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COMMUNICATIONS

Geometrical Variations of Two Manganese(II) Complexes with Closely-Related, Quinoline-Based, Tripodal Ligands

Steven T. Frey, Jasper G. Ballot, Allison Hands, Haley A. Cirka, Katheryn C. Rinaolo, Nich N. Phalkun, Manpreet Kaur and Jerry P. Jasinski

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SCIENTIFIC MANUSCRIPT

For review only.

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Category: *research communications*

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checkCIF/PLATON results for paper zl5024

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Ellipsoid plot

checkCIF/PLATON results

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sf-mndqmea

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alpha=96.842(4) beta=105.959(3) gamma=111.907(4)
Temperature: 173 K

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Hall group	-P 1	-P 1
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S = 1.008 Npar= 516

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Alert level G

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0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
8 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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alpha=90 beta=96.222(3) gamma=90
Temperature: 173 K

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Hall group	-P 2ybc	-P 2ybc
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Sum formula	C50 H52 B Mn N3 O5 [+	C50 H52 B Mn N3 O5
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Dx,g cm-3	1.296	1.295
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  0 ALERT level A = Most likely a serious problem - resolve or explain
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  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  9 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
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  2 ALERT type 5 Informative message, check
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database duplication summary

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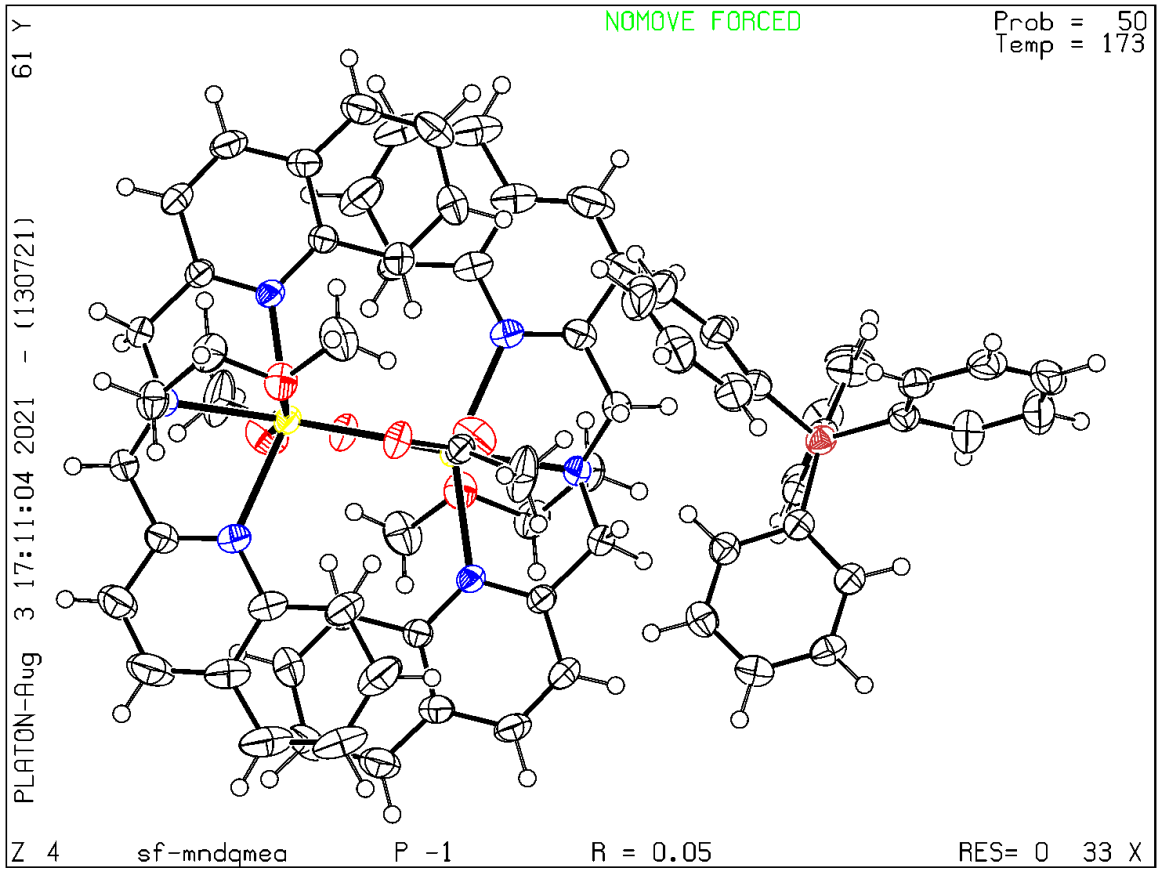

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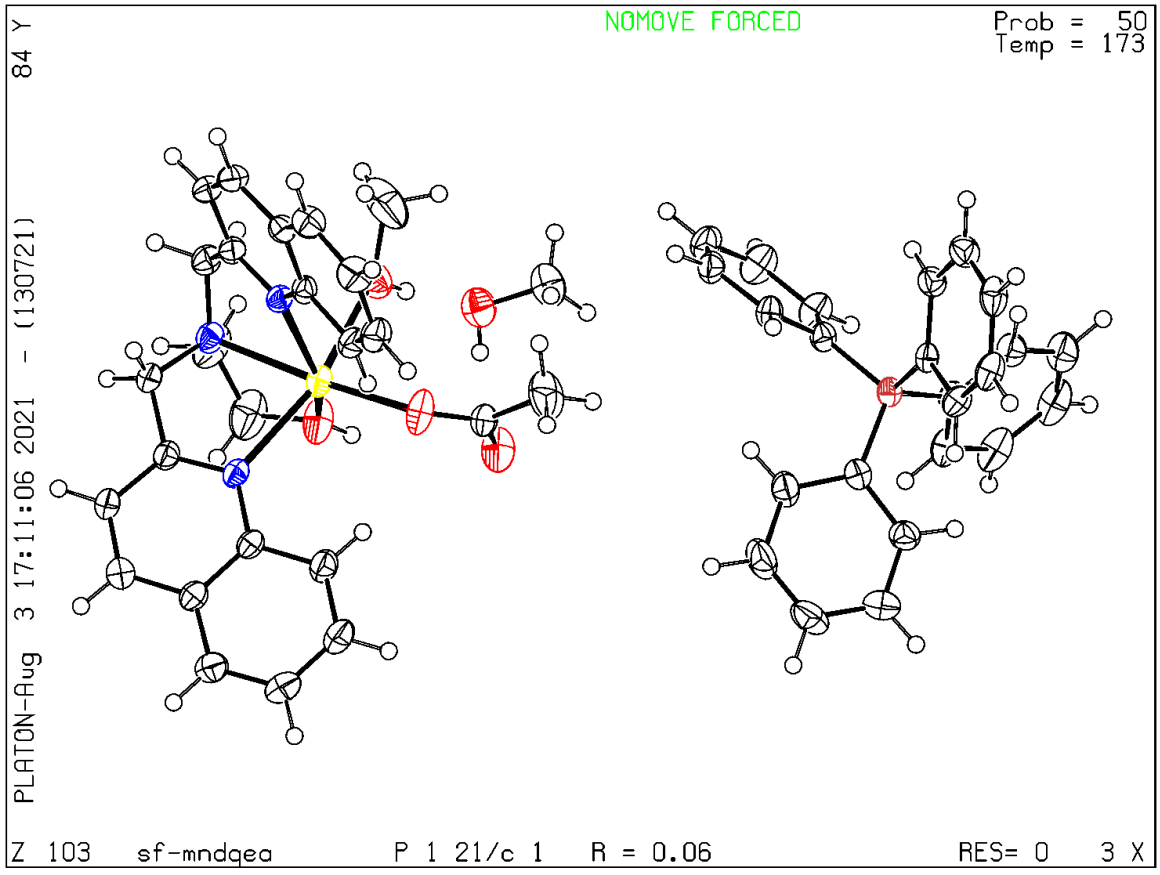

Geometrical Variations of Two Manganese(II) Complexes with Closely-Related, Quinoline-Based, Tripodal Ligands

Steven T. Frey,[a]* Jasper G. Ballot,[a] Allison Hands,[a] Haley A. Cirka,[a] Katheryn C. Rinaolo,[a] Nich N. Phalkun,[a] Manpreet Kaur[b] and Jerry P. Jasinski[b]‡

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‡ Submitted Posthumously

Abstract

Structural analyses of the compounds [Mn(DQMEA)(μ-Ac)$_2$Mn(DQMEA)](BPh$_4$)$_2$, **[1]**(BPh$_4$)$_2$, where DQMEA = *N,N*-Bis(2-quinolylmethyl)methoxyethylamine, Ac = acetate, BPh$_4$ = tetraphenylborate and [Mn(DQEA)(Ac)(CH$_3$OH)]BPh$_4$·CH$_3$OH, **[2]**BPh$_4$·CH$_3$OH where DQEA = *N,N*-Bis(2-quinolylmethyl)hydroxyethylamine), by single-crystal X-ray diffraction reveal distinct differences in the geometry of coordination of the tripodal DQEA and DQMEA ligands to Mn(II) ions. In the assymetric unit, compound **[1]**(BPh$_4$)$_2$ crystallizes as a dimer in which each manganese(II) center is coordinated by the central amine nitrogen, the nitrogen atom of each quinoline group, and the methoxy-oxygen of the tetradentate DQMEA ligand, and two bridging-acetate oxygen atoms. The symmetric Mn(II) centers have a distorted, octahedral geometry in which the quinoline nitrogen atoms are *trans* to each other resulting in co-planarity of the quinoline rings. Within each Mn(II) center, a coordinated acetate oxygen participates in C—H···O hydrogen bonding interactions with the two quinolyl moieties, further stabilizing the *trans* structure. Within the crystal, weak $\pi\cdots\pi$ stacking interactions and intermolecular cation-anion interactions stabilize the crystal packing. In the assymetric unit, cCompound **[2]**BPh$_4$·CH$_3$OH crystallizes as a monomer in which the manganese(II) ion is coordinated to the central nitrogen, the nitrogen atom of each quinoline group, and the alcohol oxygen of the tetradentate DQEA ligand, an oxygen atom of Ac, and the oxygen atom of a methanol ligand. The geometry of the Mn(II) center in **[2]**BPh$_4$·CH$_3$OH is also a distorted octahedron, but the quinoline nitrogen atoms are *cis* to each other in this structure. Hydrogen bonding between the acetate oxygen atoms and hydroxyl (O—H···O) and quinolyl (C—H···O and N—H···O) moieties of the DQEA ligand stabilize the complex in this *cis* configuration. Within the crystal, dimerization of complexes occurs by the formation of a pair of intermolecular O3—H3···O2 hydrogen bonds between the coordinated hydroxyl oxygen of DQEA ligand of one complex and an acetate oxygen of another. Additional hydrogen-bonding and intermolecular cation-anion interactions contribute to the crystal packing.

Keywords: crystal structure, manganese(II), tripodal ligand, quinoline, 6-coordinate, *cis/trans*

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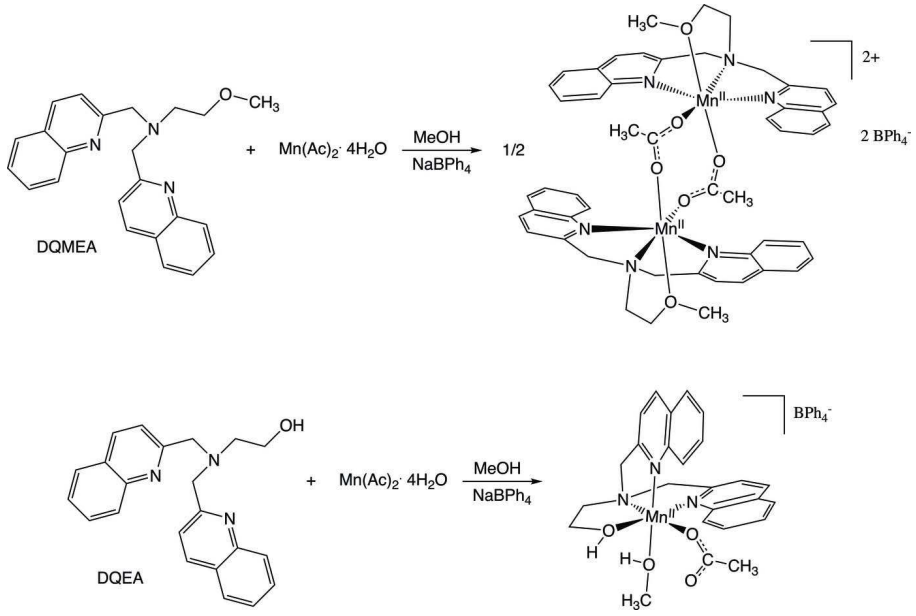


1. Chemical Context

Synthetic manganese(II) compounds have gained attention in recent years owing to their antioxidant (Signorella *et. al*., 2018; Batinic-Haberle *et. al*., 2010; Iranzo, 2011; Bani & Bancini, 2012; Miriyala *et. al*., 2012; Batinic-Haberle *et. al*., 2014; Policar, 2016), anticancer (Icsel *et. al*., 2020; Prihantono *et. al*., 2020; Liu *et. al*., 2015; Wang *et. al*., 2014; Zhou *et. al*., 2011), antibacterial (Saha *et. al*., 2020; Maurya *et. al*., 2011, Dong *et. al*., 2017), optoelectronic (Qin *et. al*., 2020), catalytic (Sarma *et. al*., 2019), and MRI enhancement (Wang *et. al*., 2019, Boros *et. al*., 2015, Gale *et. al*., 2015) properties. Manganese(II) tends to be less toxic than other metal ions (Iranzo, 2011; Bani & Bancini, 2012), can often reversibly access the Mn(III) oxidation state, and exhibits luminescence in some instances (Qin *et. al*., 2020). The ability to form stable, efficacious Mn(II) compounds for these applications is dependent upon the nature of the ligands employed, their coordinating atoms, and other groups that can alter the geometry, bulkiness, and/or optical properties of the compound (Signorella *et. al*., 2018, Policar, 2016, Qin *et. al*., 2020).

We have recently begun to study Mn(II) compounds with tetradentate, tripodal ligands (Frey *et. al*., 2018). These ligands are readily synthesized to provide a variety of N and O donors and other groups that can potentially alter the structural and/or electronic properties of the Mn(II) center. Quinoline groups, for example, provide bulkiness that can lead to distorted coordination geometries, potentially altering coordination number, redox potential, substrate specificity, and/or photophysical properties of a complex. Quinoline rings are also the basis for a number of biologically active molecules, suggesting that their presence might lead to medicinally relevant compounds (Kakoulidou *et. al*., 2021). We report here the synthesis and structural characterization of [Mn(DQMEA)(μ-Ac)$_2$Mn(DQMEA)](BPh$_4$)$_2$, **[1]**(BPh$_4$)$_2$, where DQMEA = *N,N*-Bis(2-quinolylmethyl)methoxyethylamine, Ac = acetate, BPh$_4$ = tetraphenylborate and [Mn(DQEA)(Ac)(CH$_3$OH)]BPh$_4$·CH$_3$OH, **[2]**BPh$_4$·CH$_3$OH where DQEA = *N,N*-Bis(2-quinolylmethyl)hydroxyethylamine). These compounds are prepared in a two-step reaction (see reaction scheme) in which manganese(II) acetate is reacted with either DQMEA or DQEA in methanol, followed by anion exchange with sodium tetraphenylborate. The resulting complexes demonstrate how minor alterations in ligand structure can result in significant differences in complex structure.

2. Structural commentary

Compound **[1]**$(BPh_4)_2$ crystallizes in the triclinic space group *P*1. The structure reveals a dimeric [Mn(DQMEA)(μ-Ac)$_2$Mn(DQMEA)]$^{2+}$ cation (Fig. 1) balanced by the presence of tetraphenyl borate anions. The manganese(II) ions are hexacoordinate with a distorted octahedral geometry. While this is a standard coordination number for transition metal cations, manganese(II) complexes with N-donor ligands are often heptacoordinate (Frey *et. al*., 2018*a*, Deroche *et. al*., 1996; Policar, 2001; Lessa *et. al*., 2007; Dees *et. al*., 2007; Wu *et. al*., 2010; Lieb *et. al*., 2012). The presence of the bulky quinoline rings in this compound may restrict the coordination number to six in **[1]**$(BPh_4)_2$. The DQMEA ligands are tetradentate, with the central N2 and two quinolyl nitrogen atoms (N1 and N3) in the same octahedral plane and the methoxy oxygen (O1) located perpendicular to this nitrogen plane. This configuration of the DQMEA ligand results in the quinoline groups binding Mn(II) *trans* to each other, and in coplanarity of their rings. Hydrogen-bonding interactions between quinolyl H atoms and an acetate oxygen, C—H···O, further stabilize this *trans* configuration (Table 1). O atoms from two bridging acetate ions make up the final, two coordinating atoms, with O2 *trans* to the central N2 nitrogen of DQMEA and O3 *trans* to the methoxy oxygen, O1. Distortion of the octahedral geometry of the coordination sphere is by the bite angles of the DQMEA ligands. For example, the five-membered metallacycles formed by coordination of quinoline N atoms and central nitrogen of DQMEA, produce bond angles, N2—Mn1—N3 and N2—Mn1—N1, of 73.26 (5)° and 75.52 (5)° respectively, which are significantly reduced from 90° (Table 1). This results in a *trans* N1—Mn1—N3 angle of 148.32 (5)°. Likewise, the bond angle formed by *cis* coordination of the methoxy oxygen of DQMEA and central nitrogen, N2—Mn1—O1 is 75.29 (5)°. The remaining *trans* bond angles, O2—Mn1—N2 and O3^1—Mn1—O1 are 157.92 (5)° and 163.59 (5)° respectively. The Mn—O and Mn—N bond lengths for the neutral DQMEA ligand fall in the range 2.27–2.36 Å, which is typical of manganese(II) complexes (Deroche *et. al*., 1996; Policar, 2001; Lessa *et al.*, 2007; Dees *et. al*., 2007; Wu *et. al*., 2010; Lieb *et. al*., 2012). However, the Mn1—O2 and Mn1—O3^1 acetate bond lengths, 2.062 (12) Å and 2.0899 (12) Å are significantly shorter.

The compound **[2]**$BPh_4{\cdot}CH_3OH$ crystallizes in the monoclinic space group $P2_1/c$. The structure of this compound consists of the [Mn(DQEA)(Ac)(CH_3OH)]$^+$ monocation (Fig. 2), tetraphenyl borate counter-ion, and a methanol solvent molecule. The Mn(II) ion is hexacoordinate with a distorted octahedral geometry. As with **[1]**$(BPh_4)_2$, the bulky quinoline groups likely prevent a 7-coordinate species from forming. The DQEA ligand is tetradentate, but the quinolyl nitrogen atoms in this structure, N2 and N3, are *cis* to each other, and the rings are therefore not co-planar. The central nitrogen of DQEA, N1 and the quinolyl N atoms occupy an octahedral face, while the alcohol oxygen, O3 is *trans* to the quinolyl nitrogen N3. In addition to the DQEA ligand, a monodentate acetate oxygen, O1 is *trans* to the central nitrogen of DQEA, while a methanol oxygen, O4 occupies a position *trans* to the quinolyl nitrogen, N2. Like DQMEA in **[1]**$(BPh_4)_2$, binding constraints of the DQEA ligand in **[2]**$BPh_4{\cdot}CH_3OH$ result in significant distortions of the octahedral geometry of the coordination sphere. Bond angles involving the central nitrogen of DQEA and quinolyl N atoms, N1—Mn1—N2 and N1—Mn1—N3 are 75.62 (5)° and 73.79 (5)° respectively (Table 2). The alcohol oxygen and quinolyl nitrogen that are *trans* to each other, form a bond angle with manganese, O3—Mn1—N3 of 148.81 (6)°. The remaining *trans* bond angles, O1—Mn1—N1 and N2—Mn1—O4 are 175.50 (7)° and 161.35 (6)° respectively.

The *cis* coordination of DQEA to Mn(II) in **[2]**$BPh_4{\cdot}CH_3OH$ may result from a hydrogen bonding network involving the alcohol and quinolyl groups of DQEA and acetate ligand, O—H···O and C—H···O (Table 4). A *trans* configuration of DQEA, like that of DQMEA in **[1]**$(BPh_4)_2$, would swing the alcohol hydrogen up and away from the acetate ligand, preventing this hydrogen-bonding interaction. Additional O—H···O hydrogen bonds in **[2]**$BPh_4{\cdot}CH_3OH$, between methanol molecules themselves and with the acetate ligand, provide further stabilization of the structure. This *cis* structure observed in **[2]**$BPh_4{\cdot}CH_3OH$ may not be favorable with the DQMEA ligand, since the methoxy methyl group

would disrupt this hydrogen-bonding network.

3. Supramolecular features

Within the crystal **[1]**$(BPh_4)_2$, no classical intermolecular hydrogen bonding interactions were found. The crystal packing is primarily stabilized by weak $\pi\cdots\pi$ stacking interactions (Table 3) between nearby benzene rings (*Cg*7$\cdots$*Cg*6) of a quinoline group (where *Cg*7 and *Cg*6 are the centroids of the C15–C120 and C1–C6 rings, respectively). In addition, a network of weak C—H$\cdots\pi$ [C8— H8$\cdots$*Cg*13, *X*—H, π = 78º; C11—H11B$\cdots$*Cg*13, *X*—H, π = 59º, C23—H23B$\cdots$*Cg*11, *X*—H, π = 72º], where *Cg*11 = C32–C37 and *Cg*13 = C44–C49] intermolecular cation-anion interactions (Table 3) are also present and contribute additionally to the crystal packing.

Within the crystal **[2]**$BPh_4{\cdot}CH_3OH$, dimerization of complexes occurs by the formation of a pair of intermolecular O3—H3$\cdots$O2 hydrogen bonds (Table 4) between the coordinated hydroxyl oxygen of DQEA ligand of one complex and an acetate oxygen of another (Fig. 2), forming an $R_2^2(12)$ ring-motif interaction. In addition, the methanol solvent molecule forms strong O—H$\cdots$O hydrogen bonds (Table 4), with the coordinated methanol and acetate ligands of the cationic complex forming an $R_4^4(16)$ ring motif influencing the crystal packing. Weak C11—H11A$\cdots$*Cg*12 [*X*—H, π = 58º; where *Cg*12 = C13A–C18A] intermolecular cation-anion interactions (Table 3) are also present and contribute additionally to the crystal packing.

4. Database survey

To the best of our knowledge, structures of the manganese(II) compounds described herein have not been reported previously. We have previously reported the structure of a mononuclear copper(II) complex with DQMEA (Frey *et. al*., 2018*b*). In this structure, the DQMEA ligand is tetradentate with *tris* configuration of the quinoline groups as observed in **[1]**$(BPh_4)_2$. A search of the Cambridge Crystallographic Database (updated in May 2021) revealed a related manganese(II) complex with a pentadentate, tripodal ligand containing two methyl quinolyl groups and an imine thiolate group (Coggins, *M*. K. *et. al*., 2011). This ligand binds the Mn(II) in a trigonal bipyramidal geometry with the quinoline rings *cis* to each other in the equatorial plane, similar to **[2]**$BPh_4{\cdot}CH_3OH$.

5. Synthesis and crystallization

All chemicals were obtained from commercial sources and used without further preparation. The water used was deionized. The ^{1}H and ^{13}C NMR spectra were recorded with a Jeol JNM-ECZ400s NMR spectrometer and referenced against chloroform. IR spectra were recorded with a Perkin Elmer Spectrum 100 F T—IR.

***N,N*-Bis(2-quinolylmethyl)methoxyethylamine (DQMEA)**. In a 250 ml round bottom flask, 5 g (23 mmol) 2-chlormethylquinoline hydrochloride was dissolved in 10 ml H_2O and cooled to 0°C in an ice bath. A solution of 1.9 g (47 mmol) NaOH in 10 ml H_2O was added dropwise with stirring. Following this, a solution of 0.9 g (12 mmol) 2-methoxy-ethylamine in 10 ml CH_2Cl_2 was added. The reaction mixture was then removed from the ice bath, and brought to reflux for 7 days. The mixture was then cooled to room temperature, and the CH_2Cl_2 layer was separated, washed twice with brine, and dried over anhydrous sodium sulfate. The solution was then filtered, and the filtrate was chromatographed on alumina (chromatographic grade, 80–200 mesh) eluting with 20:1 CH_2Cl_2/methanol. Fractions were collected that produced a single spot by TLC on alumina plates (eluting with 100:1, CH_2Cl_2/methanol) with an RF value of 0.33. Rotary evaporation of these fractions gave 2.4 g (58%) of a light-yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) d 2.87 (t, 2H), 3.30 (s, 3H), 3.54 (t, 2H), 4.06 (s, 4H), 7.48 (t, 2H), 7.65 (t, 2H), 7.75 (m, 4H), 8.01 (d, 2H), 8.10 (d, 2H).

***N,N*-Bis(2-quinolylmethyl)methanolamine) (DQEA)**. In a 100 ml round bottom flask, 2.5 g (12 mmol) 2-chlormethylquinoline hydrochloride was dissolved in 10 ml H_2O and cooled to 0°C in an ice bath. A solution of 0.95 g (24 mmol) NaOH in 10 ml H_2O was added dropwise with stirring. Following this, a solution of 0.36 g (6.0 mmol)

ethanolamine in 10 ml CH_2Cl_2 was added. The reaction mixture was then removed from the ice bath, and brought to reflux for 7 days. The mixture was then cooled to room temperature, and the CH_2Cl_2 layer was separated, washed twice with brine, and dried over anhydrous sodium sulfate. The solution was then filtered, and the filtrate was chromatographed on alumina (chromatographic grade, 80–200 mesh) eluting with 100:1 CH_2Cl_2/methanol. Fractions were collected that produced a single spot by TLC on alumina plates (eluting with 100:1, CH_2Cl_2/methanol) with an RF value of 0.33. Rotary evaporation of these fractions gave 0.70 g (20%) of a light-yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) d 3.02 (t, 2H), 3.54 (t, 2H), 4.17 (s, 4H), 7.51 (m, 4H), 7.74 (m, 4H), 8.07 (m, 4H).

[Mn(DQMEA)(μ-Ac)$_2$Mn(DQMEA)](BPh$_4$)$_2$. In a 100 ml round bottom flask, 0.20 g (0.56 mmol) DQEA was dissolved in 10 ml me thanol. To this solution, 0.14 g (0.58 mmol) manganese(II) acetate tetrahydrate was added, and the solution was brought to reflux for 30 minutes. A solution of 0.19 g (0.56 mmol) sodium tetraphenylborate in 10 ml of methanol was then added dropwise to the warm reaction mixture. The solution was then cooled in a refrigerator to promote crystallization of the compound. After several hours, the reaction mixture was filtered to produce light yellow microcrystals that were washed twice with cold methanol and air dried to give 0.36 g (82%) of product. Recrystallization of 20 mg of this product in a mixture of dichloromethane and methanol gave crystals suitable for X-ray diffraction. These crystals had an IR spectrum identical to the original product. IR (ATR, cm^{-1}) 2800–3200 (aromatic C—H, w), 1600 (C—O, s), 1425 (C—O, s), 731 (BPh_4^-, s), 704 (BPh_4^-, s).

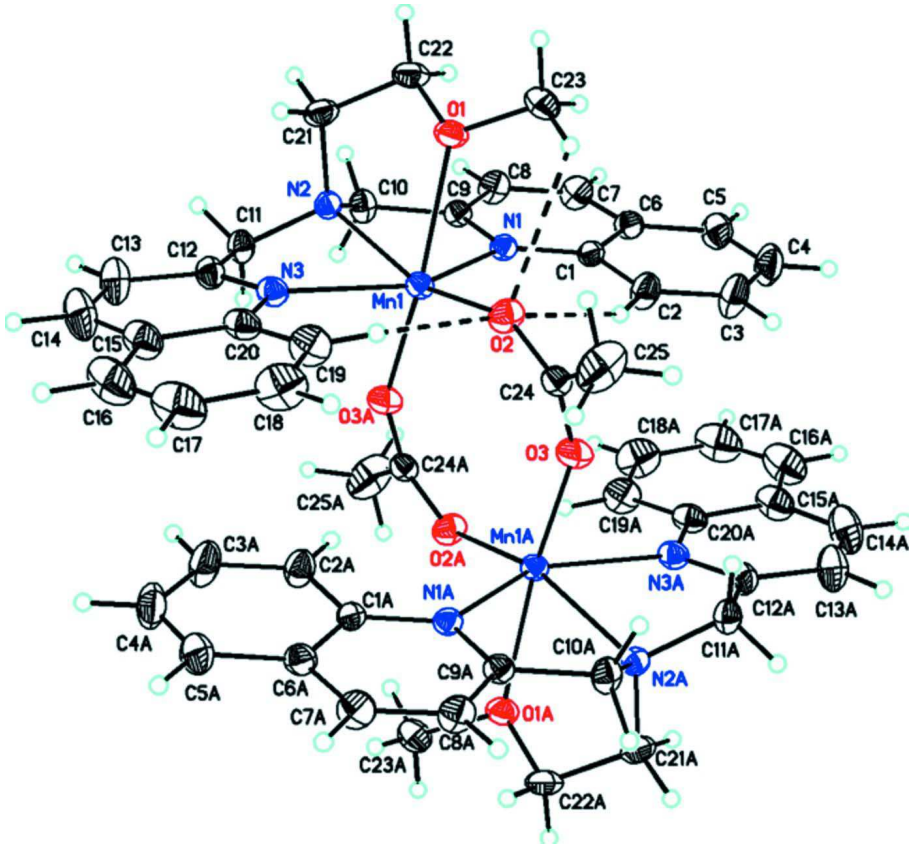
[Mn(DQEA)(Ac)(CH$_3$OH)]BPh$_4$·CH$_3$OH. In a 100 ml round bottom flask, 0.20 g (0.58 mmol) DQEA was dissolved in 10 ml me thanol. To this solution, 0.14 g (0.58 mmol) manganese(II) acetate tetrahydrate was added, and the solution was brought to reflux for 30 minutes. A solution of 0.20 g (0.58 mmol) sodium tetraphenylborate in 10 ml of methanol was then added dropwise to the warm reaction mixture. The solution was then cooled in a refrigerator to promote crystallization of the compound. After several hours, the reaction mixture was filtered to produce light yellow microcrystals that were washed twice with cold methanol and air dried to give 0.31 g (69%) of product. Recrystallization of 20 mg of this product in a mixture of dichloromethane and methanol gave crystals suitable for X-ray diffraction. These crystals had an IR spectrum identical to the original product. IR (ATR, cm^{-1}) 2800–3200 (aromatic C—H, w), 1578 (C—O, s), 1427 (C—O, s), 736 (BPh_4^-, s), 700 (BPh_4^-, s).

6. Refinement

Crystal data, data collection and structure refinement details for **[1]**$(BPh_4)_2$ are summarized in Table 5. A l l H atoms were positioned geometrically and refined using a riding model: C—H = 0.93– 0.99 A°, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(*C*-methyl). Idealized methyl groups were refined as a rotating groups:C23(H23A,H23B,H23C), C25(H25A,H25B,H25C).

Crystal data, data collection and structure refinement details for **[2]**BPh_4·CH_3OH are summarized in Table 5. The hydroxy H atoms(O3—H3, O4—H4) were located in a difference-Fourier map and refined with the distance restraint O—H = 0.87 ± 0.01 and with U_{iso}(H) = 1.5U_{eq}(O). C-bound H atoms were positioned geometrically and refined as riding: C—H = 0.95–0.99 A° with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(*C*-methyl). Idealized methyl groups were refined as rotating groups:C24(H24A,H24B,H24C), C25(H25A,H25B,H25C), C1S(H1SA,H1SB,H1SC). An idealized tetrahedral OH group was also refined as a rotating group: O1S(H1S).

fig1.tif



171 **Figure 1**

172 Structure of the $[Mn(DQMEA)(m\text{-}Ac)_2Mn(DQMEA)]^{2+}$ complex [DQMEA = *N,N*-Bis(2-quinolylmethyl)methoxyethyl-

173 amine, Ac = acetate] with atom labels. Displacement ellipsoids are drawn at the 30% probability level.

fig2.tif

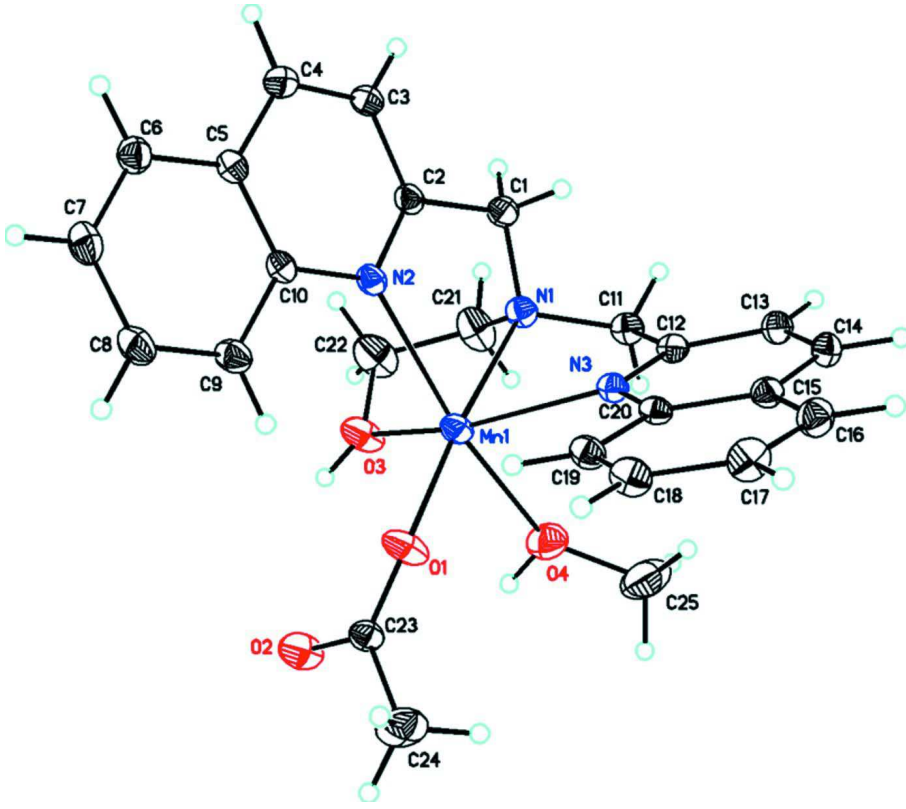


Figure 2

Structure of the [Mn(DQEA)(Ac)(CH_3OH)]$^+$ complex [DQEA = *N,N*-Bis(2-quinolylmethyl)hydroxyethylamine, Ac = acetate] with atom labels. Displacement ellipsoids are drawn at the 30% probability level.

fig3.tif

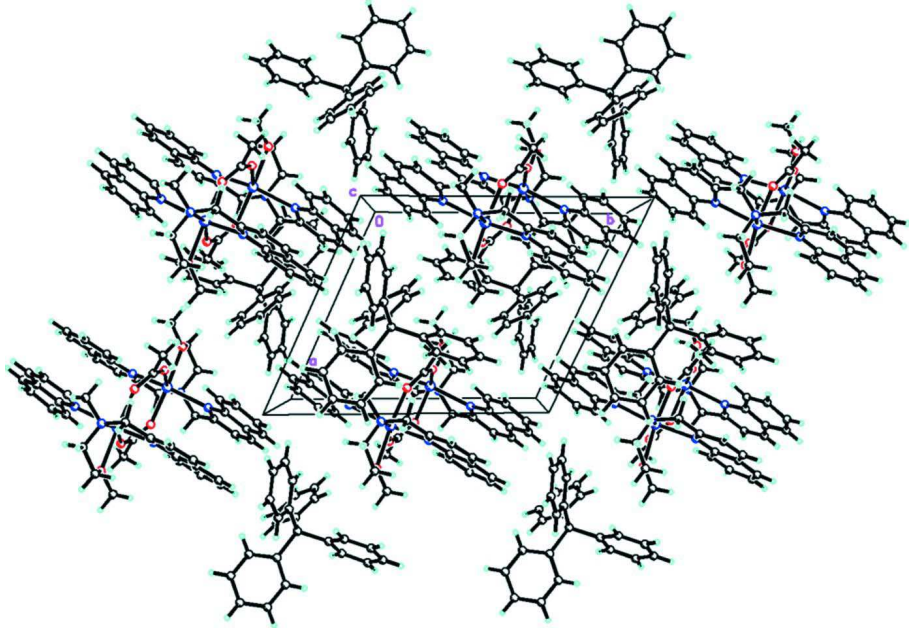


Figure 3

A view along the *c* axis of the crystal packing of **[1]**(BPh_4)$_2$.

fig4.tif

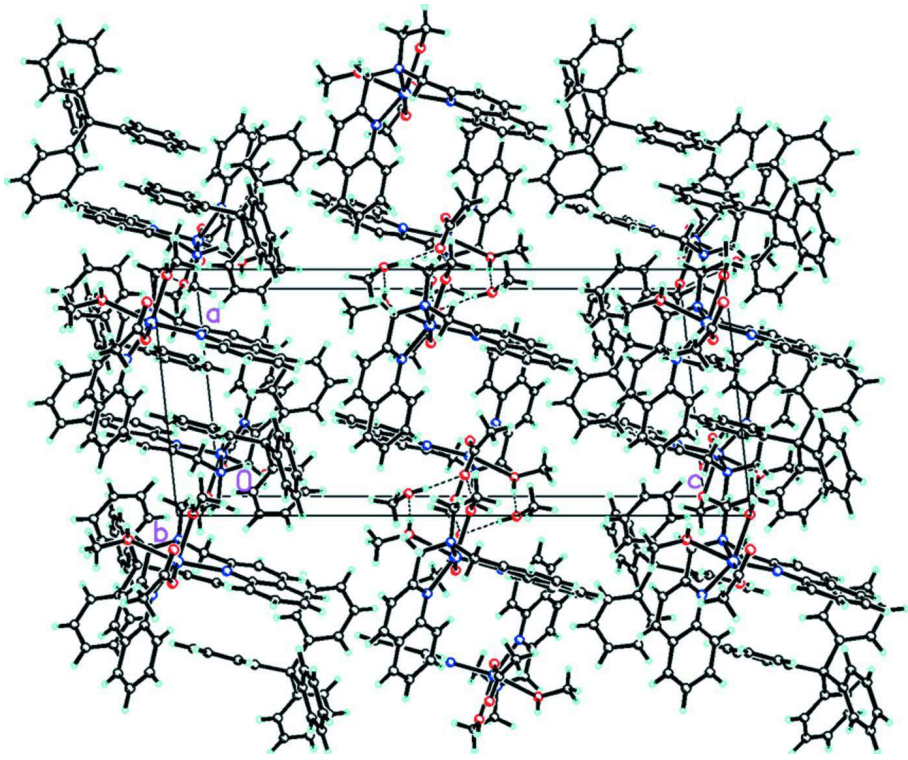


Figure 4

A view along the *b* axis of the crystal packing of **[2]**$BPh_4 \cdot CH_3OH$.

Table 1

Selected bond lengths (Å) and angles (°) of [1](BPh4)2

Mn1—O1	2.0559 (15)
Mn1—O3	2.1691 (15)
Mn1—O4	2.3200 (17)
Mn1—N1	2.2783 (15)
Mn1—N2	2.3165 (16)
Mn1—N3	2.2660 (15)
N2—Mn1—N3	73.26 (5)
N2—Mn1—N1	75.52 (5)
N1—Mn1—N3	148.32 (4)
N2—Mn1—O1	75.29 (5)
O2—Mn1—N2	157.92 (5)
O31—Mn1—O1	163.59 (5)

Table 2

Selected bond lengths (Å) and angles (°) of [2]BPh4·CH3OH

Mn1—O1	2.3235 (11)
Mn1—O2	2.0626 (12)
Mn1—O31	2.0899 (12)
Mn1—N1	2.3190 (13)

Mn1—N2	2.2734 (13)
Mn1—N3	2.3586 (14)
N1—Mn1—N2	75.62 (5)
N1—Mn1—N3	73.79 (5)
O3—Mn1—N3	148.81 (6)
O1—Mn1—N1	175.50 (7)
N2—Mn1—O4	161.35 (6)

Table 3

Hydrogen-bond geometry and π-π stacking interactions of [1](BPh4)2 (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O2	0.95	2.49	3.366 (2)	154.1
C19—H19···O2	0.95	2.31	3.201 (3)	155.1
C8—H8···*Cg*13i	0.95	2.68	3.5556 (2)	153
C11—H11B··· *Cg*13ii	0.99	2.81	3.7195 (2)	152
C23—H23B··· *Cg*11iii	0.98	2.78	3.7034 (2)	157
*Cg*6··· *Cg*7iv			3.6397 (2)	

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

Table 4

Hydrogen-bond geometry and π-π stacking interaction of [2]BPh4·CH3OH (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2i	0.873 (9)	1.786 (12)	2.632 (2)	163 (3)
O4—H4···O1S	0.883 (9)	1.770 (10)	2.648 (2)	173 (3)
C9—H9···O1	0.95	2.43	3.326 (3)	156.8
C19—H19···O1	0.95	2.39	3.181 (2)	140.8
O1S—H1S···O2i	0.84	1.92	2.693 (2)	151.6
C11—H11A···*Cg*12ii	0.99	2.70	3.4967 (1)	138

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

Table 5

Experimental details

	(sf-mndqmea)	(sf-mndqea)
Crystal data		
Chemical formula	$C_{50}H_{52}Mn_2N_6O_6\cdot2(C_{24}H_{20}B)$	$C_{25}H_{28}MnN_3O_4\cdot C_{24}H_{20}B\cdot CH_4O$
M_r	1581.27	840.69
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
Temperature (K)	173	173
a, b, c (Å)	11.6553 (5), 13.6846 (7), 16.1109 (6)	10.3504 (3), 17.4824 (5), 23.9618 (9)
α, β, γ (°)	96.842 (4), 105.959 (3), 111.907 (4)	90, 96.222 (3), 90
V (Å^3)	2220.29 (18)	4310.3 (3)
Z	1	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$

μ (mm^{-1})	0.34	0.36
Crystal size (mm)	0.32 × 0.26 × 0.18	0.34 × 0.28 × 0.26
Data collection		
Diffractometer	Rigaku Oxford Diffraction Gemini Eos	Rigaku-OxfordDiffraction Eos, Gemini
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.40.53a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.819, 1.000	0.845, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27403, 14642, 10453	31401, 14423, 10328
R_{int}	0.027	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.762	0.765
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.134, 1.01	0.058, 0.165, 1.04
No. of reflections	14642	14423
No. of parameters	516	551
No. of restraints	0	6
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})	0.97, −0.34	1.62, −0.51

Computer programs: *CrysAlis PRO* 1.171.40.53a (Rigaku OD, 2019), *CrysAlis PRO* 1.171.38.46 (Rigaku OD, 2015), ShelXT (Sheldrick, 2015), *SHELXL* (Sheldrick, 2015), Olex2 (Dolomanov *et al.*, 2009).

Acknowledgements

This publication is submitted in memory of Jerry P. Jasinski, a selfless friend, mentor and collaborator who was always generous with his time and willing to share his expertise and guidance. He will be missed.

Funding information

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References

Batinic-Haberle, I., Reboucas, J. S. & Spaojevic, I. (2010). *Antioxid. Redox Signaling*, **13**, 877-918.

Batinic-Haberle, I., Tovmasyan, A., Roberts, E. R. H., Vujaskovic, Z., Leong, K. W. & Spasojevic, I. (2014). *Antioxid. Redox Signaling*, **20**, 2372-2415.

Boros, E., Gale, E. M. & Caravan, P. (2015). *Dal. Trans*., **44**, 4804-4819.

Coggins, M. K. & Kovacs, J. A. (2011). *J. Am. Chem. Soc*., **133**, 12470-12473.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Dong, H., Yang, X., He, J., Cai, S., Xiao, K. & Zhu, L. (2017). *RSC Adv*., **7**, 53385-53396.

Dees, A., Zahl, A., Puchta, R., van Eikema Holmes, N. J. R., Heinemann, F. W. & Ivanovic-Burmazovic, I. (2007). *Inorg. Chem*., **46**, 2459-2470.

Deroche, A., Morgenstern-Badarau, I., Cesario, M., Guilhem, J., Keita, B., Nadjo, L. & Houee-Levin, C. (1996). *J. Am. Chem. Soc*., **118**, 4567-4573.

Frey, S. T., Ramirez, H. A., Kaur, M. & Jasinski, J. P. (2018). *Acta Cryst*., **E74**, 1075-1078.

Frey, S. T., Li, J., Kaur, M. & Jasinski, J. P. (2018). *Acta Cryst*., **E74**, 1138-1141.

Gale, E. M., Atanasova, I. P., Blasi, F., Ay, I. & Caravan, P. (2015). *J. Am. Chem. Soc*., **137**, 15548-15557.

Icsel, C., Yilmaz, V. T., Aydinlik, S. & Aygun, M. (2020). *Eur. J. Med. Chem*., **202**, 112535-112545.

Iranzo, O. (2011). *Bioorg. Chem.*, **39**, 73-87.

Kakoulidou, C., Hatzidimitriou, A. G., Fylaktakidou, K. C. & Psomas, G. (2021). *Polyhedron*, **195**. 114986-1144996.

Lessa, J. A., Horn, A. Jr, Pinheiro, C. B., Farah, L. L., Eberlin, M. N., Benassi, M., Catharino, R. R. & Fernandes, S. (2007). *Inorg. Chem. Comm*., **10**, 863-866.

Lieb, D., Friedel, F. C., Yawer, M., Zahl, A., Khusniyarov, M. M., Heinemann, F. W. & Ivanovic-Burmazovic, I. (2012). *Inorg. Chem*., **52**, 222-236.

Liu, J., Guo, W., Li, X., Geng, J., Chen, Q. & Gao, J. (2015). *Int. J. Mol. Med*., **35**, 607-616.

Maurya, R. C., Bohre, P., Sahu, S., Martin, M. H. & Sharma, A. K. (2011). *Arab. J. Chem*., **9**, S54-S63.

Miriyala, S., Spasojevic, I., Tovmasyan, A., Salvemini, D., Vujaskovic, Z., **St**, Clair, D. & Batinic-Haberle, I. (2012). *Biochim. Biophys. Acta*, **1822**, 794-814.

Policar, C. (2016). *Redox-Active Therapeutics*, edited by I. Batinic-Haberle *et al.*, pp. 125-164. Switzerland: Springer International Publishing.

Policar, C., Durot, S., Lambert, F., Cesario, M., Ramiandrasoa, F. & Morgenstern-Badarau, I. (2001). *Eur. J. Inorg. Chem*., 1807-1818.

Prihantono, Irfandi, R., Raya, I. & **Warsinggih** (2020). *Annal. Med. And Surg*., **60**, 396-402.

Qin, Y., She, P., Huang, X., Huang, W. & Zhao, Q. (2020). *Coord. Chem. Rev*., **416**, 213331-213350.

Saha, T., Kumar, P., Sepay, N., Ganguly, D., Tiwari, K., **Mukhopadhyay** & Das, S. (2020). *ACS Omega*, **5**, 16342-16357.

Sarma, C., Chaurasia, P. K. & Bharati, S. L. (2019). *Russ. J. Gen. Chem*., **89**, 517-531.

Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Signorella, S., Palopoli, C. & Ledesma, G. (2018). *Coord. Chem. Rev*., **365**, 75-102.

Wang, J., Wang, H., Ramsay, I. A., Erstad, D. J., Fuchs, B. C., Tanabe, K. K., Caravan, P. & Gale, E. M. (2018). *J. Med. Chem*., **61**, 8811-8824.

Wang, Z.-W., Chen, Q. Y. & Liu, Q.-S. (2014). *Transition Met. Chem*., **39**, 917-924.

Wu, H., Yuan, J., Qi, B., Kong, J., Kou, F., Fan, X. & Wang, Y. (2010). Z. Naturforsch., 65b, 1097-1100.

Zhou, D.-F., Chen, Q.-Y., Qi, Y., Fu, H.-J., Li, Z., Zhao, K.-D. & Gao, J. (2011). *Inorg. Chem*., **50**, 6929-6937.

supporting information

Geometrical Variations of Two Manganese(II) Complexes with Closely-Related, Quinoline-Based, Tripodal Ligands

Steven T. Frey,* Jasper G. Ballot, Allison Hands, Haley A. Cirka, Katheryn C. Rinaolo, Nich N. Phalkun, Manpreet Kaur and Jerry P. Jasinski

Computing details

Data collection: *CrysAlis PRO* 1.171.40.53a (Rigaku OD, 2019) for sf-mndqmea; *CrysAlis PRO* 1.171.38.46 (Rigaku OD, 2015) for sf-mndqea. Cell refinement: *CrysAlis PRO* 1.171.40.53a (Rigaku OD, 2019) for sf-mndqmea; *CrysAlis PRO* 1.171.38.46 (Rigaku OD, 2015) for sf-mndqea. Data reduction: *CrysAlis PRO* 1.171.40.53a (Rigaku OD, 2019) for sf-mndqmea; *CrysAlis PRO* 1.171.38.46 (Rigaku OD, 2015) for sf-mndqea. For both structures, program(s) used to solve structure: ShelXT (Sheldrick, 2015); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

(sf-mndqmea)

Crystal data

$C_{50}H_{52}Mn_2N_6O_6 \cdot 2(C_{24}H_{20}B)$
$M_r = 1581.27$
Triclinic, $P\overline{1}$
$a = 11.6553$ (5) Å
$b = 13.6846$ (7) Å
$c = 16.1109$ (6) Å
$\alpha = 96.842$ (4)°
$\beta = 105.959$ (3)°
$\gamma = 111.907$ (4)°
$V = 2220.29$ (18) Å^3
$Z = 1$
$F(000) = 830$
$D_x = 1.183$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6992 reflections
$\theta = 3.1$–$31.9°$
$\mu = 0.34$ mm^{-1}
$T = 173$ K
Prism, colourless
0.32 × 0.26 × 0.18 mm

Data collection

Rigaku Oxford Diffraction Gemini Eos diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan *CrysAlis PRO* 1.171.40.53a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{min} = 0.819$, $T_{max} = 1.000$
27403 measured reflections
14642 independent reflections
10453 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 32.8°$, $\theta_{min} = 2.6°$
$h = -17 \rightarrow 14$
$k = -20 \rightarrow 19$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.134$
$S = 1.01$
14642 reflections
516 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.5867P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.09230 (2)	0.45985 (2)	0.62583 (2)	0.02687 (7)
O1	0.29645 (11)	0.48109 (11)	0.71837 (8)	0.0372 (3)
O2	0.18222 (12)	0.48215 (11)	0.53140 (8)	0.0394 (3)
O3	0.09606 (12)	0.54509 (12)	0.42250 (9)	0.0482 (3)
N1	0.15844 (12)	0.62707 (10)	0.72095 (8)	0.0277 (3)
N2	0.05879 (12)	0.41905 (11)	0.75239 (8)	0.0291 (3)
N3	−0.01210 (13)	0.26858 (11)	0.59568 (9)	0.0328 (3)
C1	0.22918 (15)	0.72862 (13)	0.71242 (10)	0.0287 (3)
C2	0.2633 (2)	0.73921 (15)	0.63582 (12)	0.0436 (4)
H2	0.235495	0.676276	0.589884	0.052*
C3	0.3361 (2)	0.83935 (18)	0.62687 (16)	0.0584 (6)
H3	0.359381	0.845145	0.575019	0.070*
C4	0.3769 (2)	0.93367 (17)	0.69301 (16)	0.0594 (6)
H4	0.427551	1.002745	0.685853	0.071*
C5	0.3441 (2)	0.92638 (16)	0.76703 (14)	0.0496 (5)
H5	0.371835	0.990506	0.811705	0.060*
C6	0.26884 (17)	0.82401 (14)	0.77838 (11)	0.0352 (3)
C7	0.2307 (2)	0.81222 (15)	0.85348 (12)	0.0436 (4)
H7	0.253892	0.874524	0.898701	0.052*
C8	0.16075 (19)	0.71166 (15)	0.86098 (11)	0.0409 (4)
H8	0.134165	0.702960	0.911348	0.049*
C9	0.12752 (15)	0.61982 (13)	0.79360 (10)	0.0291 (3)
C10	0.04948 (17)	0.50959 (14)	0.80483 (11)	0.0360 (4)
H10A	0.080472	0.510083	0.868650	0.043*
H10B	−0.044338	0.496532	0.787582	0.043*
C11	−0.06475 (16)	0.32000 (14)	0.72543 (11)	0.0350 (3)
H11A	−0.140250	0.339103	0.706073	0.042*
H11B	−0.069727	0.288740	0.777377	0.042*
C12	−0.07520 (16)	0.23623 (14)	0.65097 (12)	0.0356 (3)
C13	−0.1573 (2)	0.12662 (16)	0.64185 (16)	0.0541 (5)

H13	−0.197272	0.106714	0.684990	0.065*
C14	−0.1785 (2)	0.05012 (18)	0.57089 (19)	0.0642 (6)
H14	−0.235025	−0.023876	0.563307	0.077*
C15	−0.1173 (2)	0.08012 (16)	0.50883 (14)	0.0498 (5)
C16	−0.1365 (2)	0.0053 (2)	0.43219 (18)	0.0671 (7)
H16	−0.194352	−0.069159	0.420855	0.081*
C17	−0.0736 (3)	0.0386 (2)	0.37518 (16)	0.0705 (8)
H17	−0.089164	−0.012428	0.323287	0.085*
C18	0.0141 (3)	0.1471 (2)	0.39129 (15)	0.0653 (7)
H18	0.058671	0.169009	0.350799	0.078*
C19	0.0365 (2)	0.22247 (18)	0.46537 (13)	0.0503 (5)
H19	0.097431	0.295943	0.476340	0.060*
C20	−0.03012 (17)	0.19126 (15)	0.52444 (11)	0.0382 (4)
C21	0.16969 (17)	0.39670 (17)	0.80250 (11)	0.0406 (4)
H21A	0.157688	0.324057	0.773055	0.049*
H21B	0.168590	0.395356	0.863587	0.049*
C22	0.30071 (17)	0.48023 (17)	0.80781 (11)	0.0424 (4)
H22A	0.317035	0.552757	0.840669	0.051*
H22B	0.372320	0.461335	0.839272	0.051*
C23	0.41725 (17)	0.56036 (19)	0.71645 (15)	0.0501 (5)
H23A	0.412146	0.557971	0.654455	0.075*
H23B	0.490646	0.544419	0.747593	0.075*
H23C	0.431602	0.632931	0.746002	0.075*
C24	0.17229 (15)	0.50764 (13)	0.45826 (10)	0.0305 (3)
C25	0.2630 (3)	0.4932 (3)	0.41266 (17)	0.0711 (7)
H25A	0.324836	0.471080	0.451359	0.107*
H25B	0.312151	0.561957	0.400237	0.107*
H25C	0.211191	0.436977	0.356568	0.107*
C26	0.45807 (16)	0.73424 (14)	0.27056 (11)	0.0357 (4)
C27	0.54458 (19)	0.69684 (18)	0.32056 (13)	0.0482 (5)
H27	0.576361	0.654644	0.290159	0.058*
C28	0.5858 (2)	0.7194 (2)	0.41356 (15)	0.0671 (7)
H28	0.644434	0.692533	0.445203	0.081*
C29	0.5414 (3)	0.7806 (2)	0.45937 (15)	0.0763 (9)
H29	0.568659	0.795854	0.522545	0.092*
C30	0.4580 (2)	0.8188 (2)	0.41297 (15)	0.0653 (7)
H30	0.427693	0.861668	0.444155	0.078*
C31	0.41656 (19)	0.79591 (16)	0.32066 (13)	0.0468 (5)
H31	0.357615	0.823246	0.290242	0.056*
C32	0.35685 (14)	0.56806 (13)	0.13074 (10)	0.0288 (3)
C33	0.37934 (15)	0.51455 (14)	0.06120 (10)	0.0314 (3)
H33	0.425356	0.556477	0.028073	0.038*
C34	0.33677 (16)	0.40259 (14)	0.03909 (11)	0.0356 (4)
H34	0.355659	0.369655	−0.007626	0.043*
C35	0.26740 (16)	0.33890 (15)	0.08432 (12)	0.0386 (4)
H35	0.238497	0.262287	0.069289	0.046*
C36	0.24020 (16)	0.38843 (15)	0.15247 (12)	0.0374 (4)
H36	0.190976	0.345606	0.183637	0.045*

C37	0.28504 (15)	0.49983 (14)	0.17444 (11)	0.0326 (3)
H37	0.266341	0.532064	0.221606	0.039*
C38	0.52329 (16)	0.76512 (13)	0.12295 (11)	0.0325 (3)
C39	0.4939 (2)	0.78594 (18)	0.03912 (14)	0.0482 (5)
H39	0.403927	0.759950	0.002917	0.058*
C40	0.5903 (3)	0.8431 (2)	0.00571 (16)	0.0589 (6)
H40	0.565227	0.857375	−0.051225	0.071*
C41	0.7210 (2)	0.87892 (17)	0.05458 (16)	0.0572 (6)
H41	0.787153	0.918518	0.032342	0.069*
C42	0.75487 (19)	0.85651 (16)	0.13639 (15)	0.0507 (5)
H42	0.845099	0.878560	0.170157	0.061*
C43	0.65797 (17)	0.80177 (15)	0.17014 (12)	0.0394 (4)
H43	0.684244	0.788765	0.227458	0.047*
C44	0.27983 (15)	0.72880 (14)	0.11957 (10)	0.0320 (3)
C45	0.14894 (15)	0.65105 (14)	0.07822 (10)	0.0307 (3)
H45	0.130811	0.576336	0.071878	0.037*
C46	0.04438 (16)	0.67853 (16)	0.04605 (10)	0.0359 (4)
H46	−0.042877	0.623068	0.018662	0.043*
C47	0.06724 (19)	0.78577 (18)	0.05386 (13)	0.0459 (4)
H47	−0.003859	0.805256	0.033293	0.055*
C48	0.1951 (2)	0.86474 (18)	0.09205 (16)	0.0561 (6)
H48	0.212623	0.939099	0.096337	0.067*
C49	0.29813 (19)	0.83622 (16)	0.12416 (14)	0.0475 (5)
H49	0.385122	0.892335	0.150484	0.057*
B1	0.40540 (17)	0.69964 (15)	0.16047 (11)	0.0297 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.02666 (12)	0.03045 (12)	0.02107 (10)	0.01041 (9)	0.00804 (8)	0.00418 (8)
O1	0.0264 (5)	0.0484 (7)	0.0335 (6)	0.0146 (5)	0.0069 (4)	0.0115 (5)
O2	0.0464 (7)	0.0496 (8)	0.0282 (5)	0.0217 (6)	0.0188 (5)	0.0125 (5)
O3	0.0322 (6)	0.0494 (8)	0.0538 (8)	0.0165 (6)	0.0012 (5)	0.0166 (6)
N1	0.0307 (6)	0.0278 (6)	0.0223 (5)	0.0117 (5)	0.0075 (5)	0.0044 (5)
N2	0.0306 (6)	0.0295 (7)	0.0251 (6)	0.0101 (5)	0.0101 (5)	0.0071 (5)
N3	0.0339 (7)	0.0304 (7)	0.0295 (6)	0.0128 (5)	0.0075 (5)	0.0024 (5)
C1	0.0305 (7)	0.0265 (7)	0.0264 (7)	0.0115 (6)	0.0070 (5)	0.0066 (6)
C2	0.0593 (12)	0.0348 (9)	0.0358 (9)	0.0146 (8)	0.0223 (8)	0.0102 (7)
C3	0.0814 (16)	0.0437 (12)	0.0548 (12)	0.0180 (11)	0.0380 (11)	0.0224 (10)
C4	0.0715 (15)	0.0311 (10)	0.0663 (14)	0.0089 (9)	0.0257 (11)	0.0181 (10)
C5	0.0572 (12)	0.0288 (9)	0.0524 (11)	0.0125 (8)	0.0136 (9)	0.0053 (8)
C6	0.0394 (9)	0.0279 (8)	0.0324 (8)	0.0137 (7)	0.0063 (6)	0.0034 (6)
C7	0.0598 (12)	0.0332 (9)	0.0335 (8)	0.0196 (8)	0.0143 (8)	−0.0011 (7)
C8	0.0562 (11)	0.0394 (10)	0.0281 (8)	0.0198 (8)	0.0188 (7)	0.0035 (7)
C9	0.0310 (7)	0.0299 (8)	0.0245 (7)	0.0122 (6)	0.0093 (5)	0.0038 (6)
C10	0.0429 (9)	0.0329 (8)	0.0311 (8)	0.0103 (7)	0.0206 (7)	0.0055 (6)
C11	0.0374 (8)	0.0312 (8)	0.0361 (8)	0.0103 (7)	0.0184 (7)	0.0083 (6)
C12	0.0353 (8)	0.0294 (8)	0.0405 (9)	0.0125 (6)	0.0131 (7)	0.0076 (7)

C13	0.0593 (13)	0.0320 (10)	0.0747 (15)	0.0145 (9)	0.0362 (11)	0.0118 (9)
C14	0.0622 (14)	0.0302 (10)	0.0921 (18)	0.0105 (9)	0.0333 (13)	0.0021 (11)
C15	0.0484 (11)	0.0364 (10)	0.0531 (11)	0.0181 (8)	0.0079 (9)	−0.0058 (8)
C16	0.0659 (15)	0.0477 (13)	0.0673 (15)	0.0207 (11)	0.0116 (12)	−0.0182 (11)
C17	0.0783 (17)	0.0609 (15)	0.0534 (13)	0.0310 (13)	0.0081 (12)	−0.0216 (11)
C18	0.0868 (17)	0.0700 (16)	0.0420 (11)	0.0391 (14)	0.0245 (11)	−0.0010 (11)
C19	0.0635 (13)	0.0480 (11)	0.0364 (9)	0.0235 (10)	0.0179 (9)	−0.0008 (8)
C20	0.0377 (9)	0.0360 (9)	0.0347 (8)	0.0181 (7)	0.0044 (7)	−0.0018 (7)
C21	0.0413 (9)	0.0531 (11)	0.0295 (8)	0.0225 (8)	0.0088 (7)	0.0175 (7)
C22	0.0359 (9)	0.0573 (12)	0.0276 (8)	0.0202 (8)	0.0016 (6)	0.0098 (7)
C23	0.0253 (8)	0.0611 (13)	0.0585 (12)	0.0133 (8)	0.0112 (8)	0.0210 (10)
C24	0.0283 (7)	0.0335 (8)	0.0256 (7)	0.0098 (6)	0.0098 (5)	0.0035 (6)
C25	0.0952 (19)	0.104 (2)	0.0674 (15)	0.0669 (17)	0.0625 (14)	0.0449 (15)
C26	0.0293 (8)	0.0347 (9)	0.0312 (8)	0.0040 (6)	0.0086 (6)	0.0033 (6)
C27	0.0390 (10)	0.0522 (12)	0.0375 (9)	0.0096 (8)	0.0038 (7)	0.0106 (8)
C28	0.0490 (12)	0.0764 (17)	0.0419 (11)	0.0015 (11)	−0.0024 (9)	0.0222 (11)
C29	0.0664 (15)	0.0851 (19)	0.0291 (10)	−0.0111 (13)	0.0114 (10)	0.0023 (11)
C30	0.0641 (14)	0.0669 (15)	0.0402 (11)	0.0005 (11)	0.0274 (10)	−0.0044 (10)
C31	0.0425 (10)	0.0460 (11)	0.0387 (9)	0.0043 (8)	0.0197 (8)	−0.0008 (8)
C32	0.0228 (7)	0.0336 (8)	0.0277 (7)	0.0121 (6)	0.0061 (5)	0.0058 (6)
C33	0.0256 (7)	0.0367 (8)	0.0292 (7)	0.0123 (6)	0.0083 (6)	0.0047 (6)
C34	0.0297 (8)	0.0392 (9)	0.0340 (8)	0.0157 (7)	0.0076 (6)	−0.0002 (7)
C35	0.0328 (8)	0.0323 (9)	0.0455 (9)	0.0139 (7)	0.0078 (7)	0.0052 (7)
C36	0.0322 (8)	0.0381 (9)	0.0414 (9)	0.0128 (7)	0.0130 (7)	0.0141 (7)
C37	0.0294 (8)	0.0367 (9)	0.0314 (7)	0.0139 (6)	0.0108 (6)	0.0075 (6)
C38	0.0326 (8)	0.0287 (8)	0.0369 (8)	0.0127 (6)	0.0149 (6)	0.0050 (6)
C39	0.0480 (11)	0.0596 (13)	0.0459 (10)	0.0253 (10)	0.0226 (8)	0.0212 (9)
C40	0.0782 (16)	0.0618 (14)	0.0587 (13)	0.0344 (12)	0.0429 (12)	0.0305 (11)
C41	0.0625 (14)	0.0366 (10)	0.0755 (15)	0.0093 (9)	0.0483 (12)	0.0057 (10)
C42	0.0370 (10)	0.0403 (10)	0.0600 (12)	0.0023 (8)	0.0243 (9)	−0.0095 (9)
C43	0.0338 (8)	0.0358 (9)	0.0403 (9)	0.0087 (7)	0.0142 (7)	−0.0020 (7)
C44	0.0315 (8)	0.0348 (8)	0.0292 (7)	0.0141 (6)	0.0116 (6)	0.0034 (6)
C45	0.0318 (8)	0.0364 (8)	0.0254 (7)	0.0143 (6)	0.0123 (6)	0.0079 (6)
C46	0.0306 (8)	0.0508 (10)	0.0275 (7)	0.0180 (7)	0.0108 (6)	0.0094 (7)
C47	0.0443 (10)	0.0558 (12)	0.0440 (10)	0.0319 (9)	0.0110 (8)	0.0096 (9)
C48	0.0546 (12)	0.0386 (11)	0.0716 (14)	0.0268 (9)	0.0105 (10)	0.0049 (10)
C49	0.0382 (9)	0.0353 (10)	0.0578 (12)	0.0145 (8)	0.0066 (8)	0.0003 (8)
B1	0.0269 (8)	0.0313 (9)	0.0283 (8)	0.0112 (7)	0.0087 (6)	0.0038 (7)

Geometric parameters (Å, º)

Mn1—O1	2.3235 (11)	C22—H22B	0.9900
Mn1—O2	2.0626 (12)	C23—H23A	0.9800
Mn1—O3^{i}	2.0899 (12)	C23—H23B	0.9800
Mn1—N1	2.3190 (13)	C23—H23C	0.9800
Mn1—N2	2.2734 (13)	C24—C25	1.498 (2)
Mn1—N3	2.3586 (14)	C25—H25A	0.9800
O1—C22	1.430 (2)	C25—H25B	0.9800

215	O1—C23	1.433 (2)	C25—H25C	0.9800
216	O2—C24	1.2557 (19)	C26—C27	1.401 (3)
217	O3—C24	1.230 (2)	C26—C31	1.398 (3)
218	N1—C1	1.372 (2)	C26—B1	1.653 (2)
219	N1—C9	1.3201 (19)	C27—H27	0.9500
220	N2—C10	1.470 (2)	C27—C28	1.398 (3)
221	N2—C11	1.469 (2)	C28—H28	0.9500
222	N2—C21	1.482 (2)	C28—C29	1.379 (4)
223	N3—C12	1.320 (2)	C29—H29	0.9500
224	N3—C20	1.376 (2)	C29—C30	1.360 (4)
225	C1—C2	1.404 (2)	C30—H30	0.9500
226	C1—C6	1.413 (2)	C30—C31	1.387 (3)
227	C2—H2	0.9500	C31—H31	0.9500
228	C2—C3	1.366 (3)	C32—C33	1.403 (2)
229	C3—H3	0.9500	C32—C37	1.402 (2)
230	C3—C4	1.401 (3)	C32—B1	1.636 (2)
231	C4—H4	0.9500	C33—H33	0.9500
232	C4—C5	1.352 (3)	C33—C34	1.388 (2)
233	C5—H5	0.9500	C34—H34	0.9500
234	C5—C6	1.413 (3)	C34—C35	1.376 (3)
235	C6—C7	1.406 (3)	C35—H35	0.9500
236	C7—H7	0.9500	C35—C36	1.393 (2)
237	C7—C8	1.353 (3)	C36—H36	0.9500
238	C8—H8	0.9500	C36—C37	1.378 (2)
239	C8—C9	1.410 (2)	C37—H37	0.9500
240	C9—C10	1.506 (2)	C38—C39	1.390 (3)
241	C10—H10A	0.9900	C38—C43	1.400 (2)
242	C10—H10B	0.9900	C38—B1	1.650 (2)
243	C11—H11A	0.9900	C39—H39	0.9500
244	C11—H11B	0.9900	C39—C40	1.394 (3)
245	C11—C12	1.502 (2)	C40—H40	0.9500
246	C12—C13	1.409 (3)	C40—C41	1.368 (3)
247	C13—H13	0.9500	C41—H41	0.9500
248	C13—C14	1.353 (3)	C41—C42	1.374 (3)
249	C14—H14	0.9500	C42—H42	0.9500
250	C14—C15	1.396 (3)	C42—C43	1.391 (3)
251	C15—C16	1.413 (3)	C43—H43	0.9500
252	C15—C20	1.423 (3)	C44—C45	1.402 (2)
253	C16—H16	0.9500	C44—C49	1.394 (3)
254	C16—C17	1.345 (4)	C44—B1	1.644 (2)
255	C17—H17	0.9500	C45—H45	0.9500
256	C17—C18	1.395 (4)	C45—C46	1.391 (2)
257	C18—H18	0.9500	C46—H46	0.9500
258	C18—C19	1.375 (3)	C46—C47	1.373 (3)
259	C19—H19	0.9500	C47—H47	0.9500
260	C19—C20	1.395 (3)	C47—C48	1.380 (3)
261	C21—H21A	0.9900	C48—H48	0.9500
262	C21—H21B	0.9900	C48—C49	1.385 (3)

C21—C22	1.499 (3)	C49—H49	0.9500
C22—H22A	0.9900		
O1—Mn1—N3	96.56 (5)	C22—C21—H21A	109.2
O2—Mn1—O1	84.09 (5)	C22—C21—H21B	109.2
O2—Mn1—O3^{i}	110.91 (5)	O1—C22—C21	107.13 (13)
O2—Mn1—N1	109.13 (5)	O1—C22—H22A	110.3
O2—Mn1—N2	157.92 (5)	O1—C22—H22B	110.3
O2—Mn1—N3	101.85 (5)	C21—C22—H22A	110.3
O3^{i}—Mn1—O1	163.59 (5)	C21—C22—H22B	110.3
O3^{i}—Mn1—N1	88.01 (5)	H22A—C22—H22B	108.5
O3^{i}—Mn1—N2	90.58 (5)	O1—C23—H23A	109.5
O3^{i}—Mn1—N3	87.08 (5)	O1—C23—H23B	109.5
N1—Mn1—O1	80.48 (5)	O1—C23—H23C	109.5
N1—Mn1—N3	148.32 (5)	H23A—C23—H23B	109.5
N2—Mn1—O1	75.29 (4)	H23A—C23—H23C	109.5
N2—Mn1—N1	75.52 (5)	H23B—C23—H23C	109.5
N2—Mn1—N3	73.26 (5)	O2—C24—C25	116.86 (16)
C22—O1—Mn1	112.24 (9)	O3—C24—O2	125.09 (16)
C22—O1—C23	111.33 (14)	O3—C24—C25	118.03 (17)
C23—O1—Mn1	121.82 (11)	C24—C25—H25A	109.5
C24—O2—Mn1	142.40 (11)	C24—C25—H25B	109.5
C24—O3—Mn1^{i}	151.88 (13)	C24—C25—H25C	109.5
C1—N1—Mn1	128.17 (10)	H25A—C25—H25B	109.5
C9—N1—Mn1	113.65 (10)	H25A—C25—H25C	109.5
C9—N1—C1	118.10 (13)	H25B—C25—H25C	109.5
C10—N2—Mn1	109.90 (10)	C27—C26—B1	120.62 (16)
C10—N2—C21	111.87 (13)	C31—C26—C27	114.99 (17)
C11—N2—Mn1	107.37 (9)	C31—C26—B1	124.30 (16)
C11—N2—C10	110.52 (12)	C26—C27—H27	118.8
C11—N2—C21	109.29 (14)	C28—C27—C26	122.4 (2)
C21—N2—Mn1	107.74 (10)	C28—C27—H27	118.8
C12—N3—Mn1	111.76 (11)	C27—C28—H28	120.0
C12—N3—C20	118.03 (15)	C29—C28—C27	120.0 (2)
C20—N3—Mn1	129.54 (12)	C29—C28—H28	120.0
N1—C1—C2	119.53 (14)	C28—C29—H29	120.4
N1—C1—C6	122.08 (14)	C30—C29—C28	119.2 (2)
C2—C1—C6	118.38 (16)	C30—C29—H29	120.4
C1—C2—H2	119.8	C29—C30—H30	119.6
C3—C2—C1	120.46 (18)	C29—C30—C31	120.8 (2)
C3—C2—H2	119.8	C31—C30—H30	119.6
C2—C3—H3	119.5	C26—C31—H31	118.7
C2—C3—C4	121.0 (2)	C30—C31—C26	122.7 (2)
C4—C3—H3	119.5	C30—C31—H31	118.7
C3—C4—H4	120.0	C33—C32—C37	115.07 (15)
C5—C4—C3	120.00 (19)	C33—C32—B1	124.68 (14)
C5—C4—H4	120.0	C37—C32—B1	120.24 (14)
C4—C5—H5	119.8	C32—C33—H33	118.8

311	C4—C5—C6	120.46 (18)	C34—C33—C32	122.36 (16)
312	C6—C5—H5	119.8	C34—C33—H33	118.8
313	C1—C6—C5	119.69 (17)	C33—C34—H34	119.7
314	C7—C6—C1	117.67 (16)	C35—C34—C33	120.51 (15)
315	C7—C6—C5	122.64 (16)	C35—C34—H34	119.7
316	C6—C7—H7	120.2	C34—C35—H35	120.5
317	C8—C7—C6	119.63 (16)	C34—C35—C36	119.02 (17)
318	C8—C7—H7	120.2	C36—C35—H35	120.5
319	C7—C8—H8	120.2	C35—C36—H36	120.2
320	C7—C8—C9	119.62 (16)	C37—C36—C35	119.67 (17)
321	C9—C8—H8	120.2	C37—C36—H36	120.2
322	N1—C9—C8	122.86 (15)	C32—C37—H37	118.3
323	N1—C9—C10	119.40 (13)	C36—C37—C32	123.35 (15)
324	C8—C9—C10	117.71 (14)	C36—C37—H37	118.3
325	N2—C10—C9	114.45 (13)	C39—C38—C43	114.75 (16)
326	N2—C10—H10A	108.6	C39—C38—B1	121.18 (15)
327	N2—C10—H10B	108.6	C43—C38—B1	124.06 (15)
328	C9—C10—H10A	108.6	C38—C39—H39	118.5
329	C9—C10—H10B	108.6	C38—C39—C40	123.0 (2)
330	H10A—C10—H10B	107.6	C40—C39—H39	118.5
331	N2—C11—H11A	109.2	C39—C40—H40	119.9
332	N2—C11—H11B	109.2	C41—C40—C39	120.3 (2)
333	N2—C11—C12	112.10 (13)	C41—C40—H40	119.9
334	H11A—C11—H11B	107.9	C40—C41—H41	120.6
335	C12—C11—H11A	109.2	C40—C41—C42	118.79 (19)
336	C12—C11—H11B	109.2	C42—C41—H41	120.6
337	N3—C12—C11	118.99 (15)	C41—C42—H42	119.8
338	N3—C12—C13	123.39 (17)	C41—C42—C43	120.48 (19)
339	C13—C12—C11	117.57 (16)	C43—C42—H42	119.8
340	C12—C13—H13	120.4	C38—C43—H43	118.7
341	C14—C13—C12	119.2 (2)	C42—C43—C38	122.57 (19)
342	C14—C13—H13	120.4	C42—C43—H43	118.7
343	C13—C14—H14	120.1	C45—C44—B1	124.25 (15)
344	C13—C14—C15	119.9 (2)	C49—C44—C45	114.86 (15)
345	C15—C14—H14	120.1	C49—C44—B1	120.89 (15)
346	C14—C15—C16	123.2 (2)	C44—C45—H45	118.6
347	C14—C15—C20	118.12 (18)	C46—C45—C44	122.86 (16)
348	C16—C15—C20	118.7 (2)	C46—C45—H45	118.6
349	C15—C16—H16	119.7	C45—C46—H46	120.0
350	C17—C16—C15	120.7 (2)	C47—C46—C45	120.05 (16)
351	C17—C16—H16	119.7	C47—C46—H46	120.0
352	C16—C17—H17	119.6	C46—C47—H47	120.5
353	C16—C17—C18	120.8 (2)	C46—C47—C48	118.92 (17)
354	C18—C17—H17	119.6	C48—C47—H47	120.5
355	C17—C18—H18	119.8	C47—C48—H48	119.8
356	C19—C18—C17	120.5 (2)	C47—C48—C49	120.4 (2)
357	C19—C18—H18	119.8	C49—C48—H48	119.8
358	C18—C19—H19	119.9	C44—C49—H49	118.5

C18—C19—C20	120.1 (2)	C48—C49—C44	122.90 (18)
C20—C19—H19	119.9	C48—C49—H49	118.5
N3—C20—C15	121.28 (18)	C32—B1—C26	106.60 (14)
N3—C20—C19	119.52 (17)	C32—B1—C38	111.30 (13)
C19—C20—C15	119.20 (17)	C32—B1—C44	109.27 (12)
N2—C21—H21A	109.2	C38—B1—C26	110.96 (13)
N2—C21—H21B	109.2	C44—B1—C26	110.09 (13)
N2—C21—C22	112.21 (15)	C44—B1—C38	108.61 (13)
H21A—C21—H21B	107.9		

Mn1—O1—C22—C21	38.47 (17)	C20—N3—C12—C11	−175.68 (15)
Mn1—O2—C24—O3	10.6 (3)	C20—N3—C12—C13	1.5 (3)
Mn1—O2—C24—C25	−170.74 (18)	C20—C15—C16—C17	0.0 (4)
Mn1^{i}—O3—C24—O2	−52.7 (4)	C21—N2—C10—C9	90.02 (17)
Mn1^{i}—O3—C24—C25	128.7 (3)	C21—N2—C11—C12	−73.27 (17)
Mn1—N1—C1—C2	3.8 (2)	C23—O1—C22—C21	178.92 (16)
Mn1—N1—C1—C6	−176.55 (11)	C26—C27—C28—C29	−0.1 (3)
Mn1—N1—C9—C8	178.80 (13)	C27—C26—C31—C30	0.2 (3)
Mn1—N1—C9—C10	−3.30 (18)	C27—C26—B1—C32	47.8 (2)
Mn1—N2—C10—C9	−29.62 (16)	C27—C26—B1—C38	−73.5 (2)
Mn1—N2—C11—C12	43.33 (16)	C27—C26—B1—C44	166.21 (16)
Mn1—N2—C21—C22	46.01 (16)	C27—C28—C29—C30	−0.3 (4)
Mn1—N3—C12—C11	−4.19 (19)	C28—C29—C30—C31	0.7 (4)
Mn1—N3—C12—C13	173.00 (16)	C29—C30—C31—C26	−0.6 (3)
Mn1—N3—C20—C15	−167.76 (13)	C31—C26—C27—C28	0.2 (3)
Mn1—N3—C20—C19	11.1 (2)	C31—C26—B1—C32	−128.51 (17)
N1—C1—C2—C3	−178.59 (19)	C31—C26—B1—C38	110.14 (18)
N1—C1—C6—C5	178.61 (16)	C31—C26—B1—C44	−10.1 (2)
N1—C1—C6—C7	−1.4 (2)	C32—C33—C34—C35	1.4 (2)
N1—C9—C10—N2	22.9 (2)	C33—C32—C37—C36	0.7 (2)
N2—C11—C12—N3	−26.9 (2)	C33—C32—B1—C26	−139.76 (15)
N2—C11—C12—C13	155.77 (17)	C33—C32—B1—C38	−18.6 (2)
N2—C21—C22—O1	−57.4 (2)	C33—C32—B1—C44	101.30 (16)
N3—C12—C13—C14	−3.2 (3)	C33—C34—C35—C36	0.2 (2)
C1—N1—C9—C8	1.9 (2)	C34—C35—C36—C37	−1.2 (2)
C1—N1—C9—C10	179.76 (14)	C35—C36—C37—C32	0.8 (2)
C1—C2—C3—C4	−0.9 (4)	C37—C32—C33—C34	−1.7 (2)
C1—C6—C7—C8	1.3 (3)	C37—C32—B1—C26	41.58 (18)
C2—C1—C6—C5	−1.7 (3)	C37—C32—B1—C38	162.70 (13)
C2—C1—C6—C7	178.21 (17)	C37—C32—B1—C44	−77.36 (17)
C2—C3—C4—C5	−0.1 (4)	C38—C39—C40—C41	2.1 (4)
C3—C4—C5—C6	0.1 (4)	C39—C38—C43—C42	1.1 (3)
C4—C5—C6—C1	0.8 (3)	C39—C38—B1—C26	−153.26 (17)
C4—C5—C6—C7	−179.1 (2)	C39—C38—B1—C32	88.20 (19)
C5—C6—C7—C8	−178.77 (19)	C39—C38—B1—C44	−32.1 (2)
C6—C1—C2—C3	1.7 (3)	C39—C40—C41—C42	0.6 (3)
C6—C7—C8—C9	0.3 (3)	C40—C41—C42—C43	−2.2 (3)
C7—C8—C9—N1	−2.0 (3)	C41—C42—C43—C38	1.4 (3)

C7—C8—C9—C10	−179.94 (17)	C43—C38—C39—C40	−2.8 (3)
C8—C9—C10—N2	−159.07 (15)	C43—C38—B1—C26	28.1 (2)
C9—N1—C1—C2	−179.77 (15)	C43—C38—B1—C32	−90.40 (18)
C9—N1—C1—C6	−0.1 (2)	C43—C38—B1—C44	149.27 (15)
C10—N2—C11—C12	163.19 (14)	C44—C45—C46—C47	0.2 (2)
C10—N2—C21—C22	−74.89 (18)	C45—C44—C49—C48	1.2 (3)
C11—N2—C10—C9	−147.95 (14)	C45—C44—B1—C26	−107.55 (17)
C11—N2—C21—C22	162.38 (14)	C45—C44—B1—C32	9.2 (2)
C11—C12—C13—C14	174.1 (2)	C45—C44—B1—C38	130.78 (16)
C12—N3—C20—C15	2.0 (2)	C45—C46—C47—C48	1.5 (3)
C12—N3—C20—C19	−179.14 (17)	C46—C47—C48—C49	−1.8 (3)
C12—C13—C14—C15	1.2 (4)	C47—C48—C49—C44	0.4 (4)
C13—C14—C15—C16	−178.8 (2)	C49—C44—C45—C46	−1.5 (2)
C13—C14—C15—C20	2.1 (4)	C49—C44—B1—C26	72.5 (2)
C14—C15—C16—C17	−179.2 (2)	C49—C44—B1—C32	−170.76 (16)
C14—C15—C20—N3	−3.8 (3)	C49—C44—B1—C38	−49.2 (2)
C14—C15—C20—C19	177.4 (2)	B1—C26—C27—C28	−176.47 (18)
C15—C16—C17—C18	1.4 (4)	B1—C26—C31—C30	176.68 (18)
C16—C15—C20—N3	177.03 (18)	B1—C32—C33—C34	179.53 (14)
C16—C15—C20—C19	−1.8 (3)	B1—C32—C37—C36	179.47 (14)
C16—C17—C18—C19	−0.9 (4)	B1—C38—C39—C40	178.43 (19)
C17—C18—C19—C20	−1.0 (4)	B1—C38—C43—C42	179.81 (16)
C18—C19—C20—N3	−176.55 (19)	B1—C44—C45—C46	178.51 (14)
C18—C19—C20—C15	2.4 (3)	B1—C44—C49—C48	−178.84 (19)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.95	2.49	3.366 (2)	154
C19—H19···O2	0.95	2.31	3.201 (3)	155

(sf-mndqea)

Crystal data

$C_{25}H_{28}MnN_3O_4·C_{24}H_{20}B·CH_4O$	$F(000)$ = 1772
M_r = 840.69	D_x = 1.295 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.3504 (3) Å	Cell parameters from 8395 reflections
b = 17.4824 (5) Å	θ = 2.4–32.4°
c = 23.9618 (9) Å	μ = 0.36 mm^{-1}
β = 96.222 (3)°	T = 173 K
V = 4310.3 (3) Å^3	Prism, colourless
Z = 4	0.34 × 0.28 × 0.26 mm

Data collection

Rigaku-OxfordDiffraction Eos, Gemini diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm^{-1}
ω scans

Absorption correction: multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min} = 0.845, T_{max} = 1.000
31401 measured reflections
14423 independent reflections
10328 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 32.9°, θ_{min} = 2.4°
h = −15→12
k = −25→15
l = −34→36

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.165
S = 1.04
14423 reflections
551 parameters
6 restraints
Primary atom site location: dual

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 1.8737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.62 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.51 e $Å^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
Mn1	0.20955 (3)	0.33372 (2)	0.52465 (2)	0.02887 (8)
O1	0.28260 (15)	0.44318 (8)	0.52717 (8)	0.0458 (4)
O2	0.13625 (14)	0.53269 (9)	0.50984 (8)	0.0472 (4)
O3	0.01070 (14)	0.34494 (9)	0.48643 (8)	0.0460 (4)
H3	−0.0444 (16)	0.3827 (8)	0.4808 (13)	0.069*
O4	0.11505 (18)	0.35758 (11)	0.60640 (7)	0.0522 (4)
H4	0.056 (2)	0.3940 (14)	0.6018 (7)	0.078*
N1	0.13270 (15)	0.21203 (9)	0.52930 (7)	0.0300 (3)
N2	0.25617 (14)	0.27744 (8)	0.44164 (6)	0.0263 (3)
N3	0.35826 (14)	0.26899 (8)	0.58294 (6)	0.0250 (3)
C1	0.1942 (2)	0.16293 (10)	0.48970 (8)	0.0354 (4)
H1A	0.133110	0.121253	0.477185	0.042*
H1B	0.272491	0.139095	0.509961	0.042*
C2	0.23333 (17)	0.20303 (10)	0.43876 (8)	0.0277 (3)
C3	0.2509 (2)	0.15811 (11)	0.39134 (8)	0.0332 (4)

H3A	0.232686	0.104854	0.391288	0.040*
C4	0.2941 (2)	0.19156 (12)	0.34577 (9)	0.0353 (4)
H4A	0.309254	0.161637	0.314022	0.042*
C5	0.31641 (17)	0.27116 (10)	0.34594 (8)	0.0281 (3)
C6	0.35744 (19)	0.31015 (12)	0.29956 (9)	0.0350 (4)
H6	0.371122	0.282409	0.266622	0.042*
C7	0.3778 (2)	0.38723 (12)	0.30130 (9)	0.0380 (4)
H7	0.406030	0.412913	0.269855	0.046*
C8	0.3569 (2)	0.42823 (12)	0.34957 (10)	0.0389 (4)
H8	0.370017	0.482024	0.350349	0.047*
C9	0.31788 (19)	0.39234 (11)	0.39593 (9)	0.0343 (4)
H9	0.305169	0.421153	0.428502	0.041*
C10	0.29676 (16)	0.31278 (10)	0.39504 (8)	0.0257 (3)
C11	0.17193 (18)	0.18518 (11)	0.58680 (8)	0.0310 (4)
H11A	0.163673	0.128810	0.588162	0.037*
H11B	0.113351	0.207422	0.612533	0.037*
C12	0.31032 (17)	0.20775 (10)	0.60599 (7)	0.0265 (3)
C13	0.38118 (19)	0.16441 (11)	0.64824 (8)	0.0308 (4)
H13	0.343676	0.120367	0.663213	0.037*
C14	0.50440 (19)	0.18637 (11)	0.66746 (8)	0.0316 (4)
H14	0.552505	0.158524	0.696779	0.038*
C15	0.56010 (17)	0.25042 (10)	0.64373 (7)	0.0273 (3)
C16	0.68930 (19)	0.27457 (12)	0.66033 (9)	0.0362 (4)
H16	0.740776	0.248276	0.689480	0.043*
C17	0.7399 (2)	0.33549 (13)	0.63453 (10)	0.0394 (5)
H17	0.826643	0.351320	0.645679	0.047*
C18	0.66422 (19)	0.37498 (12)	0.59152 (9)	0.0354 (4)
H18	0.700936	0.417001	0.573660	0.043*
C19	0.53881 (18)	0.35393 (10)	0.57498 (8)	0.0298 (4)
H19	0.488640	0.381618	0.546186	0.036*
C20	0.48380 (16)	0.29085 (10)	0.60079 (7)	0.0246 (3)
C21	−0.0107 (2)	0.21667 (14)	0.51666 (12)	0.0499 (6)
H21A	−0.044582	0.165746	0.504360	0.060*
H21B	−0.049139	0.230296	0.551419	0.060*
C22	−0.0523 (3)	0.27337 (15)	0.47277 (14)	0.0609 (7)
H22A	−0.029409	0.255102	0.435989	0.073*
H22B	−0.147768	0.280060	0.470040	0.073*
C23	0.24108 (17)	0.50953 (10)	0.53302 (8)	0.0300 (4)
C24	0.3268 (3)	0.56394 (16)	0.56850 (13)	0.0610 (7)
H24A	0.406476	0.573160	0.550851	0.091*
H24B	0.349107	0.541777	0.605865	0.091*
H24C	0.280812	0.612425	0.571949	0.091*
C25	0.1493 (3)	0.3478 (2)	0.66573 (14)	0.0772 (10)
H25A	0.235256	0.323941	0.672363	0.116*
H25B	0.084817	0.315080	0.680990	0.116*
H25C	0.151236	0.397853	0.684268	0.116*
C1A	0.22943 (16)	0.82382 (10)	0.66640 (8)	0.0258 (3)
C2A	0.10210 (18)	0.80893 (12)	0.67804 (9)	0.0351 (4)

H2A	0.039094	0.848465	0.672264	0.042*
C3A	0.0645 (2)	0.73836 (13)	0.69774 (11)	0.0445 (5)
H3AA	−0.022712	0.730770	0.705399	0.053*
C4A	0.1532 (2)	0.67911 (12)	0.70626 (9)	0.0386 (4)
H4AA	0.127488	0.630823	0.719490	0.046*
C5A	0.27957 (19)	0.69139 (11)	0.69522 (8)	0.0325 (4)
H5A	0.341386	0.651141	0.700295	0.039*
C6A	0.31653 (17)	0.76259 (10)	0.67667 (8)	0.0294 (4)
H6A	0.404844	0.770203	0.670653	0.035*
C7A	0.31137 (15)	0.89867 (10)	0.57753 (8)	0.0260 (3)
C8A	0.3447 (2)	0.83057 (12)	0.55253 (9)	0.0378 (4)
H8A	0.343613	0.784518	0.573514	0.045*
C9A	0.3793 (3)	0.82720 (14)	0.49815 (11)	0.0527 (6)
H9A	0.400916	0.779296	0.482891	0.063*
C10A	0.3829 (2)	0.89250 (15)	0.46604 (10)	0.0464 (5)
H10A	0.406457	0.890139	0.428849	0.056*
C11A	0.3514 (2)	0.96099 (14)	0.48912 (9)	0.0387 (4)
H11C	0.353973	1.006814	0.467957	0.046*
C12A	0.31605 (18)	0.96344 (12)	0.54321 (8)	0.0327 (4)
H12A	0.293728	1.011571	0.557872	0.039*
C13A	0.16262 (15)	0.97007 (10)	0.64702 (8)	0.0264 (3)
C14A	0.05970 (17)	0.97895 (11)	0.60440 (10)	0.0350 (4)
H14A	0.059344	0.948968	0.571322	0.042*
C15A	−0.04210 (18)	1.03004 (12)	0.60869 (11)	0.0432 (5)
H15A	−0.110568	1.033810	0.579026	0.052*
C16A	−0.0439 (2)	1.07509 (13)	0.65575 (12)	0.0475 (6)
H16A	−0.112437	1.110546	0.658519	0.057*
C17A	0.0553 (2)	1.06806 (13)	0.69882 (11)	0.0442 (5)
H17A	0.055206	1.098630	0.731589	0.053*
C18A	0.15563 (18)	1.01599 (11)	0.69416 (9)	0.0333 (4)
H18A	0.222312	1.011611	0.724513	0.040*
C19A	0.41156 (15)	0.93298 (9)	0.68196 (7)	0.0230 (3)
C20A	0.51041 (16)	0.97532 (10)	0.66118 (8)	0.0286 (3)
H20A	0.501839	0.988483	0.622491	0.034*
C21A	0.62106 (18)	0.99893 (11)	0.69510 (10)	0.0350 (4)
H21C	0.685638	1.027965	0.679305	0.042*
C22A	0.63770 (19)	0.98062 (11)	0.75125 (10)	0.0372 (4)
H22C	0.713320	0.996604	0.774318	0.045*
C23A	0.5423 (2)	0.93848 (12)	0.77358 (9)	0.0363 (4)
H23A	0.552234	0.925309	0.812271	0.044*
C24A	0.43229 (18)	0.91550 (11)	0.73941 (8)	0.0299 (4)
H24D	0.368132	0.886646	0.755632	0.036*
B1	0.27811 (17)	0.90610 (11)	0.64276 (8)	0.0241 (3)
O1S	−0.05342 (16)	0.47202 (9)	0.60058 (7)	0.0466 (4)
H1S	−0.072497	0.486612	0.567306	0.070*
C1S	−0.0044 (2)	0.53468 (15)	0.63392 (12)	0.0511 (6)
H1SA	−0.049235	0.581606	0.620435	0.077*
H1SB	0.088990	0.540071	0.631278	0.077*

H1SC	−0.019027	0.525696	0.673115	0.077*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.02861 (14)	0.02196 (13)	0.03572 (16)	−0.00182 (10)	0.00199 (11)	−0.00028 (10)
O1	0.0409 (8)	0.0229 (7)	0.0730 (11)	0.0000 (6)	0.0035 (7)	−0.0023 (7)
O2	0.0344 (7)	0.0392 (9)	0.0647 (11)	0.0034 (6)	−0.0097 (7)	−0.0074 (7)
O3	0.0318 (7)	0.0302 (8)	0.0727 (12)	0.0016 (6)	−0.0095 (7)	−0.0058 (7)
O4	0.0559 (10)	0.0559 (11)	0.0457 (10)	0.0129 (8)	0.0093 (8)	−0.0099 (8)
N1	0.0296 (7)	0.0259 (7)	0.0342 (8)	−0.0053 (6)	0.0022 (6)	0.0003 (6)
N2	0.0274 (7)	0.0211 (7)	0.0302 (7)	−0.0026 (5)	0.0015 (6)	0.0028 (5)
N3	0.0268 (7)	0.0223 (7)	0.0269 (7)	−0.0021 (5)	0.0071 (5)	0.0009 (5)
C1	0.0545 (12)	0.0206 (8)	0.0309 (9)	−0.0063 (8)	0.0041 (8)	0.0010 (7)
C2	0.0299 (8)	0.0224 (8)	0.0298 (9)	−0.0021 (6)	−0.0012 (7)	0.0012 (6)
C3	0.0442 (10)	0.0211 (8)	0.0339 (10)	−0.0023 (7)	0.0027 (8)	−0.0007 (7)
C4	0.0434 (11)	0.0294 (9)	0.0333 (10)	0.0004 (8)	0.0050 (8)	−0.0024 (7)
C5	0.0258 (8)	0.0263 (8)	0.0320 (9)	0.0022 (6)	0.0019 (7)	0.0033 (6)
C6	0.0357 (9)	0.0357 (10)	0.0342 (10)	0.0029 (8)	0.0068 (8)	0.0048 (8)
C7	0.0358 (10)	0.0380 (11)	0.0408 (11)	0.0015 (8)	0.0074 (8)	0.0123 (8)
C8	0.0426 (11)	0.0270 (9)	0.0478 (12)	−0.0027 (8)	0.0087 (9)	0.0071 (8)
C9	0.0379 (9)	0.0251 (9)	0.0407 (11)	−0.0030 (7)	0.0083 (8)	0.0010 (7)
C10	0.0222 (7)	0.0234 (8)	0.0311 (9)	0.0001 (6)	0.0015 (6)	0.0036 (6)
C11	0.0311 (9)	0.0287 (9)	0.0346 (9)	−0.0065 (7)	0.0090 (7)	0.0017 (7)
C12	0.0295 (8)	0.0245 (8)	0.0270 (8)	−0.0026 (6)	0.0095 (7)	−0.0001 (6)
C13	0.0374 (9)	0.0279 (9)	0.0281 (9)	−0.0021 (7)	0.0083 (7)	0.0043 (7)
C14	0.0373 (9)	0.0317 (9)	0.0259 (8)	0.0025 (7)	0.0040 (7)	0.0041 (7)
C15	0.0289 (8)	0.0273 (8)	0.0265 (8)	0.0026 (6)	0.0068 (6)	−0.0010 (6)
C16	0.0329 (9)	0.0400 (11)	0.0351 (10)	0.0018 (8)	0.0013 (8)	−0.0008 (8)
C17	0.0293 (9)	0.0450 (12)	0.0437 (12)	−0.0066 (8)	0.0032 (8)	−0.0022 (9)
C18	0.0316 (9)	0.0310 (9)	0.0446 (11)	−0.0067 (7)	0.0083 (8)	0.0012 (8)
C19	0.0305 (8)	0.0250 (8)	0.0348 (9)	−0.0017 (7)	0.0073 (7)	0.0024 (7)
C20	0.0249 (7)	0.0216 (7)	0.0284 (8)	0.0002 (6)	0.0075 (6)	−0.0014 (6)
C21	0.0327 (10)	0.0410 (12)	0.0730 (17)	−0.0127 (9)	−0.0081 (10)	0.0126 (11)
C22	0.0466 (13)	0.0446 (14)	0.087 (2)	−0.0067 (11)	−0.0158 (13)	0.0005 (13)
C23	0.0291 (8)	0.0251 (8)	0.0354 (9)	−0.0036 (6)	0.0026 (7)	−0.0019 (7)
C24	0.0558 (15)	0.0511 (15)	0.0708 (19)	−0.0080 (12)	−0.0170 (13)	−0.0205 (13)
C25	0.073 (2)	0.091 (2)	0.0631 (19)	0.0181 (17)	−0.0124 (15)	−0.0357 (17)
C1A	0.0237 (7)	0.0245 (8)	0.0293 (8)	−0.0041 (6)	0.0030 (6)	−0.0025 (6)
C2A	0.0228 (8)	0.0349 (10)	0.0481 (12)	−0.0037 (7)	0.0054 (8)	0.0043 (8)
C3A	0.0309 (9)	0.0422 (12)	0.0614 (15)	−0.0122 (8)	0.0091 (9)	0.0068 (10)
C4A	0.0439 (11)	0.0297 (10)	0.0418 (11)	−0.0123 (8)	0.0026 (9)	0.0039 (8)
C5A	0.0382 (9)	0.0241 (8)	0.0344 (10)	−0.0022 (7)	−0.0006 (8)	−0.0022 (7)
C6A	0.0259 (8)	0.0248 (8)	0.0375 (10)	−0.0020 (6)	0.0037 (7)	−0.0023 (7)
C7A	0.0201 (7)	0.0276 (8)	0.0301 (8)	−0.0017 (6)	0.0021 (6)	−0.0039 (6)
C8A	0.0434 (11)	0.0295 (9)	0.0434 (11)	−0.0056 (8)	0.0177 (9)	−0.0087 (8)
C9A	0.0684 (16)	0.0423 (13)	0.0531 (14)	−0.0082 (11)	0.0325 (13)	−0.0187 (10)
C10A	0.0500 (12)	0.0583 (15)	0.0331 (11)	−0.0092 (11)	0.0152 (9)	−0.0121 (10)

C11A	0.0370 (10)	0.0493 (12)	0.0297 (10)	0.0006 (9)	0.0024 (8)	0.0029 (8)
C12A	0.0344 (9)	0.0347 (10)	0.0289 (9)	0.0053 (7)	0.0027 (7)	0.0002 (7)
C13A	0.0199 (7)	0.0220 (7)	0.0384 (9)	−0.0019 (6)	0.0076 (6)	−0.0002 (6)
C14A	0.0242 (8)	0.0269 (9)	0.0528 (12)	−0.0022 (7)	−0.0004 (8)	−0.0011 (8)
C15A	0.0198 (8)	0.0340 (10)	0.0753 (16)	−0.0017 (7)	0.0027 (9)	0.0103 (10)
C16A	0.0290 (9)	0.0318 (10)	0.0865 (18)	0.0060 (8)	0.0281 (11)	0.0082 (11)
C17A	0.0425 (11)	0.0350 (11)	0.0605 (14)	0.0026 (9)	0.0301 (11)	−0.0038 (9)
C18A	0.0307 (9)	0.0306 (9)	0.0405 (10)	−0.0001 (7)	0.0134 (8)	−0.0022 (7)
C19A	0.0204 (7)	0.0185 (7)	0.0303 (8)	−0.0011 (5)	0.0038 (6)	−0.0024 (6)
C20A	0.0234 (7)	0.0266 (8)	0.0359 (9)	−0.0033 (6)	0.0038 (7)	0.0037 (7)
C21A	0.0237 (8)	0.0266 (9)	0.0542 (12)	−0.0053 (6)	0.0022 (8)	0.0023 (8)
C22A	0.0294 (9)	0.0278 (9)	0.0511 (12)	0.0004 (7)	−0.0102 (8)	−0.0074 (8)
C23A	0.0412 (10)	0.0339 (10)	0.0320 (10)	0.0005 (8)	−0.0038 (8)	−0.0042 (8)
C24A	0.0308 (8)	0.0291 (9)	0.0302 (9)	−0.0033 (7)	0.0054 (7)	−0.0031 (7)
B1	0.0204 (7)	0.0220 (8)	0.0301 (9)	−0.0018 (6)	0.0044 (7)	−0.0026 (7)
O1S	0.0450 (8)	0.0440 (9)	0.0506 (10)	−0.0038 (7)	0.0047 (7)	−0.0072 (7)
C1S	0.0467 (12)	0.0488 (14)	0.0567 (15)	0.0002 (10)	0.0002 (11)	−0.0148 (11)

Geometric parameters (Å, º)

Mn1—O1	2.0559 (15)	C23—C24	1.500 (3)
Mn1—O3	2.1691 (15)	C24—H24A	0.9800
Mn1—O4	2.3200 (17)	C24—H24B	0.9800
Mn1—N1	2.2783 (15)	C24—H24C	0.9800
Mn1—N2	2.3165 (16)	C25—H25A	0.9800
Mn1—N3	2.2660 (15)	C25—H25B	0.9800
O1—C23	1.250 (2)	C25—H25C	0.9800
O2—C23	1.232 (2)	C1A—C2A	1.401 (2)
O3—H3	0.873 (9)	C1A—C6A	1.404 (2)
O3—C22	1.432 (3)	C1A—B1	1.645 (3)
O4—H4	0.883 (9)	C2A—H2A	0.9500
O4—C25	1.438 (4)	C2A—C3A	1.391 (3)
N1—C1	1.474 (3)	C3A—H3AA	0.9500
N1—C11	1.470 (3)	C3A—C4A	1.385 (3)
N1—C21	1.485 (3)	C4A—H4AA	0.9500
N2—C2	1.323 (2)	C4A—C5A	1.379 (3)
N2—C10	1.381 (2)	C5A—H5A	0.9500
N3—C12	1.326 (2)	C5A—C6A	1.389 (3)
N3—C20	1.377 (2)	C6A—H6A	0.9500
C1—H1A	0.9900	C7A—C8A	1.393 (3)
C1—H1B	0.9900	C7A—C12A	1.403 (3)
C1—C2	1.501 (3)	C7A—B1	1.642 (3)
C2—C3	1.409 (3)	C8A—H8A	0.9500
C3—H3A	0.9500	C8A—C9A	1.390 (3)
C3—C4	1.357 (3)	C9A—H9A	0.9500
C4—H4A	0.9500	C9A—C10A	1.379 (4)
C4—C5	1.410 (3)	C10A—H10A	0.9500
C5—C6	1.408 (3)	C10A—C11A	1.373 (3)

C5—C10	1.417 (3)	C11A—H11C	0.9500
C6—H6	0.9500	C11A—C12A	1.385 (3)
C6—C7	1.364 (3)	C12A—H12A	0.9500
C7—H7	0.9500	C13A—C14A	1.402 (3)
C7—C8	1.397 (3)	C13A—C18A	1.394 (3)
C8—H8	0.9500	C13A—B1	1.648 (2)
C8—C9	1.374 (3)	C14A—H14A	0.9500
C9—H9	0.9500	C14A—C15A	1.394 (3)
C9—C10	1.408 (2)	C15A—H15A	0.9500
C11—H11A	0.9900	C15A—C16A	1.377 (4)
C11—H11B	0.9900	C16A—H16A	0.9500
C11—C12	1.509 (3)	C16A—C17A	1.380 (4)
C12—C13	1.406 (3)	C17A—H17A	0.9500
C13—H13	0.9500	C17A—C18A	1.395 (3)
C13—C14	1.363 (3)	C18A—H18A	0.9500
C14—H14	0.9500	C19A—C20A	1.397 (2)
C14—C15	1.407 (3)	C19A—C24A	1.404 (3)
C15—C16	1.418 (3)	C19A—B1	1.652 (2)
C15—C20	1.416 (2)	C20A—H20A	0.9500
C16—H16	0.9500	C20A—C21A	1.393 (3)
C16—C17	1.364 (3)	C21A—H21C	0.9500
C17—H17	0.9500	C21A—C22A	1.376 (3)
C17—C18	1.406 (3)	C22A—H22C	0.9500
C18—H18	0.9500	C22A—C23A	1.385 (3)
C18—C19	1.366 (3)	C23A—H23A	0.9500
C19—H19	0.9500	C23A—C24A	1.388 (3)
C19—C20	1.414 (2)	C24A—H24D	0.9500
C21—H21A	0.9900	O1S—H1S	0.8400
C21—H21B	0.9900	O1S—C1S	1.417 (3)
C21—C22	1.475 (4)	C1S—H1SA	0.9800
C22—H22A	0.9900	C1S—H1SB	0.9800
C22—H22B	0.9900	C1S—H1SC	0.9800

O1—Mn1—O3	104.91 (6)	O3—C22—C21	109.5 (2)
O1—Mn1—O4	89.73 (7)	O3—C22—H22A	109.8
O1—Mn1—N1	175.50 (7)	O3—C22—H22B	109.8
O1—Mn1—N2	108.08 (6)	C21—C22—H22A	109.8
O1—Mn1—N3	102.93 (6)	C21—C22—H22B	109.8
O3—Mn1—O4	82.68 (7)	H22A—C22—H22B	108.2
O3—Mn1—N1	77.57 (6)	O1—C23—C24	117.54 (19)
O3—Mn1—N2	87.26 (6)	O2—C23—O1	123.42 (18)
O3—Mn1—N3	148.81 (6)	O2—C23—C24	119.00 (19)
N1—Mn1—O4	86.86 (7)	C23—C24—H24A	109.5
N1—Mn1—N2	75.62 (5)	C23—C24—H24B	109.5
N2—Mn1—O4	161.35 (6)	C23—C24—H24C	109.5
N3—Mn1—O4	83.67 (6)	H24A—C24—H24B	109.5
N3—Mn1—N1	73.79 (5)	H24A—C24—H24C	109.5
N3—Mn1—N2	97.26 (5)	H24B—C24—H24C	109.5

718	C23—O1—Mn1	137.49 (13)	O4—C25—H25A	109.5
719	Mn1—O3—H3	135.0 (13)	O4—C25—H25B	109.5
720	C22—O3—Mn1	113.91 (14)	O4—C25—H25C	109.5
721	C22—O3—H3	110.6 (12)	H25A—C25—H25B	109.5
722	Mn1—O4—H4	112.1 (12)	H25A—C25—H25C	109.5
723	C25—O4—Mn1	137.07 (17)	H25B—C25—H25C	109.5
724	C25—O4—H4	107.6 (12)	C2A—C1A—C6A	115.07 (16)
725	C1—N1—Mn1	109.55 (11)	C2A—C1A—B1	124.12 (16)
726	C1—N1—C21	113.12 (18)	C6A—C1A—B1	120.81 (15)
727	C11—N1—Mn1	106.35 (11)	C1A—C2A—H2A	118.8
728	C11—N1—C1	108.81 (15)	C3A—C2A—C1A	122.40 (19)
729	C11—N1—C21	112.15 (16)	C3A—C2A—H2A	118.8
730	C21—N1—Mn1	106.59 (12)	C2A—C3A—H3AA	119.7
731	C2—N2—Mn1	114.19 (12)	C4A—C3A—C2A	120.54 (19)
732	C2—N2—C10	117.79 (16)	C4A—C3A—H3AA	119.7
733	C10—N2—Mn1	127.90 (12)	C3A—C4A—H4AA	120.6
734	C12—N3—Mn1	113.60 (11)	C5A—C4A—C3A	118.87 (18)
735	C12—N3—C20	118.55 (15)	C5A—C4A—H4AA	120.6
736	C20—N3—Mn1	127.43 (11)	C4A—C5A—H5A	120.0
737	N1—C1—H1A	108.5	C4A—C5A—C6A	120.05 (18)
738	N1—C1—H1B	108.5	C6A—C5A—H5A	120.0
739	N1—C1—C2	115.15 (15)	C1A—C6A—H6A	118.5
740	H1A—C1—H1B	107.5	C5A—C6A—C1A	123.04 (17)
741	C2—C1—H1A	108.5	C5A—C6A—H6A	118.5
742	C2—C1—H1B	108.5	C8A—C7A—C12A	114.32 (17)
743	N2—C2—C1	118.65 (16)	C8A—C7A—B1	124.35 (17)
744	N2—C2—C3	123.51 (17)	C12A—C7A—B1	121.21 (15)
745	C3—C2—C1	117.74 (16)	C7A—C8A—H8A	118.6
746	C2—C3—H3A	120.3	C9A—C8A—C7A	122.7 (2)
747	C4—C3—C2	119.45 (17)	C9A—C8A—H8A	118.6
748	C4—C3—H3A	120.3	C8A—C9A—H9A	119.6
749	C3—C4—H4A	120.3	C10A—C9A—C8A	120.9 (2)
750	C3—C4—C5	119.40 (18)	C10A—C9A—H9A	119.6
751	C5—C4—H4A	120.3	C9A—C10A—H10A	120.8
752	C4—C5—C10	118.11 (17)	C11A—C10A—C9A	118.4 (2)
753	C6—C5—C4	122.59 (18)	C11A—C10A—H10A	120.8
754	C6—C5—C10	119.30 (17)	C10A—C11A—H11C	119.9
755	C5—C6—H6	119.6	C10A—C11A—C12A	120.1 (2)
756	C7—C6—C5	120.9 (2)	C12A—C11A—H11C	119.9
757	C7—C6—H6	119.6	C7A—C12A—H12A	118.2
758	C6—C7—H7	120.2	C11A—C12A—C7A	123.56 (19)
759	C6—C7—C8	119.67 (19)	C11A—C12A—H12A	118.2
760	C8—C7—H7	120.2	C14A—C13A—B1	121.93 (16)
761	C7—C8—H8	119.3	C18A—C13A—C14A	115.11 (17)
762	C9—C8—C7	121.35 (19)	C18A—C13A—B1	122.87 (16)
763	C9—C8—H8	119.3	C13A—C14A—H14A	118.7
764	C8—C9—H9	120.1	C15A—C14A—C13A	122.6 (2)
765	C8—C9—C10	119.84 (19)	C15A—C14A—H14A	118.7

C10—C9—H9	120.1	C14A—C15A—H15A	119.9
N2—C10—C5	121.69 (16)	C16A—C15A—C14A	120.3 (2)
N2—C10—C9	119.35 (17)	C16A—C15A—H15A	119.9
C9—C10—C5	118.96 (17)	C15A—C16A—H16A	120.4
N1—C11—H11A	109.4	C15A—C16A—C17A	119.12 (19)
N1—C11—H11B	109.4	C17A—C16A—H16A	120.4
N1—C11—C12	111.02 (14)	C16A—C17A—H17A	120.1
H11A—C11—H11B	108.0	C16A—C17A—C18A	119.9 (2)
C12—C11—H11A	109.4	C18A—C17A—H17A	120.1
C12—C11—H11B	109.4	C13A—C18A—C17A	123.0 (2)
N3—C12—C11	118.04 (16)	C13A—C18A—H18A	118.5
N3—C12—C13	123.08 (16)	C17A—C18A—H18A	118.5
C13—C12—C11	118.86 (16)	C20A—C19A—C24A	115.13 (15)
C12—C13—H13	120.4	C20A—C19A—B1	123.19 (16)
C14—C13—C12	119.18 (17)	C24A—C19A—B1	121.67 (15)
C14—C13—H13	120.4	C19A—C20A—H20A	118.8
C13—C14—H14	120.1	C21A—C20A—C19A	122.44 (18)
C13—C14—C15	119.78 (17)	C21A—C20A—H20A	118.8
C15—C14—H14	120.1	C20A—C21A—H21C	119.7
C14—C15—C16	122.62 (17)	C22A—C21A—C20A	120.63 (18)
C14—C15—C20	118.04 (16)	C22A—C21A—H21C	119.7
C20—C15—C16	119.33 (17)	C21A—C22A—H22C	120.6
C15—C16—H16	119.9	C21A—C22A—C23A	118.87 (18)
C17—C16—C15	120.15 (19)	C23A—C22A—H22C	120.6
C17—C16—H16	119.9	C22A—C23A—H23A	120.0
C16—C17—H17	119.8	C22A—C23A—C24A	119.98 (19)
C16—C17—C18	120.33 (18)	C24A—C23A—H23A	120.0
C18—C17—H17	119.8	C19A—C24A—H24D	118.5
C17—C18—H18	119.4	C23A—C24A—C19A	122.95 (18)
C19—C18—C17	121.10 (18)	C23A—C24A—H24D	118.5
C19—C18—H18	119.4	C1A—B1—C13A	108.71 (13)
C18—C19—H19	120.1	C1A—B1—C19A	108.74 (14)
C18—C19—C20	119.89 (18)	C7A—B1—C1A	111.25 (14)
C20—C19—H19	120.1	C7A—B1—C13A	109.94 (14)
N3—C20—C15	121.34 (15)	C7A—B1—C19A	108.36 (13)
N3—C20—C19	119.45 (16)	C13A—B1—C19A	109.82 (14)
C19—C20—C15	119.20 (16)	C1S—O1S—H1S	109.5
N1—C21—H21A	109.0	O1S—C1S—H1SA	109.5
N1—C21—H21B	109.0	O1S—C1S—H1SB	109.5
H21A—C21—H21B	107.8	O1S—C1S—H1SC	109.5
C22—C21—N1	113.0 (2)	H1SA—C1S—H1SB	109.5
C22—C21—H21A	109.0	H1SA—C1S—H1SC	109.5
C22—C21—H21B	109.0	H1SB—C1S—H1SC	109.5

Mn1—O1—C23—O2	−42.4 (3)	C20—N3—C12—C13	0.6 (3)
Mn1—O1—C23—C24	140.0 (2)	C20—C15—C16—C17	−0.9 (3)
Mn1—O3—C22—C21	37.1 (3)	C21—N1—C1—C2	89.5 (2)
Mn1—N1—C1—C2	−29.2 (2)	C21—N1—C11—C12	−159.13 (17)

Mn1—N1—C11—C12	−42.98 (17)	C1A—C2A—C3A—C4A	−0.5 (4)
Mn1—N1—C21—C22	37.8 (3)	C2A—C1A—C6A—C5A	2.1 (3)
Mn1—N2—C2—C1	−5.9 (2)	C2A—C1A—B1—C7A	−110.5 (2)
Mn1—N2—C2—C3	177.87 (14)	C2A—C1A—B1—C13A	10.7 (2)
Mn1—N2—C10—C5	−177.24 (12)	C2A—C1A—B1—C19A	130.21 (19)
Mn1—N2—C10—C9	2.0 (2)	C2A—C3A—C4A—C5A	0.4 (4)
Mn1—N3—C12—C11	5.9 (2)	C3A—C4A—C5A—C6A	0.9 (3)
Mn1—N3—C12—C13	−172.43 (14)	C4A—C5A—C6A—C1A	−2.3 (3)
Mn1—N3—C20—C15	170.51 (12)	C6A—C1A—C2A—C3A	−0.7 (3)
Mn1—N3—C20—C19	−10.8 (2)	C6A—C1A—B1—C7A	69.8 (2)
N1—C1—C2—N2	24.5 (3)	C6A—C1A—B1—C13A	−168.98 (16)
N1—C1—C2—C3	−159.04 (17)	C6A—C1A—B1—C19A	−49.4 (2)
N1—C11—C12—N3	26.2 (2)	C7A—C8A—C9A—C10A	0.3 (4)
N1—C11—C12—C13	−155.39 (17)	C8A—C7A—C12A—C11A	−0.4 (3)
N1—C21—C22—O3	−50.7 (3)	C8A—C7A—B1—C1A	−23.7 (2)
N2—C2—C3—C4	0.3 (3)	C8A—C7A—B1—C13A	−144.16 (17)
N3—C12—C13—C14	1.1 (3)	C8A—C7A—B1—C19A	95.8 (2)
C1—N1—C11—C12	74.95 (18)	C8A—C9A—C10A—C11A	0.1 (4)
C1—N1—C21—C22	−82.7 (3)	C9A—C10A—C11A—C12A	−0.6 (3)
C1—C2—C3—C4	−175.88 (19)	C10A—C11A—C12A—C7A	0.8 (3)
C2—N2—C10—C5	−1.3 (2)	C12A—C7A—C8A—C9A	−0.1 (3)
C2—N2—C10—C9	177.93 (16)	C12A—C7A—B1—C1A	160.40 (15)
C2—C3—C4—C5	−2.2 (3)	C12A—C7A—B1—C13A	39.9 (2)
C3—C4—C5—C6	−178.03 (19)	C12A—C7A—B1—C19A	−80.11 (19)
C3—C4—C5—C10	2.2 (3)	C13A—C14A—C15A—C16A	0.8 (3)
C4—C5—C6—C7	179.91 (19)	C14A—C13A—C18A—C17A	−1.0 (3)
C4—C5—C10—N2	−0.4 (3)	C14A—C13A—B1—C1A	−85.8 (2)
C4—C5—C10—C9	−179.70 (17)	C14A—C13A—B1—C7A	36.2 (2)
C5—C6—C7—C8	−0.4 (3)	C14A—C13A—B1—C19A	155.34 (16)
C6—C5—C10—N2	179.78 (16)	C14A—C15A—C16A—C17A	−1.0 (3)
C6—C5—C10—C9	0.5 (3)	C15A—C16A—C17A—C18A	0.2 (3)
C6—C7—C8—C9	0.9 (3)	C16A—C17A—C18A—C13A	0.8 (3)
C7—C8—C9—C10	−0.7 (3)	C18A—C13A—C14A—C15A	0.2 (3)
C8—C9—C10—N2	−179.30 (18)	C18A—C13A—B1—C1A	90.41 (19)
C8—C9—C10—C5	0.0 (3)	C18A—C13A—B1—C7A	−147.59 (16)
C10—N2—C2—C1	177.61 (16)	C18A—C13A—B1—C19A	−28.4 (2)
C10—N2—C2—C3	1.4 (3)	C19A—C20A—C21A—C22A	0.5 (3)
C10—C5—C6—C7	−0.3 (3)	C20A—C19A—C24A—C23A	0.2 (3)
C11—N1—C1—C2	−145.11 (16)	C20A—C19A—B1—C1A	148.18 (16)
C11—N1—C21—C22	153.8 (2)	C20A—C19A—B1—C7A	27.1 (2)
C11—C12—C13—C14	−177.25 (17)	C20A—C19A—B1—C13A	−92.98 (19)
C12—N3—C20—C15	−1.5 (2)	C20A—C21A—C22A—C23A	−0.2 (3)
C12—N3—C20—C19	177.15 (16)	C21A—C22A—C23A—C24A	0.0 (3)
C12—C13—C14—C15	−1.9 (3)	C22A—C23A—C24A—C19A	0.0 (3)
C13—C14—C15—C16	−177.61 (18)	C24A—C19A—C20A—C21A	−0.4 (3)
C13—C14—C15—C20	1.0 (3)	C24A—C19A—B1—C1A	−32.9 (2)
C14—C15—C16—C17	177.70 (19)	C24A—C19A—B1—C7A	−153.93 (16)
C14—C15—C20—N3	0.7 (3)	C24A—C19A—B1—C13A	85.97 (19)

C14—C15—C20—C19	−177.98 (17)	B1—C1A—C2A—C3A	179.7 (2)
C15—C16—C17—C18	0.3 (3)	B1—C1A—C6A—C5A	−178.26 (17)
C16—C15—C20—N3	179.36 (16)	B1—C7A—C8A—C9A	−176.3 (2)
C16—C15—C20—C19	0.7 (3)	B1—C7A—C12A—C11A	175.86 (17)
C16—C17—C18—C19	0.6 (3)	B1—C13A—C14A—C15A	176.64 (17)
C17—C18—C19—C20	−0.8 (3)	B1—C13A—C18A—C17A	−177.41 (17)
C18—C19—C20—N3	−178.52 (17)	B1—C19A—C20A—C21A	178.57 (17)
C18—C19—C20—C15	0.1 (3)	B1—C19A—C24A—C23A	−178.82 (17)
C20—N3—C12—C11	178.96 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2^{i}	0.87 (1)	1.79 (1)	2.632 (2)	163 (3)
O4—H4···O1*S*	0.88 (1)	1.77 (1)	2.648 (2)	173 (3)
C9—H9···O1	0.95	2.43	3.326 (3)	157
C17—H17···O1*S*^{ii}	0.95	2.73	3.364 (3)	125
C18—H18···O1*S*^{ii}	0.95	2.73	3.366 (2)	125
C19—H19···O1	0.95	2.39	3.181 (2)	141
C25—H25*A*···N3	0.98	2.78	3.383 (4)	120
O1*S*—H1*S*···O2^{i}	0.84	1.92	2.693 (2)	152

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

other supporting information

Crystallographic Information File. zl5024.cif

Structure factors. zl5024sf-mndqmeasup2.hkl

Structure factors. zl5024sf-mndqeasup3.hkl