Our work in the area of synthesis of polynuclear manganese complexes and their magnetic properties led to the synthesis and crystalization of the title compound, \([\text{Mn}_7(\text{C}_8\text{H}_9\text{NO}_3)_4(\text{C}_8\text{H}_{10}\text{NO}_3)_4(\text{C}_2\text{H}_5\text{O})_2(\text{C}_7\text{H}_5\text{O}_2)_2\text{O}_2]/\text{C}_8\text{C}_2\text{H}_5\text{OH}\). Herein, we report the molecular and crystal structure of the title compound, which was synthesized by the reaction of \(\text{Mn}(\text{C}_6\text{H}_5\text{COO})_2\) with \(\text{pyridoxine} (\text{PNH}_2, \text{C}_8\text{H}_{11}\text{NO}_3)\) followed by the addition of tetramethylammonium hydroxide (TMAOH). The core of this centrosymmetric complex is a cage-like structure consisting of six \(\text{Mn}^{II}\) ions and one \(\text{Mn}^{III}\) ion bound together through \(\text{Mn—O}\) bonds. The compound crystallizes in hydrogen-bonded layers formed by \(\text{O—H} \cdots \text{N}\) hydrogen bonds involving the aromatic amine group of the ligand PN\(^2\) with the neighboring O atoms from the PNH\(^-\) ligand. The crystal structure has large voids present in which highly disordered solvent molecules (ethanol) sit. A solvent mask was calculated and 181 electrons were found in a volume of 843 Å\(^3\) in one void per triclinic unit cell. This is consistent with the presence of seven ethanol molecules per formula unit, which accounts for 182 electrons per unit cell. Additionally, one ethanol molecule was found to be ordered in the crystal.

**Chemical scheme**

**3D view**
The heptanuclear title compound is \([\text{Mn}_7(\text{PN})_4(\text{PNH})_4(\text{EtO})_2] \cdot 8(\text{C}_2\text{H}_6\text{O})\), where \(\text{PN}_2\) refers to the doubly deprotonated ligand pyridoxine (PNH2, IUPAC name: 5-hydroxy-6-methyl-3,4-pyridinedimethanol), a water-soluble, naturally occurring vitamer of Vitamin B6 involved in the metabolism of all three macronutrients, namely proteins, lipids, and carbohydrates. This ligand plays the pivotal role as a linker (Stouder et al., 2017).

The \(\text{PNH}_2\) ligand is comprised of aliphatic and aromatic alkoxide groups, and those in principle can adopt both bridging and chelating modes while binding with metals. The partially labeled molecular structure of the title compound is shown in Fig. 1. The core of the centrosymmetric complex (Fig. 2), is comprised of three triangular \(\text{Mn}_3\) units connected via the \(\text{Mn}3\) atom at the center of this cage-like structure. The core consists of six \(\text{Mn}^{III}\) (\(\text{Mn}1, \text{Mn}2, \text{Mn}4\)) ions and one \(\text{Mn}^{II}\) (\(\text{Mn}3\)) ion. The central \(\text{Mn}3\) ion is connected to \(\text{Mn}1\) and \(\text{Mn}2\) via a \(\mu_3\)-O oxido ion (O2) and to \(\text{Mn}4\) via \(\mu_3\)-O atoms (O1, O4) coming from the alkoxide arm of a \(\text{PN}^{2-}\) group that is chelating to \(\text{Mn}4\). Apart from that, \(\text{Mn}1\) and \(\text{Mn}2\) are connected via a bridging \(\mu\)-O atom from the ethoxide group (O3) and a carboxylate group (O11, O12). \(\text{Mn}1\) is further connected to \(\text{Mn}4\) via a bridging \(\mu\)-O (O3) from the alkoxide arm of \(\text{PN}^{2-}\) group and a \(\mu_3\)-O atom (O1) from the alkoxide arm of a \(\text{PN}^{2-}\) group. Similarly, \(\text{Mn}2\) is connected to \(\text{Mn}4\) via a bridging \(\mu\)-O (O10) from the alkoxide arms of the \(\text{PN}^{2-}\) group and a \(\mu_3\)-O atom (O4) from the alkoxide arm of a \(\text{PN}^{2-}\) group. The neutral complex is thus comprised of six \(\text{Mn}^{III}\) ions, one \(\text{Mn}^{II}\) ion, two oxide ions, two ethoxide ions, two carboxylate ions, four doubly deprotonated, and four singly deprotonated ligands. All \(\text{Mn}\) ions possess octahedral environments. Bond-valence sum (BVS) calculations (Brese & O’Keefe, 1991) show that one of the alkoxide arms of all eight \(\text{PNH}_2\) ligands is deprotonated; however, four of the ligands, namely \(\text{PN}^{2-}\), exist in the zwitterionic form where the aromatic amine functionality is protonated. BVS calculations also confirmed that \(\text{Mn}1, \text{Mn}2,\) and \(\text{Mn}4\) are \(\text{Mn}^{III}\) ions.

Inspection of the crystal packing of the complex shows that the \(\text{Mn}_7\) unit relates to its four neighboring units by \(\text{O} - \text{H} \cdots \text{N}\) hydrogen bonds involving the aromatic amine (N1, N3) group of the ligand \(\text{PN}^{2-}\) with the neighboring O atoms (O15, O14). Often such polymetallic complexes exhibit magnetic properties (Saha et al., 2011a), catalytic properties (Yamada et al., 2015), optical properties (Aboshyan-Sorgho et al., 2012) and biological activities (Kuczer et al., 2013). In order to support the network of three-dimensional polymetallic units, alkoxide-based ligands play an important role since this functionality is an excellent bridging group that fosters higher nuclearity products formation (Saha et al., 2011b). Herein, we explore the coordination chemistry of pyridoxine (\(\text{PNH}_2\), IUPAC name: 5-hydroxy-6-methyl-3,4-pyridinedimethanol), a water-soluble, naturally occurring vitamer of Vitamin B6 involved in the metabolism of all three macronutrients, namely proteins, lipids, and carbohydrates.

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

| D—H···A    | D—H   | H···A  | D···A  | D—H···A |
|------------|--------|--------|--------|---------|
| O14—H14—N3 | 0.84   | 1.80   | 2.619  | 4       | 163     |
| O15—H15—N1'' | 0.84  | 1.84   | 2.675  | 4       | 175     |
| O17—H17—O13'' | 0.84  | 1.89   | 2.684  | 5       | 158     |

Symmetry codes: (i) \(-x+1, -y, -z+2\); (ii) \(x, y, z-1\); (iii) \(-x+1, -y+1, -z+1\).
from the PNH⁻ ligand (Fig. 3). In addition to the hydrogen bonds between neighboring molecules, there is also an O—H···O hydrogen bond between two OH groups on adjacent ligands (O17, O13). Table 1 gives details of these hydrogen-bonding interactions. The solid-state structural analysis of such complexes can give us valuable insights on potential uses of such materials for catalytic, magnetic and/or biological activity.

The crystal structure has large voids present in which highly disordered solvent molecules (ethanol) sit. A solvent mask was calculated and 181 electrons were found in a volume of 843 Å³ in one void per triclinic unit cell. This is consistent with the presence of seven ethanol molecules per formula unit, which accounts for 182 electrons per unit cell. Additionally, one ethanol molecule O16/C42/C43 was found to be ordered in the crystal.

Synthesis and crystallization

The reaction was carried out in presence of air. To a stirred solution of Mn(C₆H₅COO)₂ (0.17 g, 1.0 mmol) in 12 ml of ethanol, pyridoxine (PNH₂, 0.10 g, 1.0 mmol) was added at 343 K. The solution turned from pink to light brown after the addition of PNH₂, which is an indication of oxidation of MnII to MnIII by the atmospheric O₂. After 30 min, TMAOH (0.09 g, 1.0 mmol) was added to the stirred solution. Heating was ceased and the reaction was set to stir for 3 h, after which the dark-brown solution was filtered and set for slow diffusion with Et₂O. X-ray quality crystals grew after two weeks with a yield of 23%. The crystals were stored in the mother solvent until X-ray study.

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Table 2: Experimental details.

| Crystal data | Chemical formula |
|--------------|------------------|
|              | [Mn₇(C₆H₅NO₃)₄(C₈H₁₀NO₃)₄(C₂H₅O)₂(C₇H₅O₂)₂O₂]-8C₂H₆O |
| M₀          | 2449.71          |
| Crystal system, space group | Triclinic, P      |
| Temperature (K) | 100               |
| a, b, c (Å) | 12.9774 (5), 14.6762 (7), 16.7750 (6) |
| V (Å³)    | 2859.0 (2)       |
| Z          | 1                |
| Radiation type | Mo Kα            |
| μ (mm⁻¹)  | 0.83             |
| Crystal size (mm) | 0.09 × 0.08 × 0.06 |

| Data collection | Diffractometer |
|-----------------|----------------|
|                 | Rigaku XtaLAB Synergy, Dual-flex, HyPix |

| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD: 2020) |
|-----------------------|-------------------------------------------|
| Tₘᵢₓ, Tₘᵢₜ             | 0.966, 1.000 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 34399, 10190, 7884 |
| Rₘᵢₓ                   | 0.037 |
| (sin θ/λ)ₘᵢₓ (Å⁻¹)     | 0.597 |

| Refinement | R(F² > 2σ(F²)), wR(F²), S |
|------------|---------------------------|
| No. of reflections | 10190 |
| No. of parameters | 621 |
| No. of restraints | 9 |
| H-atom treatment | H-atom parameters constrained |
| Δρₘᵢₓ, Δρₘᵢₜ (e Å⁻³) | 0.98, −0.28 |

Computer programs: CrysAlis PRO (Rigaku OD: 2020), SHELXT (Sheldrick, 2015a), SHELXL2018/5 (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).
Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Disordered molecules of ethanol were tentatively added to the model. Only one ethanol molecule, with 50% occupancy, refined well without breaking up when anisotropic temperature factors were included, and was kept. The contribution from the other seven disordered ethanol solvent molecules to the structure factors was calculated using the solvent mask tool in OLEX2 (Dolomanov et al., 2009).

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full crystallographic data

Di-µ-benzoato-di-µ-ethanolato-tetrakis[µ3-5-(hydroxymethyl)-2-methyl-4-(oxidomethyl)pyridin-1-iium-3-olato]tetrakis[µ3-5-(hydroxymethyl)-2-methyl-4-(oxidomethyl)pyridin-3-olato]di-µ3-oxido-heptamanganese(II,III) ethanol octasolvate

Arpita Saha, Clifford W. Padgett, Pierre LeMagueres, Kiana Moncur and Glory Onajobi

Di-µ-benzoato-di-µ-ethanolato-tetrakis[µ3-5-(hydroxymethyl)-2-methyl-4-(oxidomethyl)pyridin-1-iium-3-olato]tetrakis[µ3-5-(hydroxymethyl)-2-methyl-4-(oxidomethyl)pyridin-3-olato]di-µ3-oxido-heptamanganese(II,III) ethanol octasolvate

Crystal data

\[\text{[Mn}_7\text{(C}_8\text{H}_9\text{NO}_3)_4\text{Cl}_2\text{(C}_8\text{H}_10\text{NO}_3)_4\text{(C}_2\text{H}_5\text{O})_2\text{(C}_7\text{H}_5\text{O}_2)_2\text{O}_2\text{]}·8\text{C}_2\text{H}_6\text{O} F(000) = 1274}\]

\[M_r = 2449.71\]

Triclinic, P\(\bar{1}\)

\(a = 12.9774 (5) \text{ Å}\)

\(b = 14.6762 (7) \text{ Å}\)

\(c = 16.7750 (6) \text{ Å}\)

\(\alpha = 66.578 (4)^\circ\)

\(\beta = 77.956 (3)^\circ\)

\(\gamma = 81.343 (4)^\circ\)

\(V = 2859.0 (2) \text{ Å}^3\)

\(Z = 1\)

Data collection

Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer

Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm\(^{-1}\)

\(\omega\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2020)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.048\)

\(wR(F^2) = 0.141\)

\(S = 1.07\)

10190 reflections

621 parameters

9 restraints

\(\text{Primary atom site location: dual}\)

\(\text{Secondary atom site location: difference Fourier map}\)

\(\text{Hydrogen site location: inferred from neighbouring sites}\)

\(\text{H-atom parameters constrained}\)

\(w = 1/[\sigma^2(F^2) + (0.0847P)^2 + 0.6047P]\)

where \(P = (F^2 + 2F^2) / 3\)
Special details

Refinement. Hydrogen atoms were attached via the riding model at calculated positions using suitable HFIX commands.

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

|     | x          | y          | z          | U(eq)/Å² | Occ. (<1) |
|-----|------------|------------|------------|----------|-----------|
| Mn1 | 0.72295 (3)| 0.42295 (3)| 0.56146 (3)| 0.03246 (13)|          |
| Mn2 | 0.72328 (3)| 0.52363 (3)| 0.37463 (3)| 0.03223 (13)|          |
| Mn3 | 0.500000  | 0.500000  | 0.500000  | 0.02829 (15)|          |
| Mn4 | 0.49800 (4)| 0.39857 (3)| 0.70324 (3)| 0.03243 (13)|          |
| O1  | 0.55540 (16)| 0.51184 (14)| 0.60120 (12)| 0.0335 (5) | 0.035 (5)|
| O2  | 0.63608 (16)| 0.43484 (15)| 0.47679 (12)| 0.0346 (5) | 0.0346 (5)|
| O3  | 0.64800 (16)| 0.32378 (15)| 0.65648 (13)| 0.0377 (5) | 0.0377 (5)|
| O4  | 0.43587 (16)| 0.37094 (14)| 0.62110 (12)| 0.0317 (4) | 0.0317 (4)|
| O5  | 0.77496 (16)| 0.54310 (15)| 0.46695 (12)| 0.0340 (5) | 0.0340 (5)|
| O6  | 0.54308 (18)| 0.43981 (16)| 0.78180 (13)| 0.0427 (5) | 0.0427 (5)|
| O7  | 0.80492 (17)| 0.43486 (16)| 0.63726 (13)| 0.0399 (5) | 0.0399 (5)|
| O8  | 0.45964 (18)| 0.27999 (16)| 0.79730 (13)| 0.0429 (5) | 0.0429 (5)|
| O9  | 0.80638 (17)| 0.62354 (16)| 0.28792 (12)| 0.0401 (5) | 0.0401 (5)|
| O10 | 0.65480 (16)| 0.51228 (16)| 0.29100 (12)| 0.0365 (5) | 0.0365 (5)|
| O11 | 0.84197 (18)| 0.40553 (17)| 0.37249 (14)| 0.0450 (5) | 0.0450 (5)|
| O12 | 0.64048 (18)| 0.32916 (16)| 0.51759 (14)| 0.0446 (5) | 0.0446 (5)|
| O13 | 0.5745 (3)  | 0.8308 (2)  | 0.5748 (2)  | 0.0938 (11)| 0.0938 (11)|
| H13 | 0.563029   | 0.867061   | 0.604331   | 0.141*    | 0.141*|
| O14 | 0.7656 (3)  | 0.0844 (3)  | 0.9805 (2)  | 0.1267 (17)| 0.1267 (17)|
| H14 | 0.722079   | 0.044696   | 1.017122   | 0.190*    | 0.190*|
| O15 | 0.7882 (3)  | 0.6430 (4)  | -0.07481 (18)| 0.1081 (14)| 0.1081 (14)|
| H15 | 0.752050   | 0.628887   | -0.103888  | 0.162*    | 0.162*|
| O17 | 0.4330 (3)  | 0.0810 (3)  | 0.5982 (2)  | 0.0919 (11)| 0.0919 (11)|
| H17 | 0.432053   | 0.094953   | 0.546618   | 0.138*    | 0.138*|
| N1  | 0.6795 (3)  | 0.6054 (2)  | 0.82394 (19)| 0.0565 (8)| 0.0565 (8)|
| N2  | 0.8660 (2)  | 0.3582 (3)  | 0.85144 (18)| 0.0572 (8)| 0.0572 (8)|
| H2  | 0.898645   | 0.380528   | 0.880277   | 0.069*    | 0.069*|
| N3  | 0.3404 (3)  | 0.0499 (2)  | 0.8848 (2)  | 0.0625 (9)| 0.0625 (9)|
| N4  | 0.8846 (3)  | 0.7742 (2)  | 0.06429 (17)| 0.0541 (8)| 0.0541 (8)|
| H4  | 0.919064   | 0.827978   | 0.033777   | 0.065*    | 0.065*|
| C1  | 0.5477 (3)  | 0.6057 (2)  | 0.6102 (2)  | 0.0437 (8)| 0.0437 (8)|
| H1A | 0.472136   | 0.628671   | 0.620333   | 0.052*    | 0.052*|
| H1B | 0.581389   | 0.655189   | 0.554310   | 0.052*    | 0.052*|
| C2  | 0.5985 (3)  | 0.6023 (2)  | 0.68398 (19)| 0.0398 (7)| 0.0398 (7)|
| C3  | 0.5897 (2)  | 0.5214 (2)  | 0.7651 (2)  | 0.0383 (7)| 0.0383 (7)|
| C4  | 0.6299 (3)  | 0.5275 (3)  | 0.8349 (2)  | 0.0453 (8)| 0.0453 (8)|
| C5  | 0.6900 (4)  | 0.6800 (3)  | 0.7461 (3)  | 0.0668 (12)| 0.0668 (12)|
| H5  | 0.726298   | 0.734859   | 0.739336   | 0.080*    | 0.080*|
| C6  | 0.6519 (3)  | 0.6829 (3)  | 0.6746 (2)  | 0.0541 (9)| 0.0541 (9)|

IUCrData (2021). 6, x201643
|   | x     | y     | z     | u     |
|---|-------|-------|-------|-------|
| C7 | 0.6150 (3) | 0.4451 (3) | 0.9227 (2) | 0.0521 (9) |
| H7A | 0.657552 | 0.453886 | 0.960656 | 0.078* |
| H7B | 0.637445 | 0.381370 | 0.915995 | 0.078* |
| H7C | 0.540275 | 0.445717 | 0.949300 | 0.078* |
| C8 | 0.6669 (4) | 0.7730 (3) | 0.5903 (3) | 0.0711 (13) |
| H8A | 0.719651 | 0.813228 | 0.593372 | 0.085* |
| H8B | 0.694921 | 0.751164 | 0.540623 | 0.085* |
| C9 | 0.7070 (3) | 0.2479 (2) | 0.7162 (2) | 0.0480 (8) |
| H9A | 0.759715 | 0.213800 | 0.683475 | 0.058* |
| H9B | 0.658742 | 0.198088 | 0.759588 | 0.058* |
| C10 | 0.7632 (3) | 0.2870 (2) | 0.7647 (2) | 0.0438 (8) |
| C11 | 0.7743 (3) | 0.2318 (3) | 0.8526 (2) | 0.0579 (10) |
| C12 | 0.8258 (3) | 0.2700 (3) | 0.8944 (2) | 0.0657 (12) |
| H12 | 0.832882 | 0.233481 | 0.954365 | 0.079* |
| C13 | 0.8599 (3) | 0.4152 (3) | 0.7668 (2) | 0.0445 (8) |
| C14 | 0.8080 (2) | 0.3788 (2) | 0.72120 (19) | 0.0401 (7) |
| C15 | 0.7288 (3) | 0.1302 (4) | 0.9029 (3) | 0.0804 (15) |
| H15A | 0.650705 | 0.138997 | 0.914161 | 0.096* |
| H15B | 0.749629 | 0.088584 | 0.867154 | 0.096* |
| C16 | 0.9105 (3) | 0.5112 (3) | 0.7254 (2) | 0.0543 (9) |
| H16A | 0.900561 | 0.543147 | 0.768119 | 0.082* |
| H16B | 0.878194 | 0.554992 | 0.674076 | 0.082* |
| H16C | 0.986260 | 0.498703 | 0.706714 | 0.082* |
| C17 | 0.4377 (3) | 0.2715 (2) | 0.62780 (19) | 0.0396 (7) |
| H17A | 0.510846 | 0.250131 | 0.607072 | 0.048* |
| H17B | 0.392631 | 0.270284 | 0.587405 | 0.048* |
| C18 | 0.4011 (3) | 0.1963 (2) | 0.7189 (2) | 0.0404 (7) |
| C19 | 0.4165 (2) | 0.2055 (2) | 0.7954 (2) | 0.0385 (7) |
| C20 | 0.3851 (3) | 0.1288 (2) | 0.8786 (2) | 0.0470 (8) |
| C21 | 0.3266 (4) | 0.0416 (3) | 0.8115 (3) | 0.0703 (12) |
| H21 | 0.295627 | −0.015756 | 0.817061 | 0.084* |
| C22 | 0.3544 (3) | 0.1115 (3) | 0.7281 (2) | 0.0552 (10) |
| C23 | 0.4023 (3) | 0.1353 (3) | 0.9612 (2) | 0.0558 (10) |
| H23A | 0.474186 | 0.108487 | 0.971879 | 0.084* |
| H23B | 0.351217 | 0.096644 | 1.010739 | 0.084* |
| H23C | 0.392797 | 0.205080 | 0.955318 | 0.084* |
| C24 | 0.3357 (4) | 0.0933 (3) | 0.6510 (3) | 0.0709 (13) |
| H24A | 0.296834 | 0.032815 | 0.672004 | 0.085* |
| H24B | 0.291910 | 0.150337 | 0.615491 | 0.085* |
| C25 | 0.8829 (2) | 0.5660 (3) | 0.4548 (2) | 0.0438 (8) |
| H25A | 0.922119 | 0.560551 | 0.399362 | 0.053* |
| H25B | 0.917118 | 0.516849 | 0.503944 | 0.053* |
| C26 | 0.8890 (3) | 0.6662 (3) | 0.4515 (3) | 0.0716 (12) |
| H26A | 0.849209 | 0.714489 | 0.406701 | 0.107* |
| H26B | 0.962998 | 0.682037 | 0.436342 | 0.107* |
| H26C | 0.858678 | 0.669216 | 0.509054 | 0.107* |
| C27 | 0.8156 (2) | 0.6543 (2) | 0.20096 (18) | 0.0347 (7) |
| C28 | 0.8713 (3) | 0.7392 (2) | 0.1522 (2) | 0.0422 (8) |
| Atomic displacement parameters (Å²) | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------------------------------------|------|------|------|------|------|------|
| Mn1                                | 0.0324 (3) | 0.0366 (3) | 0.0289 (2) | -0.0128 (2) | -0.00724 (18) | -0.00816 (18) |
| Mn2                                | 0.0324 (3) | 0.0407 (3) | 0.0269 (2) | -0.0137 (2) | -0.00393 (18) | -0.01295 (19) |
| Mn3                                | 0.0290 (3) | 0.0337 (3) | 0.0242 (3) | -0.0124 (3) | -0.0051 (2) | -0.0093 (2) |
| Mn4                                | 0.0368 (3) | 0.0378 (3) | 0.0241 (2) | -0.0140 (2) | -0.00685 (18) | -0.00830 (18) |
| O1                                 | 0.0416 (12) | 0.0341 (11) | 0.0270 (10) | -0.0156 (9) | -0.0040 (8) | -0.0099 (8) |
| O2                                 | 0.0350 (12) | 0.0402 (11) | 0.0317 (10) | -0.0157 (9) | -0.0073 (8) | -0.0114 (9) |
| O3                                 | 0.0363 (12) | 0.0360 (11) | 0.0363 (11) | -0.0132 (9) | -0.0077 (9) | -0.0043 (9) |
| O4                                 | 0.0361 (11) | 0.0345 (11) | 0.0254 (9) | -0.0145 (9) | -0.0056 (8) | -0.0078 (8) |
| O5                                 | 0.0333 (11) | 0.0419 (11) | 0.0284 (10) | -0.0166 (9) | -0.0042 (8) | -0.0107 (8) |

IUCrData (2021). 6, x201643
| Atom | U1      | U2      | U3      | U4      | U5      | U6      |
|------|---------|---------|---------|---------|---------|---------|
| O6   | 0.0535  | 0.0479  | 0.0298  | -0.0168 | -0.0139 | -0.0098 |
| O7   | 0.0442  | 0.0449  | 0.0305  | -0.0199 | -0.0099 | -0.0065 |
| O8   | 0.0528  | 0.0455  | 0.0274  | -0.0202 | -0.0076 | -0.0044 |
| O9   | 0.0459  | 0.0528  | 0.0274  | -0.0247 | -0.0002 | -0.0169 |
| O10  | 0.0391  | 0.0462  | 0.0308  | -0.0153 | -0.0038 | -0.0189 |
| O11  | 0.0438  | 0.0499  | 0.0467  | -0.0056 | -0.0058 | -0.0241 |
| O12  | 0.0411  | 0.0443  | 0.0506  | -0.0055 | -0.0090 | -0.0187 |
| O13  | 0.140   | 0.0525  | 0.074   | 0.000   | 0.001   | -0.0191 |
| O14  | 0.099   | 0.139   | 0.078   | -0.053  | -0.034  | 0.050   |
| O15  | 0.113   | 0.189   | 0.0413  | -0.080  | -0.050  | -0.044  |
| O16  | 0.133   | 0.082   | 0.083   | 0.008   | -0.040  | -0.050  |
| N1   | 0.067   | 0.069   | 0.051   | -0.0224 | -0.0145 | -0.0322 |
| N2   | 0.0421  | 0.093   | 0.0352  | -0.0091 | -0.0118 | -0.0189 |
| N3   | 0.082   | 0.0445  | 0.0467  | -0.0233 | -0.0100 | 0.0036  |
| N4   | 0.070   | 0.0525  | 0.0327  | -0.0244 | -0.0011 | -0.0058 |
| C1   | 0.062   | 0.0350  | 0.0387  | -0.0155 | -0.0122 | -0.0127 |
| C2   | 0.0406  | 0.0474  | 0.0366  | -0.0100 | -0.0038 | -0.0200 |
| C3   | 0.0354  | 0.0479  | 0.0403  | -0.0094 | -0.0082 | -0.0227 |
| C4   | 0.048   | 0.060   | 0.0373  | -0.0073 | -0.0081 | -0.0261 |
| C5   | 0.093   | 0.064   | 0.057   | -0.037  | -0.017  | -0.025  |
| C6   | 0.065   | 0.062   | 0.0480  | -0.0258 | -0.0099 | -0.0268 |
| C7   | 0.061   | 0.065   | 0.0404  | -0.0041 | -0.0170 | -0.0265 |
| C8   | 0.103   | 0.062   | 0.059   | -0.045  | -0.015  | -0.021  |
| C9   | 0.047   | 0.0394  | 0.0468  | -0.0080 | -0.0133 | -0.0004 |
| C10  | 0.0345  | 0.0463  | 0.0381  | -0.0076 | -0.0100 | 0.0005  |
| C11  | 0.037   | 0.072   | 0.0436  | -0.0102 | -0.0120 | 0.0050  |
| C12  | 0.043   | 0.100   | 0.0308  | -0.007  | -0.0095 | 0.0026  |
| C13  | 0.0352  | 0.065   | 0.0342  | -0.0054 | -0.0066 | -0.0187 |
| C14  | 0.0334  | 0.0497  | 0.0327  | -0.0053 | -0.0083 | -0.0088 |
| C15  | 0.056   | 0.098   | 0.052   | -0.020  | -0.0154 | 0.017   |
| C16  | 0.057   | 0.068   | 0.054   | -0.0170 | -0.0147 | -0.0313 |
| C17  | 0.0459  | 0.0403  | 0.0372  | -0.0132 | -0.0083 | -0.0152 |
| C18  | 0.0438  | 0.0339  | 0.0405  | -0.0100 | -0.0091 | -0.0074 |
| C19  | 0.0384  | 0.0336  | 0.0374  | -0.0080 | -0.0057 | -0.0056 |
| C20  | 0.051   | 0.0399  | 0.0365  | -0.0065 | -0.0060 | -0.0043 |
| C21  | 0.101   | 0.042   | 0.063   | -0.035  | -0.021  | 0.0003  |
| C22  | 0.076   | 0.0410  | 0.049   | -0.0205 | -0.0168 | -0.0080 |
| C23  | 0.071   | 0.0472  | 0.0344  | -0.0994 | -0.0035 | -0.0002 |
| C24  | 0.105   | 0.047   | 0.065   | -0.034  | -0.021  | -0.0123 |
| C25  | 0.0346  | 0.062   | 0.0352  | -0.0206 | -0.0073 | -0.0121 |
| C26  | 0.058   | 0.090   | 0.090   | -0.035  | -0.002  | -0.052  |
| C27  | 0.0361  | 0.0407  | 0.0291  | -0.0071 | -0.0024 | -0.0150 |
| C28  | 0.046   | 0.0444  | 0.0360  | -0.0111 | -0.0003 | -0.0156 |
| C29  | 0.068   | 0.074   | 0.0275  | -0.019  | -0.0058 | -0.0087 |
| C30  | 0.052   | 0.068   | 0.0324  | -0.0186 | -0.0068 | -0.0208 |
| C31  | 0.0332  | 0.0505  | 0.0324  | -0.0076 | -0.0028 | -0.0202 |
| C32  | 0.048   | 0.053   | 0.0351  | -0.0161 | -0.0026 | -0.0251 |
| C33  | 0.064   | 0.052   | 0.0493  | -0.0304 | 0.0074  | -0.0244 |
|     |   |   |   |   |   |
|-----|---|---|---|---|---|
| C34 | 0.067 (3) | 0.116 (4) | 0.0329 (18) | −0.039 (3) | −0.0045 (17) | −0.023 (2) |
| C35 | 0.0377 (18) | 0.0455 (19) | 0.052 (2) | −0.0145 (15) | −0.0017 (15) | −0.0246 (16) |
| C36 | 0.041 (2) | 0.0444 (19) | 0.073 (2) | −0.0172 (16) | −0.0055 (17) | −0.0277 (18) |
| C37 | 0.050 (2) | 0.060 (2) | 0.082 (3) | −0.0166 (19) | 0.0028 (19) | −0.041 (2) |
| C38 | 0.068 (3) | 0.071 (3) | 0.098 (3) | −0.010 (2) | 0.003 (2) | −0.054 (3) |
| C39 | 0.066 (3) | 0.070 (3) | 0.128 (4) | −0.003 (2) | −0.006 (3) | −0.062 (3) |
| C40 | 0.060 (3) | 0.049 (2) | 0.124 (4) | −0.003 (2) | −0.028 (3) | −0.038 (3) |
| C41 | 0.047 (2) | 0.052 (2) | 0.083 (3) | −0.0119 (18) | −0.031 (19) | −0.036 (2) |
| O16 | 0.061 (4) | 0.071 (3) | 0.103 (4) | −0.008 (3) | −0.034 (3) | −0.032 (3) |
| C42 | 0.026 (3) | 0.066 (3) | 0.096 (5) | −0.013 (3) | −0.005 (3) | −0.031 (3) |
| C43 | 0.054 (5) | 0.077 (4) | 0.123 (7) | 0.017 (4) | −0.031 (5) | −0.050 (5) |

**Geometric parameters (Å, °)**

| Bond/Angle | Distance/° | Bond/Angle | Distance/° |
|------------|------------|------------|------------|
| Mn1—Mn2    | 2.8844 (6)  | C8—H8B     | 0.9900     |
| Mn1—Mn3    | 3.1695 (5)  | C9—H9A     | 0.9900     |
| Mn1—O1     | 2.471 (2)   | C9—H9B     | 0.9900     |
| Mn1—O2     | 1.9315 (19) | C9—C10     | 1.506 (5)  |
| Mn1—O3     | 1.8815 (19) | C10—C11    | 1.398 (4)  |
| Mn1—O5     | 1.9410 (19) | C10—C14    | 1.400 (5)  |
| Mn1—O7     | 1.891 (2)   | C11—C12    | 1.369 (6)  |
| Mn1—O12    | 2.154 (2)   | C11—C15    | 1.529 (6)  |
| Mn2—Mn3    | 3.1810 (4)  | C12—H12    | 0.9500     |
| Mn2—O2     | 1.9428 (19) | C13—C14    | 1.405 (5)  |
| Mn2—O4\[^4\] | 2.394 (2) | C13—C16    | 1.486 (5)  |
| Mn2—O5     | 1.9422 (19) | C15—H15A   | 0.9900     |
| Mn2—O9     | 1.8853 (19) | C15—H15B   | 0.9900     |
| Mn2—O10    | 1.881 (2)   | C16—H16A   | 0.9800     |
| Mn2—O11    | 2.145 (2)   | C16—H16B   | 0.9800     |
| Mn3—Mn4\[^4\] | 3.1274 (4) | C16—H16C   | 0.9800     |
| Mn3—O1     | 2.0519 (19) | C17—H17A   | 0.9900     |
| Mn3—O1\[^4\] | 2.0518 (19) | C17—C18    | 1.515 (4)  |
| Mn3—O2     | 1.920 (2)   | C18—C19    | 1.400 (4)  |
| Mn3—O2\[^4\] | 1.920 (2) | C18—C22    | 1.404 (5)  |
| Mn3—O4\[^4\] | 2.2620 (18) | C19—C20    | 1.426 (4)  |
| Mn3—O4     | 2.2620 (18) | C20—C23    | 1.490 (5)  |
| Mn4—O1     | 1.9563 (18) | C21—H21    | 0.9500     |
| Mn4—O3     | 2.239 (2)   | C21—C22    | 1.379 (5)  |
| Mn4—O4     | 1.9286 (19) | C22—C24    | 1.492 (5)  |
| Mn4—O6     | 1.873 (2)   | C23—H23A   | 0.9800     |
| Mn4—O8     | 1.875 (2)   | C23—H23B   | 0.9800     |
| Mn4—O10\[^4\] | 2.212 (2) | C23—H23C   | 0.9800     |
| O1—C1      | 1.432 (4)   | C24—H24A   | 0.9900     |
| O3—C9      | 1.417 (4)   | C24—H24B   | 0.9900     |
| O4—C17     | 1.415 (4)   | C25—H25A   | 0.9900     |
| O5—C25     | 1.445 (3)   | C25—H25B   | 0.9900     |
| O6—C3      | 1.327 (4)   | C25—C26    | 1.462 (5)  |
O7—C14 1.324 (3)  C26—H26A 0.9800
O8—C19 1.315 (4)  C26—H26B 0.9800
O9—C27 1.329 (3)  C26—H26C 0.9800
O10—C32 1.420 (3)  C27—C28 1.400 (4)
O11—C35 1.252 (4)  C27—C31 1.396 (4)
O12—C35 1.274 (4)  C28—C33 1.493 (5)
O13—H13 0.8400  C29—H29 0.9500
O13—C8 1.368 (6)  C29—C30 1.370 (5)
O14—H14 0.8400  C30—C31 1.400 (4)
O14—C15 1.356 (5)  C30—C34 1.520 (5)
O15—H15 0.8400  C31—C32 1.511 (4)
O15—C34 1.402 (4)  C32—H32A 0.9900
O17—H17 0.8400  C32—H32B 0.9900
O17—C24 1.415 (6)  C33—H33A 0.9800
N1—C4 1.327 (4)  C33—H33B 0.9800
N1—C5 1.325 (5)  C33—H33C 0.9800
N2—H2 0.8800  C34—H34A 0.9900
N2—C12 1.330 (5)  C34—H34B 0.9900
N2—C13 1.343 (4)  C35—C36 1.493 (5)
N3—C20 1.330 (5)  C36—C37 1.379 (5)
N3—C21 1.333 (5)  C36—C41 1.379 (5)
N4—H4 0.8800  C37—H37 0.9500
N4—C28 1.337 (4)  C37—C38 1.375 (6)
N4—C29 1.347 (5)  C38—H38 0.9500
C1—H1A 0.9900  C38—C39 1.359 (7)
C1—H1B 0.9900  C39—H39 0.9500
C1—C2 1.500 (4)  C39—C40 1.377 (7)
C2—C3 1.402 (4)  C40—H40 0.9500
C2—C6 1.400 (5)  C40—C41 1.396 (6)
C3—C4 1.416 (4)  C41—H41 0.9500
C4—C7 1.484 (5)  O16—H16 0.8400
C5—H5 0.9500  O16—C42 1.380 (9)
C5—C6 1.373 (5)  C42—H42A 0.9900
C6—C8 1.504 (5)  C42—H42B 0.9900
C7—H7A 0.9800  C42—C43 1.384 (12)
C7—H7B 0.9800  C43—H43A 0.9800
C7—H7C 0.9800  C43—H43B 0.9800
C8—H8A 0.9900  C43—H43C 0.9800

Mn2—Mn1—Mn3 63.190 (13)  C28—N4—H4 118.9
O1—Mn1—Mn2 93.74 (5)  C28—N4—C29 122.1 (3)
O1—Mn1—Mn3 40.33 (4)  C29—N4—H4 118.9
O2—Mn1—Mn2 42.04 (6)  O1—C1—H1A 108.9
O2—Mn1—Mn3 34.50 (6)  O1—C1—H1B 108.9
O2—Mn1—O1 74.81 (8)  O1—C1—C2 113.5 (3)
O2—Mn1—O5 81.03 (8)  H1A—C1—H1B 107.7
O2—Mn1—O12 92.21 (9)  C2—C1—H1A 108.9
O3—Mn1—Mn2 137.18 (6)  C2—C1—H1B 108.9
| Bond | Distance (Å) | Bond | Distance (Å) |
|------|-------------|------|-------------|
| O3—Mn1—Mn3 | 84.67 (6) | C3—C2—C1 | 121.5 (3) |
| O3—Mn1—O1 | 75.72 (8) | C6—C2—C1 | 120.2 (3) |
| O3—Mn1—O2 | 95.59 (8) | C6—C2—C3 | 118.2 (3) |
| O3—Mn1—O5 | 168.24 (9) | O6—C3—C2 | 124.1 (3) |
| O3—Mn1—O7 | 90.81 (9) | O6—C3—C4 | 117.3 (3) |
| O3—Mn1—O12 | 97.35 (9) | O6—C2—C4 | 118.6 (3) |
| O5—Mn1—Mn2 | 42.05 (6) | N1—C4—C3 | 121.6 (3) |
| O5—Mn1—Mn3 | 86.28 (6) | N1—C4—C7 | 119.3 (3) |
| O5—Mn1—O1 | 92.52 (8) | C3—C4—C7 | 119.1 (3) |
| O5—Mn1—O12 | 94.05 (9) | N1—C5—H5 | 117.9 |
| O7—Mn1—Mn2 | 132.02 (6) | N1—C5—C6 | 124.2 (3) |
| O7—Mn1—Mn3 | 139.87 (7) | C6—C5—H5 | 117.9 |
| O7—Mn1—O1 | 99.97 (8) | C2—C6—C8 | 122.7 (3) |
| O7—Mn1—O2 | 170.40 (9) | C5—C6—C2 | 118.3 (3) |
| O7—Mn1—O5 | 91.27 (8) | C5—C6—C8 | 119.0 (3) |
| O7—Mn1—O12 | 94.07 (9) | C4—C7—H7A | 109.5 |
| O12—Mn1—Mn3 | 86.28 (6) | C4—C7—H7B | 109.5 |
| O12—Mn1—O1 | 164.36 (8) | C4—C7—H7C | 109.5 |
| Mn1—Mn2—Mn3 | 62.784 (12) | H7A—C7—H7B | 109.5 |
| O2—Mn2—Mn1 | 41.74 (6) | H7A—C7—H7C | 109.5 |
| O2—Mn2—Mn3 | 34.32 (6) | C6—C8—H8A | 109.2 |
| O2—Mn2—O4 | 79.51 (8) | C6—C8—H8B | 109.2 |
| O2—Mn2—O11 | 92.14 (9) | O13—C8—H8B | 109.2 |
| O4—Mn2—Mn1 | 98.83 (5) | O13—C8—C6 | 112.0 (4) |
| O4—Mn2—Mn3 | 45.19 (4) | O13—C8—H8A | 109.2 |
| O5—Mn2—Mn1 | 42.02 (6) | C10—C9—H9A | 109.0 |
| O5—Mn2—Mn3 | 85.93 (6) | O3—C9—H9A | 109.0 |
| O5—Mn2—O2 | 80.72 (8) | O3—C9—H9B | 109.0 |
| O5—Mn2—O4 | 95.70 (8) | O3—C9—C10 | 112.9 (3) |
| O5—Mn2—O11 | 92.82 (9) | H9A—C9—H9B | 107.8 |
| O9—Mn2—Mn1 | 131.22 (6) | C10—C9—H9A | 109.0 |
| O9—Mn2—Mn3 | 140.22 (7) | C10—C9—H9B | 109.0 |
| O9—Mn2—O2 | 169.68 (9) | C11—C10—C9 | 121.0 (3) |
| O9—Mn2—O4 | 96.07 (8) | C11—C10—C14 | 118.9 (3) |
| O9—Mn2—O5 | 90.53 (8) | C14—C10—C9 | 120.1 (3) |
| O9—Mn2—O11 | 93.74 (9) | C10—C11—C15 | 121.1 (4) |
| O10—Mn2—Mn1 | 136.16 (6) | C12—C11—C10 | 119.2 (3) |
| O10—Mn2—Mn3 | 86.99 (6) | C12—C11—C15 | 119.7 (3) |
| O10—Mn2—O2 | 95.53 (8) | N2—C12—C11 | 120.3 (3) |
| O10—Mn2—O4 | 76.56 (8) | N2—C12—H12 | 119.8 |
| O10—Mn2—O5 | 171.95 (9) | C11—C12—H12 | 119.8 |
| O10—Mn2—O9 | 92.46 (8) | N2—C13—C14 | 117.5 (3) |
| O10—Mn2—O11 | 94.43 (9) | N2—C13—C16 | 119.1 (3) |
| O11—Mn2—Mn1 | 80.99 (6) | C14—C13—C16 | 123.4 (3) |
| O11—Mn2—Mn3 | 125.98 (6) | O7—C14—C10 | 123.4 (3) |
| O11—Mn2—O4 | 166.93 (8) | O7—C14—C13 | 116.7 (3) |
| Mn1i—Mn3—Mn1 | 180.0 | C10—C14—C13 | 119.9 (3) |
| Bond                  | Angle (deg) | Torsion (deg) | Bond Length (Å) |
|----------------------|-------------|---------------|-----------------|
| Mn1—Mn3—Mn2         | 125.975 (11)| O14—C15—C11  | 109.7 (4)       |
| Mn1—Mn3—Mn2         | 54.026 (11) | O14—C15—H15A | 109.7           |
| Mn1—Mn3—Mn2         | 125.973 (11)| O14—C15—H15B | 109.7           |
| Mn1—Mn3—Mn2         | 54.026 (11) | C11—C15—H15A | 109.7           |
| Mn2—Mn3—Mn2         | 180.0       | C11—C15—H15B | 109.7           |
| Mn4—Mn3—Mn1         | 116.284 (12)| H15A—C15—H15B| 108.2           |
| Mn4—Mn3—Mn1         | 116.285 (12)| C13—C16—H16A | 109.5           |
| Mn4—Mn3—Mn1         | 63.716 (12) | C13—C16—H16B | 109.5           |
| Mn4—Mn3—Mn1         | 63.715 (12) | C13—C16—H16C | 109.5           |
| Mn4—Mn3—Mn2         | 62.297 (12) | H16A—C16—H16B| 109.5           |
| Mn4—Mn3—Mn2         | 62.298 (12) | H16A—C16—H16C| 109.5           |
| Mn4—Mn3—Mn2         | 117.702 (12)| H16B—C16—H16C| 109.5           |
| Mn4—Mn3—Mn2         | 117.703 (12)| O4—C17—H17A  | 108.3           |
| Mn4—Mn3—Mn4         | 180.0       | O4—C17—H17B  | 108.3           |
| O1—Mn3—Mn2i         | 51.20 (6)   | O4—C17—C18   | 115.8 (3)       |
| O1—Mn3—Mn2i         | 128.80 (6)  | H17A—C17—H17B| 107.4           |
| O1—Mn3—Mn2i         | 128.80 (6)  | C18—C17—H17A | 108.3           |
| O1—Mn3—Mn2i         | 51.20 (6)   | C18—C17—H17B | 108.3           |
| O1—Mn3—Mn2i         | 94.51 (6)   | C19—C18—C17  | 122.2 (3)       |
| O1—Mn3—Mn2i         | 94.51 (6)   | C19—C18—C22  | 118.0 (3)       |
| O1—Mn3—Mn2i         | 85.49 (6)   | C22—C18—C17  | 119.8 (3)       |
| O1—Mn3—Mn2i         | 85.49 (6)   | O8—C19—C18   | 125.0 (3)       |
| O1—Mn3—Mn2i         | 142.37 (5)  | O8—C19—C20   | 116.1 (3)       |
| O1—Mn3—Mn4i         | 37.63 (5)   | C18—C19—C20  | 118.9 (3)       |
| O1—Mn3—Mn4i         | 37.64 (5)   | N3—C20—C19   | 121.4 (3)       |
| O1—Mn3—Mn4i         | 142.37 (5)  | N3—C20—C23   | 118.3 (3)       |
| O1—Mn3—Mn1i         | 180.0       | C19—C20—C23  | 120.3 (3)       |
| O1—Mn3—O1i          | 104.56 (7)  | N3—C21—H21   | 118.1           |
| O1—Mn3—O1i          | 75.44 (7)   | N3—C21—C22   | 123.8 (4)       |
| O1—Mn3—O4i          | 104.56 (7)  | C22—C21—H21  | 118.1           |
| O1—Mn3—O4i          | 75.44 (7)   | C22—C21—C24  | 122.5 (3)       |
| O2—Mn3—Mn1i         | 34.74 (6)   | C21—C22—C18  | 118.7 (3)       |
| O2—Mn3—Mn1i         | 145.26 (6)  | C21—C22—C24  | 118.8 (3)       |
| O2—Mn3—Mn1i         | 34.74 (6)   | C20—C23—H23A | 109.5           |
| O2—Mn3—Mn1i         | 145.26 (6)  | C20—C23—H23B | 109.5           |
| O2—Mn3—Mn1i         | 145.20 (6)  | C20—C23—H23C | 109.5           |
| O2—Mn3—Mn2i         | 34.80 (6)   | H23A—C23—H23B| 109.5           |
| O2—Mn3—Mn2i         | 34.80 (6)   | H23A—C23—H23C| 109.5           |
| O2—Mn3—Mn4i         | 145.21 (6)  | H23B—C23—H23C| 109.5           |
| O2—Mn3—Mn4i         | 88.58 (6)   | O17—C24—C22  | 110.3 (4)       |
| O2—Mn3—Mn4i         | 91.42 (6)   | O17—C24—H24A | 109.6           |
| O2—Mn3—Mn4i         | 91.42 (6)   | O17—C24—H24B | 109.6           |
| O2—Mn3—Mn4i         | 88.58 (6)   | C22—C24—H24A | 109.6           |
| O2—Mn3—Mn4i         | 85.92 (8)   | C22—C24—H24B | 109.6           |
| O2—Mn3—O1i          | 94.08 (8)   | H24A—C24—H24B| 108.1           |
| O2—Mn3—O1i          | 85.92 (8)   | O5—C25—H25A  | 109.3           |
| O2—Mn3—O1i          | 94.08 (8)   | O5—C25—H25B  | 109.3           |
| O2—Mn3—O1i          | 180.00 (12) | O5—C25—C26   | 111.8 (3)       |
| Bond                  | Distance (Å) | Angle (°)   |
|----------------------|--------------|-------------|
| O2—Mn3—O4           | 96.56 (8)    | H25A—C25—H25B 107.9 |
| O2—Mn3—O4i          | 83.44 (8)    | C26—C25—H25A 109.3 |
| O2—Mn3—O4           | 83.45 (8)    | C26—C25—H25B 109.3 |
| O2—Mn3—O4i          | 96.55 (8)    | C25—C26—H26A 109.5 |
| O4—Mn3—Mn1          | 94.02 (5)    | C25—C26—H26B 109.5 |
| O4—Mn3—Mn1i         | 94.02 (5)    | C25—C26—H26C 109.5 |
| O4—Mn3—Mn1i         | 85.98 (5)    | H26A—C26—H26B 109.5 |
| O4—Mn3—Mn1i         | 85.97 (5)    | H26A—C26—H26C 109.5 |
| O4—Mn3—Mn2i         | 48.66 (5)    | H26B—C26—H26C 109.5 |
| O4—Mn3—Mn2           | 131.34 (5)   | O9—C27—C28 115.6 (3) |
| O4—Mn3—Mn2          | 48.66 (5)    | O9—C27—C31 124.3 (3) |
| O4—Mn3—Mn2i         | 131.34 (5)   | C31—C27—C28 120.1 (3) |
| O4—Mn3—Mn2i         | 37.81 (5)    | N4—C28—C27 119.1 (3) |
| O4—Mn3—Mn4i         | 142.19 (5)   | N4—C28—C33 118.8 (3) |
| O4—Mn3—Mn4          | 142.19 (5)   | C27—C28—C33 122.1 (3) |
| O4—Mn3—Mn4          | 37.81 (5)    | N4—C29—H29 119.5 |
| O4—Mn3—Mn4i         | 180.0        | N4—C29—C30 120.9 (3) |
| O1—Mn4—Mn3           | 39.83 (6)    | C30—C29—H29 119.5 |
| O1—Mn4—O3           | 80.23 (8)    | C29—C30—C31 119.4 (3) |
| O1—Mn4—O10           | 88.94 (8)    | C29—C30—C34 119.9 (3) |
| O3—Mn4—Mn3           | 80.49 (5)    | C31—C30—C34 120.7 (3) |
| O4—Mn4—Mn3           | 45.98 (5)    | C27—C31—C30 118.3 (3) |
| O4—Mn4—O1            | 85.80 (8)    | C27—C31—C32 121.1 (3) |
| O4—Mn4—O3            | 86.40 (8)    | C30—C31—C32 120.6 (3) |
| O4—Mn4—O10           | 80.29 (8)    | O10—C32—C31 114.1 (2) |
| O6—Mn4—Mn3           | 131.65 (6)   | O10—C32—H32A 108.7 |
| O6—Mn4—O1            | 92.27 (9)    | O10—C32—H32B 108.7 |
| O6—Mn4—O3            | 101.04 (9)   | C31—C32—H32A 108.7 |
| O6—Mn4—O4            | 171.90 (10)  | C31—C32—H32B 108.7 |
| O6—Mn4—O8            | 89.03 (9)    | H32A—C32—H32B 107.6 |
| O6—Mn4—O10           | 91.82 (9)    | C28—C33—H33A 109.5 |
| O8—Mn4—Mn3           | 139.31 (7)   | C28—C33—H33B 109.5 |
| O8—Mn4—O1            | 172.24 (10)  | C28—C33—H33C 109.5 |
| O8—Mn4—O3            | 92.02 (9)    | H33A—C33—H33B 109.5 |
| O8—Mn4—O4            | 93.95 (9)    | H33A—C33—H33C 109.5 |
| O8—Mn4—O10           | 98.67 (9)    | H33B—C33—H33C 109.5 |
| O10—Mn4—Mn3          | 83.17 (5)    | O15—C34—C30 109.8 (3) |
| O10—Mn4—O3           | 163.43 (7)   | O15—C34—H34A 109.7 |
| Mn3—O1—Mn1           | 88.47 (7)    | O15—C34—H34B 109.7 |
| Mn4—O1—Mn1           | 96.62 (8)    | C30—C34—H34A 109.7 |
| Mn4—O1—Mn3           | 102.54 (8)   | C30—C34—H34B 109.7 |
| C1—O1—Mn1            | 124.55 (19)  | H34A—C34—H34B 108.2 |
| C1—O1—Mn3            | 120.65 (17)  | O11—C35—O12 125.0 (3) |
| C1—O1—Mn4            | 117.86 (17)  | O11—C35—C36 117.6 (3) |
| Mn1—O2—Mn2           | 96.23 (8)    | O12—C35—C36 117.5 (3) |
| Mn3—O2—Mn1           | 110.77 (10)  | C37—C36—C35 120.2 (3) |
| Mn3—O2—Mn2           | 110.88 (10)  | C41—C36—C35 120.9 (3) |
| Mn1—O3—Mn4           | 107.22 (9)   | C41—C36—C37 118.9 (4) |
C9—O3—Mn1 117.61 (19) C36—C37—H37 119.6
C9—O3—Mn4 121.6 (2) C38—C37—C36 120.7 (4)
Mn3—O4—Mn2i 86.15 (7) C38—C37—H37 119.6
Mn4—O4—Mn2i 97.47 (8) C37—C38—H37 119.8
Mn4—O4—Mn3 96.21 (8) C39—C38—C37 120.5 (5)
C17—O4—Mn2 123.30 (17) C39—C38—H37 119.8
C17—O4—Mn3 125.88 (16) C38—C39—C37 120.1
C17—O4—Mn4 119.61 (17) C38—C39—H37 119.8 (5)
Mn1—O5—Mn2 95.94 (8) C40—C39—C40 120.1
C25—O5—Mn1 120.45 (18) C36—C41—C40 119.6 (4)
C25—O5—Mn2 120.49 (17) C36—C41—H41 120.2
C3—O6—Mn4 128.97 (18) C36—C41—C40 119.6 (4)
Mn1—O1—C1—C2 −64.4 (3) O12—Mn1—O3—Mn4 −169.09 (9)
Mn1—O3—C9—C10 63.5 (3) O12—Mn1—O3—C9 49.5 (2)
Mn1—O5—C25—C26 −127.1 (3) O12—Mn1—O7—C14 −89.6 (3)
Mn1—O7—C14—C10 12.5 (5) O12—C35—C36—C41 −2.5 (5)
Mn1—O7—C14—C13 −167.8 (2) N1—C5—C6—C8 178.7 (4)
Mn1—O7—C14—C13 3.5 (4) N2—C13—C14—O7 −178.4 (3)
Mn1—O12—C35—O11 −134.58 (19) N2—C13—C14—C10 1.3 (5)
Mn1—O1—C1—C2 −64.4 (3) N3—C21—C22—C18 0.6 (7)
Mn1—C9—O4—Mn4 97.47 (8) N3—C21—C22—C24 179.5 (4)
Mn2—Mn1—O3—Mn4 −83.27 (12) N4—C29—C30—C31 −1.5 (6)
Mn2—Mn1—O3—Mn4 135.3 (2) N4—C29—C30—C34 179.7 (4)
Mn2—Mn1—O7—C14 −172.2 (2) N4—C29—C30—C31 −1.5 (6)
Mn2—C9—O4—Mn4 −74.6 (3) N4—C29—C30—C34 179.7 (4)
Mn2—O5—C25—C26 113.8 (3) C1—C2—C3—O6 4.7 (5)
Mn2—O9—C27—C28 171.4 (2) C1—C2—C3—C4 −173.4 (3)
Mn2—O9—C27—C31 −8.0 (5) C1—C2—C6—C5 174.9 (4)
Mn2—O10—C32—C31 −57.1 (3) C1—C2—C6—C8 −3.8 (6)
Mn2—O11—C35—O12 −5.1 (5) C2—C3—C4—N1 −3.1 (5)
Mn2—O11—C35—C36 174.4 (2) C2—C3—C4—C7 176.2 (3)
Mn3—Mn1—O3—Mn4 −43.35 (7) C2—C6—C8—O13 71.6 (5)
Mn3—Mn1—O3—C9 175.2 (2) C3—C2—C6—C5 179.4 (4)
Mn3—Mn1—O7—C14 90.5 (3) C3—C2—C6—C8 −1.9 (6)
Mn3—Mn2—O9—C27 −97.2 (2) C4—N1—C5—C6 0.5 (7)
Mn3—Mn2—O10—Mn4i 41.38 (7) C5—N1—C4—C3 1.1 (6)
Mn3—Mn2—O10—C32 −178.9 (2) C5—N1—C4—C7 −178.2 (4)
Mn3—Mn4—O6—C3 −2.7 (3) C5—C6—C8—O13 −107.1 (5)
Mn3—Mn4—O8—C19 −2.2 (3) C6—C2—C3—O6 −178.5 (3)
Mn3—O1—C1—C2 −176.10 (19) C6—C2—C3—C4 3.4 (5)
Mn4—O1—C1—C2 57.1 (3) C6—C2—C3—C7 176.2 (3)
Mn4—O3—C9—C10 175.2 (2) C9—C10—C11—C12 −179.9 (4)
Mn4—O3—C9—C11 175.2 (2) C9—C10—C11—C15 −0.6 (6)
Mn4—O4—C17—C18 −176.10 (19) C9—C10—C11—C15 −0.6 (6)
Mn4—O4—C17—C19 173.3 (2) C9—C10—C11—C15 −0.6 (6)
Mn4—O6—C3—C2 176.2 (3) C10—C11—C12—N2 −178.4 (4)
Mn4—O6—C3—C4 176.2 (3) C10—C11—C12—N2 −178.4 (4)
Mn4—O8—C19—C20 −173.6 (2) C10—C11—C12—N2 −178.4 (4)
Mn4i—O10—C32—C31 −176.10 (19) C10—C11—C12—N2 −178.4 (4)
O1—Mn1—O3—Mn4 −3.38 (7) C12—N2—C13—C14 −0.3 (5)
O1—Mn1—O3—C9 178.7 (3) C12—N2—C13—C14 −0.3 (5)
O1—Mn1—O7—C14 −144.8 (2) C12—C11—C15—O14 −11.5 (6)
O1—Mn1—O7—C14 83.5 (3) C12—C11—C15—O14 −11.5 (6)
O1—Mn4—O6—C3 3.8 (3) C13—N2—C12—C11 0.0 (6)
O1—Mn4—O6—C3 3.8 (3) C13—N2—C12—C11 0.0 (6)
O1—C1—C2—C3 −40.1 (4) C14—C10—C11—C15 −178.8 (4)
O1—C1—C2—C6 143.2 (3) C14—C10—C11—C15 −178.8 (4)
O2—Mn1—O3—C9 142.4 (2) C15—C11—C12—N2 179.8 (4)
O2—Mn1—O3—C9 −76.12 (10) C15—C11—C12—N2 179.8 (4)
O2—Mn1—O7—C14 142.4 (2) C16—C13—C14—O7 −0.4 (5)
O2—Mn1—O7—C14 −76.12 (10) C16—C13—C14—O7 −0.4 (5)
O2—Mn2—O9—C27 −149.7 (5) C16—C13—C14—O7 −0.4 (5)
O2—Mn2—O9—C27 −149.7 (5) C16—C13—C14—O7 −0.4 (5)
O2—Mn2—O10—Mn4i 74.66 (10) C17—C18—C22—C21 −176.8 (4)
O2—Mn2—O10—C32 −145.6 (2) C17—C18—C22—C21 −176.8 (4)
O3—Mn1—O7—C14 7.8 (3) C18—C19—C20—N3 2.5 (5)
O3—Mn4—O6—C3 84.3 (3) C18—C19—C20—N3 2.5 (5)
O3—Mn4—O6—C3 84.3 (3) C18—C19—C20—N3 2.5 (5)
O3—Mn4—O8—C19 −80.0 (3) C18—C19—C20—C23 178.8 (3)
O3—C9—C10—C11 144.1 (3) C18—C22—C24—O17 64.0 (5)
O3—C9—C10—C14 −37.7 (5) C19—C18—C22—C24 −0.2 (6)
O4—Mn2—O9—C27 −85.7 (3) C19—C18—C22—C24 −0.2 (6)
O4—Mn2—O9—C27 −85.7 (3) C19—C18—C22—C24 −0.2 (6)
O4—Mn2—O10—Mn4i −3.14 (7) C20—N3—C21—C22 −1.1 (7)
O4—Mn2—O10—Mn4i −3.14 (7) C20—N3—C21—C22 −1.1 (7)
O4—Mn2—O10—C32 136.6 (2) C21—N3—C20—C19 1.2 (6)
O4—Mn2—O10—C32 136.6 (2) C21—N3—C20—C19 1.2 (6)
O4—Mn4—O8—C19 6.6 (3) C21—N3—C20—C19 −178.5 (4)
O4—Mn4—O8—C19 6.6 (3) C21—N3—C20—C19 −178.5 (4)
O4—C17—C18—C19 −32.1 (5) C21—C22—C24—O17 −114.8 (4)
O4—C17—C18—C22 151.0 (3) C22—C18—C19—O8 179.5 (3)
O5—Mn1—O3—Mn4 −3.5 (5) C22—C18—C19—O8 179.5 (3)
O5—Mn1—O3—Mn4 −3.5 (5) C22—C18—C19—O8 179.5 (3)
O5—Mn1—O3—C9 −144.9 (4) C27—C31—C32—O10 35.1 (4)
O5—Mn1—O7—C14 176.2 (3) C28—N4—C29—C30 1.9 (6)
O5—Mn2—O9—C27 178.5 (3) C28—C27—C31—C30 1.4 (5)
O6—Mn4—O8—C19 179.0 (3) C28—C27—C31—C30 1.4 (5)
O6—C3—C4—N1 178.7 (3) C29—N4—C28—C27 −0.6 (5)
O6—C3—C4—C7  
O7—Mn1—O3—Mn4  
O7—Mn1—O3—C9  
O8—Mn4—O6—C3  
O8—C19—C20—N3  
O8—C19—C20—C23  
O9—Mn2—O10—Mn4'  
O9—Mn2—O10—C32  
O9—C27—C28—N4  
O9—C27—C28—C33  
O9—C27—C31—C30  
O9—C27—C31—C32  
O10—Mn2—O9—C27  
O10'Mn4—O6—C3  
O10'Mn4—O8—C19  
O11—Mn2—O9—C27  
O11—Mn2—O10—Mn4'  
O11—Mn2—O10—C32  
O11—C35—C36—C37  
O14—H14···N3''  
O15—H15···N1'''  
O17—H17···O13'''

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| O14—H14···N3'' | 0.84 | 1.80 | 2.619 (4) | 163 |
| O15—H15···N1''' | 0.84 | 1.84 | 2.675 (4) | 175 |
| O17—H17···O13'''' | 0.84 | 1.89 | 2.684 (5) | 158 |

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