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$[Mn_{12}O_{12}(O_2CMe)_{12}(NO_3)_4(H_2O)_4]$: facile synthesis of a new type of Mn_{12} complex

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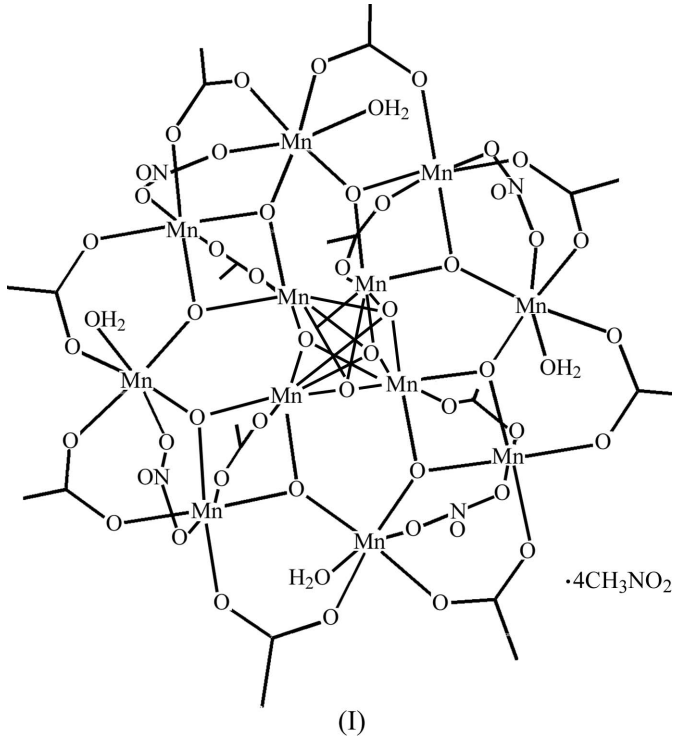
The title dodecanuclear Mn complex, namely dodeca-μ_2-acetato-$\kappa^{24}O$:O'-tetraaquatetra-μ_2-nitrato-$\kappa^{8}O$:O'-tetra-μ_4-oxido-octa-μ_3-oxido-tetramanganese(IV)octamanganese(III) nitromethane tetrasolvate, $[Mn_{12}(CH_3COO)_{12}(NO_3)_4O_{12}(H_2O)_4]\cdot 4CH_3NO_2$, was synthesized by the reaction of Mn^{2+} and Ce^{4+} sources in nitromethane with an excess of acetic acid. This compound is distinct from the previously known single-molecule magnet $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$, synthesized by Lis [*Acta Cryst.* (1980), B**36**, 2042–2044]. It is the first Mn_{12}-type molecule containing nitrate ligands to be directly synthesized without the use of a preformed cluster. Additionally, this molecule is distinct from all other known Mn_{12} complexes due to intermolecular hydrogen bonds between the nitrate and water ligands, which give rise to a three-dimensional network. The complex is compared to other known Mn_{12} molecules in terms of its structural parameters and symmetry.

Keywords: manganese clusters; single-molecule magnets; crystal structure; three-dimensional network; cluster chemistry; *in situ* formation; Mn_{12} molecule.

1. Introduction

The original 'Mn_{12}' molecule was first synthesized in 1980 and has garnered much interest in the scientific community, especially in the field of single-molecule magnets (SMMs; Lis, 1980). Herein, the term 'Mn_{12}' will be used to describe all structures containing a core similar to the molecule synthesized by Lis, which contains four Mn^{IV} ions surrounded by a ring of eight Mn^{III} ions bridged by 12 oxide (O^{2-}) ions. SMMs are molecules that behave as molecular supraparamagnets below a certain blocking temperature, T_B, and which exhibit slow magnetic relaxation, and consequently magnetic hysteresis (Bagai & Christou, 2009). The SMM properties in manganese complexes arise from the combination of a large ground-state spin, S, due to the ferromagnetic coupling of Mn^{III} ions, and a large negative anisotropy, D, which arises from the Jahn–Teller distortion of the Mn^{III} ions. Many studies have focused on changing the alkyl group of the carboxylate ligands of the complex to observe the effect on the structural and magnetic properties (Sessoli *et al.*, 1993). Herein, the structure of a new Mn_{12} cluster molecule, $[Mn_{12}O_{12}(O_2CMe)_{12}(NO_3)_4(H_2O)_4]\cdot 4CH_3NO_2$, (I), containing 12 acetate ligands, four water ligands, and four nitrate ligands, is presented. This complex has been characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction.



(I)

2. Experimental

2.1. Synthesis and crystallization

The title Mn_{12} complex was synthesized using an excess of acetic acid, manganese(II) acetate, and cerium(IV) ammonium nitrate in a 20:8:4 ratio in a solution of warm nitromethane (20 ml). The solution was filtered and the filtrate left undisturbed for 3 d, during which time brown crystals of the title complex formed in approximately 40% yield.

2.2. IR spectroscopy and elemental analysis

The identity of the complex was confirmed by IR spectroscopy and elemental analysis, which were both in good agreement with the crystal structure analysis. Selected IR data (KBr, cm^{-1}): 3598 (*s*), 3380 (*b*), 1709 (*s*), 1627 (*m*), 1384 (*s*), 1388 (*s*), 1333 (*s*), 1256 (*w*), 1042 (*s*), 741 (*s*), 813 (*s*), 673 (*s*), 641 (*m*), 610 (*m*), 563 (*m*), 518 (*w*). Analysis calculated for $C_{28}H_{56}Mn_{12}N_8O_{60}$: C 15.83, H 2.66, N 5.28%; found: C 15.92, H 2.73, N 5.33%.

 doi:10.1107/S2053229615002326

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Mn_{12}(C_2H_3O_2)_{12}(NO_3)_4O_{12}(H_2O)_4]\cdot 4CH_3NO_2$
M_r	2124.08
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature (K)	100
a, c (Å)	15.7293 (8), 27.9010 (14)
V (Å^3)	6903.0 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.24
Crystal size (mm)	0.16 × 0.10 × 0.04
Data collection	
Diffractometer	Bruker APEXII DUO diffractometer
Absorption correction	Analytical, based on measured indexed crystal faces (*SHELXTL2013*; Bruker, 2013)
T_{min}, T_{max}	0.816, 0.929
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	85988, 3974, 3287
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.066, 1.05
No. of reflections	3974
No. of parameters	254
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, −0.71

Computer programs: *APEX2* (Bruker, 2013), *SAINT* (Bruker, 2013), *SHELXTL2013* (Bruker, 2013) and *SHELXL2014* (Sheldrick, 2015).

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The Mn_{12} cluster is located on a $\overline{4}$ symmetry element at (0.5, 0.25, 0.375). Consequently, a quarter of the Mn_{12} cluster exists in the asymmetric unit, along with a nitromethane solvent molecule. The latter has the nitro group disordered and was refined in two parts with their site-occupation factors dependently refined to values of 0.526 (5) and 0.474 (5). All methyl H atoms were allowed to rotate around the vicinal C—C bonds and to ride, with U_{iso}(H) = 1.5U_{eq}(C). Water atoms H13*A* and H13*B* were located in a difference Fourier map and refined freely.

3. Results and discussion

Many derivatives of the Mn_{12} molecule have been synthesized with different bridging groups, including benzoate (Sessoli *et al.*, 1993), and its derivatives (Aubin *et al.*, 1999), *tert*-butyl acetate (Sun *et al.*, 1998), pivalate, phosphinate (Brockman *et al.*, 2003), sulfonate (Chakov *et al.*, 2003), and dichloroacetate (Eppley & Christou, 2002), to name a few. These molecules all retain similar properties in terms of magnetic character, but crystallize in a wide variety of symmetries and space groups. There are four main types of symmetry that can be considered when classifying these Mn_{12} molecules, *i.e.* S_4, D_2, C_2, and C_1 (Bagai & Christou, 2007). The title compound crystallizes in the tetragonal crystal system and has S_4 symmetry similar to the original Mn_{12} sythesized by Lis (1980).

Table 2
Selected bond lengths (Å).

Mn1—O2	1.8843 (14)	Mn2—O11	2.2583 (16)
Mn1—O3	1.8891 (14)	Mn2—Mn3	2.7473 (4)
Mn1—O4	1.9492 (15)	Mn3—O3^{ii}	1.8697 (14)
Mn1—O7^{i}	1.9538 (14)	Mn3—O2	1.8742 (13)
Mn1—O13	2.1787 (18)	Mn3—O1^{ii}	1.8979 (13)
Mn1—O10	2.2458 (16)	Mn3—O9	1.8998 (14)
Mn2—O3^{ii}	1.8913 (14)	Mn3—O1	1.9104 (14)
Mn2—O2	1.9043 (14)	Mn3—O1^{i}	1.9154 (13)
Mn2—O5	1.9375 (15)	Mn3—Mn3^{i}	2.8361 (5)
Mn2—O6	1.9401 (15)	Mn3—Mn3^{iii}	2.8753 (6)
Mn2—O8	2.1463 (16)		

Symmetry codes: (i) $y+\frac{1}{4}, -x+\frac{3}{4}, -z+\frac{3}{4}$; (ii) $-y+\frac{3}{4}, x-\frac{1}{4}, -z+\frac{3}{4}$; (iii) $-x+1, -y+\frac{1}{2}, z$.

Further experiments to study Mn_{12} have included changing the environment of these Mn_{12} moieties to include partial ligand substitution where the equatorial and axial ligands are different (Soler, Artus *et al.*, 2001), single (Tasiopoulos *et al.*, 2004) or multiple reductions of the Mn^{III} ions in the outer shell of the core (Soler, Artus *et al.*, 2001), and attempts to add nitrate ligands to a preformed Mn_{12} cluster using nitric acid (Artus *et al.*, 2001). Inclusion of nitrate ligands in such a structure has proven difficult, resulting in low synthetic yield, likely due to the weak nature of the nitrate ligand compared to carboxylates and other bridging ligands. The title material, however, contains nitrate ligands and crystallizes from a facile procedure.

A search of the Cambridge Structural Database (*ConQuest* Version 1.16; Groom & Allen, 2014) for similar structures yielded only two complexes, namely the original $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (Lis, 1980) and $[Mn_{12}O_{12}(O_2CCH_2{}^tBu)_{12}(NO_3)_4(H_2O)_4]$ (Artus *et al.*, 2001). Many other Mn_{12}

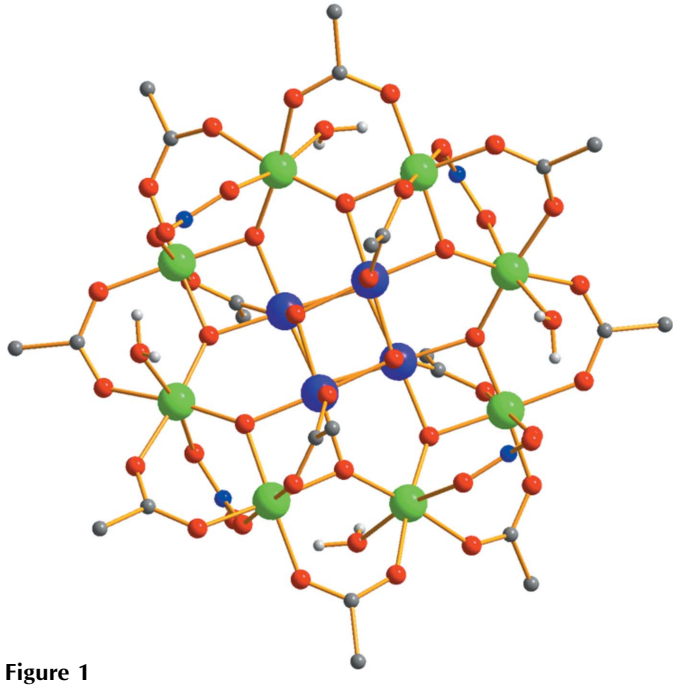


Figure 1
The structure of the title Mn_{12} molecule, with methyl H atoms omitted for clarity. Color key: Mn^{III} green, Mn^{IV} purple, O red, N blue, C grey and H white.

Table 3
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O13—H13A···O11^{i}	0.95 (3)	1.94 (3)	2.813 (2)	152 (3)
O13—H13A···O12^{i}	0.95 (3)	2.39 (3)	3.172 (3)	139 (3)
O13—H13B···O12^{iv}	0.79 (3)	1.93 (3)	2.713 (3)	171 (3)

Symmetry codes: (i) $y+\frac{1}{4}, -x+\frac{3}{4}, -z+\frac{3}{4}$; (iv) $-y+\frac{3}{4}, x+\frac{1}{4}, z+\frac{1}{4}$.

derivatives exist, and most can be found in a review article by Bagai & Christou (2009).

Similar to other Mn_{12} complexes, the title molecule, (I), contains a roughly cubic core of four Mn^{IV} ions and four μ_4-O^{2-} ions centered in a ring of eight Mn^{III} ions bound by eight μ_3-O^{2-} bridges, as shown in Figs. 1 and 2. The oxidation states of the Mn atoms were determined by bond-length considerations (Table 2), and the observation of Jahn–Teller elongation axes in the Mn^{III} ions. Atoms Mn1 and Mn2 were both assigned as Mn^{III} and Mn3 was assigned as an Mn^{IV} ion, as shown in Fig. 2. The periphery surrounding the core is completed by 12 acetate ligands, four aqua ligands, and four nitrate ligands. As expected, all Mn centers are six-coordinated and all of the acetate and nitrate ligands bridge pairs of Mn centers in a μ_2-κO:$\kappa O'$ fashion.

Similar to other Mn_{12} derivatives, the title molecule is highly symmetric. However, unlike any other Mn_{12} molecule, it contains both inter- and intramolecular hydrogen bonds (Table 3). On the molecular level, water atom H13A interacts with atoms O11 and O12 of the neighboring nitrate ligand. The extended structure exhibits hydrogen-bonding interactions between water atom H13B and nitrate atom O12^{iv} of a neighboring molecule, as shown in Fig. 3 [symmetry code: (iv) $-y+\frac{3}{4}, x+\frac{1}{4}, z+\frac{1}{4}$].

The three-dimensional network mediated by O—H···O hydrogen bonds between the water ligand on one molecule and the nitrate ligand on a neighboring molecule distinguishes this system from any other Mn_{12} derivative. To our knowledge, this is the first linked network of Mn_{12} molecules despite the many derivatives synthesized previously (Bagai & Christou, 2009). This type of network, in addition to being structurally fascinating, promises other interesting physical properties including higher-level magnetic ordering in the solid state and unique solution dynamics resulting from the labile ligand sphere.

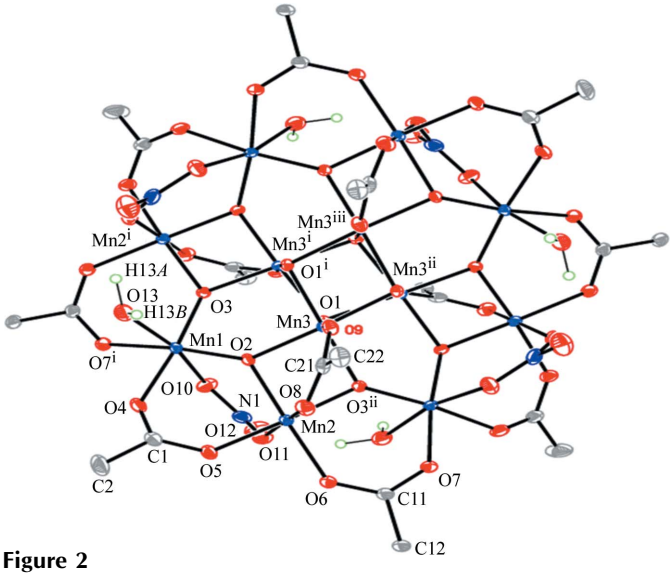


Figure 2
Displacement ellipsoid drawing (40% probability) of the title Mn_{12} molecule with the reference asymmetric unit labelled. Methyl H atoms and solvent molecules have been omitted for clarity. [Symmetry codes: (i) $y+\frac{1}{4}, -x+\frac{3}{4}, -z+\frac{3}{4}$; (ii) $-y+\frac{3}{4}, x-\frac{1}{4}, -z+\frac{3}{4}$; (iii) $-x+1, -y+\frac{1}{2}, z$.]

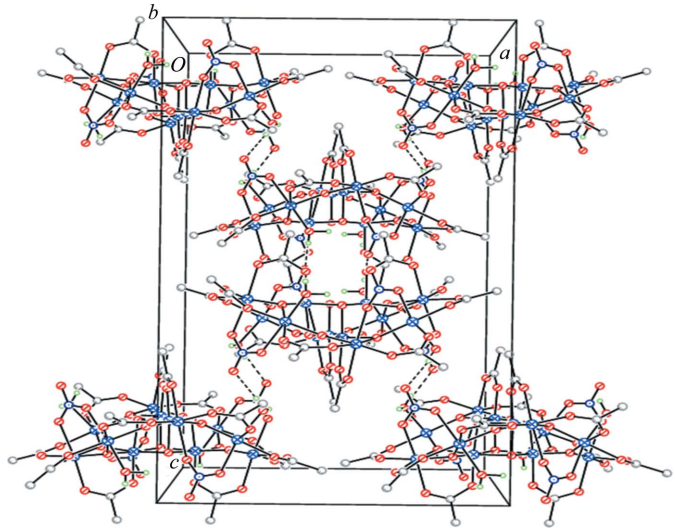


Figure 3
Packing diagram of the Mn_{12} clusters along the b axis, showing the intermolecular hydrogen-bonding network (drawn as dashed lines).

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$[Mn_{12}O_{12}(O_2CMe)_{12}(NO_3)_4(H_2O)_4]$: facile synthesis of a new type of Mn_{12} complex

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *APEX2* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXTL2013* (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL2013* (Sheldrick, 2015); software used to prepare material for publication: *SHELXTL2013* (Sheldrick, 2015).

Dodeca-μ_2-acetato-κ^{24}-*O*:*O*′-tetraaquatetra-μ_2-nitro-κ^8*O*:*O*′-octa-μ_3-oxido-tetra-μ_2-oxido-tetramanganese(IV)octamanganese(III) nitromethane tetrasolvate

Crystal data

$[Mn_{12}(C_2H_3O_2)_{12}O_{12}(NO_3)_4(H_2O)_4]\cdot 4CH_3NO_2$
M_r = 2124.08
Tetragonal, $I4_1/a$
a = 15.7293 (8) Å
c = 27.9010 (14) Å
V = 6903.0 (8) Å^3
Z = 4
$F(000)$ = 4240
D_x = 2.044 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9809 reflections
θ = 2.0–28.0°
μ = 2.24 mm^{-1}
T = 100 K
Blocks, brown
0.16 × 0.10 × 0.04 mm

Data collection

Bruker APEX-II DUO diffractometer
Radiation source: fine-focus sealed tube
phi and/or ω scans
Absorption correction: analytical based on measured indexed crystal faces, Bruker *SHELXTL* v6.14 (Bruker 2013)
T_{min} = 0.816, T_{max} = 0.929
85988 measured reflections
3974 independent reflections
3287 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.5°, θ_{min} = 1.5°
h = −20→20
k = −20→20
l = −36→36

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.066
S = 1.05
3974 reflections
254 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 5.382P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 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. All H atoms were positioned geometrically (C—H = 0.93/1.00 Å) and allowed to ride with U_{iso}(H)= 1.2/1.5U_{eq}(C). Methyl H atoms were allowed to rotate around the corresponding C—C.
The water ligand protons were obtained from a difference Fourier map and refined freely.
The Mn12 cluster methyl protons were refined using AFIX 137 in the least-squares refinement, while the solvent disordered methyl protons were constrained to the calculated positions using AFIX 33. The disorder of the methyl protons is a direct result of the disorder in the NO2 group which was refined in two parts with their site occupation factors dependently refined.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.35701 (2)	0.47156 (2)	0.37492 (2)	0.01492 (8)	
Mn2	0.24107 (2)	0.30827 (2)	0.41895 (2)	0.01474 (8)	
Mn3	0.41075 (2)	0.26971 (2)	0.41044 (2)	0.01080 (8)	
O1	0.42256 (8)	0.26785 (8)	0.34230 (5)	0.0112 (3)	
O2	0.34443 (8)	0.36865 (8)	0.40876 (5)	0.0138 (3)	
O3	0.46181 (8)	0.44239 (8)	0.34623 (5)	0.0140 (3)	
O4	0.25146 (10)	0.51348 (9)	0.40287 (6)	0.0257 (4)	
O5	0.17971 (9)	0.40843 (9)	0.43986 (6)	0.0208 (3)	
O6	0.13643 (9)	0.24322 (9)	0.42220 (6)	0.0213 (3)	
O7	0.17142 (9)	0.10596 (9)	0.41062 (6)	0.0213 (3)	
O8	0.27101 (9)	0.28661 (9)	0.49300 (5)	0.0206 (3)	
O9	0.40972 (9)	0.26266 (9)	0.47841 (5)	0.0157 (3)	
O10	0.28826 (10)	0.42650 (10)	0.30911 (6)	0.0247 (4)	
O11	0.19940 (9)	0.33803 (10)	0.34334 (6)	0.0223 (3)	
O12	0.20524 (11)	0.34684 (12)	0.26682 (6)	0.0339 (4)	
O13	0.41571 (11)	0.54253 (11)	0.43325 (7)	0.0255 (4)	
H13A	0.474 (2)	0.558 (2)	0.4331 (12)	0.052 (10)*	
H13B	0.4134 (18)	0.5217 (18)	0.4589 (11)	0.033 (9)*	
N1	0.23166 (11)	0.37124 (12)	0.30634 (7)	0.0212 (4)	
C1	0.19674 (14)	0.48579 (14)	0.43236 (9)	0.0231 (5)	
C2	0.14995 (19)	0.55029 (16)	0.46142 (12)	0.0437 (8)	
H2A	0.1419	0.6020	0.4424	0.066*	
H2B	0.1828	0.5638	0.4903	0.066*	
H2C	0.0944	0.5274	0.4707	0.066*	
C11	0.12084 (13)	0.16401 (13)	0.42315 (8)	0.0186 (4)	
C12	0.03467 (13)	0.13741 (14)	0.44059 (9)	0.0238 (5)	
H12A	0.0295	0.0754	0.4385	0.036*	
H12B	−0.0092	0.1641	0.4207	0.036*	
H12C	0.0274	0.1553	0.4740	0.036*	
C21	0.34451 (14)	0.26868 (13)	0.50633 (8)	0.0182 (4)	
C22	0.36202 (16)	0.25121 (15)	0.55825 (8)	0.0240 (5)	
H22A	0.3342	0.2946	0.5780	0.036*	
H22B	0.4235	0.2527	0.5639	0.036*	

H22C	0.3398	0.1950	0.5667	0.036*	
C31	0.13368 (16)	0.62208 (18)	0.31265 (10)	0.0352 (6)	
H31A	0.1204	0.6673	0.2897	0.053*	0.526 (5)
H31B	0.1803	0.6406	0.3335	0.053*	0.526 (5)
H31C	0.1508	0.5707	0.2953	0.053*	0.526 (5)
H31D	0.1559	0.5830	0.3370	0.053*	0.474 (5)
H31E	0.1440	0.5984	0.2807	0.053*	0.474 (5)
H31F	0.1624	0.6771	0.3155	0.053*	0.474 (5)
N32	0.0535 (3)	0.6026 (3)	0.34366 (19)	0.0359 (11)*	0.526 (5)
O33	0.0556 (2)	0.5501 (2)	0.37364 (14)	0.0408 (11)*	0.526 (5)
O34	−0.0101 (3)	0.6413 (3)	0.33603 (19)	0.0645 (15)*	0.526 (5)
N42	0.0467 (3)	0.6330 (3)	0.31944 (19)	0.0293 (11)*	0.474 (5)
O43	0.0154 (3)	0.5940 (3)	0.35468 (18)	0.0464 (13)*	0.474 (5)
O44	0.0055 (3)	0.6782 (3)	0.29394 (18)	0.0540 (15)*	0.474 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01221 (15)	0.01047 (15)	0.02207 (18)	0.00176 (11)	0.00208 (12)	0.00434 (12)
Mn2	0.01200 (15)	0.01139 (15)	0.02082 (17)	0.00170 (11)	0.00553 (12)	0.00148 (12)
Mn3	0.01111 (14)	0.00945 (14)	0.01184 (15)	0.00102 (11)	0.00147 (11)	0.00041 (11)
O1	0.0093 (6)	0.0134 (7)	0.0109 (7)	−0.0005 (5)	0.0006 (5)	0.0004 (5)
O2	0.0133 (7)	0.0107 (6)	0.0173 (8)	0.0024 (5)	0.0030 (6)	0.0019 (5)
O3	0.0117 (7)	0.0122 (7)	0.0182 (7)	−0.0003 (5)	−0.0001 (6)	0.0041 (6)
O4	0.0209 (8)	0.0152 (7)	0.0409 (10)	0.0060 (6)	0.0112 (7)	0.0065 (7)
O5	0.0191 (8)	0.0157 (7)	0.0277 (9)	0.0037 (6)	0.0084 (6)	0.0012 (6)
O6	0.0147 (7)	0.0160 (7)	0.0332 (9)	0.0015 (6)	0.0079 (7)	0.0028 (7)
O7	0.0143 (7)	0.0166 (7)	0.0331 (9)	−0.0006 (6)	0.0084 (6)	−0.0003 (7)
O8	0.0218 (8)	0.0203 (8)	0.0198 (8)	0.0036 (6)	0.0078 (6)	0.0010 (6)
O9	0.0203 (7)	0.0145 (7)	0.0123 (7)	0.0036 (6)	0.0021 (6)	−0.0002 (6)
O10	0.0213 (8)	0.0270 (8)	0.0257 (9)	−0.0065 (7)	−0.0044 (7)	0.0077 (7)
O11	0.0166 (7)	0.0261 (8)	0.0241 (8)	−0.0021 (6)	0.0000 (6)	0.0067 (7)
O12	0.0314 (10)	0.0464 (11)	0.0239 (9)	−0.0075 (8)	−0.0072 (8)	−0.0001 (8)
O13	0.0265 (9)	0.0212 (8)	0.0288 (10)	0.0035 (7)	−0.0011 (8)	−0.0026 (7)
N1	0.0146 (9)	0.0249 (10)	0.0241 (10)	0.0035 (7)	−0.0031 (8)	0.0034 (8)
C1	0.0193 (11)	0.0185 (11)	0.0315 (13)	0.0042 (8)	0.0050 (9)	0.0014 (9)
C2	0.0451 (16)	0.0210 (12)	0.065 (2)	0.0078 (11)	0.0288 (15)	−0.0027 (13)
C11	0.0140 (10)	0.0191 (10)	0.0227 (12)	0.0003 (8)	0.0028 (8)	0.0036 (9)
C12	0.0146 (10)	0.0202 (11)	0.0368 (14)	0.0013 (8)	0.0089 (10)	0.0073 (10)
C21	0.0267 (11)	0.0107 (9)	0.0170 (11)	0.0001 (8)	0.0067 (9)	−0.0006 (8)
C22	0.0335 (13)	0.0225 (11)	0.0160 (11)	0.0029 (9)	0.0047 (10)	0.0009 (9)
C31	0.0317 (14)	0.0384 (15)	0.0353 (15)	−0.0062 (11)	−0.0001 (11)	−0.0068 (12)

Geometric parameters (Å, º)

Mn1—O2	1.8843 (14)	O8—C21	1.247 (3)
Mn1—O3	1.8891 (14)	O9—C21	1.291 (2)
Mn1—O4	1.9492 (15)	O10—N1	1.247 (2)

Mn1—O7^{i}	1.9538 (14)	O11—N1	1.263 (2)
Mn1—O13	2.1787 (18)	O12—N1	1.239 (2)
Mn1—O10	2.2458 (16)	O13—H13A	0.95 (3)
Mn2—O3^{ii}	1.8913 (14)	O13—H13B	0.79 (3)
Mn2—O2	1.9043 (14)	C1—C2	1.493 (3)
Mn2—O5	1.9375 (15)	C2—H2A	0.9800
Mn2—O6	1.9401 (15)	C2—H2B	0.9800
Mn2—O8	2.1463 (16)	C2—H2C	0.9800
Mn2—O11	2.2583 (16)	C11—C12	1.500 (3)
Mn2—Mn3	2.7473 (4)	C12—H12A	0.9800
Mn3—O3^{ii}	1.8697 (14)	C12—H12B	0.9800
Mn3—O2	1.8742 (13)	C12—H12C	0.9800
Mn3—O1^{ii}	1.8979 (13)	C21—C22	1.500 (3)
Mn3—O9	1.8998 (14)	C22—H22A	0.9800
Mn3—O1	1.9104 (14)	C22—H22B	0.9800
Mn3—O1^{i}	1.9154 (13)	C22—H22C	0.9800
Mn3—Mn3^{i}	2.8361 (5)	C31—N42	1.392 (5)
Mn3—Mn3^{ii}	2.8361 (5)	C31—N32	1.560 (6)
Mn3—Mn3^{iii}	2.8753 (6)	C31—H31A	0.9800
O1—Mn3^{i}	1.8979 (13)	C31—H31B	0.9800
O1—Mn3^{ii}	1.9154 (13)	C31—H31C	0.9800
O3—Mn3^{i}	1.8697 (14)	C31—H31D	0.9800
O3—Mn2^{i}	1.8913 (14)	C31—H31E	0.9800
O4—C1	1.268 (3)	C31—H31F	0.9800
O5—C1	1.263 (3)	N32—O33	1.176 (6)
O6—C11	1.270 (3)	N32—O34	1.191 (8)
O7—C11	1.260 (3)	N42—O44	1.196 (7)
O7—Mn1^{ii}	1.9538 (14)	N42—O43	1.258 (8)

O2—Mn1—O3	95.47 (6)	O9—Mn3—Mn3^{iii}	89.76 (4)
O2—Mn1—O4	90.04 (6)	O1—Mn3—Mn3^{iii}	84.36 (4)
O3—Mn1—O4	174.24 (6)	O1^{i}—Mn3—Mn3^{iii}	40.83 (4)
O2—Mn1—O7^{i}	173.48 (6)	Mn2—Mn3—Mn3^{iii}	175.026 (9)
O3—Mn1—O7^{i}	90.09 (6)	Mn3^{i}—Mn3—Mn3^{iii}	59.541 (6)
O4—Mn1—O7^{i}	84.52 (6)	Mn3^{ii}—Mn3—Mn3^{iii}	59.540 (6)
O2—Mn1—O13	96.34 (7)	Mn3^{i}—O1—Mn3	96.27 (6)
O3—Mn1—O13	94.08 (7)	Mn3^{i}—O1—Mn3^{ii}	97.88 (6)
O4—Mn1—O13	83.61 (7)	Mn3—O1—Mn3^{ii}	95.69 (6)
O7^{i}—Mn1—O13	86.63 (7)	Mn3—O2—Mn1	131.87 (8)
O2—Mn1—O10	95.05 (6)	Mn3—O2—Mn2	93.28 (6)
O3—Mn1—O10	89.83 (6)	Mn1—O2—Mn2	126.37 (7)
O4—Mn1—O10	91.36 (7)	Mn3^{i}—O3—Mn1	132.68 (7)
O7^{i}—Mn1—O10	81.54 (6)	Mn3^{i}—O3—Mn2^{i}	93.85 (6)
O13—Mn1—O10	167.55 (6)	Mn1—O3—Mn2^{i}	131.34 (8)
O3^{ii}—Mn2—O2	83.93 (6)	C1—O4—Mn1	136.19 (14)
O3^{ii}—Mn2—O5	174.53 (7)	C1—O5—Mn2	128.88 (14)
O2—Mn2—O5	93.71 (6)	C11—O6—Mn2	133.01 (13)
O3^{ii}—Mn2—O6	93.26 (6)	C11—O7—Mn1^{ii}	132.72 (14)

O2—Mn2—O6	173.88 (7)	C21—O8—Mn2	121.77 (13)
O5—Mn2—O6	89.55 (6)	C21—O9—Mn3	127.20 (14)
O3^{ii}—Mn2—O8	88.10 (6)	N1—O10—Mn1	127.92 (14)
O2—Mn2—O8	92.04 (6)	N1—O11—Mn2	137.10 (13)
O5—Mn2—O8	87.05 (6)	Mn1—O13—H13A	122 (2)
O6—Mn2—O8	93.30 (6)	Mn1—O13—H13B	116 (2)
O3^{ii}—Mn2—O11	96.76 (6)	H13A—O13—H13B	99 (3)
O2—Mn2—O11	90.27 (6)	O12—N1—O10	120.70 (19)
O5—Mn2—O11	88.17 (6)	O12—N1—O11	117.66 (18)
O6—Mn2—O11	84.65 (6)	O10—N1—O11	121.64 (19)
O8—Mn2—O11	174.82 (6)	O5—C1—O4	125.6 (2)
O3^{ii}—Mn2—Mn3	42.77 (4)	O5—C1—C2	117.4 (2)
O2—Mn2—Mn3	42.93 (4)	O4—C1—C2	117.0 (2)
O5—Mn2—Mn3	133.59 (5)	C1—C2—H2A	109.5
O6—Mn2—Mn3	135.38 (4)	C1—C2—H2B	109.5
O8—Mn2—Mn3	80.50 (4)	H2A—C2—H2B	109.5
O11—Mn2—Mn3	104.29 (4)	C1—C2—H2C	109.5
O3^{ii}—Mn3—O2	85.36 (6)	H2A—C2—H2C	109.5
O3^{ii}—Mn3—O1^{ii}	96.73 (6)	H2B—C2—H2C	109.5
O2—Mn3—O1^{ii}	175.52 (6)	O7—C11—O6	125.66 (19)
O3^{ii}—Mn3—O9	93.64 (6)	O7—C11—C12	117.28 (19)
O2—Mn3—O9	93.94 (6)	O6—C11—C12	117.06 (18)
O1^{ii}—Mn3—O9	89.90 (6)	C11—C12—H12A	109.5
O3^{ii}—Mn3—O1	88.74 (6)	C11—C12—H12B	109.5
O2—Mn3—O1	92.40 (6)	H12A—C12—H12B	109.5
O1^{ii}—Mn3—O1	83.69 (6)	C11—C12—H12C	109.5
O9—Mn3—O1	173.39 (6)	H12A—C12—H12C	109.5
O3^{ii}—Mn3—O1^{i}	171.95 (6)	H12B—C12—H12C	109.5
O2—Mn3—O1^{i}	95.44 (6)	O8—C21—O9	125.0 (2)
O1^{ii}—Mn3—O1^{i}	81.93 (6)	O8—C21—C22	119.98 (19)
O9—Mn3—O1^{i}	94.30 (6)	O9—C21—C22	115.05 (19)
O1—Mn3—O1^{i}	83.23 (6)	C21—C22—H22A	109.5
O3^{ii}—Mn3—Mn2	43.38 (4)	C21—C22—H22B	109.5
O2—Mn3—Mn2	43.79 (4)	H22A—C22—H22B	109.5
O1^{ii}—Mn3—Mn2	139.12 (4)	C21—C22—H22C	109.5
O9—Mn3—Mn2	85.31 (4)	H22A—C22—H22C	109.5
O1—Mn3—Mn2	100.60 (4)	H22B—C22—H22C	109.5
O1^{i}—Mn3—Mn2	138.87 (4)	N32—C31—H31A	109.5
O3^{ii}—Mn3—Mn3^{i}	130.01 (5)	N32—C31—H31B	109.5
O2—Mn3—Mn3^{i}	89.92 (4)	H31A—C31—H31B	109.5
O1^{ii}—Mn3—Mn3^{i}	85.70 (4)	N32—C31—H31C	109.5
O9—Mn3—Mn3^{i}	136.36 (5)	H31A—C31—H31C	109.5
O1—Mn3—Mn3^{i}	41.70 (4)	H31B—C31—H31C	109.5
O1^{i}—Mn3—Mn3^{i}	42.09 (4)	N42—C31—H31D	109.5
Mn2—Mn3—Mn3^{i}	124.210 (15)	N42—C31—H31E	109.5
O3^{ii}—Mn3—Mn3^{ii}	88.34 (4)	H31D—C31—H31E	109.5
O2—Mn3—Mn3^{ii}	134.35 (5)	N42—C31—H31F	109.5
O1^{ii}—Mn3—Mn3^{ii}	42.03 (4)	H31D—C31—H31F	109.5

O9—Mn3—Mn3^{ii}	131.61 (4)	H31E—C31—H31F	109.5
O1—Mn3—Mn3^{ii}	42.22 (4)	O33—N32—O34	120.7 (6)
O1^{i}—Mn3—Mn3^{ii}	85.38 (4)	O33—N32—C31	120.7 (4)
Mn2—Mn3—Mn3^{ii}	124.639 (16)	O34—N32—C31	118.6 (5)
Mn3^{i}—Mn3—Mn3^{ii}	60.916 (12)	O44—N42—O43	122.8 (5)
O3^{ii}—Mn3—Mn3^{iii}	137.92 (4)	O44—N42—C31	121.7 (5)
O2—Mn3—Mn3^{iii}	136.27 (4)	O43—N42—C31	115.5 (5)
O1^{ii}—Mn3—Mn3^{iii}	41.29 (4)		

Symmetry codes: (i) y+1/4, −x+3/4, −z+3/4; (ii) −y+3/4, x−1/4, −z+3/4; (iii) −x+1, −y+1/2, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13*A*···O11^{i}	0.95 (3)	1.94 (3)	2.813 (2)	152 (3)
O13—H13*A*···O12^{i}	0.95 (3)	2.39 (3)	3.172 (3)	139 (3)
O13—H13*B*···O12^{iv}	0.79 (3)	1.93 (3)	2.713 (3)	171 (3)

Symmetry codes: (i) y+1/4, −x+3/4, −z+3/4; (iv) −y+3/4, x+1/4, z+1/4.