Nitrato(5,10,15,20-tetraphenylporphinato)-manganese(III)–benzene–n-hexane (2/1/1)

Hongli Cao,[a] Junwen Wang[a]* and Jianfeng Li[b]*

[a]Key Laboratory of Magnetic Molecules, Magnetic Information Materials, Ministry of Education, School of Chemical and Material Science, Shanxi Normal University, Taiyu Road, Taiyuan 030032, People's Republic of China, and [b]College of Materials Science and Opto-electronic Technology, CAS Center for Excellence in Topological Quantum Computation & Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Yanqi Lake, Huairou District, Beijing 101408, People's Republic of China. *Correspondence e-mail: wangjunwen2013@126.com, jfli@ucas.ac.cn

The crystal structure of solvated [Mn(TPP)(NO$_3$)] (TPP = 5,10,15,20-tetraphenylporphyrinato, C$_{44}$H$_{28}$N$_4$), [Mn(C$_{44}$H$_{28}$N$_4$O$_3$)(NO$_3$)]·0.5C$_6$H$_{14}$·0.5C$_6$H$_6$, has been determined in the space group *Pccn*. The Mn^{III} atom has a distorted square-pyramidal environment, being coordinated by four pyrrole N atoms of the porphyrin ligand in the basal plane and an O atom of the nitrato ligand in the apical site. The Mn^{III} atom is displaced out of the porphyrin plane by 0.22 (4) Å with the average Mn—Np distance being 2.011 (6) Å (where Np is a porphyrin N atom). The Mn—O bond length is 2.1246 (18) Å. Two kinds of intermolecular C—H···O hydrogen bonds exist in the crystal structure, with the apical nitrato ligands interacting with solvent molecules and adjacent molecules, respectively.

3D view
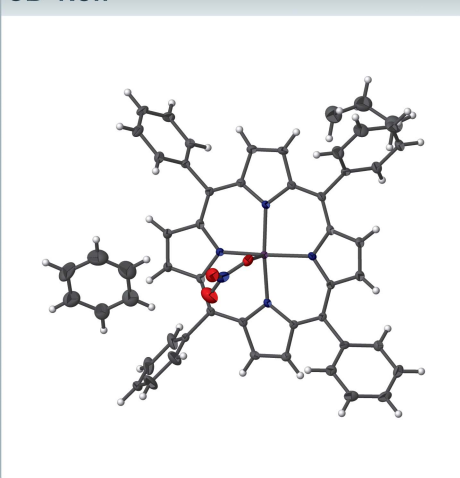
Chemical scheme
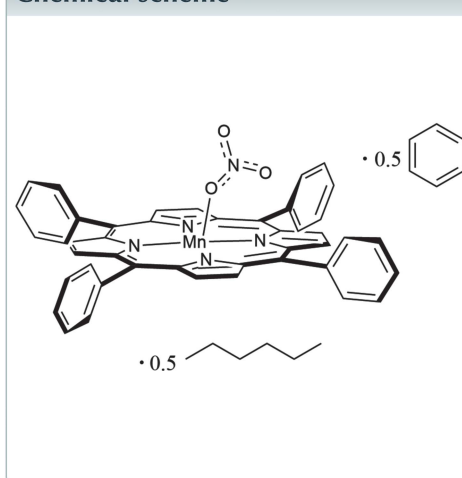
Structure description

Interactions between metalloporphyrins and nitrate ligands occur in many areas of bioinorganic chemistry. Nitrates play a key role in fixing atmospheric nitrogen into a more bioavailable form, as detailed in the nitrogen cycle (Averill, 1996). A series of nitrate-coordinating Fe^{III} derivatives have been reported, whereby the denticity of the nitrate ligands shows differences for complexes of the general type [Fe(Por)(NO$_3$)] (where Por is porphyrin). Among them, [Fe(OEP)(NO$_3$)] (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato, space group *P*$\bar{1}$; Ellison *et al.*, 1996), [Fe(OEP)(NO$_3$)] (space group *P*2$_1$/*c*, Wyllie *et al.*, 2007) and [Fe(4-Me-TTP)(NO$_3$)] (TTP = 5,10,15,20-tetrakis(4-methylphenyl)porphyrinato; Bhuyan & Sarkar, 2013) have a nitrate group monodentately binding to the central metal cation, while [Fe(TPP)(NO$_3$)] (Wyllie *et al.*, 2007),

Table 1
Selected structural parameters (Å) for related metalloporphyrin nitrato complexes.

Δ_4 is the displacement of the metal atom from the mean plane of the four pyrrole nitrogen atoms and Δ_{24} is the displacement of the metal atom from the 24-atom mean plane.

Complex	Δ_4	Δ_{24}	$M-O$	$N-O1$	$M-N_p$	Ref.
[Mn(TPP)(NO$_3$)] (Pccn) benzene and n-hexane hemisolvate	0.23	0.22	2.1246 (18)	1.260 (3) 1.236 (3) 1.230 (3)	2.011 (6)	This work
[Mn(TPP)(NO$_3$)] ($P\bar{1}$) benzene disolvate	0.21	0.20	2.101 (3)	1.298 (4) 1.226 (5) 1.226 (5)	2.007 (9)	(Suslick & Watson, 1991)
[Fe(OEP)(NO$_3$)] ($P2_1/c$)	0.40	0.45	1.966 (2)	1.301 (3) 1.199 (3) 1.212 (3)	2.047 (6)	(Wyllie et al., 2007)
[Fe(OEP)(NO$_3$)] ($P\bar{1}$)	0.46	0.50	2.016 (3)	1.206 (5) 1.198 (4) 1.208 (6)	2.056 (1)	(Ellison et al., 1996)
[Fe(4−Me-TTP)(NO$_3$)]	0.47	0.53	1.971 (3)	1.262 (5) 1.252 (5) 1.221 (4)	2.063 (13)	(Bhuyan & Sarkar, 2013)
[Fe(TPP)(NO$_3$)]	0.54	0.63	2.121 (6) 2.19 (10)	1.27 (10) 1.285 (21) 1.217 (3)	2.085 (10)	(Wyllie et al., 2007)
[Fe(TpivPP)(NO$_3$)]	0.42	0.49	2.123 (3) 2.226 (3)	1.271 (4) 1.252 (4) 1.214 (3)	2.070 (16)	(Munro & Scheidt, 1998)
[Fe(4-OMe-TPP)(NO$_3$)]	0.55	0.62	2.169 (5) 2.169 (5)	1.216 (5) 1.276 (8) 1.216 (5)	2.05 (3)	(Bhuyan & Sarkar, 2013)

[Fe(4-OMe-TPP)(NO$_3$) (4-OMe-TPP = 5,10,15,20-tetrakis(4-methoxyphenyl)-porphyrinato; Bhuyan & Sarkar, 2013) and [Fe(TpivPP)(NO$_3$)] (TpivPP = $\alpha,\alpha,\alpha,\alpha$-tetrakis(o-pival-amidophenyl)porphyrinato; Munro & Scheidt, 1998) have a nitrate group bidentately binding to the central cation. Herein, we report the structural properties of a related manganese(III) compound, viz. [Mn(TPP)(NO$_3$)], crystallizing as a hemisolvate of benzene and n-hexane. In accordance with the benzene disolvate of [Mn(TPP)(NO$_3$)] (Suslick & Watson, 1991), the nitrato ligand binds monodentately. The key crystal structural parameters of all the above-mentioned metalloporphyrin nitrate complexes are given in Table 1. It is seen that the average Mn−Np bond length and the Mn−O1 bond length of the title complex are 2.011 (6) and 2.1246 (18) Å, respectively, both of which are slightly longer than the values of 2.007 (9) and 2.101 (3) Å found in the structure of the triclinic benzene disolvate [Mn(TPP)(NO$_3$)]·2C$_6$H$_6$ (Suslick & Watson, 1991).

In the crystal structure of the title five-coordinate manganese(III) nitrate complex (Fig. 1), the asymmetric unit contains one porphyrin molecule, half of a benzene solvate molecule, and half of an n-hexane solvate molecule. The Mn1^{III} atom has a distorted square-pyramidal environment, defined by the four pyrrole N atoms of the porphyrin ligand in the basal plane and an O atom of the nitrato ligand in the apical site. Additional quantitative information about the structure is given in Fig. 2, which includes the displacement of each porphyrin core atom (in units of 0.01 Å) from the 24-atom mean plane. Averaged values of the chemically unique bond lengths (in Å) and angles (in °) are also shown. The
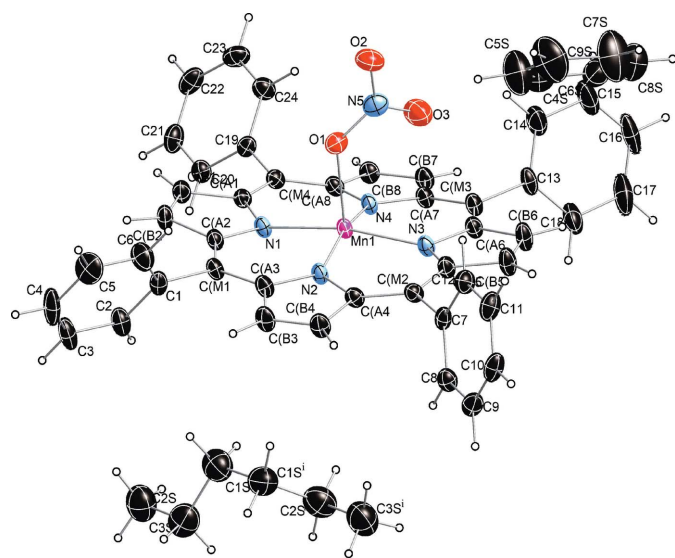
Figure 1
The molecular structure of the title compound, drawn with displacement ellipsoids at the 50% probability level. Only one of the two orientations of the disordered benzene solvate molecules is shown. [Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$.]
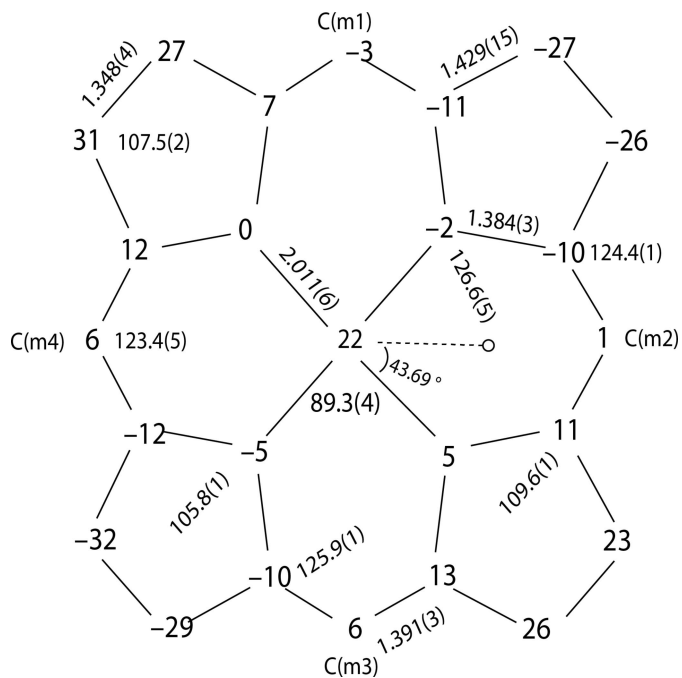
Figure 2
A formal diagram of the porphyrin core of the title compound. Averaged values of the chemically unique bond lengths (Å) and angles (°) are shown. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed. The positive numbers indicate a displacement towards the nitrate ligand, the dashed line indicates the plane of the nitrate ligand on the unhindered porphyrin side.

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C4S-H4S\cdots O3$	0.95	2.38	3.177 (8)	141
$C10-H10\cdots O2^i$	0.95	2.50	3.182 (3)	129
$C17-H17\cdots O2^{ii}$	0.95	2.53	3.350 (4)	145
$C22-H22\cdots O2^{iii}$	0.95	2.49	3.085 (3)	120

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

Figure 4
C—H···O hydrogen-bonding interactions between adjacent porphyrin molecules (dashed lines).

mean absolute core-atom displacements of C_a, C_b, C_m and C_{av} are 0.11 (2), 0.28 (3), 0.04 (2) and 0.16 (10) Å, respectively, and the monodentate nitrato ligand forms a dihedral angle of 43.69 (13)° with the plane defined by the Mn1, N3 and O1 atoms.

The porphyrin core shows a characteristic saddle-shaped distortion and the Mn1^{III} atom is displaced by 0.22 (4) Å from the 24-atom porphyrin plane in the direction of the nitrato ligand. This value is smaller than the displacement of the iron atom (0.63 Å) in [Fe(TPP)(NO)$_3$] reported by Wyllie *et al.* (2007). This difference is explained by the high-spin config-uration of $3d^5$ Fe^{III} where the occupied $d_{(x2-y2)}$ orbital 'pushes' the metal out of the porphyrin plane, and the empty $d_{(x2-y2)}$ orbital of $3d^4$ Mn^{III} allows a more in-plane conformation (Suslick & Watson, 1991).

In the title compound, C—H···O hydrogen-bonding inter-actions are found between the disordered benzene solvent molecule (C4S) and the apical nitrato ligand (O3), as illus-trated in Fig. 3 and detailed in Table 2. Similar hydrogen bonds are also found between the apical ligand and phenyl rings of adjacent porphyrin molecules (Fig. 4, Table 2). All these structural parameters are consistent with literature data where C—H···O bonds range from 3.00–4.00 Å (Desiraju, 1996), with angles of 120–180° (Steiner & Desiraju, 1998). The molecular packing of the title compound is shown in Fig. 5.

Synthesis and crystallization

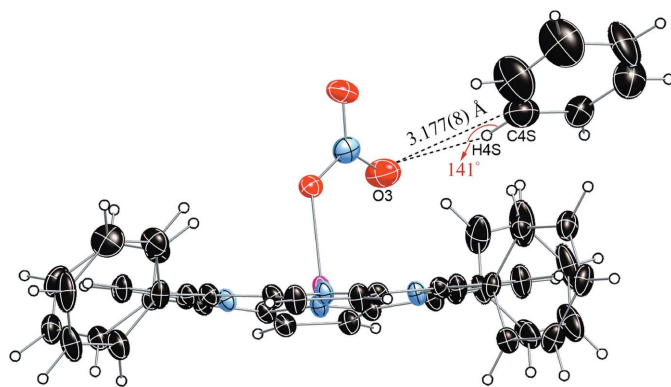**General information**. All experimental manipulations were performed under a purified nitrogen atmosphere using Schlenk techniques. Except for the solvent used in column chromatography, all solvents used in the experimental process were treated under dry conditions and exclusion of oxygen. Benzene and *n*-hexane were distilled under argon protection, and then refluxed over sodium/benzophenone and potassium–sodium alloy, respectively. All solvents used in the anhydrous and anaerobic operation (Schlenk system) were treated with the pump–freeze–thaw method three times before use.

The title compound was obtained serendipitously in an unsuccessful attempt to isolate the five-coordinate manganese(II) nitrosyl species [Mn(TPP)(NO)]. [Mn(TPP)OH] was prepared according to a reported method (He *et al.*, 2016). The purple [Mn(TPP)OH] powder (10 mg, 0.0015 mmol) was reduced by ethyl mercaptan for 48 h with benzene as solvent, then the solution was evaporated to dryness. NO gas was then bubbled slowly in a solution of the residue in degassed benzene for 5 minutes under an argon atmosphere. There was a dramatic color change from greenish yellow to red. The red solution was finally layered with hexanes. Black, block-shaped crystals were obtained several weeks later.

Figure 3
The C—H···O interactions between the apical nitrato ligand and the benzene solvent molecule.

Figure 5
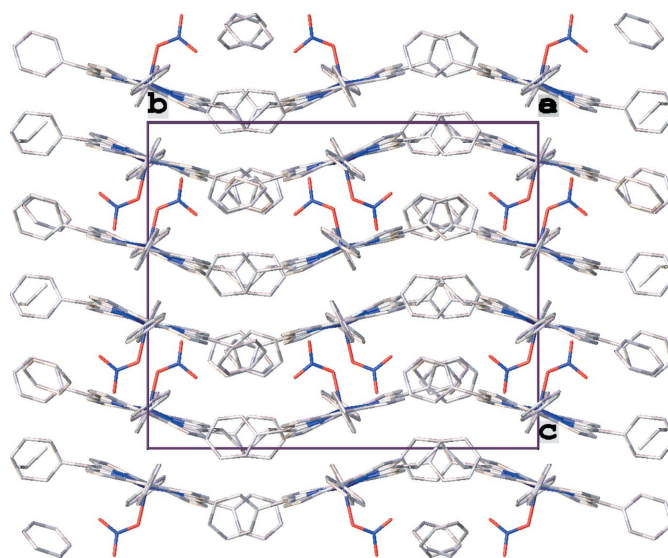A view of the molecular packing of the title compound in the crystal structure, as seen in a projection along [100]. H atoms have been omitted for clarity.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Mn(C_{44}H_{28}N_4O_3)(NO_3)]\cdot$ $0.5C_6H_{14}\cdot0.5C_6H_6$
M_r	811.79
Crystal system, space group	Orthorhombic, $Pccn$
Temperature (K)	100
a, b, c (Å)	20.1021 (10), 21.5505 (9), 17.9807 (9)
V (Å^3)	7789.4 (6)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.39
Crystal size (mm)	$0.33 \times 0.29 \times 0.12$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.763, 0.865
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	58775, 8270, 6163
R_{int}	0.058
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.633
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.148, 1.07
No. of reflections	8270
No. of parameters	560
No. of restraints	37
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.80, −0.48

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The benzene molecule is disordered around a twofold rotation axis. Thus, the occupancy of all atoms was constrained to 1/2, and the C4*S*—C9*S* distance constrained to 1.45 Å. One outlier reflection, 332, was omitted from the refinement.

References

Averill, B. A. (1996). *Chem. Rev.* **96**, 2951–2964.
Bhuyan, J. & Sarkar, S. (2013). *J. Chem. Sci.* **125**, 707–714.
Bruker (2014). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Ellison, M. K., Shang, M., Kim, J. & Scheidt, W. R. (1996). *Acta Cryst.* **C52**, 3040–3043.
He, M., Li, X., Liu, Y. & Li, J. (2016). *Inorg. Chem.* **55**, 5871–5879.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Munro, O. Q. & Scheidt, W. R. (1998). *Inorg. Chem.* **37**, 2308–2316.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* **A71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* **C71**, 3–8.
Steiner, T. & Desiraju, G. R. (1998). *Chem. Commun.* pp. 891–892.
Suslick, K. S. & Watson, R. A. (1991). *Inorg. Chem.* **30**, 912–919.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wyllie, G. R., Munro, O. Q., Schulz, C. E. & Scheidt, W. R. (2007). *Polyhedron*, **26**, 4664–4672.

full crystallographic data

Nitrato(5,10,15,20-tetraphenylporphinato)manganese(III)–benzene–*n*-hexane (2/1/1)

Hongli Cao, Junwen Wang and Jianfeng Li

Nitrato(5,10,15,20-tetraphenylporphinato)manganese(III)–benzene–*n*-hexane (2/1/1)

Crystal data

$[Mn(C_{44}H_{28}N_4O_3)(NO_3)]\cdot 0.5C_6H_{14}\cdot 0.5C_6H_6$
$M_r = 811.79$
Orthorhombic, $Pccn$
$a = 20.1021 (10)$ Å
$b = 21.5505 (9)$ Å
$c = 17.9807 (9)$ Å
$V = 7789.4 (6)$ Å^3
$Z = 8$
$F(000) = 3376$

$D_x = 1.384$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9845 reflections
$\theta = 2.5$–$26.7°$
$\mu = 0.39$ mm^{-1}
$T = 100$ K
Block, black
$0.33 \times 0.29 \times 0.12$ mm

Data collection

Bruker APEXII CCD
    diffractometer
φ and ω scans
Absorption correction: multi-scan
    (*SADABS*; Krause *et al.*, 2015)
$T_{min} = 0.763$, $T_{max} = 0.865$
58775 measured reflections

8270 independent reflections
6163 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 26.7°$, $\theta_{min} = 2.3°$
$h = -25 \rightarrow 23$
$k = -27 \rightarrow 24$
$l = -22 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.148$
$S = 1.07$
8270 reflections
560 parameters
37 restraints
Primary atom site location: dual

Hydrogen site location: inferred from
    neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2 + 10.1161P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.097$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ 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.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.42182 (2)	0.50321 (2)	0.38016 (2)	0.01235 (11)	
O1	0.42711 (8)	0.52498 (8)	0.26507 (10)	0.0206 (4)	
O2	0.41592 (10)	0.58633 (9)	0.17166 (11)	0.0311 (5)	
O3	0.42351 (12)	0.62345 (10)	0.28275 (12)	0.0416 (6)	
N1	0.49166 (9)	0.43691 (8)	0.36975 (11)	0.0144 (4)	
N2	0.35071 (9)	0.43777 (8)	0.36889 (11)	0.0148 (4)	
N3	0.35138 (9)	0.56361 (9)	0.41173 (11)	0.0151 (4)	
N4	0.49211 (9)	0.56102 (8)	0.41874 (11)	0.0147 (4)	
N5	0.42152 (11)	0.57920 (11)	0.23960 (13)	0.0259 (5)	
C1	0.42051 (11)	0.28091 (11)	0.31319 (15)	0.0183 (5)	
C2	0.44918 (13)	0.23571 (11)	0.35761 (16)	0.0259 (6)	
H2	0.467963	0.247013	0.404159	0.031*	
C3	0.45086 (14)	0.17416 (12)	0.33504 (18)	0.0304 (6)	
H3	0.470578	0.143610	0.366108	0.036*	
C4	0.42397 (14)	0.15745 (12)	0.26773 (19)	0.0341 (7)	
H4	0.425615	0.115394	0.251982	0.041*	
C5	0.39436 (16)	0.20192 (13)	0.22261 (18)	0.0369 (7)	
H5	0.375509	0.190271	0.176218	0.044*	
C6	0.39240 (14)	0.26347 (12)	0.24550 (16)	0.0298 (6)	
H6	0.371794	0.293805	0.214858	0.036*	
C7	0.17559 (12)	0.50079 (10)	0.38931 (13)	0.0158 (5)	
C8	0.14138 (12)	0.47327 (11)	0.44853 (15)	0.0198 (5)	
H8	0.165523	0.456573	0.489306	0.024*	
C9	0.07229 (12)	0.47019 (12)	0.44807 (16)	0.0243 (6)	
H9	0.049340	0.451340	0.488358	0.029*	
C10	0.03678 (13)	0.49480 (12)	0.38843 (15)	0.0244 (6)	
H10	−0.010419	0.492704	0.387856	0.029*	
C11	0.07056 (13)	0.52232 (13)	0.33002 (16)	0.0256 (6)	
H11	0.046353	0.539209	0.289402	0.031*	
C12	0.13958 (12)	0.52542 (11)	0.33034 (15)	0.0217 (5)	
H12	0.162274	0.544480	0.290016	0.026*	
C13	0.42453 (11)	0.72160 (11)	0.45726 (15)	0.0189 (5)	
C14	0.45003 (16)	0.75859 (13)	0.4016 (2)	0.0404 (8)	
H14	0.466560	0.740272	0.357213	0.048*	
C15	0.45157 (18)	0.82290 (14)	0.4103 (2)	0.0527 (10)	
H15	0.468977	0.848052	0.371515	0.063*	
C16	0.42877 (14)	0.84987 (13)	0.4729 (2)	0.0398 (8)	
H16	0.429418	0.893761	0.477800	0.048*	
C17	0.40443 (17)	0.81338 (14)	0.5299 (2)	0.0430 (9)	
H17	0.389609	0.832124	0.574726	0.052*	
C18	0.40157 (16)	0.74907 (13)	0.52169 (17)	0.0338 (7)	
H18	0.383801	0.724157	0.560487	0.041*	
C19	0.66708 (12)	0.50305 (10)	0.38165 (13)	0.0154 (5)	
C20	0.70957 (12)	0.45885 (11)	0.41236 (14)	0.0198 (5)	
H20	0.691967	0.426573	0.442483	0.024*	

C21	0.77752 (13)	0.46181 (13)	0.39912 (15)	0.0256 (6)
H21	0.806087	0.431261	0.419872	0.031*
C22	0.80410 (13)	0.50902 (13)	0.35582 (16)	0.0271 (6)
H22	0.850647	0.510865	0.346956	0.032*
C23	0.76238 (13)	0.55324 (13)	0.32574 (15)	0.0277 (6)
H23	0.780381	0.585843	0.296427	0.033*
C24	0.69414 (13)	0.55040 (12)	0.33805 (15)	0.0226 (5)
H24	0.665777	0.580821	0.316693	0.027*
C(A1	0.55989 (11)	0.44641 (10)	0.36743 (13)	0.0146 (5)
C(A2	0.48166 (12)	0.37726 (10)	0.34335 (13)	0.0157 (5)
C(A3	0.35993 (12)	0.37606 (10)	0.35121 (14)	0.0169 (5)
C(A4	0.28251 (12)	0.44579 (10)	0.37543 (13)	0.0159 (5)
C(A5	0.28327 (12)	0.55656 (11)	0.40428 (14)	0.0174 (5)
C(A6	0.36142 (12)	0.62527 (10)	0.43015 (14)	0.0173 (5)
C(A7	0.48260 (12)	0.62090 (10)	0.44399 (13)	0.0162 (5)
C(A8	0.56024 (11)	0.55124 (10)	0.42006 (13)	0.0150 (5)
C(B1	0.59185 (12)	0.39247 (11)	0.33697 (14)	0.0194 (5)
H(B1	0.638168	0.387514	0.328321	0.023*
C(B2	0.54403 (12)	0.35015 (11)	0.32289 (14)	0.0191 (5)
H(B2	0.550561	0.309748	0.303040	0.023*
C(B3	0.29657 (12)	0.34533 (11)	0.34796 (15)	0.0216 (5)
H(B3	0.289310	0.302652	0.337501	0.026*
C(B4	0.24941 (12)	0.38788 (11)	0.36239 (15)	0.0213 (5)
H(B4	0.202762	0.380878	0.363712	0.026*
C(B5	0.25083 (13)	0.61474 (11)	0.41847 (15)	0.0230 (6)
H(B5	0.204257	0.622200	0.417728	0.028*
C(B6	0.29864 (12)	0.65671 (11)	0.43303 (16)	0.0230 (6)
H(B6	0.291982	0.699496	0.443361	0.028*
C(B7	0.54509 (12)	0.64704 (11)	0.46568 (14)	0.0182 (5)
H(B7	0.551968	0.687212	0.486043	0.022*
C(B8	0.59258 (12)	0.60410 (11)	0.45188 (14)	0.0176 (5)
H(B8	0.638833	0.608255	0.461525	0.021*
C(M1	0.42063 (12)	0.34755 (10)	0.33679 (13)	0.0162 (5)
C(M2	0.25010 (12)	0.50150 (10)	0.38919 (13)	0.0153 (5)
C(M3	0.42232 (11)	0.65274 (10)	0.44520 (14)	0.0168 (5)
C(M4	0.59319 (12)	0.49958 (10)	0.39124 (13)	0.0145 (5)
C1S	0.28678 (18)	0.23978 (17)	0.4985 (2)	0.0488 (9)
H1SA	0.315264	0.276355	0.508279	0.059*
H1SB	0.298393	0.223535	0.448647	0.059*
C2S	0.30152 (18)	0.18932 (17)	0.5575 (2)	0.0509 (9)
H2SA	0.289087	0.204976	0.607336	0.061*
H2SB	0.274282	0.152072	0.546955	0.061*
C3S	0.37423 (19)	0.17186 (17)	0.5572 (2)	0.0571 (10)
H3SA	0.387512	0.159787	0.506761	0.086*
H3SB	0.381507	0.136996	0.591202	0.086*
H3SC	0.400895	0.207461	0.573341	0.086*
C4S	0.3238 (4)	0.7350 (3)	0.2525 (4)	0.0454 (15)	0.5
H4S	0.363543	0.718301	0.272952	0.054*	0.5

C5S	0.2861 (11)	0.7015 (10)	0.2020 (13)	0.069 (6)	0.5
H5S	0.299310	0.660302	0.190509	0.083*	0.5
C6S	0.2325 (5)	0.7245 (4)	0.1690 (6)	0.077 (3)	0.5
H6S	0.210217	0.701910	0.131113	0.093*	0.5
C7S	0.2079 (11)	0.7868 (11)	0.1930 (17)	0.075 (6)	0.5
H7S	0.167838	0.803904	0.173935	0.090*	0.5
C8S	0.2462 (4)	0.8181 (4)	0.2438 (5)	0.0518 (19)	0.5
H8S	0.233013	0.858391	0.259270	0.062*	0.5
C9S	0.3018 (3)	0.7930 (3)	0.2721 (4)	0.0414 (15)	0.5
H9S	0.326862	0.816292	0.307085	0.050*	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01075 (19)	0.00928 (18)	0.0170 (2)	0.00011 (12)	−0.00051 (13)	−0.00002 (13)
O1	0.0168 (9)	0.0267 (9)	0.0183 (9)	0.0015 (7)	−0.0016 (7)	0.0008 (7)
O2	0.0329 (11)	0.0353 (11)	0.0252 (11)	−0.0007 (8)	−0.0020 (8)	0.0095 (9)
O3	0.0610 (15)	0.0309 (11)	0.0328 (12)	−0.0039 (10)	0.0025 (10)	−0.0002 (9)
N1	0.0149 (10)	0.0101 (9)	0.0181 (10)	−0.0004 (7)	−0.0014 (8)	−0.0002 (8)
N2	0.0134 (10)	0.0104 (9)	0.0206 (11)	−0.0001 (7)	0.0007 (8)	0.0002 (8)
N3	0.0117 (9)	0.0115 (9)	0.0220 (11)	−0.0004 (7)	0.0000 (8)	0.0009 (8)
N4	0.0149 (10)	0.0100 (9)	0.0191 (11)	0.0013 (7)	0.0001 (8)	0.0005 (8)
N5	0.0201 (11)	0.0309 (12)	0.0268 (13)	−0.0047 (9)	0.0010 (9)	−0.0002 (10)
C1	0.0126 (11)	0.0137 (11)	0.0286 (14)	−0.0017 (9)	0.0024 (10)	−0.0036 (10)
C2	0.0255 (14)	0.0180 (12)	0.0342 (15)	0.0028 (10)	−0.0041 (12)	−0.0024 (11)
C3	0.0262 (14)	0.0138 (12)	0.0511 (19)	0.0033 (10)	−0.0036 (13)	−0.0017 (12)
C4	0.0252 (14)	0.0164 (13)	0.061 (2)	0.0002 (11)	−0.0031 (14)	−0.0159 (13)
C5	0.0428 (18)	0.0290 (15)	0.0390 (18)	−0.0024 (13)	−0.0086 (14)	−0.0149 (13)
C6	0.0345 (15)	0.0233 (14)	0.0317 (16)	0.0017 (11)	−0.0060 (13)	−0.0038 (11)
C7	0.0138 (11)	0.0128 (11)	0.0209 (12)	−0.0001 (8)	0.0010 (9)	−0.0044 (9)
C8	0.0176 (12)	0.0173 (12)	0.0247 (13)	−0.0006 (9)	−0.0012 (10)	0.0000 (10)
C9	0.0196 (13)	0.0219 (13)	0.0313 (15)	−0.0043 (10)	0.0077 (11)	−0.0043 (11)
C10	0.0120 (12)	0.0269 (14)	0.0343 (16)	−0.0011 (10)	0.0009 (10)	−0.0107 (11)
C11	0.0172 (13)	0.0303 (14)	0.0293 (15)	0.0033 (10)	−0.0036 (11)	−0.0083 (12)
C12	0.0183 (13)	0.0225 (12)	0.0243 (14)	0.0032 (10)	0.0001 (10)	0.0005 (10)
C13	0.0128 (11)	0.0130 (11)	0.0309 (14)	0.0013 (9)	−0.0068 (10)	−0.0024 (10)
C14	0.0412 (18)	0.0175 (14)	0.062 (2)	0.0008 (12)	0.0178 (16)	0.0018 (14)
C15	0.044 (2)	0.0170 (14)	0.097 (3)	−0.0012 (13)	0.024 (2)	0.0097 (17)
C16	0.0225 (14)	0.0127 (12)	0.084 (3)	0.0005 (11)	−0.0136 (15)	−0.0049 (15)
C17	0.052 (2)	0.0296 (16)	0.048 (2)	0.0194 (14)	−0.0259 (16)	−0.0189 (15)
C18	0.0496 (18)	0.0196 (13)	0.0321 (16)	0.0122 (12)	−0.0080 (14)	−0.0017 (12)
C19	0.0130 (11)	0.0159 (11)	0.0173 (12)	−0.0024 (9)	0.0003 (9)	−0.0027 (9)
C20	0.0194 (13)	0.0184 (12)	0.0216 (13)	0.0013 (9)	−0.0010 (10)	−0.0002 (10)
C21	0.0183 (13)	0.0278 (14)	0.0308 (15)	0.0066 (10)	−0.0019 (11)	−0.0055 (11)
C22	0.0155 (13)	0.0340 (15)	0.0317 (15)	−0.0039 (10)	0.0045 (11)	−0.0089 (12)
C23	0.0241 (14)	0.0313 (14)	0.0276 (14)	−0.0080 (11)	0.0063 (11)	0.0013 (12)
C24	0.0212 (13)	0.0217 (13)	0.0249 (14)	−0.0017 (10)	−0.0010 (10)	0.0026 (10)
C(A1	0.0141 (11)	0.0130 (11)	0.0167 (12)	0.0011 (8)	0.0011 (9)	0.0022 (9)

C(A2	0.0184 (12)	0.0117 (10)	0.0171 (12)	0.0026 (9)	−0.0004 (9)	0.0006 (9)
C(A3	0.0170 (12)	0.0122 (11)	0.0214 (13)	−0.0010 (9)	−0.0021 (10)	0.0002 (9)
C(A4	0.0148 (11)	0.0143 (11)	0.0185 (12)	−0.0012 (9)	−0.0007 (9)	0.0010 (9)
C(A5	0.0150 (12)	0.0139 (11)	0.0232 (13)	0.0020 (9)	0.0011 (10)	0.0011 (9)
C(A6	0.0165 (12)	0.0126 (11)	0.0227 (13)	0.0011 (9)	0.0008 (10)	0.0011 (9)
C(A7	0.0167 (12)	0.0127 (11)	0.0191 (12)	0.0001 (9)	−0.0012 (9)	−0.0002 (9)
C(A8	0.0132 (11)	0.0139 (11)	0.0180 (12)	−0.0005 (8)	−0.0014 (9)	0.0016 (9)
C(B1	0.0176 (12)	0.0161 (11)	0.0245 (14)	0.0023 (9)	0.0023 (10)	−0.0003 (10)
C(B2	0.0182 (12)	0.0133 (11)	0.0258 (13)	0.0031 (9)	0.0009 (10)	−0.0029 (10)
C(B3	0.0175 (12)	0.0138 (11)	0.0336 (15)	−0.0041 (9)	−0.0002 (11)	−0.0024 (10)
C(B4	0.0149 (12)	0.0170 (11)	0.0320 (15)	−0.0030 (9)	0.0005 (10)	−0.0003 (10)
C(B5	0.0147 (12)	0.0158 (11)	0.0386 (16)	0.0022 (9)	−0.0011 (11)	−0.0022 (11)
C(B6	0.0162 (12)	0.0141 (11)	0.0386 (16)	0.0024 (9)	−0.0017 (11)	−0.0025 (11)
C(B7	0.0192 (12)	0.0131 (11)	0.0224 (13)	−0.0021 (9)	−0.0011 (10)	−0.0018 (9)
C(B8	0.0156 (12)	0.0170 (11)	0.0202 (13)	−0.0011 (9)	−0.0021 (9)	−0.0007 (9)
C(M1	0.0179 (12)	0.0112 (10)	0.0196 (13)	0.0007 (9)	−0.0016 (9)	0.0001 (9)
C(M2	0.0135 (11)	0.0149 (11)	0.0175 (12)	0.0002 (9)	−0.0002 (9)	0.0025 (9)
C(M3	0.0173 (12)	0.0114 (10)	0.0215 (13)	0.0006 (9)	−0.0012 (10)	−0.0003 (9)
C(M4	0.0119 (11)	0.0145 (11)	0.0170 (12)	0.0007 (8)	−0.0007 (8)	0.0019 (9)
C1S	0.059 (2)	0.0438 (19)	0.043 (2)	0.0006 (17)	−0.0063 (17)	−0.0030 (16)
C2S	0.049 (2)	0.046 (2)	0.057 (2)	−0.0065 (16)	0.0016 (18)	−0.0077 (17)
C3S	0.060 (2)	0.045 (2)	0.067 (3)	−0.0008 (18)	−0.001 (2)	−0.0046 (18)
C4S	0.050 (4)	0.048 (4)	0.038 (4)	0.001 (3)	0.003 (3)	0.004 (3)
C5S	0.074 (10)	0.046 (7)	0.087 (12)	0.001 (6)	−0.014 (9)	−0.015 (8)
C6S	0.068 (6)	0.060 (5)	0.104 (8)	−0.016 (4)	−0.024 (5)	−0.012 (5)
C7S	0.046 (7)	0.077 (9)	0.103 (11)	0.010 (6)	−0.043 (7)	−0.015 (8)
C8S	0.044 (4)	0.053 (4)	0.059 (5)	−0.001 (3)	−0.006 (4)	−0.011 (4)
C9S	0.042 (3)	0.044 (3)	0.038 (4)	0.004 (3)	0.006 (3)	−0.001 (3)

Geometric parameters (Å, º)

Mn1—O1	2.1246 (18)	C21—H21	0.9500
Mn1—N1	2.0119 (19)	C21—C22	1.388 (4)
Mn1—N2	2.0184 (19)	C22—H22	0.9500
Mn1—N3	2.0052 (19)	C22—C23	1.380 (4)
Mn1—N4	2.0074 (19)	C23—H23	0.9500
O1—N5	1.260 (3)	C23—C24	1.391 (4)
O2—N5	1.236 (3)	C24—H24	0.9500
O3—N5	1.230 (3)	C(A1—C(B1	1.437 (3)
N1—C(A1	1.387 (3)	C(A1—C(M4	1.394 (3)
N1—C(A2	1.385 (3)	C(A2—C(B2	1.431 (3)
N2—C(A3	1.380 (3)	C(A2—C(M1	1.389 (3)
N2—C(A4	1.387 (3)	C(A3—C(B3	1.437 (3)
N3—C(A5	1.384 (3)	C(A3—C(M1	1.391 (3)
N3—C(A6	1.384 (3)	C(A4—C(B4	1.434 (3)
N4—C(A7	1.381 (3)	C(A4—C(M2	1.388 (3)
N4—C(A8	1.386 (3)	C(A5—C(B5	1.436 (3)
C1—C2	1.385 (4)	C(A5—C(M2	1.388 (3)

C1—C6	1.394 (4)	C(A6—C(B6	1.433 (3)
C1—C(M1	1.497 (3)	C(A6—C(M3	1.386 (3)
C2—H2	0.9500	C(A7—C(B7	1.431 (3)
C2—C3	1.388 (3)	C(A7—C(M3	1.393 (3)
C3—H3	0.9500	C(A8—C(B8	1.431 (3)
C3—C4	1.374 (4)	C(A8—C(M4	1.395 (3)
C4—H4	0.9500	C(B1—H(B1	0.9500
C4—C5	1.390 (4)	C(B1—C(B2	1.349 (3)
C5—H5	0.9500	C(B2—H(B2	0.9500
C5—C6	1.389 (4)	C(B3—H(B3	0.9500
C6—H6	0.9500	C(B3—C(B4	1.344 (3)
C7—C8	1.399 (3)	C(B4—H(B4	0.9500
C7—C12	1.389 (3)	C(B5—H(B5	0.9500
C7—C(M2	1.498 (3)	C(B5—C(B6	1.346 (3)
C8—H8	0.9500	C(B6—H(B6	0.9500
C8—C9	1.391 (3)	C(B7—H(B7	0.9500
C9—H9	0.9500	C(B7—C(B8	1.353 (3)
C9—C10	1.393 (4)	C(B8—H(B8	0.9500
C10—H10	0.9500	C1S—C1S^{i}	1.543 (7)
C10—C11	1.384 (4)	C1S—H1SA	0.9900
C11—H11	0.9500	C1S—H1SB	0.9900
C11—C12	1.389 (4)	C1S—C2S	1.548 (5)
C12—H12	0.9500	C2S—H2SA	0.9900
C13—C14	1.379 (4)	C2S—H2SB	0.9900
C13—C18	1.380 (4)	C2S—C3S	1.509 (5)
C13—C(M3	1.500 (3)	C3S—H3SA	0.9800
C14—H14	0.9500	C3S—H3SB	0.9800
C14—C15	1.395 (4)	C3S—H3SC	0.9800
C15—H15	0.9500	C4S—H4S	0.9500
C15—C16	1.347 (5)	C4S—C5S	1.38 (2)
C16—H16	0.9500	C4S—C9S	1.372 (9)
C16—C17	1.381 (5)	C5S—H5S	0.9500
C17—H17	0.9500	C5S—C6S	1.33 (2)
C17—C18	1.395 (4)	C6S—H6S	0.9500
C18—H18	0.9500	C6S—C7S	1.49 (3)
C19—C20	1.393 (3)	C7S—H7S	0.9500
C19—C24	1.397 (3)	C7S—C8S	1.37 (2)
C19—C(M4	1.497 (3)	C8S—H8S	0.9500
C20—H20	0.9500	C8S—C9S	1.342 (10)
C20—C21	1.388 (4)	C9S—H9S	0.9500
N1—Mn1—O1	91.79 (7)	C23—C24—H24	119.8
N1—Mn1—N2	89.34 (8)	N1—C(A1—C(B1	109.5 (2)
N2—Mn1—O1	95.27 (7)	N1—C(A1—C(M4	125.9 (2)
N3—Mn1—O1	99.66 (7)	C(M4—C(A1—C(B1	124.6 (2)
N3—Mn1—N1	168.53 (8)	N1—C(A2—C(B2	109.9 (2)
N3—Mn1—N2	88.96 (8)	N1—C(A2—C(M1	125.8 (2)
N3—Mn1—N4	89.79 (8)	C(M1—C(A2—C(B2	124.3 (2)

N4—Mn1—O1	99.46 (7)	N2—C(A3—C(B3	109.5 (2)
N4—Mn1—N1	88.95 (8)	N2—C(A3—C(M1	125.9 (2)
N4—Mn1—N2	165.21 (8)	C(M1—C(A3—C(B3	124.5 (2)
N5—O1—Mn1	123.66 (15)	N2—C(A4—C(B4	109.7 (2)
C(A1—N1—Mn1	126.01 (15)	N2—C(A4—C(M2	125.9 (2)
C(A2—N1—Mn1	126.15 (15)	C(M2—C(A4—C(B4	124.3 (2)
C(A2—N1—C(A1	105.67 (18)	N3—C(A5—C(B5	109.7 (2)
C(A3—N2—Mn1	126.98 (16)	N3—C(A5—C(M2	126.0 (2)
C(A3—N2—C(A4	105.81 (19)	C(M2—C(A5—C(B5	124.3 (2)
C(A4—N2—Mn1	127.19 (15)	N3—C(A6—C(B6	109.5 (2)
C(A5—N3—Mn1	126.86 (16)	N3—C(A6—C(M3	125.8 (2)
C(A6—N3—Mn1	126.00 (15)	C(M3—C(A6—C(B6	124.6 (2)
C(A6—N3—C(A5	105.82 (18)	N4—C(A7—C(B7	109.6 (2)
C(A7—N4—Mn1	126.58 (15)	N4—C(A7—C(M3	125.9 (2)
C(A7—N4—C(A8	105.85 (18)	C(M3—C(A7—C(B7	124.4 (2)
C(A8—N4—Mn1	127.38 (15)	N4—C(A8—C(B8	109.6 (2)
O2—N5—O1	118.8 (2)	N4—C(A8—C(M4	125.7 (2)
O3—N5—O1	119.1 (2)	C(M4—C(A8—C(B8	124.6 (2)
O3—N5—O2	122.0 (2)	C(A1—C(B1—H(B1	126.3
C2—C1—C6	118.9 (2)	C(B2—C(B1—C(A1	107.5 (2)
C2—C1—C(M1	120.7 (2)	C(B2—C(B1—H(B1	126.3
C6—C1—C(M1	120.5 (2)	C(A2—C(B2—H(B2	126.3
C1—C2—H2	119.5	C(B1—C(B2—C(A2	107.4 (2)
C1—C2—C3	120.9 (3)	C(B1—C(B2—H(B2	126.3
C3—C2—H2	119.5	C(A3—C(B3—H(B3	126.2
C2—C3—H3	120.0	C(B4—C(B3—C(A3	107.6 (2)
C4—C3—C2	119.9 (3)	C(B4—C(B3—H(B3	126.2
C4—C3—H3	120.0	C(A4—C(B4—H(B4	126.3
C3—C4—H4	119.9	C(B3—C(B4—C(A4	107.3 (2)
C3—C4—C5	120.1 (2)	C(B3—C(B4—H(B4	126.3
C5—C4—H4	119.9	C(A5—C(B5—H(B5	126.4
C4—C5—H5	120.1	C(B6—C(B5—C(A5	107.3 (2)
C6—C5—C4	119.9 (3)	C(B6—C(B5—H(B5	126.4
C6—C5—H5	120.1	C(A6—C(B6—H(B6	126.1
C1—C6—H6	119.8	C(B5—C(B6—C(A6	107.7 (2)
C5—C6—C1	120.3 (3)	C(B5—C(B6—H(B6	126.2
C5—C6—H6	119.8	C(A7—C(B7—H(B7	126.3
C8—C7—C(M2	119.8 (2)	C(B8—C(B7—C(A7	107.5 (2)
C12—C7—C8	119.1 (2)	C(B8—C(B7—H(B7	126.3
C12—C7—C(M2	121.1 (2)	C(A8—C(B8—H(B8	126.3
C7—C8—H8	119.8	C(B7—C(B8—C(A8	107.3 (2)
C9—C8—C7	120.4 (2)	C(B7—C(B8—H(B8	126.3
C9—C8—H8	119.8	C(A2—C(M1—C1	117.9 (2)
C8—C9—H9	120.1	C(A2—C(M1—C(A3	123.7 (2)
C8—C9—C10	119.9 (2)	C(A3—C(M1—C1	118.4 (2)
C10—C9—H9	120.1	C(A4—C(M2—C7	117.4 (2)
C9—C10—H10	120.1	C(A5—C(M2—C7	119.3 (2)
C11—C10—C9	119.7 (2)	C(A5—C(M2—C(A4	123.3 (2)

C11—C10—H10	120.1	C(A6—C(M3—C13	118.5 (2)
C10—C11—H11	119.8	C(A6—C(M3—C(A7	123.7 (2)
C10—C11—C12	120.5 (3)	C(A7—C(M3—C13	117.6 (2)
C12—C11—H11	119.8	C(A1—C(M4—C19	118.8 (2)
C7—C12—H12	119.8	C(A1—C(M4—C(A8	122.8 (2)
C11—C12—C7	120.3 (2)	C(A8—C(M4—C19	118.3 (2)
C11—C12—H12	119.8	C1S[i]—C1S—H1SA	109.1
C14—C13—C18	119.1 (2)	C1S[i]—C1S—H1SB	109.1
C14—C13—C(M3	118.5 (2)	C1S[i]—C1S—C2S	112.6 (3)
C18—C13—C(M3	122.4 (2)	H1SA—C1S—H1SB	107.8
C13—C14—H14	120.0	C2S—C1S—H1SA	109.1
C13—C14—C15	120.1 (3)	C2S—C1S—H1SB	109.1
C15—C14—H14	120.0	C1S—C2S—H2SA	109.4
C14—C15—H15	119.5	C1S—C2S—H2SB	109.4
C16—C15—C14	121.0 (3)	H2SA—C2S—H2SB	108.0
C16—C15—H15	119.5	C3S—C2S—C1S	111.0 (3)
C15—C16—H16	120.2	C3S—C2S—H2SA	109.4
C15—C16—C17	119.6 (3)	C3S—C2S—H2SB	109.4
C17—C16—H16	120.2	C2S—C3S—H3SA	109.5
C16—C17—H17	119.9	C2S—C3S—H3SB	109.5
C16—C17—C18	120.1 (3)	C2S—C3S—H3SC	109.5
C18—C17—H17	119.9	H3SA—C3S—H3SB	109.5
C13—C18—C17	120.1 (3)	H3SA—C3S—H3SC	109.5
C13—C18—H18	120.0	H3SB—C3S—H3SC	109.5
C17—C18—H18	120.0	C5S—C4S—H4S	121.1
C20—C19—C24	118.9 (2)	C5S—C4S—C9S	117.8 (11)
C20—C19—C(M4	121.9 (2)	C9S—C4S—H4S	121.1
C24—C19—C(M4	119.2 (2)	C4S—C5S—H5S	118.5
C19—C20—H20	119.9	C6S—C5S—C4S	122.9 (16)
C21—C20—C19	120.3 (2)	C6S—C5S—H5S	118.6
C21—C20—H20	119.9	C5S—C6S—H6S	120.8
C20—C21—H21	119.7	C5S—C6S—C7S	118.4 (12)
C22—C21—C20	120.6 (2)	C7S—C6S—H6S	120.8
C22—C21—H21	119.7	C6S—C7S—H7S	121.6
C21—C22—H22	120.3	C8S—C7S—C6S	116.7 (14)
C23—C22—C21	119.5 (2)	C8S—C7S—H7S	121.7
C23—C22—H22	120.3	C7S—C8S—H8S	119.3
C22—C23—H23	119.8	C9S—C8S—C7S	121.5 (11)
C22—C23—C24	120.4 (2)	C9S—C8S—H8S	119.3
C24—C23—H23	119.8	C4S—C9S—H9S	118.7
C19—C24—H24	119.8	C8S—C9S—C4S	122.6 (7)
C23—C24—C19	120.4 (2)	C8S—C9S—H9S	118.7
Mn1—O1—N5—O2	−169.95 (16)	C18—C13—C(M3—C(A7	−110.9 (3)
Mn1—O1—N5—O3	11.9 (3)	C19—C20—C21—C22	0.6 (4)
Mn1—N1—C(A1—C(B1	−162.14 (16)	C20—C19—C24—C23	−0.1 (4)
Mn1—N1—C(A1—C(M4	18.3 (3)	C20—C19—C(M4—C(A1	−57.4 (3)
Mn1—N1—C(A2—C(B2	162.58 (16)	C20—C19—C(M4—C(A8	125.9 (2)

Mn1—N1—C(A2—C(M1	−17.0 (3)	C20—C21—C22—C23	−0.1 (4)
Mn1—N2—C(A3—C(B3	−179.46 (17)	C21—C22—C23—C24	−0.6 (4)
Mn1—N2—C(A3—C(M1	−0.9 (4)	C22—C23—C24—C19	0.6 (4)
Mn1—N2—C(A4—C(B4	179.21 (16)	C24—C19—C20—C21	−0.5 (4)
Mn1—N2—C(A4—C(M2	1.9 (4)	C24—C19—C(M4—C(A1	119.8 (2)
Mn1—N3—C(A5—C(B5	−167.60 (17)	C24—C19—C(M4—C(A8	−56.8 (3)
Mn1—N3—C(A5—C(M2	15.5 (4)	C(A1—N1—C(A2—C(B2	−1.3 (3)
Mn1—N3—C(A6—C(B6	166.81 (17)	C(A1—N1—C(A2—C(M1	179.1 (2)
Mn1—N3—C(A6—C(M3	−14.5 (4)	C(A1—C(B1—C(B2—C(A2	0.8 (3)
Mn1—N4—C(A7—C(B7	−179.11 (16)	C(A2—N1—C(A1—C(B1	1.8 (3)
Mn1—N4—C(A7—C(M3	−2.0 (4)	C(A2—N1—C(A1—C(M4	−177.7 (2)
Mn1—N4—C(A8—C(B8	179.77 (16)	C(A3—N2—C(A4—C(B4	0.7 (3)
Mn1—N4—C(A8—C(M4	3.1 (3)	C(A3—N2—C(A4—C(M2	−176.7 (2)
N1—C(A1—C(B1—C(B2	−1.6 (3)	C(A3—C(B3—C(B4—C(A4	−0.4 (3)
N1—C(A1—C(M4—C19	−177.4 (2)	C(A4—N2—C(A3—C(B3	−0.9 (3)
N1—C(A1—C(M4—C(A8	−1.0 (4)	C(A4—N2—C(A3—C(M1	177.6 (2)
N1—C(A2—C(B2—C(B1	0.4 (3)	C(A5—N3—C(A6—C(B6	−0.8 (3)
N1—C(A2—C(M1—C1	−174.8 (2)	C(A5—N3—C(A6—C(M3	177.9 (2)
N1—C(A2—C(M1—C(A3	4.9 (4)	C(A5—C(B5—C(B6—C(A6	−1.5 (3)
N2—C(A3—C(B3—C(B4	0.9 (3)	C(A6—N3—C(A5—C(B5	−0.1 (3)
N2—C(A3—C(M1—C1	−175.7 (2)	C(A6—N3—C(A5—C(M2	−177.1 (2)
N2—C(A3—C(M1—C(A2	4.6 (4)	C(A7—N4—C(A8—C(B8	4.5 (3)
N2—C(A4—C(B4—C(B3	−0.2 (3)	C(A7—N4—C(A8—C(M4	−172.3 (2)
N2—C(A4—C(M2—C7	176.1 (2)	C(A7—C(B7—C(B8—C(A8	1.1 (3)
N2—C(A4—C(M2—C(A5	−5.4 (4)	C(A8—N4—C(A7—C(B7	−3.7 (3)
N3—C(A5—C(B5—C(B6	1.1 (3)	C(A8—N4—C(A7—C(M3	173.4 (2)
N3—C(A5—C(M2—C7	174.8 (2)	C(B1—C(A1—C(M4—C19	3.1 (3)
N3—C(A5—C(M2—C(A4	−3.7 (4)	C(B1—C(A1—C(M4—C(A8	179.5 (2)
N3—C(A6—C(B6—C(B5	1.5 (3)	C(B2—C(A2—C(M1—C1	5.7 (4)
N3—C(A6—C(M3—C13	174.4 (2)	C(B2—C(A2—C(M1—C(A3	−174.6 (2)
N3—C(A6—C(M3—C(A7	−0.3 (4)	C(B3—C(A3—C(M1—C1	2.6 (4)
N4—C(A7—C(B7—C(B8	1.6 (3)	C(B3—C(A3—C(M1—C(A2	−177.1 (2)
N4—C(A7—C(M3—C13	−165.7 (2)	C(B4—C(A4—C(M2—C7	−0.9 (4)
N4—C(A7—C(M3—C(A6	9.0 (4)	C(B4—C(A4—C(M2—C(A5	177.6 (2)
N4—C(A8—C(B8—C(B7	−3.5 (3)	C(B5—C(A5—C(M2—C7	−1.7 (4)
N4—C(A8—C(M4—C19	166.2 (2)	C(B5—C(A5—C(M2—C(A4	179.8 (2)
N4—C(A8—C(M4—C(A1	−10.3 (4)	C(B6—C(A6—C(M3—C13	−7.1 (4)
C1—C2—C3—C4	0.2 (4)	C(B6—C(A6—C(M3—C(A7	178.2 (2)
C2—C1—C6—C5	−1.2 (4)	C(B7—C(A7—C(M3—C13	11.0 (4)
C2—C1—C(M1—C(A2	64.2 (3)	C(B7—C(A7—C(M3—C(A6	−174.2 (2)
C2—C1—C(M1—C(A3	−115.5 (3)	C(B8—C(A8—C(M4—C19	−10.0 (4)
C2—C3—C4—C5	−0.8 (5)	C(B8—C(A8—C(M4—C(A1	173.5 (2)
C3—C4—C5—C6	0.4 (5)	C(M1—C1—C2—C3	−178.2 (2)
C4—C5—C6—C1	0.6 (5)	C(M1—C1—C6—C5	177.8 (3)
C6—C1—C2—C3	0.8 (4)	C(M1—C(A2—C(B2—C(B1	180.0 (2)
C6—C1—C(M1—C(A2	−114.8 (3)	C(M1—C(A3—C(B3—C(B4	−177.7 (2)
C6—C1—C(M1—C(A3	65.5 (3)	C(M2—C7—C8—C9	−177.6 (2)
C7—C8—C9—C10	−0.2 (4)	C(M2—C7—C12—C11	177.6 (2)

C8—C7—C12—C11	−0.5 (4)	C(M2—C(A4—C(B4—C(B3	177.2 (2)
C8—C7—C(M2—C(A4	72.7 (3)	C(M2—C(A5—C(B5—C(B6	178.1 (2)
C8—C7—C(M2—C(A5	−105.9 (3)	C(M3—C13—C14—C15	178.7 (3)
C8—C9—C10—C11	−0.1 (4)	C(M3—C13—C18—C17	−179.6 (3)
C9—C10—C11—C12	0.2 (4)	C(M3—C(A6—C(B6—C(B5	−177.3 (3)
C10—C11—C12—C7	0.1 (4)	C(M3—C(A7—C(B7—C(B8	−175.6 (2)
C12—C7—C8—C9	0.5 (3)	C(M4—C19—C20—C21	176.7 (2)
C12—C7—C(M2—C(A4	−105.3 (3)	C(M4—C19—C24—C23	−177.4 (2)
C12—C7—C(M2—C(A5	76.1 (3)	C(M4—C(A1—C(B1—C(B2	177.9 (2)
C13—C14—C15—C16	0.4 (6)	C(M4—C(A8—C(B8—C(B7	173.2 (2)
C14—C13—C18—C17	−0.1 (4)	C1Sⁱ—C1S—C2S—C3S	−178.4 (3)
C14—C13—C(M3—C(A6	−105.4 (3)	C4S—C5S—C6S—C7S	−6 (3)
C14—C13—C(M3—C(A7	69.6 (3)	C5S—C4S—C9S—C8S	−0.6 (15)
C14—C15—C16—C17	1.0 (5)	C5S—C6S—C7S—C8S	5 (3)
C15—C16—C17—C18	−2.0 (5)	C6S—C7S—C8S—C9S	−2 (3)
C16—C17—C18—C13	1.5 (5)	C7S—C8S—C9S—C4S	−0.2 (19)
C18—C13—C14—C15	−0.8 (5)	C9S—C4S—C5S—C6S	4 (3)
C18—C13—C(M3—C(A6	74.1 (3)		

Symmetry code: (i) −x+1/2, −y+1/2, z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C4*S*—H4*S*···O3	0.95	2.38	3.177 (8)	141
C10—H10···O2ⁱⁱ	0.95	2.50	3.182 (3)	129
C17—H17···O2ⁱⁱⁱ	0.95	2.53	3.350 (4)	145
C22—H22···O2ⁱᵛ	0.95	2.49	3.085 (3)	120

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