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fac-Bromido/chlorido(0.50/0.50)[3-carbamoyl-1-(1,10-phenanthrolin-2-ylmethyl)pyridinium-κ^2N,N']tricarbonylmanganese(I) 0.49-bromide 0.51-chloride methanol monosolvate

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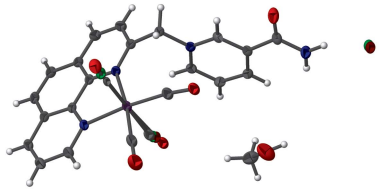
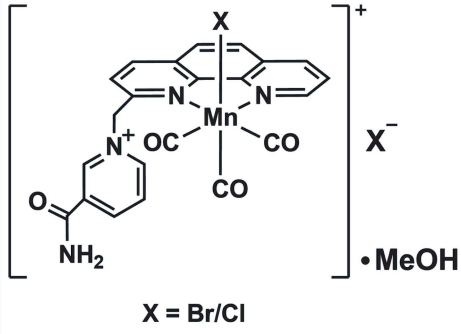
Structural data: full structural data are available from iucrdata.iucr.org

The title complex, $[MnBr_{0.50}Cl_{0.50}(C_{19}H_{15}N_4O)(CO)_3]Br_{0.49}Cl_{0.51}\cdot CH_3OH$, exhibits substitutional disorder of the halogen ligand in the asymmetric unit, with almost the same occupancies for Br and Cl. The Mn^I atom is coordinated in a distorted octahedral environment by three carbonyl C atoms, the disordered X^- ligand (X = Br or Cl) and two N atoms from the 1,10-phenanthroline ligand bearing a nicotinamide pendant moiety. The cation displays a *fac* configuration of the carbonyl ligands. There is another disorder between the chloride ligand and its *trans*-situated carbonyl ligand, and between Cl^- and Br^- at the position of the counter-anion. In the crystal, intermolecular C—H···X, N—H···X, O—H···X (X = Br or Cl) and C—H···O hydrogen bonds lead to the formation of a three-dimensional network.

3D view



Chemical scheme



Structure description

The group 7 metal complexes of general formula $[MX(CO)_3(N\text{^}N)]$ (M = Mn^I, Re^I; X = Br, Cl; N^N = 2,2′-bipyridine or 1,10-phenanthroline derivatives) have been extensively studied for their catalytic CO_2 reduction abilities over recent decades (Francke *et al.*, 2018). Because the single-electron reduction of CO_2 is highly unfavorable, the reduction of CO_2 via proton-assisted multi-electron transfer is one of the best strategies (Tanaka & Ooyama, 2002). In fact, the introduction of phenolic functional groups into the bipyridyl supporting ligands, which can act as proton donors, have shown enhanced catalytic performance (Agarwal *et al.*, 2015). Thus, we focused on simulating the biological

function of coenzyme nicotinamide adenine dinucleotide (NAD) that can transfer a hydride ion reversibly.

Herein we report on the synthesis and structural characterization of a new complex of the type *fac*-[Mn*X*(CO)$_3$(N^N)]$^+$, in which the phenanthroline ligand (N^N) contains an NAD-mimic moiety (*N*-methylated nicotinamide).

The title complex was synthesized by reacting bromidopentacarbonylmanganese(I) with 3-carbamoyl-1-(1,10-phenanthrolin-2-ylmethyl)pyridinium chloride. As a consequence, the compound exhibits substitutional disorder of Cl and Br at the two halogen sites in the asymmetric unit. The halogen site (*X*1) bonded to Mn shows an occupancy of 1:1 for Br and Cl, just like the halogen site of the counter-anion (*X*2). The coordination environment of the central Mn^I atom in the complex cation is distorted octahedral, defined by two N atoms of the bidentate phenanthroline ligand, the X^- ligand and three carbonyl C atoms, whereby the carbonyl ligands are arranged in a *fac* configuration (Fig. 1). The Mn—N bond lengths [2.054 (3) and 2.117 (2) Å] are similar to those previously reported for complexes of this type (*fac*-[MnBr(CO)$_3$(N^N)], where N^N = 1,10-phenanthroline derivatives; Jimenez *et al.*, 2015; Kurtz *et al.*, 2015). Of the three Mn—C bond lengths, the axial Mn—C one [1.846 (7) Å] is considerably longer compared to the equatorial Mn—C ones [1.807 (3) and 1.811 (3) Å] due to the *trans* influence of the halide ligands. In addition, there is another disorder of the Cl1 ligand that is split into one position near the Br1 ligand and a position opposite to that (Cl3) where it is positionally disordered with a carbonyl ligand (C1≡O1). The occupancies of Cl3 and C1≡O1 are 0.225 (6):0.775 (6). Due to the observed disorder, the compound crystallizes as a racemate, *i.e.* a mixture of *C* and *A* isomers in the unit cell. The nicotinamide moiety is located at the 2-position of the phenanthroline ligand, and is close to being perpendicular to the latter, with a dihedral angle of 84.2 (7)°. Also, there is intramolecular C—H···O interaction in the complex cation (Table 1).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H1···Br2*a*	0.88	2.68	3.478 (3)	152
N4—H1···Cl2*b*	0.88	2.46	3.279 (6)	155
N4—H2···Br2*a*^{i}	0.88	2.48	3.326 (3)	162
N4—H2···Cl2*b*^{i}	0.88	2.40	3.239 (6)	160
O5—H19···Br2*a*^{i}	0.84	2.47	3.276 (3)	161
O5—H19···Cl2*b*^{i}	0.84	2.41	3.218 (5)	163
C5—H4···O5^{ii}	0.95	2.49	3.370 (4)	154
C6—H5···Br1*b*^{iii}	0.95	2.90	3.735 (4)	147
C16—H10···O4^{iv}	0.99	2.39	3.120 (4)	130
C16—H11···Br2*a*^{v}	0.99	2.78	3.678 (3)	150
C17—H12···O1*c*^{vi}	0.95	2.46	3.224 (5)	137
C19—H14···Br2*a*^{i}	0.95	2.72	3.667 (3)	172
C19—H14···Cl2*b*^{i}	0.95	2.77	3.702 (6)	167
C21—H15···O4	0.95	2.35	2.702 (4)	101
C21—H15···O4^{iv}	0.95	2.33	3.074 (4)	135

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

In the crystal structure, a methanol solvent molecule is incorporated per formula unit. There are weak C—H···*X*, N—H···*X*, O—H···*X* (*X* = Br or Cl) and C—H···O hydrogen bonds between the complex cation, the counter-anion and/or the solvent molecule, leading to the formation of a three-dimensional network structure (Table 1, Fig. 2).

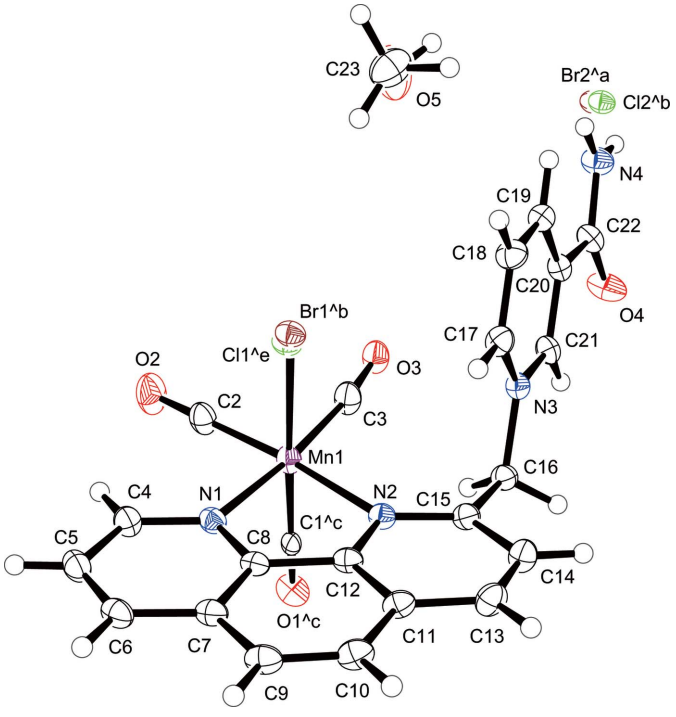


Figure 1
The structures of the molecular components in the title salt (*C* isomer; *i.e.* only the major components of the disorder between *X*1 and C1≡O1 are shown), with atom labels and displacement ellipsoids for non-H atoms drawn at the 50% probability level.

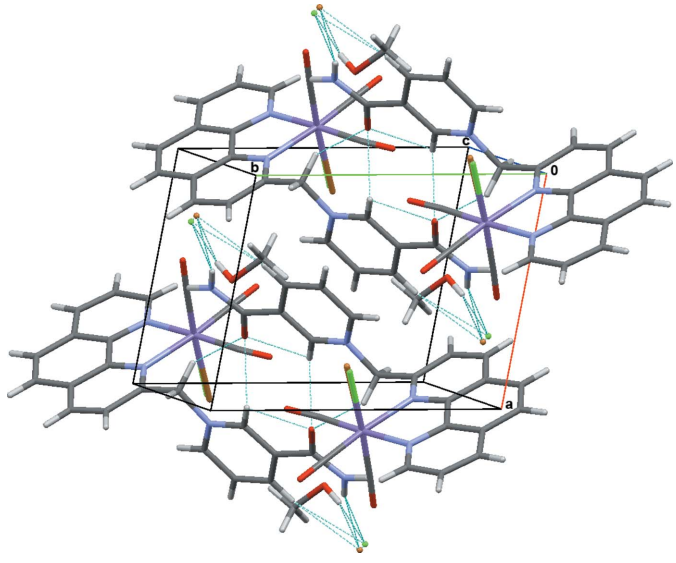


Figure 2
The crystal packing of the title compound with hydrogen bonds shown as dashed lines (for numerical values, see: Table 1).

Table 2
Experimental details.

Crystal data	
Chemical formula	$[MnBr_{0.50}Cl_{0.50}(C_{19}H_{15}N_4O)(CO)_3]Br_{0.49}Cl_{0.51}\cdot CH_4O$
M_r	601.72
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	93
a, b, c (Å)	7.9489 (2), 9.3587 (3), 16.6744 (5)
α, β, γ (°)	87.3910 (8), 76.4891 (8), 80.8427 (8)
V (Å^3)	1190.69 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.39
Crystal size (mm)	0.20 × 0.15 × 0.05
Data collection	
Diffractometer	Rigaku Saturn70
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.517, 0.620
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12472, 5395, 5073
R_{int}	0.017
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.088, 1.15
No. of reflections	5395
No. of parameters	324
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.14, −0.62

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *SIR97* (Altomare *et al.*, 1999), *SHELXL2018* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *ORTEP-3 for Windows* (Farrugia, 2012), *CrystalStructure* (Rigaku, 2010), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

The ligand, 3-carbamoyl-1-(1,10-phenanthrolin-2-ylmethyl)-pyridinium chloride (pnaCl), was prepared as described by Engbersen *et al.* (1990). It proved to be analytically and spectroscopically pure (IR and ^{1}H NMR data). $[MnBr(CO)_5]$ (85 mg, 0.31 mmol) and pnaCl (106 mg, 0.27 mmol) were dissolved in methanol (15 ml). The reaction mixture was stirred in the dark at room temperature for 24 h. An excess of Et_2O was added to the solution, and then it was allowed to stand at 277 K overnight. The resultant orange-coloured precipitate was collected by filtration and washed with Et_2O, and then dried under vacuum (yield 144 mg, 94%). Crystals suitable for the X-ray diffraction experiment were grown by diffusion of Et_2O into a methanol solution of the complex over a few days. From energy-dispersive X-ray (EDX) analysis of the crystals, the Mn/Br/Cl molar ratio could be estimated to be nearly 1:1:1.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The two halide sites were refined as being substitutionally disordered between bromine and chlorine, with an occupancy of 0.5071 (10) for Br1 and of 0.507 (6) for {Cl1+Cl3}, and with 0.4929 (10) for Br2 and 0.5071 (10) for Cl2. The CO group (C1≡O1) and the Cl3 atom *trans* to this group were refined as being disordered over two sets of sites, with occupancies of 0.775 (6) for the carbonyl group and 0.225 (6) for the Cl3 ligand.

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full crystallographic data

IUCrData (2019). **4**, x181792 [https://doi.org/10.1107/S2414314618017923]

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γ = 80.8427 (8)°
V = 1190.69 (6) Å^3
Z = 2
$F(000)$ = 604.00
D_x = 1.678 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 11817 reflections
θ = 3.2–27.5°
μ = 2.39 mm^{-1}
T = 93 K
Prism, yellow
0.20 × 0.15 × 0.05 mm

Data collection

Rigaku Saturn70 diffractometer
Detector resolution: 29.257 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.517, T_{max} = 0.620
12472 measured reflections
5395 independent reflections
5073 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.017
θ_{max} = 27.5°
h = −10→10
k = −12→12
l = −21→21

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.088
S = 1.15
5395 reflections
324 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 2.2804P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 1.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Special details

Geometry. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1b	0.8929 (5)	0.3755 (3)	0.63846 (13)	0.02015 (14)	0.5071 (10)
Br2a	0.7235 (3)	1.08330 (19)	1.08656 (7)	0.02015 (14)	0.4929 (10)
Mn1	1.16958 (5)	0.27016 (4)	0.67869 (2)	0.01900 (10)	
Cl1e	0.9096 (19)	0.3654 (13)	0.6366 (7)	0.02015 (14)	0.282 (6)
Cl2b	0.6988 (8)	1.0673 (5)	1.08955 (18)	0.02015 (14)	0.5071 (10)
Cl3d	1.4134 (8)	0.1740 (6)	0.7245 (3)	0.02015 (14)	0.225 (6)
O1c	1.4948 (5)	0.1658 (3)	0.73470 (17)	0.0267 (7)	0.775 (6)
O2	1.3608 (3)	0.4822 (3)	0.57446 (14)	0.0396 (6)	
O3	1.0876 (3)	0.5106 (2)	0.79685 (11)	0.0256 (4)	
O4	0.8059 (3)	0.6321 (3)	1.04873 (13)	0.0320 (5)	
O5	0.5308 (4)	0.8025 (4)	0.73664 (16)	0.0522 (7)	
O30d	0.8464 (19)	0.4043 (14)	0.6329 (7)	0.0256 (4)	0.225 (6)
N1	1.2160 (3)	0.1257 (3)	0.58401 (13)	0.0188 (4)	
N2	1.0398 (3)	0.1015 (2)	0.74008 (13)	0.0177 (4)	
N3	0.8143 (3)	0.3242 (3)	0.88439 (13)	0.0184 (4)	
N4	0.5950 (3)	0.7904 (3)	1.00838 (14)	0.0259 (5)	
C1c	1.3725 (8)	0.2021 (5)	0.7131 (3)	0.0178 (10)	0.775 (6)
C2	1.2855 (4)	0.3997 (3)	0.61360 (16)	0.0253 (6)	
C3	1.1152 (4)	0.4113 (3)	0.75533 (16)	0.0256 (4)	
C4	1.3042 (4)	0.1405 (3)	0.50646 (16)	0.0228 (5)	
C5	1.3240 (4)	0.0364 (3)	0.44579 (16)	0.0244 (6)	
C6	1.2507 (4)	−0.0874 (3)	0.46607 (16)	0.0232 (6)	
C7	1.1544 (4)	−0.1062 (3)	0.54725 (16)	0.0206 (5)	
C8	1.1403 (3)	0.0044 (3)	0.60407 (15)	0.0178 (5)	
C9	1.0684 (4)	−0.2294 (3)	0.57349 (17)	0.0243 (6)	
C10	0.9738 (4)	−0.2399 (3)	0.65167 (17)	0.0237 (6)	
C11	0.9597 (4)	−0.1300 (3)	0.71097 (16)	0.0205 (5)	
C12	1.0435 (4)	−0.0076 (3)	0.68730 (15)	0.0182 (5)	
C13	0.8665 (4)	−0.1387 (3)	0.79310 (17)	0.0248 (6)	
C14	0.8659 (4)	−0.0318 (3)	0.84659 (16)	0.0238 (6)	
C15	0.9550 (4)	0.0861 (3)	0.81856 (15)	0.0192 (5)	
C16	0.9553 (4)	0.1955 (3)	0.88158 (15)	0.0196 (5)	
C17	0.6990 (4)	0.3362 (3)	0.83615 (15)	0.0219 (5)	
C18	0.5748 (4)	0.4589 (3)	0.83982 (16)	0.0246 (6)	
C19	0.5704 (4)	0.5694 (3)	0.89289 (16)	0.0218 (5)	
C20	0.6896 (4)	0.5542 (3)	0.94311 (15)	0.0195 (5)	
C21	0.8099 (4)	0.4289 (3)	0.93797 (15)	0.0195 (5)	
C22	0.7012 (4)	0.6639 (3)	1.00468 (16)	0.0221 (5)	
C23	0.4337 (5)	0.7208 (4)	0.7017 (3)	0.0389 (8)	

C30d	0.954 (3)	0.358 (3)	0.6374 (13)	0.0256 (4)	0.225 (6)
H1	0.5976	0.8564	1.0438	0.0310*	
H2	0.5222	0.8078	0.9754	0.0310*	
H3	1.3560	0.2255	0.4916	0.0273*	
H4	1.3876	0.0514	0.3911	0.0293*	
H5	1.2647	−0.1596	0.4258	0.0278*	
H6	1.0779	−0.3045	0.5355	0.0292*	
H7	0.9159	−0.3216	0.6675	0.0284*	
H8	0.8048	−0.2176	0.8113	0.0298*	
H9	0.8053	−0.0370	0.9027	0.0286*	
H10	1.0706	0.2292	0.8689	0.0235*	
H11	0.9393	0.1484	0.9366	0.0235*	
H12	0.7026	0.2604	0.7995	0.0263*	
H13	0.4927	0.4672	0.8060	0.0295*	
H14	0.4869	0.6548	0.8951	0.0262*	
H15	0.8905	0.4165	0.9727	0.0234*	
H16	0.3446	0.6846	0.7454	0.0467*	
H17	0.5120	0.6390	0.6718	0.0467*	
H18	0.3766	0.7818	0.6633	0.0467*	
H19	0.4638	0.8519	0.7755	0.1825*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1b	0.0210 (7)	0.0174 (4)	0.02220 (16)	−0.00054 (14)	−0.0062 (2)	−0.00383 (13)
Br2a	0.0210 (7)	0.0174 (4)	0.02220 (16)	−0.00054 (14)	−0.0062 (2)	−0.00383 (13)
Mn1	0.02252 (19)	0.01739 (18)	0.01732 (18)	−0.00680 (14)	−0.00191 (14)	−0.00348 (14)
Cl1e	0.0210 (7)	0.0174 (4)	0.02220 (16)	−0.00054 (14)	−0.0062 (2)	−0.00383 (13)
Cl2b	0.0210 (7)	0.0174 (4)	0.02220 (16)	−0.00054 (14)	−0.0062 (2)	−0.00383 (13)
Cl3d	0.0210 (7)	0.0174 (4)	0.02220 (16)	−0.00054 (14)	−0.0062 (2)	−0.00383 (13)
O1c	0.0226 (18)	0.0307 (15)	0.0298 (15)	−0.0056 (11)	−0.0096 (13)	−0.0077 (11)
O2	0.0465 (14)	0.0328 (12)	0.0350 (12)	−0.0179 (10)	0.0081 (10)	−0.0012 (9)
O3	0.0338 (9)	0.0217 (7)	0.0209 (7)	−0.0097 (6)	−0.0015 (7)	−0.0035 (6)
O4	0.0281 (11)	0.0317 (11)	0.0388 (12)	0.0044 (9)	−0.0161 (9)	−0.0150 (9)
O5	0.0521 (16)	0.0661 (18)	0.0409 (14)	−0.0272 (14)	−0.0018 (12)	−0.0081 (13)
O30d	0.0338 (9)	0.0217 (7)	0.0209 (7)	−0.0097 (6)	−0.0015 (7)	−0.0035 (6)
N1	0.0193 (10)	0.0184 (10)	0.0182 (10)	−0.0010 (8)	−0.0043 (8)	−0.0031 (8)
N2	0.0189 (10)	0.0166 (10)	0.0181 (10)	−0.0026 (8)	−0.0053 (8)	−0.0023 (8)
N3	0.0182 (10)	0.0193 (10)	0.0172 (10)	−0.0040 (8)	−0.0025 (8)	0.0000 (8)
N4	0.0285 (12)	0.0218 (11)	0.0280 (12)	−0.0009 (9)	−0.0089 (10)	−0.0062 (9)
C1c	0.027 (3)	0.0108 (18)	0.0118 (17)	−0.0012 (16)	0.0020 (16)	−0.0024 (13)
C2	0.0287 (14)	0.0241 (13)	0.0219 (13)	−0.0064 (11)	−0.0006 (11)	−0.0058 (10)
C3	0.0338 (9)	0.0217 (7)	0.0209 (7)	−0.0097 (6)	−0.0015 (7)	−0.0035 (6)
C4	0.0229 (13)	0.0237 (13)	0.0206 (12)	−0.0032 (10)	−0.0028 (10)	−0.0021 (10)
C5	0.0226 (13)	0.0300 (14)	0.0190 (12)	0.0002 (11)	−0.0033 (10)	−0.0040 (10)
C6	0.0240 (13)	0.0258 (13)	0.0202 (12)	0.0028 (10)	−0.0089 (10)	−0.0073 (10)
C7	0.0228 (13)	0.0188 (12)	0.0218 (12)	0.0012 (10)	−0.0101 (10)	−0.0043 (10)
C8	0.0176 (11)	0.0162 (11)	0.0198 (12)	0.0004 (9)	−0.0064 (9)	−0.0028 (9)

C9	0.0306 (14)	0.0180 (12)	0.0274 (14)	−0.0009 (10)	−0.0132 (11)	−0.0069 (10)
C10	0.0306 (14)	0.0168 (12)	0.0274 (14)	−0.0058 (10)	−0.0121 (11)	−0.0028 (10)
C11	0.0253 (13)	0.0157 (11)	0.0229 (13)	−0.0041 (10)	−0.0096 (10)	−0.0011 (10)
C12	0.0198 (12)	0.0157 (11)	0.0206 (12)	−0.0015 (9)	−0.0079 (10)	−0.0025 (9)
C13	0.0303 (14)	0.0201 (12)	0.0259 (14)	−0.0095 (11)	−0.0069 (11)	0.0022 (10)
C14	0.0276 (14)	0.0241 (13)	0.0208 (13)	−0.0079 (11)	−0.0048 (11)	0.0004 (10)
C15	0.0216 (12)	0.0181 (11)	0.0185 (12)	−0.0020 (9)	−0.0061 (10)	−0.0010 (9)
C16	0.0218 (12)	0.0187 (12)	0.0183 (12)	−0.0013 (10)	−0.0055 (10)	−0.0013 (9)
C17	0.0268 (13)	0.0226 (12)	0.0181 (12)	−0.0049 (10)	−0.0076 (10)	−0.0015 (10)
C18	0.0274 (14)	0.0260 (13)	0.0222 (13)	−0.0022 (11)	−0.0108 (11)	−0.0003 (10)
C19	0.0226 (13)	0.0208 (12)	0.0209 (12)	−0.0024 (10)	−0.0035 (10)	0.0012 (10)
C20	0.0185 (12)	0.0210 (12)	0.0179 (12)	−0.0040 (9)	−0.0012 (9)	−0.0018 (9)
C21	0.0183 (12)	0.0227 (12)	0.0173 (11)	−0.0039 (10)	−0.0024 (9)	−0.0036 (9)
C22	0.0190 (12)	0.0230 (13)	0.0235 (13)	−0.0032 (10)	−0.0019 (10)	−0.0052 (10)
C23	0.0406 (18)	0.0377 (17)	0.0436 (19)	−0.0116 (14)	−0.0181 (15)	0.0081 (14)
C30d	0.0338 (9)	0.0217 (7)	0.0209 (7)	−0.0097 (6)	−0.0015 (7)	−0.0035 (6)

Geometric parameters (Å, º)

Br1b—Mn1	2.489 (4)	C10—C11	1.433 (4)
Mn1—Cl1e	2.365 (15)	C11—C12	1.411 (4)
Mn1—Cl3d	2.285 (7)	C11—C13	1.402 (4)
Mn1—N1	2.054 (3)	C13—C14	1.370 (4)
Mn1—N2	2.117 (2)	C14—C15	1.408 (4)
Mn1—C1c	1.846 (7)	C15—C16	1.501 (4)
Mn1—C2	1.807 (3)	C17—C18	1.384 (4)
Mn1—C3	1.811 (3)	C18—C19	1.383 (4)
Mn1—C30d	2.03 (3)	C19—C20	1.392 (4)
Cl3d—O1c	0.699 (8)	C20—C21	1.382 (4)
O1c—C1c	1.113 (8)	C20—C22	1.513 (4)
O2—C2	1.140 (4)	O5—H19	0.840
O3—C3	1.146 (4)	N4—H1	0.880
O4—C22	1.228 (4)	N4—H2	0.880
O5—C23	1.399 (6)	C4—H3	0.950
O30d—C30d	0.91 (3)	C5—H4	0.950
N1—C4	1.332 (4)	C6—H5	0.950
N1—C8	1.360 (4)	C9—H6	0.950
N2—C12	1.370 (4)	C10—H7	0.950
N2—C15	1.338 (3)	C13—H8	0.950
N3—C16	1.503 (3)	C14—H9	0.950
N3—C17	1.343 (4)	C16—H10	0.990
N3—C21	1.346 (4)	C16—H11	0.990
N4—C22	1.335 (4)	C17—H12	0.950
C4—C5	1.401 (4)	C18—H13	0.950
C5—C6	1.372 (4)	C19—H14	0.950
C6—C7	1.409 (4)	C21—H15	0.950
C7—C8	1.409 (4)	C23—H16	0.980
C7—C9	1.433 (4)	C23—H17	0.980

C8—C12	1.430 (4)	C23—H18	0.980
C9—C10	1.352 (4)		
Br1b···C17	3.328 (4)	O1c···H4^{iv}	2.8763
Mn1···C16	3.508 (3)	O1c···H5^{iv}	2.8998
Cl1e···C8	3.578 (12)	O1c···H12^{v}	2.4627
Cl1e···C17	3.378 (11)	O1c···H13^{v}	3.1062
O1c···C2	3.412 (5)	O1c···H19^{iii}	3.0213
O1c···C3	3.447 (5)	O2···H6^{vii}	2.9319
O2···C1c	3.420 (5)	O2···H16^{v}	3.4596
O2···C3	3.290 (4)	O2···H17^{v}	2.8145
O2···C4	3.570 (4)	O2···H18^{v}	3.2633
O2···C30d	3.52 (3)	O3···H7^{vii}	3.0598
O3···N3	3.063 (3)	O3···H8^{vii}	3.0929
O3···C1c	3.496 (5)	O3···H13^{v}	3.2199
O3···C2	3.227 (3)	O3···H16^{v}	2.7709
O3···C16	3.422 (4)	O4···H10^{ii}	2.3939
O3···C20	3.492 (3)	O4···H11^{ii}	3.1595
O3···C21	2.990 (3)	O4···H13^{viii}	3.1904
O3···C30d	3.52 (3)	O4···H15^{ii}	2.3286
O4···C21	2.702 (4)	O5···H4^{x}	2.4901
O30d···N1	3.568 (13)	O5···H7^{vii}	3.0641
O30d···C2	3.423 (16)	O5···H8^{vii}	2.7287
O30d···C3	3.292 (16)	O5···H13	3.3285
O30d···C17	3.384 (12)	O5···H14	2.8980
N1···C6	2.801 (4)	O30d···H5^{xi}	2.8691
N2···N3	3.256 (3)	O30d···H6^{xi}	2.8960
N2···C13	2.823 (4)	O30d···H7^{vii}	2.8209
N2···C17	3.336 (3)	O30d···H17	3.1266
N3···C3	3.012 (4)	N1···H4^{iv}	3.4254
N3···C14	3.361 (4)	N1···H6^{xi}	3.5858
N3···C19	2.744 (4)	N1···H18^{iii}	3.5819
N4···C19	2.948 (4)	N3···H2^{viii}	3.4669
C2···C4	3.042 (4)	N4···H1^{i}	3.5748
C3···C15	3.509 (4)	N4···H8^{vii}	3.3172
C3···C16	3.051 (4)	N4···H9^{vii}	2.7806
C3···C17	3.439 (4)	N4···H12^{viii}	3.5726
C3···C21	3.414 (4)	C1c···H4^{iv}	3.1097
C4···C7	2.750 (4)	C1c···H5^{iv}	3.2305
C4···C12	3.595 (4)	C1c···H12^{v}	3.3991
C4···C30d	3.525 (18)	C1c···H13^{v}	3.3559
C5···C8	2.730 (4)	C1c···H19^{iii}	3.4121
C7···C11	2.825 (4)	C2···H6^{vii}	3.3623
C8···C10	2.814 (4)	C2···H7^{vii}	3.5759
C8···C30d	3.421 (19)	C2···H17^{v}	3.3903
C9···C12	2.828 (4)	C3···H7^{vii}	3.2235
C11···C15	2.754 (4)	C3···H13^{v}	3.4225
C12···C14	2.719 (4)	C3···H16^{v}	3.3464

C12···C30d	3.49 (2)	C4···H4^{iv}	3.5245
C14···C17	3.500 (4)	C4···H6^{xi}	3.3882
C15···C17	2.824 (4)	C4···H18^{x}	3.4677
C17···C20	2.751 (4)	C5···H3^{iv}	3.5488
C17···C30d	3.475 (19)	C5···H18^{x}	3.2944
C18···C21	2.733 (5)	C6···H3^{iv}	3.4069
Br2a···O5^{i}	3.276 (3)	C7···H18^{iii}	2.9645
Br2a···N4	3.478 (4)	C8···H5^{xi}	3.4524
Br2a···N4^{i}	3.326 (4)	C8···H18^{iii}	2.8771
Br2a···C15^{ii}	3.452 (4)	C9···H18^{iii}	3.1731
Br2a···C16^{ii}	3.464 (3)	C10···H4^{xi}	3.3326
Cl2b···O5^{i}	3.218 (4)	C10···H18^{iii}	3.2910
Cl2b···N4	3.279 (6)	C11···H4^{xi}	3.5345
Cl2b···N4^{i}	3.238 (6)	C11···H16^{iii}	3.4264
Cl2b···C15^{ii}	3.535 (6)	C11···H18^{iii}	3.2024
Cl2b···C16^{ii}	3.493 (6)	C12···H5^{xi}	3.5607
Cl3d···O5^{iii}	3.463 (6)	C12···H18^{iii}	2.9951
Cl3d···C5^{iv}	3.567 (6)	C13···H19^{xii}	3.2971
O1c···O5^{iii}	3.366 (4)	C14···H2^{xii}	3.5494
O1c···C5^{iv}	3.513 (4)	C17···H1^{viii}	3.4103
O1c···C6^{iv}	3.525 (4)	C17···H2^{viii}	3.5459
O1c···C17^{v}	3.223 (5)	C18···H16	3.1787
O1c···C18^{v}	3.537 (5)	C18···H17	3.3003
O2···O2^{vi}	2.961 (3)	C19···H8^{vii}	3.0075
O2···C9^{vii}	3.271 (4)	C19···H16	3.4117
O2···C23^{v}	3.353 (5)	C19···H19	3.3354
O3···O4^{ii}	3.079 (3)	C20···H8^{vii}	3.0797
O3···C10^{vii}	3.459 (4)	C20···H14^{viii}	3.4206
O3···C13^{vii}	3.473 (3)	C21···H14^{viii}	3.3546
O4···O3^{ii}	3.079 (3)	C21···H15^{ii}	3.5967
O4···N3^{ii}	3.540 (4)	C22···H8^{vii}	3.3205
O4···C3^{ii}	3.463 (4)	C22···H9^{vii}	3.3249
O4···C16^{ii}	3.120 (4)	C22···H10^{ii}	3.3594
O4···C18^{viii}	3.374 (4)	C22···H13^{viii}	3.4392
O4···C21^{ii}	3.075 (4)	C22···H15^{ii}	3.3182
O5···Br2a^{i}	3.276 (3)	C23···H3^{x}	3.3217
O5···Cl2b^{i}	3.218 (4)	C23···H4^{x}	2.9310
O5···Cl3d^{ix}	3.463 (6)	C23···H13	2.9204
O5···O1c^{ix}	3.366 (4)	C23···H14	3.3662
O5···C5^{x}	3.370 (4)	C30d···H5^{xi}	3.1093
O5···C10^{vii}	3.441 (4)	C30d···H6^{xi}	3.0245
O5···C11^{vii}	3.491 (4)	C30d···H7^{vii}	3.0143
O5···C13^{vii}	3.162 (5)	H1···Br2a	2.6768
O5···C18	3.583 (4)	H1···Cl2b	2.4605
O5···C19	3.360 (4)	H1···Cl2b^{i}	3.5747
N3···O4^{ii}	3.540 (4)	H1···O1c^{ii}	3.5958
N4···Br2a	3.478 (4)	H1···N4^{i}	3.5748
N4···Br2a^{i}	3.326 (4)	H1···C17^{viii}	3.4103

N4···Cl2b	3.279 (6)	H1···H1^{i}	3.3390
N4···Cl2b^{i}	3.238 (6)	H1···H2^{i}	3.1598
N4···C14^{vii}	3.564 (4)	H1···H9^{vii}	2.7846
N4···C17^{viii}	3.370 (4)	H1···H9^{viii}	3.3154
N4···C18^{viii}	3.541 (4)	H1···H10^{ii}	3.2747
C3···O4^{ii}	3.463 (4)	H1···H12^{viii}	3.3723
C4···C5^{iv}	3.396 (4)	H2···Br2a^{i}	2.4764
C4···C9^{xi}	3.493 (5)	H2···Cl2b^{i}	2.3966
C5···Cl3d^{iv}	3.567 (6)	H2···N3^{viii}	3.4669
C5···O1c^{iv}	3.513 (4)	H2···C14^{vii}	3.5494
C5···O5^{x}	3.370 (4)	H2···C17^{viii}	3.5459
C5···C4^{iv}	3.396 (4)	H2···H1^{i}	3.1598
C5···C9^{xi}	3.423 (4)	H2···H8^{vii}	3.0982
C5···C10^{xi}	3.458 (4)	H2···H9^{vii}	2.8713
C6···O1c^{iv}	3.525 (4)	H2···H9^{viii}	3.4147
C6···C7^{xi}	3.484 (4)	H2···H11^{viii}	3.5835
C6···C8^{xi}	3.533 (4)	H2···H19	3.4677
C7···C6^{xi}	3.484 (4)	H3···C5^{iv}	3.5488
C7···C7^{xi}	3.525 (4)	H3···C6^{iv}	3.4069
C8···C6^{xi}	3.533 (4)	H3···C23^{x}	3.3217
C9···O2^{xii}	3.271 (4)	H3···H5^{iv}	3.5554
C9···C4^{xi}	3.493 (5)	H3···H6^{xi}	3.5399
C9···C5^{xi}	3.423 (4)	H3···H17^{x}	2.9846
C10···O3^{xii}	3.459 (4)	H3···H18^{x}	2.9324
C10···O5^{xii}	3.441 (4)	H4···Cl3d^{iv}	2.9236
C10···C5^{xi}	3.458 (4)	H4···O1c^{iv}	2.8763
C11···O5^{xii}	3.491 (4)	H4···O5^{x}	2.4901
C13···O3^{xii}	3.473 (3)	H4···N1^{iv}	3.4254
C13···O5^{xii}	3.162 (5)	H4···C1c^{iv}	3.1097
C14···N4^{xii}	3.564 (4)	H4···C4^{iv}	3.5245
C15···Br2a^{ii}	3.452 (4)	H4···C10^{xi}	3.3326
C15···Cl2b^{ii}	3.535 (6)	H4···C11^{xi}	3.5345
C16···Br2a^{ii}	3.464 (3)	H4···C23^{x}	2.9310
C16···Cl2b^{ii}	3.493 (6)	H4···H7^{xi}	3.4793
C16···O4^{ii}	3.120 (4)	H4···H17^{x}	3.1945
C17···O1c^{xiii}	3.223 (5)	H4···H18^{x}	2.6041
C17···N4^{viii}	3.370 (4)	H4···H19^{x}	2.9179
C18···O1c^{xiii}	3.537 (5)	H5···Br1b^{xi}	2.9032
C18···O4^{viii}	3.374 (4)	H5···Cl1e^{xi}	2.9010
C18···O5	3.583 (4)	H5···Cl3d^{iv}	3.1256
C18···N4^{viii}	3.541 (4)	H5···O1c^{iv}	2.8998
C18···C22^{viii}	3.276 (4)	H5···O30d^{xi}	2.8691
C18···C23	3.520 (5)	H5···C1c^{iv}	3.2305
C19···O5	3.360 (4)	H5···C8^{xi}	3.4524
C19···C20^{viii}	3.305 (4)	H5···C12^{xi}	3.5607
C19···C22^{viii}	3.433 (4)	H5···C30d^{xi}	3.1093
C20···C19^{viii}	3.305 (4)	H5···H3^{iv}	3.5554
C20···C20^{viii}	3.441 (4)	H6···Br1b^{xi}	2.9532

C21···O4^{ii}	3.075 (4)	H6···Cl1e^{xi}	2.9268
C22···C18^{viii}	3.276 (4)	H6···O2^{xii}	2.9319
C22···C19^{viii}	3.433 (4)	H6···O30d^{xi}	2.8960
C23···O2^{xiii}	3.353 (5)	H6···N1^{xi}	3.5858
C23···C18	3.520 (5)	H6···C2^{xii}	3.3623
Br1b···H12	3.0025	H6···C4^{xi}	3.3882
Mn1···H3	3.1408	H6···C30d^{xi}	3.0245
Mn1···H10	3.1062	H6···H3^{xi}	3.5399
Cl1e···H12	3.0389	H7···Br1b^{xii}	2.9393
Cl3d···H10	3.1769	H7···Cl1e^{xii}	3.0081
O1c···H10	3.5624	H7···O3^{xii}	3.0598
O2···H3	2.8354	H7···O5^{xii}	3.0641
O3···H10	2.8542	H7···O30d^{xii}	2.8209
O3···H15	3.1437	H7···C2^{xii}	3.5759
O4···H1	2.4684	H7···C3^{xii}	3.2235
O4···H2	3.0347	H7···C30d^{xii}	3.0143
O4···H15	2.3527	H7···H4^{xi}	3.4793
O30d···H12	3.0829	H7···H17^{xii}	3.2739
O30d···H13	3.5235	H8···O3^{xii}	3.0929
N1···H4	3.2469	H8···O5^{xii}	2.7287
N2···H9	3.2548	H8···N4^{xii}	3.3172
N2···H10	2.5845	H8···C19^{xii}	3.0075
N2···H11	3.2203	H8···C20^{xii}	3.0797
N2···H12	2.8282	H8···C22^{xii}	3.3205
N3···H9	3.3914	H8···H2^{xii}	3.0982
N3···H13	3.2172	H8···H14^{xii}	2.9863
N4···H14	2.6912	H8···H19^{xii}	2.8784
C1c···H10	3.0870	H9···Br2a^{xii}	3.2000
C2···H3	2.5668	H9···Cl2b^{xii}	3.1874
C3···H10	2.4909	H9···N4^{xii}	2.7806
C4···H5	3.2584	H9···C22^{xii}	3.3249
C6···H3	3.2427	H9···H1^{xii}	2.7846
C6···H6	2.6997	H9···H1^{viii}	3.3154
C7···H4	3.2643	H9···H2^{xii}	2.8713
C7···H7	3.2789	H9···H2^{viii}	3.4147
C8···H3	3.1640	H10···Br2a^{ii}	3.2602
C8···H5	3.2753	H10···Cl2b^{ii}	3.2155
C8···H6	3.3067	H10···O4^{ii}	2.3939
C9···H5	2.7033	H10···C22^{ii}	3.3594
C10···H8	2.6885	H10···H1^{ii}	3.2747
C11···H6	3.2820	H11···Br2a^{xii}	2.7844
C11···H9	3.2502	H11···Br2a^{ii}	3.1272
C12···H7	3.3110	H11···Cl2b^{xii}	2.9562
C12···H8	3.2745	H11···Cl2b^{ii}	3.1918
C13···H7	2.6820	H11···O4^{ii}	3.1595
C14···H10	3.2221	H11···H2^{viii}	3.5835
C14···H11	2.5282	H11···H11^{xiv}	3.5606
C14···H12	2.9878	H12···Cl3d^{xiii}	3.0874

C15···H8	3.2700	H12···O1c^{xiii}	2.4627
C15···H12	2.4487	H12···N4^{viii}	3.5726
C16···H9	2.6158	H12···C1c^{xiii}	3.3991
C16···H12	2.6637	H12···H1^{viii}	3.3723
C16···H15	2.5356	H13···Cl3d^{xiii}	3.3265
C17···H10	3.1293	H13···O1c^{xiii}	3.1062
C17···H11	3.1153	H13···O3^{xiii}	3.2199
C17···H14	3.2541	H13···O4^{viii}	3.1904
C17···H15	3.1945	H13···O5	3.3285
C19···H2	2.6032	H13···C1c^{xiii}	3.3559
C19···H12	3.2517	H13···C3^{xiii}	3.4225
C19···H15	3.2470	H13···C22^{viii}	3.4392
C20···H1	3.2488	H13···C23	2.9204
C20···H2	2.5439	H13···H16	2.4806
C20···H13	3.2541	H13···H17	2.6833
C21···H10	2.6383	H13···H19	3.5907
C21···H11	2.6614	H14···Br2a^{i}	2.7246
C21···H12	3.1977	H14···Cl2b^{i}	2.7695
C21···H14	3.2504	H14···O5	2.8980
C22···H14	2.7865	H14···C20^{viii}	3.4206
C22···H15	2.5574	H14···C21^{viii}	3.3546
C30d···H12	3.1595	H14···C23	3.3662
H1···H14	3.5302	H14···H8^{vii}	2.9863
H2···H14	2.0979	H14···H15^{viii}	3.4238
H3···H4	2.3341	H14···H16	2.9568
H4···H5	2.3311	H14···H19	2.6711
H5···H6	2.5565	H15···O4^{ii}	2.3286
H6···H7	2.2889	H15···C21^{ii}	3.5967
H7···H8	2.5350	H15···C22^{ii}	3.3182
H8···H9	2.3269	H15···H14^{viii}	3.4238
H9···H10	3.4588	H15···H15^{ii}	2.8357
H9···H11	2.3297	H16···Br2a^{i}	3.5121
H9···H12	3.2974	H16···O2^{xiii}	3.4596
H10···H12	3.3559	H16···O3^{xiii}	2.7709
H10···H15	2.5364	H16···C3^{xiii}	3.3464
H11···H12	3.3215	H16···C11^{ix}	3.4264
H11···H15	2.5539	H16···C18	3.1787
H12···H13	2.3344	H16···C19	3.4117
H13···H14	2.3391	H16···H13	2.4806
H16···H19	2.0894	H16···H14	2.9568
H17···H19	2.6208	H17···Br1b	3.5386
H18···H19	2.2963	H17···O2^{xiii}	2.8145
Br1b···H5^{xi}	2.9032	H17···O30d	3.1266
Br1b···H6^{xi}	2.9532	H17···C2^{xiii}	3.3903
Br1b···H7^{vii}	2.9393	H17···C18	3.3003
Br1b···H17	3.5386	H17···H3^{x}	2.9846
Br2a···H1	2.6768	H17···H4^{x}	3.1945
Br2a···H2^{i}	2.4764	H17···H7^{vii}	3.2739

Br2a···H9^{vii}	3.2000	H17···H13	2.6833
Br2a···H10^{ii}	3.2602	H18···O2^{xiii}	3.2633
Br2a···H11^{vii}	2.7844	H18···N1^{ix}	3.5819
Br2a···H11^{ii}	3.1272	H18···C4^{x}	3.4677
Br2a···H14^{i}	2.7246	H18···C5^{x}	3.2944
Br2a···H16^{i}	3.5121	H18···C7^{ix}	2.9645
Br2a···H19^{i}	2.4721	H18···C8^{ix}	2.8771
Cl1e···H5^{xi}	2.9010	H18···C9^{ix}	3.1731
Cl1e···H6^{xi}	2.9268	H18···C10^{ix}	3.2910
Cl1e···H7^{vii}	3.0081	H18···C11^{ix}	3.2024
Cl2b···H1	2.4605	H18···C12^{ix}	2.9951
Cl2b···H1^{i}	3.5747	H18···H3^{x}	2.9324
Cl2b···H2^{i}	2.3966	H18···H4^{x}	2.6041
Cl2b···H9^{vii}	3.1874	H19···Br2a^{i}	2.4721
Cl2b···H10^{ii}	3.2155	H19···Cl2b^{i}	2.4058
Cl2b···H11^{vii}	2.9562	H19···Cl3d^{ix}	3.0845
Cl2b···H11^{ii}	3.1918	H19···O1c^{ix}	3.0213
Cl2b···H14^{i}	2.7695	H19···C1c^{ix}	3.4121
Cl2b···H19^{i}	2.4058	H19···C13^{vii}	3.2971
Cl3d···H4^{iv}	2.9236	H19···C19	3.3354
Cl3d···H5^{iv}	3.1256	H19···H2	3.4677
Cl3d···H12^{v}	3.0874	H19···H4^{x}	2.9179
Cl3d···H13^{v}	3.3265	H19···H8^{vii}	2.8784
Cl3d···H19^{iii}	3.0845	H19···H13	3.5907
O1c···H1^{ii}	3.5958	H19···H14	2.6711

Br1b—Mn1—Cl1e	1.9 (3)	C10—C11—C12	119.6 (3)
Br1b—Mn1—Cl3d	176.22 (13)	C10—C11—C13	122.8 (3)
Br1b—Mn1—N1	88.09 (9)	C12—C11—C13	117.6 (3)
Br1b—Mn1—N2	88.39 (9)	N2—C12—C8	117.2 (3)
Br1b—Mn1—C1c	176.27 (15)	N2—C12—C11	123.7 (3)
Br1b—Mn1—C2	90.72 (11)	C8—C12—C11	119.1 (3)
Br1b—Mn1—C3	86.27 (12)	C11—C13—C14	118.9 (3)
Br1b—Mn1—C30d	4.2 (6)	C13—C14—C15	120.1 (3)
Cl1e—Mn1—Cl3d	177.5 (3)	N2—C15—C14	122.9 (3)
Cl1e—Mn1—N1	86.2 (3)	N2—C15—C16	120.0 (3)
Cl1e—Mn1—N2	88.3 (4)	C14—C15—C16	117.0 (2)
Cl1e—Mn1—C1c	178.0 (4)	N3—C16—C15	113.0 (3)
Cl1e—Mn1—C2	90.5 (3)	N3—C17—C18	120.0 (3)
Cl1e—Mn1—C3	88.1 (3)	C17—C18—C19	119.9 (3)
Cl1e—Mn1—C30d	3.3 (7)	C18—C19—C20	119.2 (3)
Cl3d—Mn1—N1	94.57 (14)	C19—C20—C21	118.8 (3)
Cl3d—Mn1—N2	89.46 (15)	C19—C20—C22	125.8 (3)
Cl3d—Mn1—C1c	3.5 (2)	C21—C20—C22	115.4 (3)
Cl3d—Mn1—C2	91.83 (16)	N3—C21—C20	120.8 (3)
Cl3d—Mn1—C3	91.20 (16)	O4—C22—N4	123.6 (3)
Cl3d—Mn1—C30d	179.1 (6)	O4—C22—C20	118.7 (3)
N1—Mn1—N2	79.58 (9)	N4—C22—C20	117.7 (3)

N1—Mn1—C1c	95.58 (15)	Mn1—C30d—O30d	165 (2)
N1—Mn1—C2	92.57 (11)	C23—O5—H19	109.468
N1—Mn1—C3	173.59 (11)	C22—N4—H1	120.002
N1—Mn1—C30d	85.7 (6)	C22—N4—H2	119.996
N2—Mn1—C1c	92.89 (16)	H1—N4—H2	120.002
N2—Mn1—C2	172.13 (11)	N1—C4—H3	118.518
N2—Mn1—C3	103.30 (10)	C5—C4—H3	118.509
N2—Mn1—C30d	91.4 (6)	C4—C5—H4	120.287
C1c—Mn1—C2	88.49 (18)	C6—C5—H4	120.290
C1c—Mn1—C3	90.03 (17)	C5—C6—H5	120.347
C1c—Mn1—C30d	175.7 (6)	C7—C6—H5	120.350
C2—Mn1—C3	84.44 (12)	C7—C9—H6	119.614
C2—Mn1—C30d	87.4 (6)	C10—C9—H6	119.610
C3—Mn1—C30d	88.4 (6)	C9—C10—H7	119.472
Mn1—Cl3d—O1c	162.1 (6)	C11—C10—H7	119.465
Cl3d—O1c—C1c	12.5 (5)	C11—C13—H8	120.538
Mn1—N1—C4	127.60 (19)	C14—C13—H8	120.552
Mn1—N1—C8	114.51 (16)	C13—C14—H9	119.946
C4—N1—C8	117.8 (3)	C15—C14—H9	119.946
Mn1—N2—C12	111.76 (15)	N3—C16—H10	108.976
Mn1—N2—C15	131.55 (18)	N3—C16—H11	108.972
C12—N2—C15	116.7 (2)	C15—C16—H10	108.971
C16—N3—C17	122.5 (3)	C15—C16—H11	108.966
C16—N3—C21	116.3 (3)	H10—C16—H11	107.774
C17—N3—C21	121.2 (2)	N3—C17—H12	119.984
Mn1—C1c—O1c	177.6 (4)	C18—C17—H12	119.985
Mn1—C2—O2	177.9 (3)	C17—C18—H13	120.074
Mn1—C3—O3	172.5 (3)	C19—C18—H13	120.073
N1—C4—C5	123.0 (3)	C18—C19—H14	120.380
C4—C5—C6	119.4 (3)	C20—C19—H14	120.381
C5—C6—C7	119.3 (3)	N3—C21—H15	119.573
C6—C7—C8	117.4 (3)	C20—C21—H15	119.578
C6—C7—C9	123.3 (3)	O5—C23—H16	109.472
C8—C7—C9	119.3 (3)	O5—C23—H17	109.465
N1—C8—C7	123.0 (3)	O5—C23—H18	109.465
N1—C8—C12	116.8 (3)	H16—C23—H17	109.478
C7—C8—C12	120.2 (3)	H16—C23—H18	109.473
C7—C9—C10	120.8 (3)	H17—C23—H18	109.474
C9—C10—C11	121.1 (3)		

Br1b—Mn1—N1—C4	91.10 (18)	C17—N3—C16—C15	1.4 (3)
Br1b—Mn1—N1—C8	−86.13 (15)	C16—N3—C21—C20	177.54 (18)
Br1b—Mn1—N2—C12	84.85 (13)	C21—N3—C16—C15	−178.19 (18)
Br1b—Mn1—N2—C15	−93.67 (18)	C17—N3—C21—C20	−2.0 (4)
Cl1e—Mn1—N1—C4	90.8 (4)	C21—N3—C17—C18	1.2 (4)
Cl1e—Mn1—N1—C8	−86.4 (4)	N1—C4—C5—C6	−0.2 (4)
Cl1e—Mn1—N2—C12	83.0 (3)	C4—C5—C6—C7	1.1 (4)
Cl1e—Mn1—N2—C15	−95.5 (3)	C5—C6—C7—C8	−0.7 (4)

Cl3d—Mn1—N1—C4	−91.6 (2)	C5—C6—C7—C9	177.9 (3)
Cl3d—Mn1—N1—C8	91.19 (19)	C6—C7—C8—N1	−0.5 (4)
Cl3d—Mn1—N2—C12	−98.25 (17)	C6—C7—C8—C12	179.6 (2)
Cl3d—Mn1—N2—C15	83.2 (2)	C6—C7—C9—C10	−178.2 (3)
N1—Mn1—N2—C12	−3.51 (13)	C8—C7—C9—C10	0.3 (4)
N1—Mn1—N2—C15	177.97 (19)	C9—C7—C8—N1	−179.2 (3)
N2—Mn1—N1—C4	179.82 (19)	C9—C7—C8—C12	1.0 (4)
N2—Mn1—N1—C8	2.59 (14)	N1—C8—C12—N2	−1.9 (4)
C1c—Mn1—N1—C4	−88.3 (3)	N1—C8—C12—C11	178.8 (2)
C1c—Mn1—N1—C8	94.5 (2)	C7—C8—C12—N2	177.9 (2)
C2—Mn1—N1—C4	0.5 (2)	C7—C8—C12—C11	−1.3 (4)
C2—Mn1—N1—C8	−176.77 (16)	C7—C9—C10—C11	−1.3 (5)
C30d—Mn1—N1—C4	87.6 (6)	C9—C10—C11—C12	0.9 (4)
C30d—Mn1—N1—C8	−89.6 (6)	C9—C10—C11—C13	−178.4 (3)
C1c—Mn1—N2—C12	−98.65 (18)	C10—C11—C12—N2	−178.8 (3)
C1c—Mn1—N2—C15	82.8 (3)	C10—C11—C12—C8	0.4 (4)
C3—Mn1—N2—C12	170.64 (15)	C10—C11—C13—C14	177.2 (3)
C3—Mn1—N2—C15	−7.9 (2)	C12—C11—C13—C14	−2.1 (4)
C30d—Mn1—N2—C12	81.9 (6)	C13—C11—C12—N2	0.5 (4)
C30d—Mn1—N2—C15	−96.6 (6)	C13—C11—C12—C8	179.7 (3)
Mn1—N1—C4—C5	−178.11 (15)	C11—C13—C14—C15	1.2 (4)
Mn1—N1—C8—C7	178.88 (15)	C13—C14—C15—N2	1.4 (4)
Mn1—N1—C8—C12	−1.3 (3)	C13—C14—C15—C16	−177.3 (3)
C4—N1—C8—C7	1.4 (4)	N2—C15—C16—N3	85.2 (3)
C4—N1—C8—C12	−178.8 (2)	C14—C15—C16—N3	−96.0 (3)
C8—N1—C4—C5	−1.0 (4)	N3—C17—C18—C19	0.4 (4)
Mn1—N2—C12—C8	4.0 (3)	C17—C18—C19—C20	−1.2 (4)
Mn1—N2—C12—C11	−176.83 (16)	C18—C19—C20—C21	0.4 (4)
Mn1—N2—C15—C14	175.56 (14)	C18—C19—C20—C22	−179.5 (2)
Mn1—N2—C15—C16	−5.7 (4)	C19—C20—C21—N3	1.2 (4)
C12—N2—C15—C14	−2.9 (4)	C19—C20—C22—O4	175.4 (3)
C12—N2—C15—C16	175.8 (2)	C19—C20—C22—N4	−4.1 (4)
C15—N2—C12—C8	−177.3 (2)	C21—C20—C22—O4	−4.5 (4)
C15—N2—C12—C11	1.9 (4)	C21—C20—C22—N4	176.0 (2)
C16—N3—C17—C18	−178.30 (19)	C22—C20—C21—N3	−178.89 (19)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H1···Br2*a*	0.88	2.68	3.478 (3)	152
N4—H1···Cl2*b*	0.88	2.46	3.279 (6)	155
N4—H2···Br2*a*^{i}	0.88	2.48	3.326 (3)	162
N4—H2···Cl2*b*^{i}	0.88	2.40	3.239 (6)	160
O5—H19···Br2*a*^{i}	0.84	2.47	3.276 (3)	161
O5—H19···Cl2*b*^{i}	0.84	2.41	3.218 (5)	163
C5—H4···O5^{x}	0.95	2.49	3.370 (4)	154

C6—H5···Br1*b*^{xi}	0.95	2.90	3.735 (4)	147
C16—H10···O4^{ii}	0.99	2.39	3.120 (4)	130
C16—H11···Br2*a*^{xii}	0.99	2.78	3.678 (3)	150
C17—H12···O1*c*^{xiii}	0.95	2.46	3.224 (5)	137
C19—H14···Br2*a*^{i}	0.95	2.72	3.667 (3)	172
C19—H14···Cl2*b*^{i}	0.95	2.77	3.702 (6)	167
C21—H15···O4	0.95	2.35	2.702 (4)	101
C21—H15···O4^{ii}	0.95	2.33	3.074 (4)	135

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) −*x*+2, −*y*+1, −*z*+2; (x) −*x*+2, −*y*+1, −*z*+1; (xi) −*x*+2, −*y*, −*z*+1; (xii) *x*, *y*−1, *z*; (xiii) *x*−1, *y*, *z*.