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X-ray characterization and magnetic properties of dioxygen-bridged Cu^{II} and Mn^{III} Schiff base complexes

Yasemin Yahsi*

Department of Physics, Balikesir University, Balikesir 10145, Turkey. *Correspondence e-mail: yaseminyahsi@gmail.com

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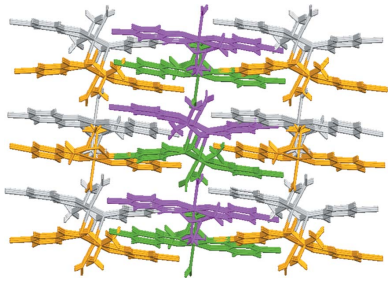
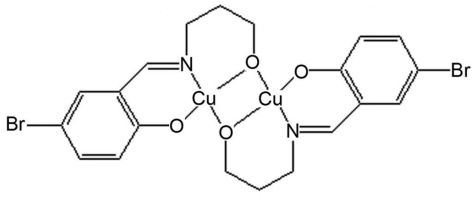
The coordination chemistry of multinuclear metal compounds is important because of their relevance to the multi-metal active sites of various metalloproteins and metalloenzymes. Multinuclear Cu^{II} and Mn^{III} compounds are of interest due to their various properties in the fields of coordination chemistry, inorganic biochemistry, catalysis, and optical and magnetic materials. Oxygen-bridged binuclear Mn^{III} complexes generally exhibit antiferromagnetic interactions and a few examples of ferromagnetic interactions have also been reported. Binuclear Cu^{II} complexes are important due to the fact that they provide examples of the simplest case of magnetic interaction involving only two unpaired electrons. Two novel dioxygen-bridged copper(II) and manganese(III) Schiff base complexes, namely bis(μ-4-bromo-2-{[(3-oxidopropyl)imino]methyl}-phenolato)dicopper(II), $[Cu_2(C_{10}H_{10}BrNO_2)_2]$, (1), and bis(diaqua{4,4′-dichloro-2,2′-[(1,1-dimethylethane-1,2-diyl)bis(nitrilomethanylylidene)]diphenolato}manganese(III)) bis{μ-4,4′-dichloro-2,2′-[(1,1-dimethylethane-1,2-diyl)bis(nitrilomethanylylidene)]diphenolato}bis[aquamanganese(III)] tetrakis(perchlorate) ethanol disolvate, $[Mn(C_{18}H_{16}Cl_2N_2O_2)(H_2O)_2]_2[Mn_2(C_{18}H_{16}Cl_2N_2O_2)_2(H_2O)_2](ClO_4)_4\cdot 2C_2H_5OH$, (2), have been synthesized and single-crystal X-ray diffraction has been used to analyze their crystal structures. The structure analyses of (1) and (2) show that each Cu^{II} atom is four-coordinated, with long weak Cu···O interactions of 2.8631 (13) Å linking the dinuclear halves of the centrosymmetric tetranucelar molecules, while each Mn^{III} atom is six-coordinated. The shortest intra- and intermolecular nonbonding Mn···Mn separations are 3.3277 (16) and 5.1763 (19) Å for (2), while the Cu···Cu separations are 3.0237 (3) and 3.4846 (3) Å for (1). The magnetic susceptibilities of (1) and (2) in the solid state were measured in the temperature range 2–300 K and reveal the presence of antiferromagnetic spin-exchange interactions between the transition metal ions.

1. Introduction

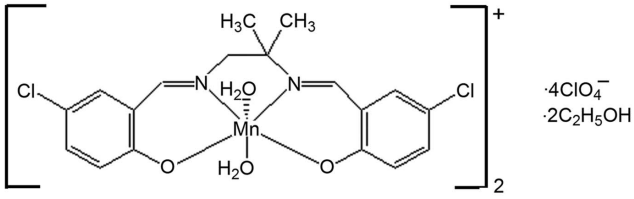
In recent years, the coordination chemistry of multinuclear metal compounds has gained importance because of their relevance to the multi-metal active sites of various metalloproteins and metalloenzymes (Waldron *et al.*, 2009; Bhowmik *et al.*, 2013; Zhang *et al.*, 2001). The synthesis and characterization of multinuclear Cu^{II} and Mn^{III} compounds have attracted considerable interest due to their various interesting properties in the fields of coordination chemistry, as well as inorganic biochemistry, catalysis, and optical and magnetic materials (Christou, 1989; Larson *et al.*, 1992; Choi *et al.*, 2004; Liu *et al.*, 2007; Surati, 2011; Hopa & Cokay, 2016). High-valent manganese complexes in dimeric or higher nuclearity forms are important due to their relevance to the active sites of oxygen-evolving complexes (OEC) in photosystem II (PS II) of green plants, and are also present in several metalloproteins, such as manganese catalase and manganese ribonu-

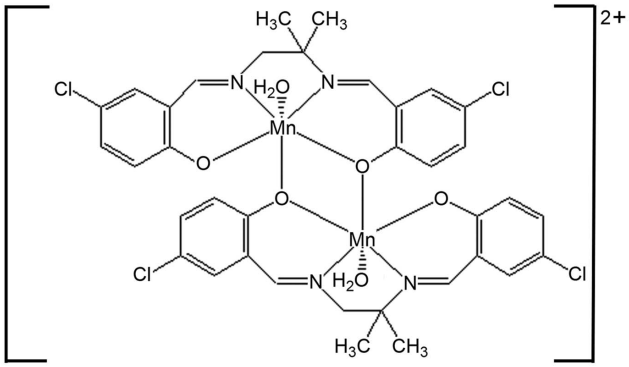


cleotide reductase (Saha *et al.*, 2004; Dismukes, 1996; Law *et al.*, 1999).



(1)





(2)

ONO- and/or ONNO-type Schiff base ligands which contain potentially bridging phenoxide or alkoxide O- and N-donor atoms have been mostly used for synthesizing multinuclear transition-metal complexes (Yahsi *et al.*, 2011; Yardan *et al.*, 2015; Vafazadeh *et al.*, 2012; Anbu & Kandaswamy, 2011). Generally Mn^{II} complexes which contain hydroxy-rich ligands are air-sensitive. The presence of atmospheric oxygen and also the phenoxide O atoms of tetranuclear Schiff base ligand are possible agents for the oxidation of Mn^{II} to Mn^{III} in the preparation of complex (2) (Yahsi & Kara, 2013; Pradeep *et al.*, 2005). Manganese and copper complexes have also been paid considerable attention because of their structural, electronic and magnetic properties (Zhang *et al.*, 2001; Armi *et al.*, 1998; Matthews *et al.*, 1999; Liu *et al.*, 2010; Safaei *et al.*, 2010). In general, oxygen-bridged binuclear Mn^{III} complexes exhibit antiferromagnetic interactions (Matsumoto *et al.*, 1988, 1989; Mikuriya *et al.*, 1992) and a few examples of ferromagnetic interactions have also been reported (Shyu *et al.*, 1999; Karmakar *et al.*, 2004). However, binuclear Cu^{II} complexes are important due to the fact that they provide examples of the simplest case of magnetic interaction involving only two unpaired electrons (Karmakar *et al.*, 2004).

In recent years, my research group and others have reported the structural and magnetic characterization of mono- and dinuclear manganese(III) (Yahsi & Kara, 2013, 2014; Kara, 2007, 2008*a*,*b*,*c*; Gungor & Kara, 2011; Feng *et al.*, 2008; Bhargavi *et al.*, 2009; Surati & Thaker, 2010) and copper(II) complexes containing ONNO- and/or ONO-type Schiff base ligands (Safaei *et al.*, 2011; Haddow *et al.*, 2009; Gungor & Kara, 2012; Yardan *et al.*, 2014). In view of the importance of Mn^{III} and Cu^{II} complexes and in an effort to enlarge the library of such complexes, the syntheses of two new doubly oxygen-bridged Mn^{III} and Cu^{II} complexes, namely bis(μ-4-bromo-2-{[(3-oxidopropyl)imino]methyl}phenolato)dicopper(II), (1), and bis(diaqua{4,4′-dichloro-2,2′-[(1,1-dimethylethane-1,2-diyl)bis(nitrilomethanylylidene)]diphenolato}manganese(III)) bis{μ-4,4′-dichloro-2,2′-[(1,1-dimethylethane-1,2-diyl)bis(nitrilomethanylylidene)]diphenolato}bis[aquamanganese(III)] tetrakis(perchlorate) ethanol disolvate, (2), are reported along with their characterization and single-crystal X-ray structures, and the results of low-temperature magnetic studies. The structures of (1) and (2) contain an alkoxide oxygen-bridged dinuclear Cu^{II} unit and a phenoxide oxygen-bridged dinuclear Mn^{III} unit, respectively. Magnetic studies indicate that the complexes exhibit antiferromagnetic coupling between two Cu^{II} ions and also between two Mn^{III} ions.

2. Experimental

2.1. Synthesis and crystallization

To a methanol solution (40 ml) of 5-bromosalicylaldehyde (1 mmol) was added 3-aminopropan-1-ol (1 mmol) with stirring at room temperature over a period of 1 h. To the resulting yellow solution was added a solution of $Cu(CO_2CH_3)_2·H_2O$ (1 mmol) in methanol (50 ml). The reaction mixture turned green quickly and, after stirring in air for 1 h, was allowed to stand at room temperature for a few weeks. The resulting powder was recrystallized from methanol and after two weeks, green crystals of (1) suitable for X-ray analysis were obtained (yield: 0.34 g, 71%).

4,4′-Dichloro-2,2′-[(1,1-dimethylethane-1,2-diyl)bis(nitrilomethanylylidene)]diphenol (5-ClL2H_2) was prepared by reaction of 1,2-diamino-2-methylpropane (1 mmol) with 5-chlorosalicylaldehyde (2 mmol) in hot ethanol (50 ml). A yellow product precipitated from the solution on cooling. Complex (2) was prepared by the addition of solutions of $Mn(CO_2CH_3)_3·2H_2O$ (1 mmol) in hot ethanol (30 ml) and $NaClO_4$ (1.7 mmol) in hot ethanol (10 ml) and hot water (10 ml) to a solution of 5-ClL2H_2 (1 mmol) in hot ethanol (40 ml). This solution was warmed to 353 K and stirred for 1 h. The resulting solution was filtered rapidly and then allowed to stand at room temperature. After several weeks, needle-like crystals of (2) suitable for X-ray analysis were obtained (yield: 0.57 g, 65%).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were included in idealized positions, with U_{iso}(H) values constrained to 1.5 times the U_{eq} value of the parent C or O atom for methyl

Table 1
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$[Cu_2(C_{10}H_{10}BrNO_2)_2]$	$[Mn(C_{18}H_{16}Cl_2N_2O_2)(H_2O)_2]_2[Mn_2(C_{18}H_{16}Cl_2N_2O_2)_2(H_2O)_2](ClO_4)_4\cdot 2C_2H_6O$
M_r	639.28	2270.70
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	293
a, b, c (Å)	9.0043 (2), 10.2212 (2), 22.7814 (5)	14.126 (3), 19.394 (4), 17.020 (3)
β (°)	92.085 (1)	91.66 (3)
V (Å^3)	2095.29 (8)	4660.9 (16)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	5.87	0.96
Crystal size (mm)	0.45 × 0.34 × 0.21	0.71 × 0.14 × 0.08
Data collection		
Diffractometer	Bruker APEXII CCD area-detector	Bruker APEXII CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.120, 0.324	0.551, 0.928
No. of measured, independent and observed - $[I > 2\sigma(I)]$ reflections	35997, 4843, 4450	25449, 8761, 3921
R_{int}	0.023	0.111
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.651	0.609
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.052, 1.03	0.081, 0.188, 1.02
No. of reflections	4843	8761
No. of parameters	271	779
No. of restraints	0	718
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −0.32	0.32, −0.33

Computer programs: *APEX2* (Bruker, 2007), *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *SHELXTL* (Sheldrick, 2008).

groups, hydroxy groups and water ligands, and to 1.2 times the U_{eq} value of the parent C atom for all other H atoms. For weakly diffracting complex (2), the H atoms of the coordinated water molecules were located in difference Fourier maps and then refined using O—H and H···H distance restraints in order to maintain optimal geometry. The disordered 2-methylpropane-1,2-diamine fragment of the mononuclear cation, the ethanol solvent molecule and the two independent perchlorate counter-ions are each disordered over two unequally occupied orientations. During refinement, distance and similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, as well as to the O···O distances in the perchlorate anions and some nonbonded distances in the ethanol solvent molecule. Neighbouring atoms within and between each orientation of the disordered groups were restrained to have similar and pseudo-isotropic atomic displacement parameters.

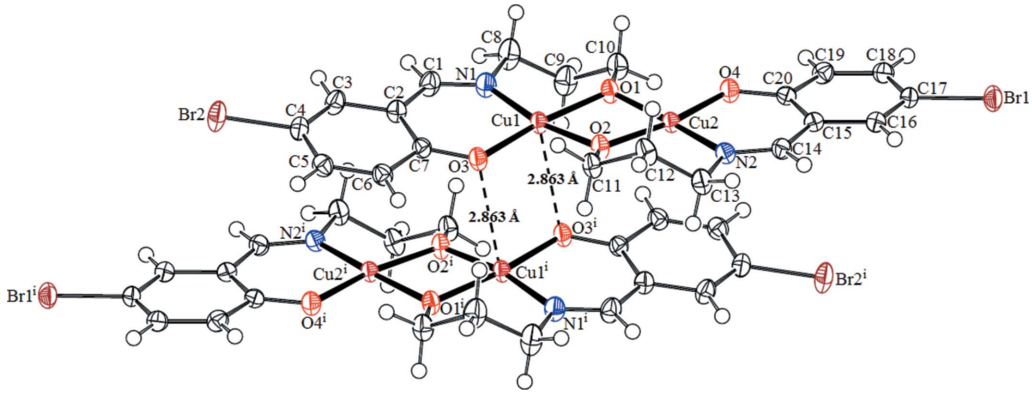


Figure 1
The molecular structure of complex (1), showing the atom-labelling scheme and weak Cu···O interactions (dashed lines) between dinuclear units. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, -y+1, -z+1$.]

3. Results and discussion

3.1. Crystal structures

The X-ray structure analysis of $[Cu_2(5\text{-BrL1})_2]$ (5-BrL1 is 4-bromo-2-{[(3-oxidopropyl)imino]methyl}phenol), (1), shows that each Schiff base ligand coordinates one Cu^{II} atom in a tridentate manner *via* phenolate and alkoxide O atoms and imine N atoms. Two Cu^{II} ions are bridged by alkoxide O atoms of the 'propanolamine' fragment (Fig. 1). The complex is a di-μ_2-alkoxide-bridged dinuclear Cu^{II} complex and each Cu^{II} atom has a four-coordinated square-planar environment. The coordination sphere around each Cu^{II} atom deviates slightly from planarity, with a Cu1—O1—Cu2—O2 torsion angle of −5.36 (5)° and a deviation of the Cu^{II} ions from the NO_3 coordination plane (atoms O1, O2, N2 and O4) of 0.025 Å. Selected bond lengths and angles are listed in Table 2 for complex (1). The intramolecular nonbonding Cu1···Cu2 distance of 3.0237 (3) Å is comparable with the values (in the range 2.994–3.023 Å) found in similar compounds (Yahsi & Kara, 2013; Bertrand & Kelley, 1970; Wang & Zheng, 2007; Yanagi & Minobe, 1987). Each dinuclear molecule is further linked into a discrete centrosymmetric tetranuclear dimer by a pair of long weak Cu···O interactions [$Cu1\cdots O3^{i}$ = 2.8631 (13) Å; symmetry code: (i) $-x, -y+1, -z+1$]. The $Cu1\cdots Cu1^{i}$ distance within this dimer is 3.4846 (3) Å (Fig. 1). If this weak Cu···O interaction is considered as part of the coordination geometry of the Cu^{II} ion, the geometry is best described as distorted square pyramidal.

The crystal packing diagram of the square-planar dinuclear Cu^{II} complex shows that neighbouring dimers are linked by nested zigzags through weak ligand–ligand interactions, with $C1\cdots H11A^{i}$ and $Br1\cdots H18^{ii}$ distances of 2.89 and 3.01 Å, respectively [symmetry code: (ii) $-x, -y+1, -z$]. There are also face-to-face π–π stacking interactions within the tetranuclear dimer between the benzene rings of the Schiff base ligands, with centroid–centroid distances between aromatic rings in the range 3.7334 (10)–4.5527 (9) Å. Hydrogen-bond geometry and the distances between ring centroids for complex (1) are given in Table 3. Neighbouring dimers are formed into three-dimensional networks which lie in the *ab* plane and stack along the *c* axis (Fig. 2), and the closest centroid–centroid distance of Cu1—O1—Cu2—O2 units is 5.2076 (6) Å (Macrae *et al.*, 2008).

The X-ray structural analysis shows that complex (2), represented as $[Mn(5\text{-ClL2})(H_2O)_2]_2[Mn_2(5\text{-ClL2})_2(H_2O)_2](ClO_4)_4\cdot 2C_2H_5OH$, contains a 2:1 ratio of mononuclear Mn^{III} $[Mn(5\text{-ClL2})(H_2O)_2]_2$ and di-μ_2-phenoxide-bridged dinuclear

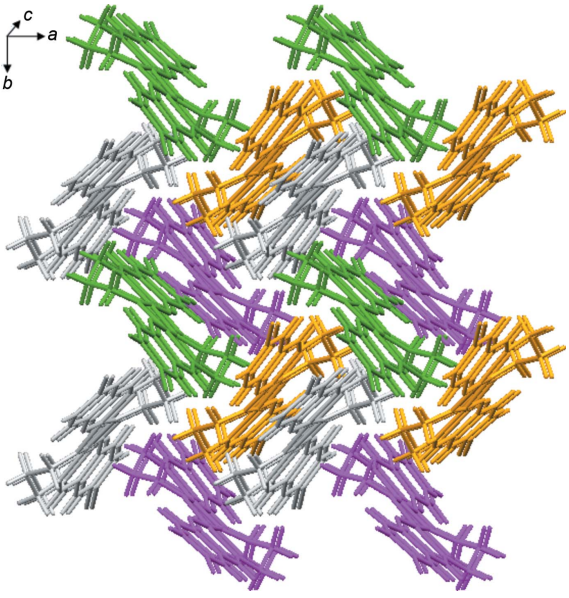


Figure 2
The molecular packing diagram of complex (1), viewed in the *ab* plane.

Table 2
Selected geometric parameters (Å, °) for (1).

Cu1—O1	1.9244 (13)	Cu2—O1	1.9253 (12)
Cu1—O2	1.9338 (12)	Cu2—O2	1.9170 (13)
Cu1—O3	1.9098 (13)	Cu2—O4	1.8905 (13)
Cu1—N1	1.9556 (16)	Cu2—N2	1.9350 (15)
O1—Cu1—O2	76.07 (5)	O3—Cu1—O2	93.48 (5)
O1—Cu1—N1	95.25 (6)	O3—Cu1—N1	95.10 (6)
O1—Cu2—N2	172.86 (6)	O4—Cu2—O1	91.24 (5)
O2—Cu2—O1	76.44 (5)	O4—Cu2—O2	167.67 (5)
O2—Cu1—N1	169.53 (6)	O4—Cu2—N2	95.22 (6)
O2—Cu2—N2	97.11 (6)	Cu1—O1—Cu2	103.52 (6)
O3—Cu1—O1	169.55 (5)	Cu2—O2—Cu1	103.48 (6)

Table 3
Hydrogen-bond geometry (Å, °) and centroid–centroid distances (Å) for complex (1).

*Cg*1 is the centroid of the Cu1/O3/C7/C2/C1/N1 ring, *Cg*2 is the centroid of the Cu2/O4/C20/C15/C14/N2 ring and *Cg*3 is the centroid of the C2–C7 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16···O1^{iii}	0.95	2.45	3.394 (2)	172
C10—H10*A*—O4	0.99	2.41	2.905 (2)	110
Centroid–centroid distances				
*Cg*1···*Cg*1^{i}			4.5527 (9)	
*Cg*2···*Cg*3^{i}			3.7334 (10)	

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

Table 4
Selected geometric parameters (Å, °) for (2).

Mn1—O1	1.851 (5)	Mn2—O4	1.880 (5)
Mn1—O2	1.895 (5)	Mn2—O5	1.873 (5)
Mn1—N1	1.977 (6)	Mn2—N3	1.969 (6)
Mn1—N2	1.955 (6)	Mn2—N4	1.964 (6)
Mn1—O3	2.221 (5)	Mn2—O6	2.270 (6)
Mn1—O2^{i}	2.425 (4)	Mn2—O7	2.241 (5)
O1—Mn1—O2	93.3 (2)	O4—Mn2—N3	94.5 (3)
O1—Mn1—N1	94.2 (2)	O4—Mn2—N4	175.2 (3)
O1—Mn1—N2	176.3 (2)	O4—Mn2—O7	90.2 (2)
O2—Mn1—N1	167.8 (2)	O5—Mn2—N3	173.8 (3)
O2—Mn1—N2	90.4 (2)	O5—Mn2—N4	93.0 (2)
O2—Mn1—O3	91.8 (2)	O5—Mn2—O4	91.7 (2)
O2—Mn1—O2^{i}	79.98 (18)	O5—Mn2—O7	89.2 (2)
N1—Mn1—O3	97.6 (2)	N3—Mn2—O6	89.6 (3)
O3—Mn1—O2^{i}	170.68 (17)	N4—Mn2—O7	90.9 (2)
Mn1—O2—Mn1^{i}	100.02 (18)	O7—Mn2—O6	177.3 (2)

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

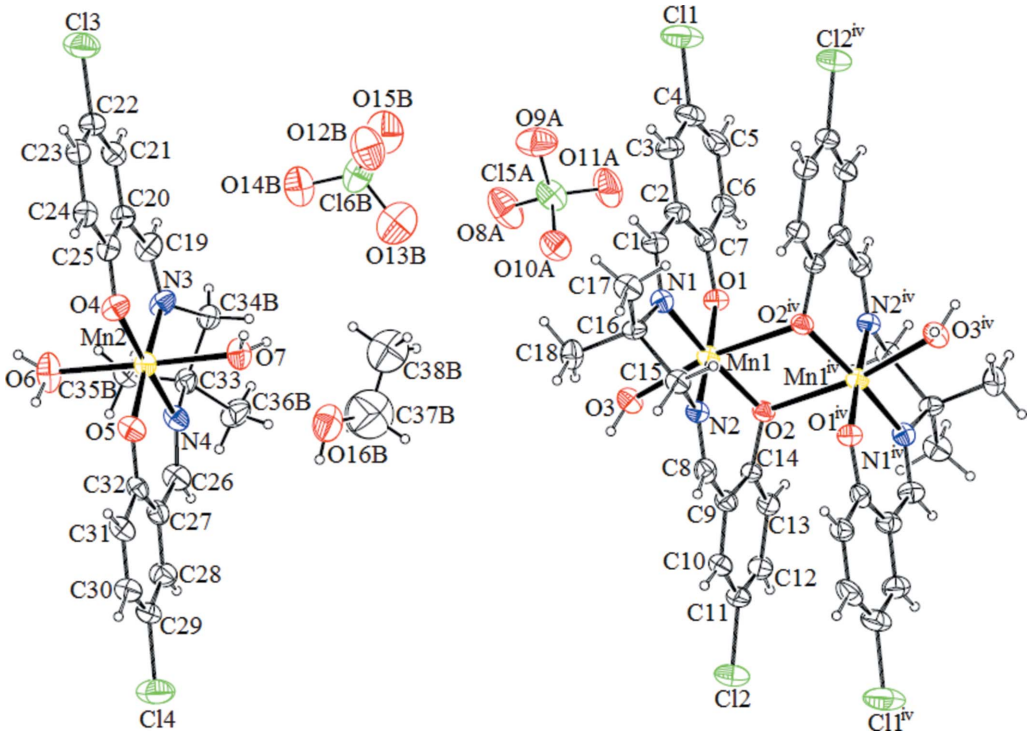


Figure 3
The unique species present in the structure of complex (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (iv) $-x+1, -y, -z+1$.]

Mn^{III} $[Mn_2(5\text{-ClL2})_2(H_2O)_2]$ unit with the latter sitting around an inversion centre. Each Mn^{III} ion is six-coordinated, with an environment that can be described as distorted octahedral, by an N_2O_2 donor set from the tetradentate Schiff base ligands in the equatorial plane and by axial O atoms (Fig. 3). The deviations of the Mn1 and Mn2 atoms from the N_2O_2 coordination planes are 0.082 and 0.012 Å, respectively. In the Mn_2O_2 bridging group, which is strictly planar with a torsion angle of 0° for Mn1—O2—$Mn1^{iv}$—$O2^{iv}$ due to the centre of inversion, the Mn1—O2—$Mn1^{iv}$ angle is 100.02 (18)° [symmetry code: (iv) $-x+1, -y, -z+1$]. The axial bonds to the water O atoms are longer than the equatorial Mn—O bond lengths due to Jahn–Teller distortion, as is usually observed for octahedral Mn^{III} ions (Table 4). The bond lengths and angles lie well within the range of corresponding values reported for other Mn^{III} complexes (Bermejo *et al.*, 1996; Yahsi & Kara, 2014; Lu *et al.*, 2006).

In the crystal structure of (2), one dinuclear and two mononuclear units are linked by hydrogen bonds to form a hydrogen-bonded linear chain along the *a* axis (Fig. 4*a*).

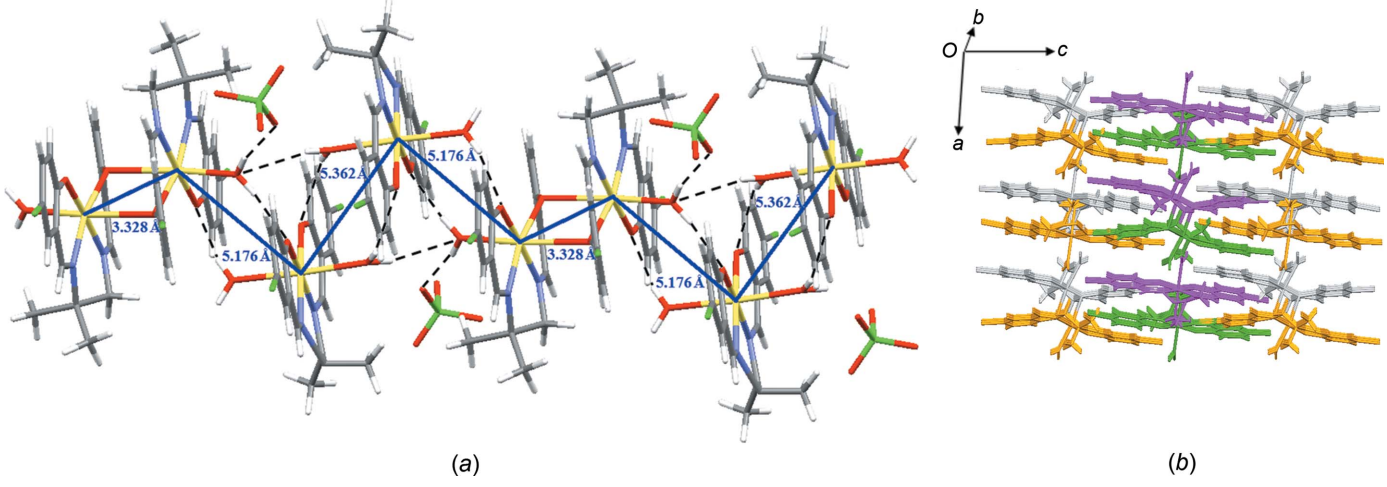


Figure 4
(*a*) A representation of the hydrogen-bonded (dashed lines) linear chain formed in complex (2). The dark-blue lines indicate the Mn···Mn distances within the chain. (*b*) The molecular packing diagram of complex (2), viewed in the *ac* plane. Ethanol solvent molecules and perchlorate counter-ions have been omitted for clarity.

Furthermore, there are also face-to-face π–π stacking interactions between the benzene rings of the Schiff base ligands, with centroid–centroid distances between the aromatic rings in the range 3.608 (4)–4.181 (5) Å (Table 5). The mononuclear and dinuclear units are linked by coordinated water molecules to form hydrogen bonds, with O3···O5^{v} = 2.781 (8) Å and O7···O1^{ix} = 2.915 (8) Å. The shortest nonbonding Mn···Mn separations are Mn1···Mn1^{iv} = 3.3277 (16) Å, Mn1^{v}···Mn2 = 5.1763 (19) Å and Mn2···Mn2^{vii} = 5.362 (2) Å (see Table 5 for symmetry codes). As shown in Fig. 4(*b*), the polymeric network lies in the *ac* plane and stacks along the *b* axis.

3.2. Magnetic properties

The variable-temperature magnetic susceptibilities for complexes (1) and (2) were measured between 2 and 300 K using a Cryogenic S600 SQUID magnetometer and are shown as $\chi_m T$ *versus* T plots in Fig. 5. The effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$ (Kahn, 1993), where χ_m is the molar susceptibility per monomeric unit and was set equal to M_m/H.

For complex (1), the $\chi_m T$ value at room temperature is 0.350 cm^3 K mol^{-1} (μ_{eff} = 1.66 μ_B), which is close to the spin-only value of 0.375 cm^3 K mol^{-1} (μ_{eff} = 1.73 μ_B) for independent Cu^{II} ($S = \frac{1}{2}$) ions with g = 2.00. Upon cooling, the $\chi_m T$ value decreases continuously to attain a minimum value of 0.0027 cm^3 K mol^{-1} at 2 K. This is a clear indication that a strong antiferromagnetic interaction operates between the two Cu^{II} ions. The experimental magnetic susceptibility data were analysed with the Bleaney–Bowers equation for dinuclear Cu^{II} complexes ($S_1 = S_2 = \frac{1}{2}$) based on the Heisenberg Hamiltonian ($H = -2JS_1S_2$), and considering the presence of some mononuclear impurities (ρ) and the temperature-independent paramagnetism (TIP) (Bleaney & Bowers, 1952). The best fit was obtained with a value of J = −351 cm^{-1}, g = 2.16, ρ = 0.0034 and TIP = 0.000033, with an $R = 5 \times 10^{-5}$ agreement factor $\{R = \Sigma[(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2/\Sigma[(\chi_m T)_{obs}]^2\}$, indicating that strong antiferromagnetic interactions exist between the Cu^{II} ions in the dinuclear entity; this is similar to values reported previously in the literature (Davis & Sinn, 1976; Zhu *et al.*, 2002; Karabach *et al.*, 2010).

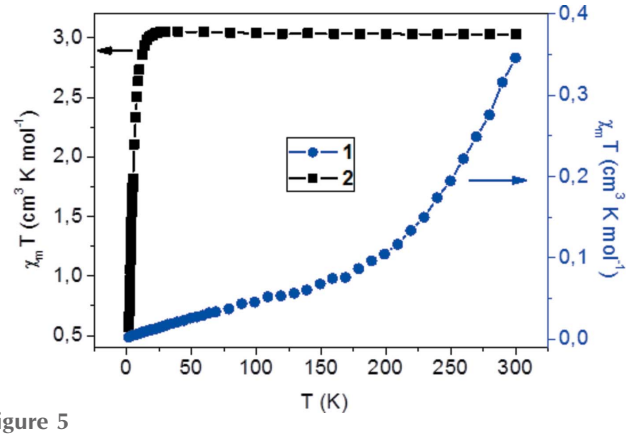


Figure 5
Temperature dependence of $\chi_m T$ for complexes (1) and (2).

For complex (2), the $\chi_m T$ value at room temperature is 3.03 cm^3 K mol^{-1} (μ_{eff} = 4.92 μ_B), which is close to the expected value of 3.00 cm^3 K mol^{-1} (μ_{eff} = 4.89 μ_B) for independent Mn^{III} (S = 2) ions with g = 2.00. Upon cooling, the $\chi_m T$ value remains almost constant until 20 K, then sharply decreases to a value of 0.57 cm^3 K mol^{-1} at 2 K. The drop in the $\chi_m T$ value below 20 K suggests the presence of magnetic anisotropy expected for Mn^{III} ions or intermolecular antiferromagnetic couplings (Mandal *et al.*, 2009). The experimental magnetic susceptibility data were analysed according to the equation for dinuclear Mn^{III} complexes ($S_1 = S_2 = 2$) based on the Heisenberg Hamiltonian ($H = -2JS_1S_2$) (Saha *et al.*, 2004). The best fit was obtained with a value of J = −0.93 cm^{-1} and g = 2.04, with an $R = 5.7 \times 10^{-4}$ agreement factor $\{R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calc}]2/\Sigma^2;[(\chi_M T)_{obs}]^2\}$, indicating that weak antiferromagnetic interactions exist between the Mn^{III} ions in the dinuclear cation; this is similar to values reported in the literature (Matsumoto *et al.*, 1989; Saha *et al.*, 2004; Yahsi & Kara, 2014).

The magneto-structural correlation including theoretical calculations of oxygen-bridged Cu^{II} and Mn^{III} complexes has been studied widely in the literature (Thompson *et al.*, 1996; Saha *et al.*, 2004). In dinuclear Cu^{II} and Mn^{III} complexes whose metal centres are doubly bridged by O atoms, different structural features were found to affect the strength of the magnetic super-exchange coupling constant, J, such as the geometry around the metal centres, the $M\cdots M$ (M = Cu and Mn) distance, the average M—O$_{bridge}$ bond lengths between the metal atom and the bridging O atoms, and the M—O$_{bridge}$—M bridging angle (Ray *et al.*, 2003; Saha *et al.*, 2004). However, the accidental orthogonality is associated with the bridging angle between the paramagnetic centres and thus the magnetic behaviour of the complexes will primarily be angle dependent (Thompson *et al.*, 1996). The alkoxide or phen-

Table 5
Hydrogen-bond geometry (Å, °) and centroid–centroid distances (Å) for complex (2).

*Cg*1 is the centroid of the Mn1/O1/C7/C2/C1/N1 ring, *Cg*2 is the centroid of the C2–C7 ring, *Cg*3 is the centroid of the C9–C14 ring, *Cg*4 is the centroid of the C20–C25 ring and *Cg*5 is the centroid of the C27—C32 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O5^{v}	0.84 (4)	1.98 (5)	2.781 (8)	158 (5)
O3—H3*B*···O10*A*^{vi}	0.84 (4)	2.23 (5)	3.016 (18)	157 (4)
O6—H6*B*···O4^{vii}	0.84 (3)	2.25 (3)	2.899 (8)	134 (3)
O6—H6*A*···O3^{viii}	0.84 (3)	2.33 (3)	3.139 (7)	164 (4)
O7—H7*B*···O1^{ix}	0.84 (8)	2.09 (7)	2.915 (8)	168 (7)
O7—H7*A*···O16*B*	0.84 (5)	2.33 (8)	2.731 (16)	110 (7)
C24—H24···O15*B*^{x}	0.93	2.43	3.19 (3)	139
C28—H28···O8*A*^{xi}	0.93	2.51	3.23 (2)	135
C31—H31···O10*A*^{xii}	0.93	2.43	3.34 (2)	169
Centroid–centroid distances				
*Cg*1···*Cg*3^{iv}			3.608 (4)	
*Cg*2···*Cg*3^{iv}			3.697 (4)	
*Cg*2···*Cg*4^{v}			3.636 (5)	
*Cg*3···*Cg*5^{v}			4.181 (5)	
*Cg*4···*Cg*5^{vii}			3.860 (5)	

Symmetry codes: (iv) $-x+1, -y, -z+1$; (v) $x, y-1, z$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+2, -y+2, -z+1$; (viii) $-x+2, -y+1, -z+1$; (ix) $x, y+1, z$; (x) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (xi) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (xii) $-x+1, -y+2, -z+1$.

oxide-bridged species exhibit an antiferromagnetic interaction when the angle is larger than 98° and the antiferromagnetic character increases with increasing angle (Ray *et al.*, 2003; Karabach *et al.*, 2010). In our case, the observed strong antiferromagnetic interaction in complex (1) is expected considering the larger $Cu-O_{alkoxide}-Cu$ bridging angles [103.48 (6)°]. On the other hand, a weak antiferromagnetic interaction is expected considering the low $Mn-O_{phenoxide}-Mn$ bridging angle [100.02 (18)°] for complex (2).

4. Conclusions

The synthesis and structural characterization of two novel dioxygen-bridged copper(II) and manganese(III) Schiff base complexes have been reported, together with an investigation into their magnetic properties. The X-ray structure analyses show that two Cu^{II} ions are bridged by the alkoxide O atoms of the 'propanolamine' fragment in the dinuclear unit of complex (1). The intramolecular nonbonding Cu1···Cu1 distance is 3.0237 (3) Å. The dinuclear Cu^{II} units are further linked into tetranuclear dimers by a weak Cu···O coordination bond. X-ray structure analysis shows that complex (2) has dinuclear Mn^{III} units about an inversion centre, as well as mononuclear Mn^{III} complex cations. In the dinuclear units, the Mn^{III} ions are surrounded by an N_2O_2 donor set of the tetradentate Schiff base ligands in the equatorial plane and by axial O atoms. One dinuclear and two mononuclear units are linked by hydrogen bonds to form a hydrogen-bonded linear chain. The temperature-dependent magnetic susceptibilities for (1) and (2) in the solid state were measured over the temperature range 2–300 K. Magnetic studies reveal that the title dioxygen-bridged complexes exhibit an antiferromagnetic interaction between two Cu^{II} ions for complex (1) and between two Mn^{III} ions for complex (2) *via* the bridging O atoms of the Schiff base ligands.

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X-ray characterization and magnetic properties of dioxygen-bridged Cu^{II} and Mn^{III} Schiff base complexes

Yasemin Yahsi

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) for (1); *SHELXL2014* (Sheldrick, 2015) for (2). For both compounds, molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(1) Bis(*μ*-4-bromo-2-{[(3-oxidopropyl)imino]methyl}phenolato)dicopper(II)

Crystal data

$[Cu_2(C_{10}H_{10}BrNO_2)_2]$
M_r = 639.28
Monoclinic, $P2_1/n$
a = 9.0043 (2) Å
b = 10.2212 (2) Å
c = 22.7814 (5) Å
β = 92.085 (1)°
V = 2095.29 (8) Å^3
Z = 4
$F(000)$ = 1256
D_x = 2.027 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9935 reflections
θ = 2.4–27.6°
μ = 5.87 mm^{-1}
T = 100 K
Block, green
0.45 × 0.34 × 0.21 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2007)
T_{min} = 0.120, T_{max} = 0.324
35997 measured reflections
4843 independent reflections
4450 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.6°, θ_{min} = 1.8°
h = −11→11
k = −13→13
l = −29→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.052
S = 1.03
4843 reflections
271 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 1.5617P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-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. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.16334 (2)	0.336543 (19)	0.030007 (8)	0.02506 (6)
Br2	0.04394 (2)	0.88982 (2)	0.762701 (9)	0.02814 (6)
Cu1	0.05380 (2)	0.63650 (2)	0.460192 (9)	0.01638 (6)
Cu2	0.12915 (2)	0.52892 (2)	0.341273 (9)	0.01537 (6)
O2	0.18938 (14)	0.51891 (13)	0.42273 (5)	0.0190 (3)
O1	0.00727 (14)	0.65831 (12)	0.37766 (5)	0.0181 (3)
C10	−0.1159 (2)	0.7236 (2)	0.35059 (8)	0.0229 (4)
H10A	−0.1576	0.6695	0.3179	0.027*
H10B	−0.0827	0.8078	0.3340	0.027*
C15	0.18423 (19)	0.41592 (17)	0.21023 (8)	0.0173 (3)
C14	0.2771 (2)	0.36885 (18)	0.25848 (8)	0.0188 (4)
H14	0.3516	0.3071	0.2494	0.023*
O3	0.12733 (14)	0.59354 (13)	0.53749 (6)	0.0192 (3)
N2	0.26911 (17)	0.40224 (15)	0.31282 (7)	0.0176 (3)
C3	−0.0041 (2)	0.83912 (18)	0.64133 (9)	0.0218 (4)
H3	−0.0679	0.9130	0.6428	0.026*
C2	0.0119 (2)	0.77242 (18)	0.58767 (8)	0.0191 (4)
N1	−0.07829 (18)	0.77575 (16)	0.48557 (7)	0.0214 (3)
C20	0.06881 (19)	0.50932 (17)	0.21698 (8)	0.0170 (3)
C17	0.1268 (2)	0.40594 (18)	0.10609 (8)	0.0189 (4)
C4	0.0713 (2)	0.79846 (18)	0.69122 (8)	0.0203 (4)
C18	0.0111 (2)	0.49481 (18)	0.11173 (8)	0.0190 (4)
H18	−0.0466	0.5218	0.0781	0.023*
C5	0.1644 (2)	0.68899 (18)	0.69030 (8)	0.0198 (4)
H5	0.2158	0.6608	0.7252	0.024*
C19	−0.0192 (2)	0.54332 (18)	0.16634 (8)	0.0195 (4)
H19	−0.1011	0.6010	0.1702	0.023*
C13	0.3784 (2)	0.34272 (19)	0.35488 (8)	0.0228 (4)
H13A	0.4639	0.3097	0.3331	0.027*
H13B	0.3319	0.2671	0.3742	0.027*
C16	0.2120 (2)	0.36551 (18)	0.15371 (8)	0.0188 (4)
H16	0.2896	0.3039	0.1489	0.023*
C7	0.10711 (19)	0.66146 (17)	0.58503 (8)	0.0169 (3)
C9	−0.2356 (2)	0.7493 (2)	0.39461 (9)	0.0288 (4)
H9A	−0.3234	0.7883	0.3739	0.035*

H9B	−0.2666	0.6650	0.4118	0.035*
C1	−0.0771 (2)	0.81953 (19)	0.53844 (9)	0.0225 (4)
H1	−0.1419	0.8906	0.5458	0.027*
C12	0.4345 (2)	0.4389 (2)	0.40165 (8)	0.0220 (4)
H12A	0.5262	0.4035	0.4210	0.026*
H12B	0.4605	0.5223	0.3824	0.026*
C6	0.1810 (2)	0.62245 (18)	0.63841 (8)	0.0188 (4)
H6	0.2439	0.5479	0.6383	0.023*
C11	0.3221 (2)	0.46629 (19)	0.44810 (8)	0.0202 (4)
H11A	0.2995	0.3841	0.4689	0.024*
H11B	0.3651	0.5288	0.4772	0.024*
C8	−0.1833 (3)	0.8396 (2)	0.44329 (9)	0.0308 (5)
H8A	−0.1344	0.9166	0.4260	0.037*
H8B	−0.2705	0.8711	0.4645	0.037*
O4	0.04083 (14)	0.56615 (13)	0.26658 (6)	0.0204 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03541 (11)	0.02557 (10)	0.01405 (10)	0.00466 (8)	−0.00131 (8)	−0.00297 (7)
Br2	0.03430 (11)	0.03154 (11)	0.01818 (10)	0.00891 (8)	−0.00451 (8)	−0.00987 (8)
Cu1	0.01757 (11)	0.01904 (11)	0.01257 (11)	0.00489 (8)	0.00107 (8)	−0.00069 (8)
Cu2	0.01586 (10)	0.01750 (11)	0.01280 (11)	0.00238 (8)	0.00127 (8)	−0.00047 (8)
O2	0.0177 (6)	0.0257 (7)	0.0135 (6)	0.0067 (5)	−0.0003 (5)	−0.0019 (5)
O1	0.0185 (6)	0.0229 (6)	0.0129 (6)	0.0057 (5)	−0.0005 (5)	−0.0011 (5)
C10	0.0228 (9)	0.0278 (10)	0.0178 (9)	0.0092 (7)	−0.0025 (7)	−0.0006 (7)
C15	0.0192 (8)	0.0162 (8)	0.0166 (9)	−0.0015 (6)	0.0008 (7)	−0.0001 (7)
C14	0.0205 (9)	0.0179 (8)	0.0181 (9)	0.0025 (7)	0.0039 (7)	0.0001 (7)
O3	0.0223 (6)	0.0215 (6)	0.0138 (6)	0.0066 (5)	0.0022 (5)	0.0001 (5)
N2	0.0179 (7)	0.0193 (7)	0.0157 (7)	0.0021 (6)	0.0014 (6)	0.0008 (6)
C3	0.0238 (9)	0.0207 (9)	0.0205 (10)	0.0054 (7)	−0.0015 (8)	−0.0049 (7)
C2	0.0197 (8)	0.0208 (9)	0.0168 (9)	0.0014 (7)	0.0000 (7)	−0.0017 (7)
N1	0.0240 (8)	0.0226 (8)	0.0175 (8)	0.0076 (6)	−0.0020 (6)	−0.0008 (6)
C20	0.0179 (8)	0.0167 (8)	0.0166 (9)	−0.0028 (6)	0.0029 (7)	0.0000 (7)
C17	0.0247 (9)	0.0180 (8)	0.0142 (8)	−0.0035 (7)	0.0021 (7)	−0.0024 (7)
C4	0.0223 (9)	0.0220 (9)	0.0166 (9)	−0.0001 (7)	0.0015 (7)	−0.0046 (7)
C18	0.0207 (8)	0.0192 (8)	0.0168 (9)	−0.0030 (7)	−0.0038 (7)	0.0009 (7)
C5	0.0194 (8)	0.0227 (9)	0.0170 (9)	−0.0001 (7)	−0.0021 (7)	0.0008 (7)
C19	0.0194 (8)	0.0188 (8)	0.0203 (9)	0.0004 (7)	−0.0015 (7)	−0.0009 (7)
C13	0.0250 (9)	0.0259 (10)	0.0174 (9)	0.0101 (7)	0.0006 (7)	0.0003 (7)
C16	0.0226 (9)	0.0170 (8)	0.0169 (9)	0.0003 (7)	0.0016 (7)	−0.0004 (7)
C7	0.0164 (8)	0.0179 (8)	0.0164 (9)	−0.0004 (6)	0.0032 (7)	−0.0008 (7)
C9	0.0278 (10)	0.0328 (11)	0.0257 (11)	0.0103 (8)	−0.0029 (8)	−0.0048 (8)
C1	0.0244 (9)	0.0221 (9)	0.0210 (10)	0.0084 (7)	−0.0006 (8)	−0.0031 (7)
C12	0.0171 (8)	0.0326 (10)	0.0163 (9)	0.0062 (7)	0.0000 (7)	0.0019 (8)
C6	0.0184 (8)	0.0203 (9)	0.0179 (9)	0.0024 (7)	0.0024 (7)	0.0008 (7)
C11	0.0190 (8)	0.0263 (9)	0.0153 (9)	0.0068 (7)	−0.0002 (7)	0.0002 (7)
C8	0.0378 (12)	0.0331 (11)	0.0208 (10)	0.0189 (9)	−0.0071 (9)	−0.0041 (8)

O4	0.0230 (6)	0.0224 (6)	0.0158 (6)	0.0051 (5)	0.0008 (5)	−0.0011 (5)

Geometric parameters (Å, º)

Br1—C17	1.9124 (18)	N1—C8	1.477 (2)
Br2—C4	1.9010 (18)	C20—O4	1.303 (2)
Cu1—O1	1.9244 (13)	C20—C19	1.419 (3)
Cu1—O2	1.9338 (12)	C17—C16	1.370 (3)
Cu1—O3	1.9098 (13)	C17—C18	1.392 (3)
Cu1—N1	1.9556 (16)	C4—C5	1.399 (3)
Cu2—O1	1.9253 (12)	C18—C19	1.376 (3)
Cu2—O2	1.9170 (13)	C18—H18	0.9500
Cu2—O4	1.8905 (13)	C5—C6	1.377 (3)
Cu2—N2	1.9350 (15)	C5—H5	0.9500
O2—C11	1.415 (2)	C19—H19	0.9500
O1—C10	1.416 (2)	C13—C12	1.522 (3)
C10—C9	1.521 (3)	C13—H13A	0.9900
C10—H10A	0.9900	C13—H13B	0.9900
C10—H10B	0.9900	C16—H16	0.9500
C15—C16	1.418 (3)	C7—C6	1.422 (3)
C15—C20	1.424 (2)	C9—C8	1.505 (3)
C15—C14	1.439 (3)	C9—H9A	0.9900
C14—N2	1.289 (2)	C9—H9B	0.9900
C14—H14	0.9500	C1—H1	0.9500
O3—C7	1.305 (2)	C12—C11	1.516 (2)
N2—C13	1.479 (2)	C12—H12A	0.9900
C3—C4	1.367 (3)	C12—H12B	0.9900
C3—C2	1.412 (3)	C6—H6	0.9500
C3—H3	0.9500	C11—H11A	0.9900
C2—C7	1.424 (2)	C11—H11B	0.9900
C2—C1	1.438 (3)	C8—H8A	0.9900
N1—C1	1.285 (2)	C8—H8B	0.9900
O1—Cu1—O2	76.07 (5)	C19—C18—C17	119.51 (17)
O1—Cu1—N1	95.25 (6)	C19—C18—H18	120.2
O1—Cu2—N2	172.86 (6)	C17—C18—H18	120.2
O2—Cu2—O1	76.44 (5)	C6—C5—C4	119.44 (17)
O2—Cu1—N1	169.53 (6)	C6—C5—H5	120.3
O2—Cu2—N2	97.11 (6)	C4—C5—H5	120.3
O3—Cu1—O1	169.55 (5)	C18—C19—C20	121.57 (17)
O3—Cu1—O2	93.48 (5)	C18—C19—H19	119.2
O3—Cu1—N1	95.10 (6)	C20—C19—H19	119.2
O4—Cu2—O1	91.24 (5)	N2—C13—C12	112.54 (15)
O4—Cu2—O2	167.67 (5)	N2—C13—H13A	109.1
O4—Cu2—N2	95.22 (6)	C12—C13—H13A	109.1
C11—O2—Cu2	128.37 (11)	N2—C13—H13B	109.1
C11—O2—Cu1	126.41 (11)	C12—C13—H13B	109.1
C10—O1—Cu1	128.26 (11)	H13A—C13—H13B	107.8

C10—O1—Cu2	125.87 (11)	C17—C16—C15	119.82 (17)
Cu1—O1—Cu2	103.52 (6)	C17—C16—H16	120.1
Cu2—O2—Cu1	103.48 (6)	C15—C16—H16	120.1
O1—C10—C9	110.88 (15)	O3—C7—C6	119.06 (16)
O1—C10—H10A	109.5	O3—C7—C2	124.14 (17)
C9—C10—H10A	109.5	C6—C7—C2	116.79 (16)
O1—C10—H10B	109.5	C8—C9—C10	112.41 (19)
C9—C10—H10B	109.5	C8—C9—H9A	109.1
H10A—C10—H10B	108.1	C10—C9—H9A	109.1
C16—C15—C20	119.71 (16)	C8—C9—H9B	109.1
C16—C15—C14	117.08 (16)	C10—C9—H9B	109.1
C20—C15—C14	123.21 (17)	H9A—C9—H9B	107.9
N2—C14—C15	126.44 (17)	N1—C1—C2	126.88 (17)
N2—C14—H14	116.8	N1—C1—H1	116.6
C15—C14—H14	116.8	C2—C1—H1	116.6
C7—O3—Cu1	126.08 (11)	C11—C12—C13	113.27 (16)
C14—N2—C13	117.01 (15)	C11—C12—H12A	108.9
C14—N2—Cu2	123.97 (13)	C13—C12—H12A	108.9
C13—N2—Cu2	118.97 (12)	C11—C12—H12B	108.9
C4—C3—C2	120.64 (17)	C13—C12—H12B	108.9
C4—C3—H3	119.7	H12A—C12—H12B	107.7
C2—C3—H3	119.7	C5—C6—C7	122.29 (17)
C3—C2—C7	120.12 (17)	C5—C6—H6	118.9
C3—C2—C1	116.24 (17)	C7—C6—H6	118.9
C7—C2—C1	123.58 (17)	O2—C11—C12	111.11 (15)
C1—N1—C8	116.17 (16)	O2—C11—H11A	109.4
C1—N1—Cu1	123.12 (13)	C12—C11—H11A	109.4
C8—N1—Cu1	120.69 (13)	O2—C11—H11B	109.4
O4—C20—C19	118.42 (16)	C12—C11—H11B	109.4
O4—C20—C15	123.88 (16)	H11A—C11—H11B	108.0
C19—C20—C15	117.70 (16)	N1—C8—C9	112.67 (17)
C16—C17—C18	121.57 (17)	N1—C8—H8A	109.1
C16—C17—Br1	119.73 (14)	C9—C8—H8A	109.1
C18—C17—Br1	118.68 (14)	N1—C8—H8B	109.1
C3—C4—C5	120.71 (17)	C9—C8—H8B	109.1
C3—C4—Br2	119.12 (14)	H8A—C8—H8B	107.8
C5—C4—Br2	120.15 (14)	C20—O4—Cu2	127.04 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16···O1^{i}	0.95	2.45	3.394 (2)	172
C10—H10*A*···O4	0.99	2.41	2.905 (2)	110

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

(2) Bis(diaqua{4,4′-dichloro-2,2′-[(1,1-dimethylethane-1,2-diyl)bis(nitrilomethanylylidene)]diphenolato}manganese(III)) bis{μ-4,4′-dichloro-2,2′-[(1,1-dimethylethane-1,2-diyl)bis(nitrilomethanylylidene)]diphenolato}bis[aquamanganese(III)] tetrakis(perchlorate) ethanol disolvate

Crystal data

$[Mn(C_{18}H_{16}Cl_2N_2O_2)(H_2O)_2]_2[Mn_2(C_{18}H_{16}Cl_2N_2O_2)_2(H_2O)_2](ClO_4)_4\cdot 2C_2H_6O$
$M_r = 2270.70$
Monoclinic, $P2_1/n$
$a = 14.126$ (3) Å
$b = 19.394$ (4) Å
$c = 17.020$ (3) Å
$\beta = 91.66$ (3)°
$V = 4660.9$ (16) Å^3
$Z = 2$
$F(000) = 2320$
$D_x = 1.618$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 18864 reflections
$\theta = 1.2$–$26.1°$
$\mu = 0.96$ mm^{-1}
$T = 293$ K
Prismatic stick, brown
0.71 × 0.14 × 0.08 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2007)
$T_{min} = 0.551$, $T_{max} = 0.928$
25449 measured reflections
8761 independent reflections
3921 reflections with $I > 2\sigma(I)$
$R_{int} = 0.111$
$\theta_{max} = 25.7°$, $\theta_{min} = 1.6°$
$h = -17\rightarrow15$
$k = -23\rightarrow22$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.188$
$S = 1.02$
8761 reflections
779 parameters
718 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
$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-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. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.60282 (7)	0.04061 (6)	0.51427 (6)	0.0537 (3)	
Mn2	0.89784 (8)	0.88349 (6)	0.49822 (6)	0.0573 (3)	

N1	0.6210 (4)	0.1205 (3)	0.5853 (3)	0.0554 (15)
N2	0.5566 (4)	0.1123 (3)	0.4421 (3)	0.0544 (14)
N3	0.9319 (5)	0.8134 (3)	0.5778 (4)	0.0728 (18)
N4	0.9094 (4)	0.8030 (3)	0.4291 (4)	0.0683 (17)
O1	0.6483 (3)	−0.0228 (3)	0.5874 (3)	0.0620 (13)
O2	0.5589 (3)	−0.0286 (2)	0.4436 (2)	0.0564 (12)
O3	0.7418 (3)	0.0460 (3)	0.4567 (3)	0.0683 (14)
H3B	0.755 (5)	0.0692 (17)	0.417 (2)	0.102*
H3A	0.772 (4)	0.0089 (15)	0.453 (3)	0.102*
O4	0.8916 (4)	0.9561 (3)	0.5711 (3)	0.0753 (15)
O5	0.8670 (4)	0.9427 (3)	0.4144 (3)	0.0710 (14)
Cl1	0.7021 (2)	0.0044 (2)	0.92858 (14)	0.1476 (13)
Cl2	0.5916 (2)	−0.01498 (18)	0.10161 (13)	0.1290 (11)
Cl3	0.9666 (2)	0.95883 (17)	0.91094 (14)	0.1278 (10)
Cl4	0.8513 (3)	0.89463 (17)	0.07437 (14)	0.1330 (11)
C1	0.6425 (5)	0.1150 (4)	0.6607 (4)	0.0608 (19)
H1	0.6471	0.1553	0.6901	0.073*
C2	0.6592 (5)	0.0512 (5)	0.7002 (4)	0.064 (2)
C3	0.6723 (5)	0.0560 (5)	0.7836 (5)	0.079 (3)
H3	0.6698	0.0987	0.8082	0.095*
C4	0.6885 (6)	−0.0018 (7)	0.8268 (5)	0.089 (3)
C5	0.6947 (6)	−0.0660 (6)	0.7912 (5)	0.089 (3)
H5	0.7070	−0.1051	0.8214	0.107*
C6	0.6824 (5)	−0.0717 (5)	0.7102 (4)	0.069 (2)
H6	0.6871	−0.1145	0.6861	0.083*
C7	0.6633 (5)	−0.0137 (4)	0.6655 (4)	0.0578 (19)
C8	0.5453 (5)	0.1045 (4)	0.3657 (5)	0.063 (2)
H8	0.5255	0.1421	0.3356	0.076*
C9	0.5622 (5)	0.0405 (5)	0.3272 (4)	0.061 (2)
C10	0.5680 (5)	0.0420 (5)	0.2442 (4)	0.072 (2)
H10	0.5596	0.0835	0.2174	0.086*
C11	0.5859 (6)	−0.0175 (6)	0.2032 (4)	0.078 (3)
C12	0.6013 (6)	−0.0784 (6)	0.2415 (5)	0.081 (3)
H12	0.6173	−0.1176	0.2133	0.097*
C13	0.5932 (5)	−0.0822 (4)	0.3235 (4)	0.066 (2)
H13	0.6010	−0.1240	0.3496	0.080*
C14	0.5734 (5)	−0.0228 (4)	0.3648 (4)	0.0542 (18)
C15	0.5358 (5)	0.1777 (4)	0.4807 (4)	0.0605 (19)
H15A	0.4725	0.1764	0.5012	0.073*
H15B	0.5387	0.2151	0.4430	0.073*
C16	0.6089 (5)	0.1897 (4)	0.5482 (4)	0.0573 (18)
C17	0.5733 (6)	0.2450 (4)	0.6022 (5)	0.078 (2)
H17A	0.5529	0.2842	0.5717	0.117*
H17B	0.6233	0.2586	0.6384	0.117*
H17C	0.5210	0.2275	0.6310	0.117*
C18	0.7046 (6)	0.2116 (4)	0.5155 (5)	0.081 (2)
H18A	0.7306	0.1741	0.4861	0.122*
H18B	0.7474	0.2234	0.5582	0.122*

H18C	0.6956	0.2508	0.4817	0.122*	
C19	0.9467 (6)	0.8288 (5)	0.6502 (6)	0.085 (3)	
H19	0.9660	0.7923	0.6822	0.102*	
C20	0.9381 (5)	0.8937 (4)	0.6894 (4)	0.0619 (19)	
C21	0.9570 (6)	0.8962 (5)	0.7706 (5)	0.078 (2)	
H21	0.9776	0.8571	0.7979	0.093*	
C22	0.9443 (6)	0.9570 (6)	0.8087 (5)	0.080 (2)	
C23	0.9168 (6)	1.0155 (5)	0.7722 (5)	0.077 (2)	
H23	0.9090	1.0558	0.8009	0.093*	
C24	0.9004 (5)	1.0152 (4)	0.6922 (5)	0.068 (2)	
H24	0.8829	1.0557	0.6666	0.081*	
C25	0.9100 (5)	0.9539 (4)	0.6487 (5)	0.066 (2)	
C26	0.9036 (6)	0.8048 (4)	0.3523 (5)	0.079 (2)	
H26	0.9134	0.7637	0.3256	0.095*	
C27	0.8833 (5)	0.8646 (4)	0.3064 (4)	0.063 (2)	
C28	0.8799 (6)	0.8537 (5)	0.2259 (5)	0.082 (2)	
H28	0.8930	0.8103	0.2056	0.098*	
C29	0.8570 (6)	0.9075 (5)	0.1761 (4)	0.079 (3)	
C30	0.8389 (6)	0.9718 (5)	0.2052 (5)	0.078 (2)	
H30	0.8238	1.0076	0.1708	0.093*	
C31	0.8429 (5)	0.9838 (5)	0.2848 (5)	0.071 (2)	
H31	0.8311	1.0277	0.3041	0.085*	
C32	0.8650 (5)	0.9291 (4)	0.3374 (4)	0.0573 (19)	
C33A	0.9614 (12)	0.7450 (6)	0.5419 (9)	0.060 (4)	0.488 (13)
C36A	0.9347 (13)	0.6860 (9)	0.5960 (9)	0.084 (6)	0.488 (13)
H36A	0.8755	0.6963	0.6197	0.126*	0.488 (13)
H36B	0.9830	0.6804	0.6363	0.126*	0.488 (13)
H36C	0.9286	0.6442	0.5660	0.126*	0.488 (13)
C35A	1.0655 (14)	0.7374 (18)	0.5234 (15)	0.093 (8)	0.488 (13)
H35A	1.1033	0.7428	0.5708	0.139*	0.488 (13)
H35B	1.0827	0.7720	0.4861	0.139*	0.488 (13)
H35C	1.0762	0.6925	0.5016	0.139*	0.488 (13)
C34A	0.9011 (14)	0.7356 (6)	0.4662 (10)	0.064 (5)	0.488 (13)
H34A	0.9264	0.6995	0.4335	0.077*	0.488 (13)
H34B	0.8359	0.7250	0.4776	0.077*	0.488 (13)
C33B	0.9521 (14)	0.7372 (8)	0.4771 (11)	0.065 (5)	0.512 (13)
C36B	0.9160 (14)	0.6722 (9)	0.4363 (10)	0.100 (7)	0.512 (13)
H36D	0.9236	0.6336	0.4712	0.149*	0.512 (13)
H36E	0.9514	0.6643	0.3898	0.149*	0.512 (13)
H36F	0.8502	0.6777	0.4220	0.149*	0.512 (13)
C35B	1.0608 (14)	0.7392 (15)	0.4857 (12)	0.072 (6)	0.512 (13)
H35D	1.0876	0.7427	0.4346	0.109*	0.512 (13)
H35E	1.0831	0.6979	0.5111	0.109*	0.512 (13)
H35F	1.0797	0.7785	0.5167	0.109*	0.512 (13)
C34B	0.9085 (14)	0.7424 (9)	0.5602 (10)	0.071 (5)	0.512 (13)
H34C	0.8406	0.7347	0.5583	0.085*	0.512 (13)
H34D	0.9384	0.7108	0.5974	0.085*	0.512 (13)
Cl6A	0.6513 (16)	0.7253 (10)	0.7491 (12)	0.128 (7)	0.43 (3)

O12A	0.7325 (16)	0.7630 (15)	0.7680 (17)	0.131 (10)	0.43 (3)
O13A	0.5802 (14)	0.7682 (11)	0.717 (2)	0.137 (9)	0.43 (3)
O14A	0.619 (2)	0.6869 (15)	0.8136 (15)	0.132 (10)	0.43 (3)
O15A	0.672 (3)	0.6743 (12)	0.6892 (16)	0.205 (12)	0.43 (3)
Cl6B	0.6451 (12)	0.7348 (8)	0.7472 (10)	0.123 (5)	0.57 (3)
O12B	0.5857 (15)	0.7835 (10)	0.7791 (17)	0.161 (8)	0.57 (3)
O13B	0.599 (2)	0.7030 (18)	0.6827 (12)	0.221 (11)	0.57 (3)
O14B	0.7364 (14)	0.7549 (14)	0.7297 (17)	0.146 (8)	0.57 (3)
O15B	0.652 (2)	0.6748 (13)	0.8005 (17)	0.157 (9)	0.57 (3)
Cl5A	0.2133 (8)	0.8144 (6)	0.7192 (7)	0.097 (3)	0.75 (2)
O8A	0.3081 (9)	0.8034 (11)	0.7021 (11)	0.156 (7)	0.75 (2)
O9A	0.2064 (12)	0.8563 (7)	0.7876 (6)	0.143 (6)	0.75 (2)
O10A	0.1693 (14)	0.8528 (9)	0.6537 (9)	0.102 (6)	0.75 (2)
O11A	0.1630 (9)	0.7540 (6)	0.7290 (10)	0.146 (6)	0.75 (2)
Cl5B	0.208 (2)	0.8058 (18)	0.7032 (18)	0.093 (7)	0.25 (2)
O8B	0.150 (3)	0.813 (3)	0.768 (2)	0.148 (14)	0.25 (2)
O9B	0.189 (3)	0.7412 (15)	0.667 (3)	0.148 (14)	0.25 (2)
O10B	0.304 (3)	0.809 (3)	0.735 (3)	0.129 (15)	0.25 (2)
O11B	0.192 (4)	0.856 (2)	0.646 (2)	0.081 (13)	0.25 (2)
O16A	0.6738 (16)	0.7300 (11)	0.5408 (14)	0.167 (9)	0.454 (12)
H16A	0.6857	0.7278	0.5882	0.250*	0.454 (12)
C38A	0.682 (4)	0.6168 (15)	0.485 (3)	0.262 (18)	0.454 (12)
H38A	0.7014	0.5857	0.5260	0.392*	0.454 (12)
H38B	0.7371	0.6377	0.4628	0.392*	0.454 (12)
H38C	0.6477	0.5919	0.4444	0.392*	0.454 (12)
C37A	0.621 (2)	0.6706 (19)	0.517 (3)	0.243 (17)	0.454 (12)
H37A	0.5742	0.6839	0.4769	0.292*	0.454 (12)
H37B	0.5884	0.6523	0.5612	0.292*	0.454 (12)
O16B	0.6680 (9)	0.7576 (8)	0.4231 (9)	0.136 (6)	0.546 (12)
H16B	0.6744	0.7651	0.3761	0.204*	0.546 (12)
C38B	0.640 (3)	0.6679 (13)	0.5170 (17)	0.194 (13)	0.546 (12)
H38D	0.6316	0.6189	0.5211	0.291*	0.546 (12)
H38E	0.6940	0.6818	0.5487	0.291*	0.546 (12)
H38F	0.5845	0.6909	0.5350	0.291*	0.546 (12)
C37B	0.655 (3)	0.6863 (10)	0.4352 (16)	0.279 (15)	0.546 (12)
H37C	0.7101	0.6618	0.4171	0.335*	0.546 (12)
H37D	0.6007	0.6710	0.4035	0.335*	0.546 (12)
O6	1.0535 (4)	0.9097 (3)	0.4871 (4)	0.113 (2)	
H6A	1.1061 (16)	0.916 (3)	0.5101 (19)	0.169*	
H6B	1.052 (3)	0.9369 (16)	0.4487 (15)	0.169*	
O7	0.7432 (4)	0.8624 (3)	0.5121 (4)	0.0834 (16)	
H7A	0.728 (6)	0.8232 (16)	0.528 (5)	0.125*	
H7B	0.710 (6)	0.891 (3)	0.536 (5)	0.125*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0575 (6)	0.0522 (7)	0.0517 (6)	0.0069 (6)	0.0049 (5)	−0.0006 (5)

Mn2	0.0617 (7)	0.0426 (7)	0.0677 (7)	0.0029 (6)	0.0022 (5)	−0.0010 (6)
N1	0.054 (3)	0.051 (4)	0.062 (4)	0.009 (3)	0.011 (3)	−0.006 (3)
N2	0.052 (3)	0.060 (4)	0.051 (3)	0.010 (3)	0.004 (3)	0.003 (3)
N3	0.092 (5)	0.046 (4)	0.079 (5)	−0.001 (3)	−0.022 (4)	−0.001 (4)
N4	0.086 (5)	0.045 (4)	0.075 (4)	0.003 (3)	0.022 (4)	0.002 (3)
O1	0.067 (3)	0.067 (4)	0.052 (3)	0.008 (3)	0.001 (2)	−0.001 (2)
O2	0.064 (3)	0.057 (3)	0.049 (2)	−0.002 (2)	0.010 (2)	−0.004 (2)
O3	0.062 (3)	0.067 (4)	0.076 (3)	0.016 (3)	0.016 (2)	0.006 (3)
O4	0.095 (4)	0.051 (3)	0.079 (4)	0.010 (3)	−0.012 (3)	−0.006 (3)
O5	0.095 (4)	0.045 (3)	0.074 (3)	0.014 (3)	0.021 (3)	0.000 (3)
Cl1	0.163 (3)	0.223 (4)	0.0567 (13)	0.039 (2)	0.0056 (15)	0.0175 (18)
Cl2	0.158 (2)	0.174 (3)	0.0562 (13)	−0.016 (2)	0.0276 (14)	−0.0170 (15)
Cl3	0.177 (3)	0.133 (3)	0.0748 (16)	−0.004 (2)	0.0239 (16)	−0.0113 (16)
Cl4	0.213 (3)	0.118 (3)	0.0684 (15)	−0.008 (2)	0.0062 (17)	−0.0092 (15)
C1	0.064 (5)	0.065 (5)	0.054 (4)	0.023 (4)	0.006 (3)	−0.010 (4)
C2	0.058 (5)	0.080 (6)	0.053 (4)	0.016 (4)	0.006 (3)	0.001 (4)
C3	0.075 (6)	0.105 (8)	0.057 (5)	0.010 (5)	0.001 (4)	−0.009 (5)
C4	0.077 (6)	0.136 (10)	0.055 (5)	0.020 (6)	0.014 (4)	0.009 (6)
C5	0.070 (6)	0.119 (9)	0.080 (6)	0.004 (5)	0.007 (5)	0.052 (6)
C6	0.068 (5)	0.074 (6)	0.063 (5)	−0.003 (4)	−0.003 (4)	0.021 (4)
C7	0.042 (4)	0.063 (5)	0.068 (5)	0.004 (3)	0.008 (3)	0.010 (4)
C8	0.047 (4)	0.070 (6)	0.073 (5)	0.005 (4)	0.003 (4)	0.009 (4)
C9	0.051 (4)	0.082 (6)	0.053 (4)	0.001 (4)	0.013 (3)	−0.005 (4)
C10	0.067 (5)	0.095 (7)	0.054 (4)	−0.009 (5)	0.010 (4)	0.005 (5)
C11	0.070 (5)	0.116 (8)	0.049 (5)	−0.013 (5)	0.014 (4)	−0.012 (5)
C12	0.074 (6)	0.103 (8)	0.066 (6)	−0.011 (5)	0.021 (4)	−0.030 (5)
C13	0.062 (5)	0.080 (6)	0.058 (5)	−0.006 (4)	0.012 (4)	−0.011 (4)
C14	0.051 (4)	0.065 (6)	0.047 (4)	−0.003 (4)	0.008 (3)	−0.011 (4)
C15	0.067 (5)	0.050 (5)	0.066 (4)	0.013 (4)	0.012 (4)	−0.006 (4)
C16	0.073 (5)	0.053 (5)	0.046 (4)	0.006 (4)	0.000 (3)	−0.005 (3)
C17	0.099 (6)	0.053 (5)	0.083 (5)	0.016 (4)	0.019 (5)	−0.009 (4)
C18	0.071 (5)	0.068 (6)	0.104 (6)	−0.011 (4)	0.000 (5)	0.009 (5)
C19	0.097 (7)	0.057 (6)	0.098 (7)	0.002 (5)	−0.020 (5)	0.009 (5)
C20	0.077 (5)	0.051 (5)	0.059 (5)	−0.001 (4)	0.001 (4)	0.002 (4)
C21	0.086 (6)	0.079 (7)	0.069 (5)	−0.012 (5)	0.010 (4)	0.005 (5)
C22	0.090 (6)	0.089 (7)	0.061 (5)	−0.007 (6)	0.010 (4)	−0.013 (5)
C23	0.079 (6)	0.076 (7)	0.077 (6)	−0.008 (5)	0.018 (4)	−0.021 (5)
C24	0.061 (5)	0.063 (6)	0.080 (6)	0.008 (4)	0.010 (4)	−0.009 (4)
C25	0.060 (5)	0.057 (6)	0.081 (6)	0.005 (4)	0.001 (4)	−0.009 (5)
C26	0.114 (7)	0.044 (5)	0.081 (6)	0.003 (5)	0.026 (5)	−0.017 (4)
C27	0.066 (5)	0.055 (6)	0.070 (5)	−0.006 (4)	0.016 (4)	−0.005 (4)
C28	0.105 (7)	0.069 (6)	0.071 (6)	−0.003 (5)	0.014 (5)	−0.011 (5)
C29	0.096 (6)	0.092 (8)	0.051 (5)	−0.020 (5)	0.014 (4)	0.001 (5)
C30	0.090 (6)	0.079 (7)	0.064 (5)	0.003 (5)	0.008 (4)	0.006 (5)
C31	0.072 (5)	0.071 (6)	0.071 (5)	0.009 (4)	0.022 (4)	0.011 (4)
C32	0.058 (4)	0.050 (5)	0.065 (5)	0.002 (3)	0.019 (4)	0.001 (4)
C33A	0.067 (8)	0.048 (7)	0.064 (8)	−0.001 (6)	0.009 (7)	0.004 (6)
C36A	0.114 (12)	0.058 (11)	0.079 (10)	0.004 (9)	−0.003 (9)	0.017 (8)

C35A	0.080 (12)	0.102 (14)	0.098 (15)	0.012 (10)	0.012 (12)	0.006 (15)
C34A	0.068 (8)	0.058 (8)	0.066 (8)	−0.001 (7)	0.012 (7)	−0.012 (6)
C33B	0.073 (8)	0.045 (7)	0.076 (8)	−0.007 (6)	0.004 (7)	−0.007 (6)
C36B	0.126 (13)	0.076 (12)	0.096 (11)	−0.008 (10)	−0.013 (10)	−0.027 (9)
C35B	0.066 (10)	0.075 (11)	0.077 (12)	0.015 (8)	0.005 (9)	0.015 (12)
C34B	0.078 (8)	0.064 (8)	0.071 (8)	−0.009 (7)	0.001 (7)	−0.003 (7)
Cl6A	0.129 (10)	0.098 (11)	0.156 (10)	0.015 (8)	−0.020 (8)	0.018 (8)
O12A	0.115 (15)	0.122 (16)	0.153 (19)	−0.016 (12)	−0.052 (13)	0.044 (14)
O13A	0.101 (12)	0.094 (14)	0.21 (2)	0.023 (10)	−0.074 (13)	0.037 (14)
O14A	0.137 (19)	0.094 (17)	0.166 (17)	0.015 (13)	0.021 (13)	0.028 (14)
O15A	0.21 (2)	0.150 (18)	0.25 (2)	0.016 (16)	0.009 (18)	−0.020 (17)
Cl6B	0.122 (8)	0.070 (6)	0.175 (9)	0.003 (5)	−0.042 (7)	0.001 (6)
O12B	0.155 (14)	0.106 (13)	0.223 (19)	−0.004 (11)	0.034 (14)	0.019 (13)
O13B	0.200 (19)	0.25 (2)	0.208 (17)	−0.025 (18)	−0.031 (15)	−0.011 (16)
O14B	0.123 (13)	0.131 (14)	0.185 (18)	−0.020 (11)	0.012 (11)	0.015 (13)
O15B	0.159 (17)	0.098 (13)	0.214 (19)	0.024 (12)	−0.011 (13)	0.039 (14)
Cl5A	0.092 (4)	0.086 (4)	0.113 (6)	0.022 (3)	0.025 (4)	0.013 (4)
O8A	0.110 (10)	0.162 (14)	0.198 (15)	0.030 (9)	0.051 (9)	0.066 (12)
O9A	0.211 (14)	0.125 (11)	0.095 (7)	0.020 (10)	0.014 (8)	−0.020 (7)
O10A	0.105 (11)	0.095 (10)	0.106 (12)	0.015 (7)	0.007 (8)	0.022 (8)
O11A	0.160 (10)	0.097 (9)	0.181 (14)	−0.043 (8)	0.023 (9)	0.044 (10)
Cl5B	0.107 (13)	0.092 (14)	0.083 (10)	0.004 (10)	0.035 (8)	0.029 (9)
O8B	0.16 (3)	0.16 (3)	0.13 (2)	0.00 (2)	0.07 (2)	0.01 (2)
O9B	0.20 (3)	0.09 (2)	0.15 (3)	−0.02 (2)	−0.01 (2)	0.03 (2)
O10B	0.09 (3)	0.11 (2)	0.18 (3)	−0.02 (2)	−0.03 (2)	0.01 (2)
O11B	0.12 (3)	0.07 (2)	0.048 (16)	0.000 (18)	0.059 (17)	0.018 (15)
O16A	0.144 (13)	0.150 (15)	0.208 (16)	−0.010 (11)	0.040 (13)	−0.009 (13)
C38A	0.26 (2)	0.26 (2)	0.27 (2)	−0.013 (18)	0.020 (17)	0.018 (18)
C37A	0.242 (19)	0.240 (19)	0.247 (19)	0.005 (10)	0.000 (10)	−0.002 (10)
O16B	0.090 (8)	0.153 (12)	0.166 (12)	−0.005 (8)	0.030 (8)	−0.065 (9)
C38B	0.185 (18)	0.179 (19)	0.217 (19)	0.018 (16)	−0.004 (15)	−0.025 (16)
C37B	0.273 (17)	0.281 (17)	0.284 (17)	0.006 (10)	0.007 (10)	−0.004 (10)
O6	0.070 (4)	0.076 (4)	0.191 (6)	−0.005 (3)	−0.001 (4)	0.022 (4)
O7	0.068 (4)	0.068 (4)	0.115 (5)	0.002 (3)	0.016 (3)	−0.007 (4)

Geometric parameters (Å, º)

Mn1—O1	1.851 (5)	C23—C24	1.374 (10)
Mn1—O2	1.895 (5)	C23—H23	0.9300
Mn1—N1	1.977 (6)	C24—C25	1.409 (10)
Mn1—N2	1.955 (6)	C24—H24	0.9300
Mn1—O3	2.221 (5)	C26—C27	1.423 (11)
Mn1—O2^{i}	2.425 (4)	C26—H26	0.9300
Mn2—O4	1.880 (5)	C27—C32	1.385 (10)
Mn2—O5	1.873 (5)	C27—C28	1.387 (10)
Mn2—N3	1.969 (6)	C28—C29	1.376 (12)
Mn2—N4	1.964 (6)	C28—H28	0.9300
Mn2—O6	2.270 (6)	C29—C30	1.368 (12)

Mn2—O7	2.241 (5)	C30—C31	1.374 (10)
N1—C1	1.314 (8)	C30—H30	0.9300
N1—C16	1.491 (9)	C31—C32	1.418 (10)
N2—C8	1.313 (8)	C31—H31	0.9300
N2—C15	1.462 (8)	C33A—C35A	1.519 (10)
N3—C19	1.279 (10)	C33A—C36A	1.523 (15)
N3—C34B	1.445 (18)	C33A—C34A	1.53 (3)
N3—C33A	1.522 (9)	C36A—H36A	0.9600
N4—C26	1.307 (9)	C36A—H36B	0.9600
N4—C34A	1.458 (9)	C36A—H36C	0.9600
N4—C33B	1.624 (19)	C35A—H35A	0.9600
O1—C7	1.352 (8)	C35A—H35B	0.9600
O2—C14	1.367 (7)	C35A—H35C	0.9600
O2—Mn1^{i}	2.425 (4)	C34A—H34A	0.9700
O3—H3B	0.840 (10)	C34A—H34B	0.9700
O3—H3A	0.838 (10)	C33B—C36B	1.520 (15)
O4—C25	1.338 (9)	C33B—C35B	1.54 (3)
O5—C32	1.336 (8)	C33B—C34B	1.56 (3)
Cl1—C4	1.742 (9)	C36B—H36D	0.9600
Cl2—C11	1.733 (8)	C36B—H36E	0.9600
Cl3—C22	1.760 (8)	C36B—H36F	0.9600
Cl4—C29	1.749 (8)	C35B—H35D	0.9600
C1—C2	1.424 (10)	C35B—H35E	0.9600
C1—H1	0.9300	C35B—H35F	0.9600
C2—C7	1.393 (10)	C34B—H34C	0.9700
C2—C3	1.428 (10)	C34B—H34D	0.9700
C3—C4	1.357 (13)	Cl6A—O12A	1.390 (15)
C3—H3	0.9300	Cl6A—O13A	1.401 (13)
C4—C5	1.388 (13)	Cl6A—O14A	1.413 (16)
C5—C6	1.388 (11)	Cl6A—O15A	1.456 (15)
C5—H5	0.9300	Cl6B—O12B	1.385 (18)
C6—C7	1.380 (10)	Cl6B—O14B	1.387 (19)
C6—H6	0.9300	Cl6B—O13B	1.403 (16)
C8—C9	1.427 (10)	Cl6B—O15B	1.477 (17)
C8—H8	0.9300	Cl5A—O11A	1.384 (11)
C9—C14	1.390 (10)	Cl5A—O8A	1.395 (12)
C9—C10	1.418 (9)	Cl5A—O9A	1.425 (12)
C10—C11	1.377 (12)	Cl5A—O10A	1.463 (11)
C10—H10	0.9300	Cl5B—O11B	1.40 (2)
C11—C12	1.364 (12)	Cl5B—O8B	1.40 (2)
C12—C13	1.406 (10)	Cl5B—O9B	1.42 (2)
C12—H12	0.9300	Cl5B—O10B	1.46 (2)
C13—C14	1.382 (10)	O16A—C37A	1.422 (10)
C13—H13	0.9300	O16A—H16A	0.8200
C15—C16	1.541 (10)	C38A—C37A	1.466 (10)
C15—H15A	0.9700	C38A—H38A	0.9600
C15—H15B	0.9700	C38A—H38B	0.9600
C16—C17	1.509 (9)	C38A—H38C	0.9600

C16—C18	1.536 (10)	C37A—H37A	0.9700
C17—H17A	0.9600	C37A—H37B	0.9700
C17—H17B	0.9600	O16B—C37B	1.412 (10)
C17—H17C	0.9600	O16B—H16B	0.8200
C18—H18A	0.9600	C38B—C37B	1.458 (10)
C18—H18B	0.9600	C38B—H38D	0.9600
C18—H18C	0.9600	C38B—H38E	0.9600
C19—C20	1.431 (11)	C38B—H38F	0.9600
C19—H19	0.9300	C37B—H37C	0.9700
C20—C21	1.402 (10)	C37B—H37D	0.9700
C20—C25	1.409 (10)	O6—H6A	0.8402 (12)
C21—C22	1.360 (12)	O6—H6B	0.8401 (11)
C21—H21	0.9300	O7—H7A	0.837 (10)
C22—C23	1.345 (12)	O7—H7B	0.838 (10)

O1—Mn1—O2	93.3 (2)	C22—C23—H23	120.3
O1—Mn1—N1	94.2 (2)	C24—C23—H23	120.3
O1—Mn1—N2	176.3 (2)	C23—C24—C25	120.6 (8)
O2—Mn1—N1	167.8 (2)	C23—C24—H24	119.7
O2—Mn1—N2	90.4 (2)	C25—C24—H24	119.7
O2—Mn1—O3	91.8 (2)	O4—C25—C20	123.7 (7)
O2—Mn1—O2^{i}	79.98 (18)	O4—C25—C24	118.3 (7)
N1—Mn1—O3	97.6 (2)	C20—C25—C24	118.0 (8)
O3—Mn1—O2^{i}	170.68 (17)	N4—C26—C27	125.2 (7)
Mn1—O2—Mn1^{i}	100.02 (18)	N4—C26—H26	117.4
N2—Mn1—N1	82.1 (3)	C27—C26—H26	117.4
O1—Mn1—O3	92.0 (2)	C32—C27—C28	120.8 (8)
N2—Mn1—O3	88.4 (2)	C32—C27—C26	124.3 (7)
O1—Mn1—O2^{i}	92.81 (18)	C28—C27—C26	114.8 (8)
N2—Mn1—O2^{i}	87.34 (19)	C29—C28—C27	119.6 (8)
N1—Mn1—O2^{i}	90.07 (19)	C29—C28—H28	120.2
O4—Mn2—N3	94.5 (3)	C27—C28—H28	120.2
O4—Mn2—N4	175.2 (3)	C30—C29—C28	120.7 (7)
O4—Mn2—O7	90.2 (2)	C30—C29—Cl4	119.0 (7)
O5—Mn2—N3	173.8 (3)	C28—C29—Cl4	120.3 (8)
O5—Mn2—N4	93.0 (2)	C29—C30—C31	120.6 (8)
O5—Mn2—O4	91.7 (2)	C29—C30—H30	119.7
O5—Mn2—O7	89.2 (2)	C31—C30—H30	119.7
N3—Mn2—O6	89.6 (3)	C30—C31—C32	119.9 (8)
N4—Mn2—O7	90.9 (2)	C30—C31—H31	120.1
O7—Mn2—O6	177.3 (2)	C32—C31—H31	120.1
N4—Mn2—N3	80.8 (3)	O5—C32—C27	123.6 (7)
N3—Mn2—O7	91.2 (3)	O5—C32—C31	118.0 (7)
O5—Mn2—O6	90.2 (2)	C27—C32—C31	118.4 (7)
O4—Mn2—O6	87.2 (3)	C35A—C33A—N3	116.5 (16)
N4—Mn2—O6	91.8 (3)	C35A—C33A—C36A	108.1 (16)
C1—N1—C16	120.4 (6)	N3—C33A—C36A	109.7 (12)
C1—N1—Mn1	123.7 (5)	C35A—C33A—C34A	109.3 (15)

C16—N1—Mn1	115.8 (4)	N3—C33A—C34A	106.8 (11)
C8—N2—C15	121.6 (6)	C36A—C33A—C34A	106.1 (12)
C8—N2—Mn1	124.7 (5)	C33A—C36A—H36A	109.5
C15—N2—Mn1	113.7 (4)	C33A—C36A—H36B	109.5
C19—N3—C34B	116.9 (9)	H36A—C36A—H36B	109.5
C19—N3—C33A	123.5 (9)	C33A—C36A—H36C	109.5
C19—N3—Mn2	122.0 (6)	H36A—C36A—H36C	109.5
C34B—N3—Mn2	117.8 (8)	H36B—C36A—H36C	109.5
C33A—N3—Mn2	112.9 (7)	C33A—C35A—H35A	109.5
C26—N4—C34A	116.9 (9)	C33A—C35A—H35B	109.5
C26—N4—C33B	122.4 (8)	H35A—C35A—H35B	109.5
C26—N4—Mn2	125.1 (6)	C33A—C35A—H35C	109.5
C34A—N4—Mn2	116.3 (8)	H35A—C35A—H35C	109.5
C33B—N4—Mn2	111.1 (7)	H35B—C35A—H35C	109.5
C7—O1—Mn1	128.0 (5)	N4—C34A—C33A	102.0 (12)
C14—O2—Mn1	120.6 (4)	N4—C34A—H34A	111.4
C14—O2—Mn1^{i}	117.8 (4)	C33A—C34A—H34A	111.4
Mn1—O3—H3B	127 (4)	N4—C34A—H34B	111.4
Mn1—O3—H3A	116 (4)	C33A—C34A—H34B	111.4
H3B—O3—H3A	106.0 (13)	H34A—C34A—H34B	109.2
C25—O4—Mn2	128.0 (5)	C36B—C33B—C35B	112.7 (17)
C32—O5—Mn2	128.6 (5)	C36B—C33B—C34B	109.4 (14)
N1—C1—C2	124.2 (7)	C35B—C33B—C34B	109.4 (16)
N1—C1—H1	117.9	C36B—C33B—N4	107.8 (14)
C2—C1—H1	117.9	C35B—C33B—N4	112.5 (14)
C7—C2—C1	126.4 (6)	C34B—C33B—N4	104.7 (14)
C7—C2—C3	118.3 (8)	C33B—C36B—H36D	109.5
C1—C2—C3	115.4 (8)	C33B—C36B—H36E	109.5
C4—C3—C2	120.0 (9)	H36D—C36B—H36E	109.5
C4—C3—H3	120.0	C33B—C36B—H36F	109.5
C2—C3—H3	120.0	H36D—C36B—H36F	109.5
C3—C4—C5	121.1 (8)	H36E—C36B—H36F	109.5
C3—C4—Cl1	119.6 (9)	C33B—C35B—H35D	109.5
C5—C4—Cl1	119.3 (8)	C33B—C35B—H35E	109.5
C6—C5—C4	119.8 (8)	H35D—C35B—H35E	109.5
C6—C5—H5	120.1	C33B—C35B—H35F	109.5
C4—C5—H5	120.1	H35D—C35B—H35F	109.5
C7—C6—C5	120.0 (9)	H35E—C35B—H35F	109.5
C7—C6—H6	120.0	N3—C34B—C33B	98.9 (12)
C5—C6—H6	120.0	N3—C34B—H34C	112.0
O1—C7—C6	117.3 (7)	C33B—C34B—H34C	112.0
O1—C7—C2	121.8 (7)	N3—C34B—H34D	112.0
C6—C7—C2	120.8 (7)	C33B—C34B—H34D	112.0
N2—C8—C9	122.5 (7)	H34C—C34B—H34D	109.7
N2—C8—H8	118.7	O12A—Cl6A—O13A	110.8 (14)
C9—C8—H8	118.7	O12A—Cl6A—O14A	112.2 (14)
C14—C9—C10	117.9 (8)	O13A—Cl6A—O14A	112.0 (16)
C14—C9—C8	125.0 (6)	O12A—Cl6A—O15A	109.9 (15)

C10—C9—C8	117.0 (8)	O13A—Cl6A—O15A	106.6 (13)
C11—C10—C9	120.3 (9)	O14A—Cl6A—O15A	105.1 (13)
C11—C10—H10	119.9	O12B—Cl6B—O14B	118.0 (14)
C9—C10—H10	119.9	O12B—Cl6B—O13B	109.4 (17)
C12—C11—C10	120.9 (8)	O14B—Cl6B—O13B	111.7 (19)
C12—C11—Cl2	119.3 (7)	O12B—Cl6B—O15B	109.0 (18)
C10—C11—Cl2	119.8 (8)	O14B—Cl6B—O15B	108.0 (16)
C11—C12—C13	120.2 (8)	O13B—Cl6B—O15B	99.0 (16)
C11—C12—H12	119.9	O11A—Cl5A—O8A	113.2 (11)
C13—C12—H12	119.9	O11A—Cl5A—O9A	109.7 (10)
C14—C13—C12	119.0 (8)	O8A—Cl5A—O9A	110.3 (10)
C14—C13—H13	120.5	O11A—Cl5A—O10A	108.4 (10)
C12—C13—H13	120.5	O8A—Cl5A—O10A	108.0 (10)
O2—C14—C13	117.9 (7)	O9A—Cl5A—O10A	107.1 (10)
O2—C14—C9	120.4 (6)	O11B—Cl5B—O8B	113 (3)
C13—C14—C9	121.5 (7)	O11B—Cl5B—O9B	107 (2)
N2—C15—C16	109.1 (6)	O8B—Cl5B—O9B	110 (2)
N2—C15—H15A	109.9	O11B—Cl5B—O10B	111 (3)
C16—C15—H15A	109.9	O8B—Cl5B—O10B	105 (3)
N2—C15—H15B	109.9	O9B—Cl5B—O10B	111 (3)
C16—C15—H15B	109.9	C37A—O16A—H16A	109.5
H15A—C15—H15B	108.3	C37A—C38A—H38A	109.5
N1—C16—C17	114.8 (6)	C37A—C38A—H38B	109.5
N1—C16—C18	108.1 (6)	H38A—C38A—H38B	109.5
C17—C16—C18	109.7 (7)	C37A—C38A—H38C	109.5
N1—C16—C15	104.2 (6)	H38A—C38A—H38C	109.5
C17—C16—C15	109.5 (6)	H38B—C38A—H38C	109.5
C18—C16—C15	110.4 (6)	O16A—C37A—C38A	112.2 (11)
C16—C17—H17A	109.5	O16A—C37A—H37A	109.2
C16—C17—H17B	109.5	C38A—C37A—H37A	109.2
H17A—C17—H17B	109.5	O16A—C37A—H37B	109.2
C16—C17—H17C	109.5	C38A—C37A—H37B	109.2
H17A—C17—H17C	109.5	H37A—C37A—H37B	107.9
H17B—C17—H17C	109.5	C37B—O16B—H16B	109.5
C16—C18—H18A	109.5	C37B—C38B—H38D	109.5
C16—C18—H18B	109.5	C37B—C38B—H38E	109.5
H18A—C18—H18B	109.5	H38D—C38B—H38E	109.5
C16—C18—H18C	109.5	C37B—C38B—H38F	109.5
H18A—C18—H18C	109.5	H38D—C38B—H38F	109.5
H18B—C18—H18C	109.5	H38E—C38B—H38F	109.5
N3—C19—C20	129.9 (8)	O16B—C37B—C38B	113.7 (11)
N3—C19—H19	115.0	O16B—C37B—H37C	108.8
C20—C19—H19	115.0	C38B—C37B—H37C	108.8
C21—C20—C25	120.0 (8)	O16B—C37B—H37D	108.8
C21—C20—C19	118.3 (8)	C38B—C37B—H37D	108.8
C25—C20—C19	121.7 (7)	H37C—C37B—H37D	107.7
C22—C21—C20	118.4 (8)	Mn2—O6—H6A	147 (3)
C22—C21—H21	120.8	Mn2—O6—H6B	101 (3)

C20—C21—H21	120.8	H6A—O6—H6B	105.77 (18)
C23—C22—C21	123.5 (8)	Mn2—O7—H7A	118 (6)
C23—C22—Cl3	118.7 (8)	Mn2—O7—H7B	120 (6)
C21—C22—Cl3	117.8 (8)	H7A—O7—H7B	106.5 (18)
C22—C23—C24	119.4 (8)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O5^{ii}	0.84 (4)	1.98 (5)	2.781 (8)	158 (5)
O3—H3*B*···O10*A*^{iii}	0.84 (4)	2.23 (5)	3.016 (18)	157 (4)
O6—H6*B*···O4^{iv}	0.84 (3)	2.25 (3)	2.899 (8)	134 (3)
O6—H6*A*···O3^{v}	0.84 (3)	2.33 (3)	3.139 (7)	164 (4)
O7—H7*B*···O1^{vi}	0.84 (8)	2.09 (7)	2.915 (8)	168 (7)
O7—H7*A*···O16*B*	0.84 (5)	2.33 (8)	2.731 (16)	110 (7)
C24—H24···O15*B*^{vii}	0.93	2.43	3.19 (3)	139
C28—H28···O8*A*^{viii}	0.93	2.51	3.23 (2)	135
C31—H31···O10*A*^{ix}	0.93	2.43	3.34 (2)	169

Symmetry codes: (ii) *x*, *y*−1, *z*; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+2, −*y*+2, −*z*+1; (v) −*x*+2, −*y*+1, −*z*+1; (vi) *x*, *y*+1, *z*; (vii) −*x*+3/2, *y*+1/2, −*z*+3/2; (viii) *x*+1/2, −*y*+3/2, *z*−1/2; (ix) −*x*+1, −*y*+2, −*z*+1.