁱ —Mn1—N1 ⁱ	90.59 (8)	C7—C6—H6	119.7
O1—Mn1—N1 ⁱ	87.90 (7)	O3—C7—C6	117.3 (2)
O6 ⁱ —Mn1—O2	101.75 (7)	O3—C7—C2	124.3 (2)
O1—Mn1—O2	79.66 (7)	C6—C7—C2	118.4 (2)
N1 ⁱ —Mn1—O2	166.99 (7)	O5—C8—N1	120.2 (2)

O6 ⁱ —Mn1—O9	87.57 (8)	O5—C8—C9	120.09 (19)
O1—Mn1—O9	93.84 (8)	N1—C8—C9	119.7 (2)
N1 ⁱ —Mn1—O9	93.75 (8)	C10—C9—C14	118.9 (2)
O2—Mn1—O9	90.88 (8)	C10—C9—C8	117.4 (2)
O6 ⁱ —Mn1—O10	88.50 (8)	C14—C9—C8	123.6 (2)
O1—Mn1—O10	90.20 (8)	C11—C10—C9	121.3 (2)
N1 ⁱ —Mn1—O10	90.55 (8)	C11—C10—H10	119.4
O2—Mn1—O10	85.74 (8)	C9—C10—H10	119.4
O9—Mn1—O10	174.20 (8)	C10—C11—C12	119.7 (2)
O3—Mn2—O4	176.03 (8)	C10—C11—H11	120.2
O3—Mn2—N2	88.18 (8)	C12—C11—H11	120.2
O4—Mn2—N2	93.66 (7)	C13—C12—C11	120.3 (2)
O3—Mn2—O5	98.67 (7)	C13—C12—H12	119.9
O4—Mn2—O5	79.85 (7)	C11—C12—H12	119.9
N2—Mn2—O5	171.17 (7)	C12—C13—C14	121.4 (2)
O3—Mn2—O8	93.89 (8)	C12—C13—H13	119.3
O4—Mn2—O8	89.72 (7)	C14—C13—H13	119.3
N2—Mn2—O8	86.94 (8)	O6—C14—C13	116.8 (2)
O5—Mn2—O8	87.05 (7)	O6—C14—C9	124.7 (2)
O3—Mn2—O11	87.30 (8)	C13—C14—C9	118.5 (2)
O4—Mn2—O11	89.15 (7)	O8—C15—O7	124.9 (2)
N2—Mn2—O11	91.20 (8)	O8—C15—C16	118.4 (2)
O5—Mn2—O11	94.65 (7)	O7—C15—C16	116.7 (2)
O8—Mn2—O11	177.77 (7)	C15—C16—H16A	109.5
N2—O1—Mn1	115.37 (13)	C15—C16—H16B	109.5
N2—O1—Ni1	116.20 (13)	H16A—C16—H16B	109.5
Mn1—O1—Ni1	121.46 (8)	C15—C16—H16C	109.5
C1—O2—Mn1	111.39 (15)	H16A—C16—H16C	109.5
C7—O3—Mn2	126.39 (15)	H16B—C16—H16C	109.5
N1—O4—Mn2	112.52 (12)	O9—C17—H17A	109.5
N1—O4—Ni1	114.00 (12)	O9—C17—H17B	109.5
Mn2—O4—Ni1	109.98 (8)	H17A—C17—H17B	109.5
C8—O5—Mn2	111.06 (13)	O9—C17—H17C	109.5
C14—O6—Mn1 ⁱ	129.29 (16)	H17A—C17—H17C	109.5
C15—O7—Ni1	126.98 (16)	H17B—C17—H17C	109.5
C15—O8—Mn2	132.85 (17)	O10—C18—H18A	109.5
C17—O9—Mn1	127.6 (2)	O10—C18—H18B	109.5
C17—O9—H9O	111 (3)	H18A—C18—H18B	109.5
Mn1—O9—H9O	113 (3)	O10—C18—H18C	109.5
C18—O10—Mn1	126.2 (2)	H18A—C18—H18C	109.5
C18—O10—H10O	111 (3)	H18B—C18—H18C	109.5
Mn1—O10—H10O	108 (3)	O11—C19—H19A	109.5
C19—O11—Mn2	127.54 (17)	O11—C19—H19B	109.5
C19—O11—H11O	104 (3)	H19A—C19—H19B	109.5
Mn2—O11—H11O	128 (3)	O11—C19—H19C	109.5
C20—O12—H12A	109.5	H19A—C19—H19C	109.5
H13A—O13—H13B	97.8	H19B—C19—H19C	109.5
C8—N1—O4	111.81 (18)	O12—C20—H20A	109.5

C8—N1—Mn1 ⁱ	129.84 (16)	O12—C20—H20B	109.5
O4—N1—Mn1 ⁱ	118.35 (13)	H20A—C20—H20B	109.5
C1—N2—O1	111.30 (18)	O12—C20—H20C	109.5
C1—N2—Mn2	131.90 (16)	H20A—C20—H20C	109.5
O1—N2—Mn2	115.94 (14)	H20B—C20—H20C	109.5
O2—C1—N2	120.4 (2)		
N1 ⁱ —Mn1—O1—N2	-163.95 (16)	Mn2—O3—C7—C6	153.19 (19)
O2—Mn1—O1—N2	12.24 (15)	Mn2—O3—C7—C2	-30.0 (3)
O9—Mn1—O1—N2	102.43 (16)	C5—C6—C7—O3	178.2 (2)
O10—Mn1—O1—N2	-73.40 (15)	C5—C6—C7—C2	1.2 (4)
N1 ⁱ —Mn1—O1—Ni1	-14.29 (10)	C3—C2—C7—O3	-178.3 (2)
O2—Mn1—O1—Ni1	161.89 (11)	C1—C2—C7—O3	-0.3 (4)
O9—Mn1—O1—Ni1	-107.91 (11)	C3—C2—C7—C6	-1.4 (4)
O10—Mn1—O1—Ni1	76.26 (10)	C1—C2—C7—C6	176.6 (2)
N2—Mn2—O3—C7	32.0 (2)	Mn2—O5—C8—N1	-11.7 (3)
O5—Mn2—O3—C7	-153.54 (19)	Mn2—O5—C8—C9	168.76 (16)
O8—Mn2—O3—C7	118.9 (2)	O4—N1—C8—O5	-4.0 (3)
O11—Mn2—O3—C7	-59.2 (2)	Mn1 ⁱ —N1—C8—O5	175.17 (16)
Mn2—O4—N1—C8	18.3 (2)	O4—N1—C8—C9	175.55 (18)
Ni1—O4—N1—C8	144.44 (16)	Mn1 ⁱ —N1—C8—C9	-5.3 (3)
Mn2—O4—N1—Mn1 ⁱ	-160.92 (9)	O5—C8—C9—C10	-2.0 (3)
Ni1—O4—N1—Mn1 ⁱ	-34.81 (17)	N1—C8—C9—C10	178.5 (2)
Mn1—O1—N2—C1	-14.5 (2)	O5—C8—C9—C14	176.4 (2)
Ni1—O1—N2—C1	-165.81 (15)	N1—C8—C9—C14	-3.1 (3)
Mn1—O1—N2—Mn2	174.82 (9)	C14—C9—C10—C11	0.5 (4)
Ni1—O1—N2—Mn2	23.53 (19)	C8—C9—C10—C11	179.0 (2)
Mn1—O2—C1—N2	2.2 (3)	C9—C10—C11—C12	0.1 (4)
Mn1—O2—C1—C2	-178.51 (18)	C10—C11—C12—C13	-0.5 (5)
O1—N2—C1—O2	7.6 (3)	C11—C12—C13—C14	0.4 (4)
Mn2—N2—C1—O2	176.28 (17)	Mn1 ⁱ —O6—C14—C13	-167.37 (18)
O1—N2—C1—C2	-171.72 (19)	Mn1 ⁱ —O6—C14—C9	14.8 (4)
Mn2—N2—C1—C2	-3.0 (3)	C12—C13—C14—O6	-177.8 (2)
O2—C1—C2—C3	14.8 (4)	C12—C13—C14—C9	0.2 (4)
N2—C1—C2—C3	-165.9 (2)	C10—C9—C14—O6	177.2 (2)
O2—C1—C2—C7	-163.2 (2)	C8—C9—C14—O6	-1.2 (4)
N2—C1—C2—C7	16.1 (3)	C10—C9—C14—C13	-0.6 (3)
C7—C2—C3—C4	0.8 (4)	C8—C9—C14—C13	-179.1 (2)
C1—C2—C3—C4	-177.3 (2)	Mn2—O8—C15—O7	2.6 (4)
C2—C3—C4—C5	0.2 (4)	Mn2—O8—C15—C16	-176.5 (2)
C3—C4—C5—C6	-0.5 (4)	Ni1—O7—C15—O8	13.4 (4)
C4—C5—C6—C7	-0.2 (4)	Ni1—O7—C15—C16	-167.5 (2)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9O \cdots O12 ⁱⁱ	0.82 (2)	1.82 (2)	2.630 (4)	172 (4)

O10—H10O···O7 ⁱ	0.84 (2)	1.97 (3)	2.713 (3)	148 (4)
O11—H11O···O5 ⁱⁱⁱ	0.83 (2)	1.95 (2)	2.778 (2)	178 (4)
O12—H12A···O8	0.84	1.94	2.743 (3)	159

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