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Selective synthesis and crystal structures of manganese(I) complexes with a bi- or tridentate terpyridine ligand

Kosei Wadayama,[a] Tsugiko Takase[b] and Dai Oyama[b]*

[a]Graduate School of Science and Engineering, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan, and [b]Department of Natural Sciences and Informatics, Fukushima University, 1, Kanayagawa, Fukushima 960-1296, Japan. *Correspondence e-mail: daio@sss.fukushima-u.ac.jp

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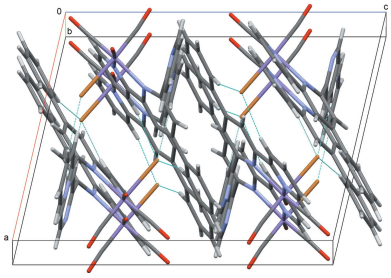
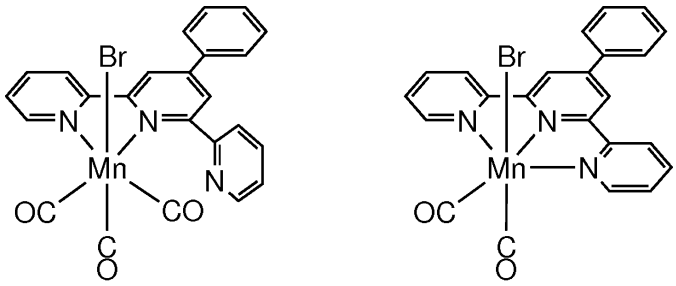
The crystal structures of two manganese(I) complexes with a different coordination mode of the supporting ligand are reported: *fac*-bromidotricarbonyl(4′-phenyl-2,2′:6′,2″-terpyridine-κ^2N,N')manganese(I), [MnBr($C_{21}H_{15}N_3$)(CO)$_3$], **I**, and *cis*-bromidodicarbonyl(4′-phenyl-2,2′:6′,2″-terpyridine-κ^3N,N',N'')manganese(I), [MnBr($C_{21}H_{15}N_3$)(CO)$_2$], **II**. In both complexes, the manganese(I) atom is coordinated by terminal carbonyl ligands, a bromide ion, and a 4′-phenyl-2,2′:6′,2″-terpyridine ligand within a distorted octahedral environment. In **I**, the metal ion is facially coordinated by three carbonyl ligands and the terpyridine ligand binds in a bidentate fashion. The non-coordinating nitrogen atom in the terpyridine ligand is positioned on the side opposite to the bromido ligand. In **II**, the metal ion is coordinated by two carbonyl ligands in a *cis* configuration and the terpyridine ligand binds in a tridentate fashion; notably, one carbonyl and the *trans* bromido ligand are mutually disordered over two positions. In **I**, the complex molecules are linked by C—H···Br hydrogen bonds. In **II**, aromatic π–π contacts are present, as well as pairs of C—H···Br and C—H···O hydrogen bonds.

1. Chemical context

Carbonylmanganese(I) complexes with polypyridyl ligands are of particular interest as novel active molecules that are able to release CO in response to photoirradiation (Carrington *et al.*, 2013; Chakraborty *et al.*, 2014; Jimenez *et al.*, 2015) or as electrocatalysts of CO_2 reduction (Grills *et al.*, 2018; Stanbury *et al.*, 2017). Among these compounds, studies have concentrated mainly on tricarbonyl complexes comprising bidentate polypyridyl supporting ligands; by contrast, only few reports exist on dicarbonyl complexes bearing tridentate ligands (Compain *et al.*, 2015; Machan & Kubiak, 2016). In fact, even though the typically tridentate ligands 2,2′:6′,2″-terpyridine and derivatives thereof coordinate to an Mn^I ion, the majority of them bind the metal ion in a bidentate manner (Compain *et al.*, 2014; Moya *et al.*, 2001).

As indicated by the results of studies focusing on the comparison between carbonylmanganese complexes containing bidentate and tridentate terpyridines (Compain *et al.*, 2015; Machan & Kubiak, 2016), investigating the relationship between reactivity and molecular structure is a key research objective. However, comparing these two systems experimentally is difficult, particularly considering that available structural data on complexes comprising tridentate terpyridine ligands are quite scarce.





I II

Herein, we report the structural characterization of complex *fac*(CO)-[Mn(tpyPh-κ^2N,N')$(CO)_3$Br] (**I**; tpyPh = 4′-phenyl-2,2′:6′,2″-terpyridine) comprising a bidentate terpyridine-based ligand, which has been synthesized by Moya *et al.* (2001), and the synthesis and characterization of the corresponding complex *cis*(CO)-[Mn(tpyPh-κ^3N,N',N'')$(CO)_2$Br] (**II**), whereby the same terpyridine-based ligand is tridentate.

2. Structural commentary

The molecular structures of compounds **I** and **II** are displayed in Figs. 1 and 2, respectively. Although **I** was prepared by Moya *et al.* (2001), its structure has not previously been determined. In **I** and **II**, the manganese(I) atoms exhibit distorted octahedral coordination environments, similar to those reported for other structurally related complexes (Compain *et al.*, 2014, 2015). In **I**, the *fac* configuration of the three CO ligands around the central manganese(I) atom is in agreement with the IR data of the complex and similar to those previously reported for complexes of this type (Compain *et al.*, 2014, 2015). As can be evinced from Fig. 1, the terpyridine ligand exhibits a bidentate coordination with respect to the central Mn^I atom, so that one of the outer pyridyl rings remains outside the coordination sphere. The corresponding non-coordinating N atom, N3, is positioned on the side opposite to the Br atom. As a result, the torsion angle between the coordinating and non-coordinating pyridyl rings in **I** (N2—C13—C14—N3) is much smaller [47.9 (3)°] than those reported for related Mn^I complexes with bidentate terpyridine derivatives (Compain *et al.*, 2014, 2015). The non-coordinating N atom is positioned in proximity of the equatorial carbonyl ligand (C2≡O2), with a short value for the interatomic distance between C2 and N3 [2.900 (4) Å]. Since this distance is considerably shorter than the sum of the two atoms' van der Waals radii (3.25 Å; Bondi, 1964), evidence suggests that an interaction exists between the free pyridine and the adjacent CO ligand. This interaction may explain the observation that the Mn1—C2 distance [1.840 (3) Å] is longer than the other two corresponding distances in **I** [Mn1—C1 = 1.805 (3) and Mn1—C3 = 1.796 (3) Å].

The crystal structures of Mn^I dicarbonyl complexes with tridentate terpyridines have very rarely been reported (Compain *et al.*, 2015), because of the instability in solution of compounds of this type. In **II**, the carbonyl ligands are in *cis* configuration, again in accordance with IR data. Differently from **I**, in **II** the Mn^I ion is coordinated by a tridentate terpyridyl ligand, as well as two CO ligands and a Br^- ion. Only the central Mn—N2 bond is slightly shortened (by ∼0.05 Å) as a result of geometric constraints. In contrast to **I**, where no disorder is observed, in **II** one of the CO ligands (C2≡O2) and the Br^- ligand are mutually disordered over two positions. The dihedral angle between the phenyl pendant and the central pyridyl ring in **II** is slightly larger than the corresponding angle in **I**. Specifically, the C10—C11—C19—C20 torsion angle has a value of −19.3 (5)° in **II** and −9.9 (4)° in **I**, but both values indicate an essential quasi-coplanarity. Notably, the extended conjugation made possible by the mentioned quasi-planarity may contribute to an increased stability of these compounds.

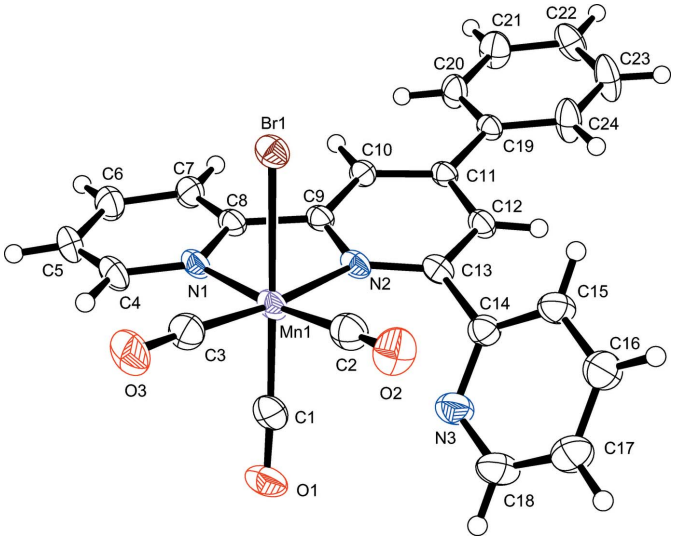


Figure 1
The molecular structure of compound **I**, with atom labeling and displacement ellipsoids drawn at the 50% probability level.

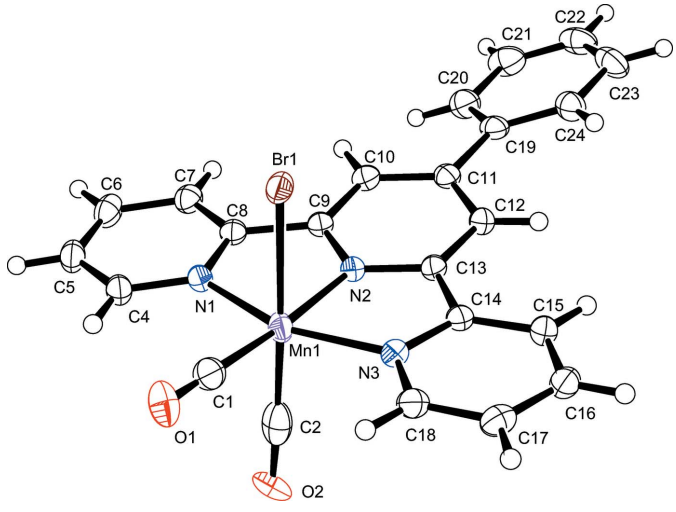


Figure 2
The molecular structure of compound **II**, with atom labeling and displacement ellipsoids drawn at the 50% probability level. Only the major components (Br1/C2≡O2) of the disordered groups are shown.

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H4···Br1^{i}	0.95	2.83	3.754 (3)	165
C16—H8···Br1^{ii}	0.95	2.88	3.612 (4)	135
C20—H11···Br1^{i}	0.95	2.92	3.844 (2)	163

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

3. Supramolecular features

In the crystal structure of **I**, complex molecules display three kinds of C—H···Br hydrogen bonds (*i.e.*, between the Br^{-} ligand and the C—H groups in the coordinating pyridyl ring, the free pyridyl ring, and the phenyl pendant), forming a three-dimensional supramolecular structure (Table 1 and Fig. 3).

In the crystal structure of **II**, weak C—H···Br and C—H···O hydrogen bonding interactions (Table 2) exist between the terpyridyl ligand and the disordered CO/Br ligands. Additional π–π interactions [$Cg3\cdots Cg2^{iv}$ = 4.000 (2) and $Cg1\cdots Cg1^{i}$ = 4.128 (3) Å; $Cg1$, $Cg2$ and $Cg3$ are the centroids of the N1/C4–C8, N2/C9–C13 and N3/C14–C18 rings, respectively; symmetry codes: (i) $1-x, -y, 2-z$; (iv) $x, -y+\frac{1}{2}, z-\frac{1}{2}$] consolidate the crystal packing. These interactions lead to the formation of a three-dimensional network structure (Fig. 4).

4. Database survey

With respect to manganese(I) complexes with a tridentate terpyridine derivative ligand of the form *cis*(CO)-[Mn(tpy*R*)(CO)$_2$Br], only a single structure, whereby *R* = *p*-tolyl, has been reported (Compain *et al.*, 2015). In contrast, some structures of bidentate terpyridine derivative-coordinated manganese(I) complexes have been reported by Compain *et al.* (2014, 2015).

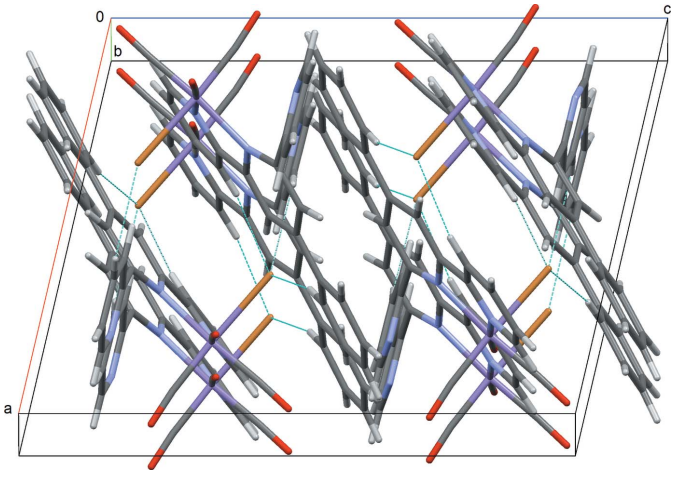


Figure 3
The crystal packing of compound **I** with C—H···Br hydrogen bonds shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H2···Br1^{i}	0.95	2.84	3.528 (4)	130
C7—H4···Br1^{ii}	0.95	2.86	3.771 (4)	162
C12—H6···Br2^{iii}	0.95	2.75	3.688 (7)	171
C12—H6···O2^{iii}	0.95	2.55	3.491 (7)	173
C15—H7···Br2^{iii}	0.95	2.81	3.759 (7)	175
C15—H7···O2^{iii}	0.95	2.50	3.447 (7)	172
C16—H8···Br2^{iv}	0.95	2.52	3.286 (7)	138
C16—H8···O2^{iv}	0.95	2.57	3.363 (7)	141
C20—H11···Br1^{ii}	0.95	2.81	3.743 (4)	168
C20—H11···O3^{ii}	0.95	2.55	3.446 (18)	158
C24—H15···Br2^{iii}	0.95	2.84	3.611 (7)	139

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

5. Synthesis and crystallization

All the manganese(I) complexes were handled and stored in the dark to minimize exposure to light. Compound **I** was synthesized as described by Moya *et al.* (2001). The compound thus obtained proved to be analytically and spectroscopically pure (as determined by microanalysis, IR, UV–vis, and ^{1}H NMR data). Crystals suitable for use in X-ray diffraction experiments were grown by vapor diffusion of diethyl ether into an acetone solution of **I**.

For the synthesis of compound **II**, bromidopentacarbonylmanganese(I) (30 mg, 0.11 mmol) and 4′-phenyl-2,2′:6′,2″-terpyridine (31 mg, 0.10 mmol) were dissolved in an acetone–water mixture (20/30 ml). The solution thus obtained was refluxed for 24 h; the solvent was then evaporated under reduced pressure, and the resulting solid was placed in diethyl ether (50 ml); the resulting mixture was stirred for 30 min to remove the starting materials and subsequently filtered; the isolated residue was washed with diethyl ether to obtain a yield for the desired complex of 43 mg (86%). Single crystals suitable for X-ray diffraction experiments were grown by slow vapor diffusion of *n*-hexane into an acetone solution of **II**. FTIR ν_{CO} (KBr pellet): 1916 (*s*), 1838 (*s*) cm^{-1}.

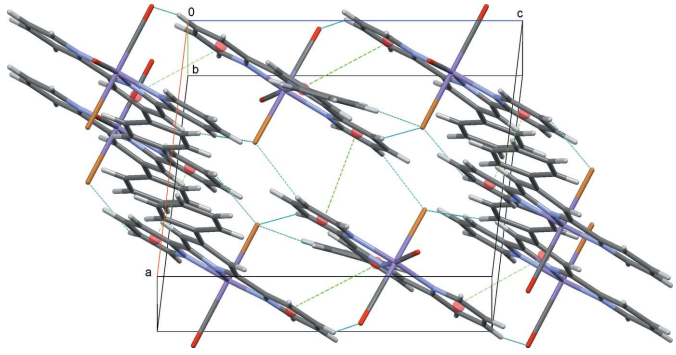


Figure 4
The crystal packing of compound **II** with C—H···Br and C—H···O hydrogen bonds (blue) and π–π contacts (green) shown as dashed lines; ring centroids are shown as red spheres.

Table 3
Experimental details.

	I	II
Crystal data		
Chemical formula	$[MnBr(C_{21}H_{15}N_3)(CO)_3]$	$[MnBr(C_{21}H_{15}N_3)(CO)_2]$
M_r	528.24	500.23
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	93	93
a, b, c (Å)	11.6630 (3), 11.6691 (3), 15.8892 (4)	10.497 (3), 14.123 (5), 13.504 (4)
β (°)	103.0774 (7)	96.767 (3)
V (Å^3)	2106.39 (10)	1988.0 (11)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.56	2.71
Crystal size (mm)	0.15 × 0.08 × 0.03	0.20 × 0.08 × 0.05
Data collection		
Diffractometer	Rigaku Saturn70	Rigaku Saturn70
Absorption correction	Multi-scan (*REQAB*, Rigaku, 1998)	Multi-scan (*REQAB*, Rigaku, 1998)
T_{min}, T_{max}	0.774, 0.926	0.795, 0.873
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	21455, 4813, 4253	19872, 4518, 4016
R_{int}	0.030	0.028
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.092, 1.06	0.046, 0.096, 1.27
No. of reflections	4813	4518
No. of parameters	289	289
No. of restraints	0	3
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.96, −0.32	0.83, −0.80

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *CrystalClear* (Rigaku, 2008), *SIR97* (Altomare *et al.*, 1999), *SHELXL2018/3* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020), *ORTEP-3 for Windows* (Farrugia, 2012), *CrystalStructure* (Rigaku, 2019), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3. All hydrogen atoms were placed at calculated positions (C—H = 0.95 Å) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(C). In compound **II**, the CO group and the Br atom *trans* to it were refined as being disordered over two sets of sites, (Br1/C2≡O2) and (Br2/C3≡O3), respectively, with an occupancy ratio of 0.807 (2): 0.193 (2).

Funding information

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Carrington, S. J., Chakraborty, I. & Mascharak, P. K. (2013). *Chem. Commun.* **49**, 11254–11256.
Chakraborty, I., Carrington, S. J. & Mascharak, P. K. (2014). *ChemMedChem*, **9**, 1266–1274.
Compain, J.-D., Bourrez, M., Haukka, M., Deronzier, A. & Chardon-Noblat, S. (2014). *Chem. Commun.* **50**, 2539–2542.
Compain, J.-D., Stanbury, M., Trejo, M. & Chardon-Noblat, S. (2015). *Eur. J. Inorg. Chem.* pp. 5757–5766.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Grills, D. C., Ertem, M. Z., McKinnon, M., Ngo, K. T. & Rochford, J. (2018). *Coord. Chem. Rev.* **374**, 173–217.
Jimenez, J., Chakraborty, I. & Mascharak, P. K. (2015). *Eur. J. Inorg. Chem.* pp. 5021–5026.
Machan, C. W. & Kubiak, C. P. (2016). *Dalton Trans.* **45**, 17179–17186.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Moya, S. A., Pastene, R., Le Bozec, H., Baricelli, P. J., Pardey, A. J. & Gimeno, J. (2001). *Inorg. Chim. Acta*, **312**, 7–14.
Rigaku (1998). *REQAB* and *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2008). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2019). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.
Stanbury, M., Compain, J.-D., Trejo, M., Smith, P., Gouré, E. & Chardon-Noblat, S. (2017). *Electrochim. Acta*, **240**, 288–299.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

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Computing details

Data collection: *PROCESS-AUTO* (Rigaku, 1998) for (I); *CrystalClear* (Rigaku, 2008) for (II). Cell refinement: *PROCESS-AUTO* (Rigaku, 1998) for (I); *CrystalClear* (Rigaku, 2008) for (II). Data reduction: *PROCESS-AUTO* (Rigaku, 1998) for (I); *CrystalClear* (Rigaku, 2008) for (II). For both structures, program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2020), *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2019), *PLATON* (Spek, 2020), *publCIF* (Westrip, 2010).

fac-Bromidotricarbonyl(4′-phenyl-2,2′:6′,2″-terpyridine-κ^2N,N')manganese(I) (I)

Crystal data

$[MnBr(C_{21}H_{15}N_3)(CO)_3]$
M_r = 528.24
Monoclinic, $P2_1/c$
a = 11.6630 (3) Å
b = 11.6691 (3) Å
c = 15.8892 (4) Å
β = 103.0774 (7)°
V = 2106.39 (10) Å^3
Z = 4
$F(000)$ = 1056.00
D_x = 1.666 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 18973 reflections
θ = 3.0–27.5°
μ = 2.56 mm^{-1}
T = 93 K
Platelet, orange
0.15 × 0.08 × 0.03 mm

Data collection

Rigaku Saturn70 diffractometer
Detector resolution: 7.143 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*, Rigaku, 1998)
T_{min} = 0.774, T_{max} = 0.926
21455 measured reflections
4813 independent reflections
4253 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.030
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −15→15
k = −15→15
l = −20→19

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 1.06
4813 reflections
289 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 2.6282P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.96$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

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}
Br1	0.61476 (2)	0.17999 (2)	0.88742 (2)	0.02812 (9)
Mn1	0.78248 (3)	0.17015 (3)	0.81054 (2)	0.02513 (10)
O1	0.99149 (17)	0.17222 (19)	0.73649 (14)	0.0400 (5)
O2	0.7925 (2)	0.42515 (18)	0.81993 (14)	0.0444 (5)
O3	0.95375 (19)	0.1798 (2)	0.97692 (14)	0.0457 (5)
N1	0.76212 (17)	−0.00325 (19)	0.81015 (13)	0.0252 (4)
N2	0.65411 (17)	0.14582 (19)	0.69692 (13)	0.0238 (4)
N3	0.7794 (2)	0.3305 (2)	0.62983 (17)	0.0359 (5)
C1	0.9075 (2)	0.1690 (2)	0.76117 (18)	0.0320 (6)
C2	0.7848 (3)	0.3278 (3)	0.81319 (19)	0.0354 (6)
C3	0.8852 (2)	0.1758 (2)	0.91343 (18)	0.0327 (6)
C4	0.8291 (2)	−0.0776 (2)	0.86473 (17)	0.0313 (6)
H1	0.893046	−0.048384	0.907298	0.038*
C5	0.8095 (2)	−0.1941 (3)	0.86198 (19)	0.0358 (6)
H2	0.860275	−0.243958	0.900658	0.043*
C6	0.7144 (2)	−0.2373 (3)	0.80188 (19)	0.0350 (6)
H3	0.698453	−0.317169	0.798723	0.042*
C7	0.6431 (2)	−0.1615 (2)	0.74643 (18)	0.0313 (6)
H4	0.576614	−0.188952	0.705236	0.038*
C8	0.6693 (2)	−0.0454 (2)	0.75134 (15)	0.0247 (5)
C9	0.6038 (2)	0.0406 (2)	0.69157 (15)	0.0232 (5)
C10	0.4996 (2)	0.0143 (2)	0.63271 (15)	0.0232 (5)
H5	0.466483	−0.060220	0.632112	0.028*
C11	0.44359 (19)	0.0971 (2)	0.57461 (15)	0.0214 (5)
C12	0.5003 (2)	0.2023 (2)	0.57681 (16)	0.0248 (5)
H6	0.467288	0.260028	0.536409	0.030*
C13	0.6042 (2)	0.2244 (2)	0.63698 (16)	0.0254 (5)
C14	0.6644 (2)	0.3362 (2)	0.63063 (17)	0.0280 (5)
C15	0.6033 (2)	0.4378 (2)	0.62349 (19)	0.0326 (6)
H7	0.522062	0.438538	0.624227	0.039*
C16	0.6619 (3)	0.5393 (3)	0.6152 (2)	0.0418 (7)
H8	0.621545	0.610530	0.610537	0.050*
C17	0.7798 (3)	0.5349 (3)	0.6138 (2)	0.0446 (7)
H9	0.822144	0.602872	0.607979	0.054*
C18	0.8345 (3)	0.4297 (3)	0.6212 (2)	0.0403 (7)
H10	0.915543	0.426919	0.620071	0.048*
C19	0.3301 (2)	0.0749 (2)	0.51219 (15)	0.0215 (5)

C20	0.2826 (2)	−0.0347 (2)	0.49944 (17)	0.0316 (6)
H11	0.324220	−0.097276	0.530401	0.038*
C21	0.1756 (3)	−0.0542 (3)	0.44231 (19)	0.0389 (7)
H12	0.144475	−0.129640	0.434142	0.047*
C22	0.1145 (2)	0.0361 (3)	0.39740 (19)	0.0373 (6)
H13	0.039539	0.023966	0.359983	0.045*
C23	0.1626 (3)	0.1429 (3)	0.4072 (2)	0.0453 (8)
H14	0.122516	0.204709	0.374184	0.054*
C24	0.2688 (3)	0.1626 (2)	0.4644 (2)	0.0402 (7)
H15	0.300073	0.238042	0.470790	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02474 (13)	0.03228 (14)	0.02610 (14)	0.00130 (9)	0.00315 (10)	−0.00370 (10)
Mn1	0.01744 (18)	0.0327 (2)	0.0221 (2)	−0.00087 (14)	−0.00207 (14)	−0.00159 (15)
O1	0.0209 (9)	0.0603 (14)	0.0372 (11)	−0.0046 (9)	0.0033 (8)	−0.0054 (10)
O2	0.0517 (13)	0.0352 (11)	0.0424 (12)	−0.0087 (10)	0.0023 (10)	−0.0043 (9)
O3	0.0325 (11)	0.0571 (14)	0.0377 (12)	−0.0050 (9)	−0.0125 (9)	−0.0002 (10)
N1	0.0163 (9)	0.0359 (11)	0.0211 (10)	0.0032 (8)	−0.0007 (8)	−0.0008 (8)
N2	0.0168 (9)	0.0321 (11)	0.0209 (10)	0.0015 (8)	0.0005 (8)	−0.0036 (8)
N3	0.0263 (11)	0.0384 (13)	0.0427 (14)	−0.0042 (9)	0.0072 (10)	−0.0009 (10)
C1	0.0241 (13)	0.0399 (15)	0.0271 (13)	−0.0049 (10)	−0.0045 (10)	−0.0031 (11)
C2	0.0300 (14)	0.0417 (16)	0.0323 (15)	−0.0015 (11)	0.0028 (11)	−0.0017 (12)
C3	0.0303 (14)	0.0343 (14)	0.0312 (14)	−0.0039 (11)	0.0019 (11)	−0.0009 (11)
C4	0.0212 (12)	0.0407 (15)	0.0271 (13)	0.0043 (10)	−0.0049 (10)	−0.0010 (11)
C5	0.0266 (13)	0.0432 (16)	0.0323 (15)	0.0071 (11)	−0.0041 (11)	0.0091 (12)
C6	0.0300 (13)	0.0368 (15)	0.0345 (15)	−0.0005 (11)	−0.0005 (11)	0.0060 (12)
C7	0.0252 (12)	0.0385 (15)	0.0266 (13)	−0.0036 (10)	−0.0017 (10)	0.0053 (11)
C8	0.0178 (11)	0.0354 (13)	0.0198 (11)	0.0014 (9)	0.0019 (9)	0.0013 (10)
C9	0.0178 (10)	0.0328 (13)	0.0186 (11)	0.0010 (9)	0.0031 (9)	0.0008 (9)
C10	0.0187 (10)	0.0280 (12)	0.0212 (11)	−0.0022 (9)	0.0009 (9)	0.0020 (9)
C11	0.0165 (10)	0.0282 (12)	0.0184 (11)	0.0000 (9)	0.0016 (8)	−0.0003 (9)
C12	0.0185 (11)	0.0276 (12)	0.0263 (12)	0.0017 (9)	0.0007 (9)	0.0011 (10)
C13	0.0196 (11)	0.0287 (12)	0.0267 (13)	0.0008 (9)	0.0027 (10)	−0.0034 (10)
C14	0.0246 (12)	0.0308 (13)	0.0276 (13)	−0.0025 (10)	0.0038 (10)	−0.0005 (10)
C15	0.0259 (12)	0.0313 (13)	0.0412 (15)	−0.0036 (10)	0.0089 (11)	−0.0030 (11)
C16	0.0374 (15)	0.0309 (14)	0.0568 (19)	−0.0007 (12)	0.0103 (14)	0.0005 (13)
C17	0.0380 (16)	0.0354 (15)	0.060 (2)	−0.0105 (13)	0.0105 (14)	0.0009 (14)
C18	0.0279 (14)	0.0428 (16)	0.0506 (18)	−0.0074 (12)	0.0100 (13)	−0.0054 (14)
C19	0.0179 (10)	0.0283 (12)	0.0172 (11)	0.0023 (9)	0.0018 (9)	−0.0002 (9)
C20	0.0300 (13)	0.0320 (13)	0.0278 (13)	−0.0007 (10)	−0.0039 (11)	0.0056 (11)
C21	0.0344 (15)	0.0347 (15)	0.0399 (16)	−0.0088 (12)	−0.0078 (12)	0.0015 (12)
C22	0.0246 (13)	0.0417 (16)	0.0368 (15)	0.0031 (11)	−0.0115 (11)	−0.0062 (12)
C23	0.0420 (17)	0.0332 (15)	0.0465 (18)	0.0079 (13)	−0.0194 (14)	0.0018 (13)
C24	0.0377 (16)	0.0266 (13)	0.0432 (17)	−0.0041 (11)	−0.0182 (13)	0.0049 (12)

Geometric parameters (Å, º)

Br1—Mn1	2.5325 (5)	C10—H5	0.9500
Mn1—C3	1.796 (3)	C11—C12	1.390 (3)
Mn1—C1	1.805 (3)	C11—C19	1.486 (3)
Mn1—C2	1.840 (3)	C12—C13	1.388 (3)
Mn1—N1	2.037 (2)	C12—H6	0.9500
Mn1—N2	2.088 (2)	C13—C14	1.496 (3)
O1—C1	1.135 (4)	C14—C15	1.375 (4)
O2—C2	1.143 (3)	C15—C16	1.388 (4)
O3—C3	1.138 (3)	C15—H7	0.9500
N1—C4	1.345 (3)	C16—C17	1.381 (4)
N1—C8	1.353 (3)	C16—H8	0.9500
N2—C9	1.355 (3)	C17—C18	1.376 (4)
N2—C13	1.355 (3)	C17—H9	0.9500
N3—C18	1.346 (4)	C18—H10	0.9500
N3—C14	1.347 (3)	C19—C24	1.374 (3)
C4—C5	1.377 (4)	C19—C20	1.391 (4)
C4—H1	0.9500	C20—C21	1.386 (4)
C5—C6	1.384 (4)	C20—H11	0.9500
C5—H2	0.9500	C21—C22	1.377 (4)
C6—C7	1.385 (4)	C21—H12	0.9500
C6—H3	0.9500	C22—C23	1.361 (4)
C7—C8	1.387 (4)	C22—H13	0.9500
C7—H4	0.9500	C23—C24	1.379 (4)
C8—C9	1.471 (3)	C23—H14	0.9500
C9—C10	1.390 (3)	C24—H15	0.9500
C10—C11	1.393 (3)		
C3—Mn1—C1	87.58 (13)	C9—C10—H5	120.0
C3—Mn1—C2	86.53 (13)	C11—C10—H5	120.0
C1—Mn1—C2	90.48 (13)	C12—C11—C10	116.6 (2)
C3—Mn1—N1	95.30 (10)	C12—C11—C19	121.2 (2)
C1—Mn1—N1	95.53 (11)	C10—C11—C19	122.3 (2)
C2—Mn1—N1	173.78 (11)	C13—C12—C11	121.2 (2)
C3—Mn1—N2	172.86 (11)	C13—C12—H6	119.4
C1—Mn1—N2	96.60 (10)	C11—C12—H6	119.4
C2—Mn1—N2	99.18 (11)	N2—C13—C12	121.9 (2)
N1—Mn1—N2	78.58 (8)	N2—C13—C14	120.3 (2)
C3—Mn1—Br1	89.33 (9)	C12—C13—C14	117.7 (2)
C1—Mn1—Br1	176.28 (9)	N3—C14—C15	122.7 (2)
C2—Mn1—Br1	87.27 (9)	N3—C14—C13	116.2 (2)
N1—Mn1—Br1	86.80 (6)	C15—C14—C13	121.0 (2)
N2—Mn1—Br1	86.69 (6)	C14—C15—C16	119.1 (3)
C4—N1—C8	117.9 (2)	C14—C15—H7	120.4
C4—N1—Mn1	126.07 (17)	C16—C15—H7	120.4
C8—N1—Mn1	115.98 (16)	C17—C16—C15	118.9 (3)
C9—N2—C13	117.3 (2)	C17—C16—H8	120.6

C9—N2—Mn1	113.14 (16)	C15—C16—H8	120.6
C13—N2—Mn1	128.74 (17)	C18—C17—C16	118.4 (3)
C18—N3—C14	117.3 (2)	C18—C17—H9	120.8
O1—C1—Mn1	174.2 (2)	C16—C17—H9	120.8
O2—C2—Mn1	175.2 (3)	N3—C18—C17	123.6 (3)
O3—C3—Mn1	177.3 (3)	N3—C18—H10	118.2
N1—C4—C5	123.3 (2)	C17—C18—H10	118.2
N1—C4—H1	118.4	C24—C19—C20	117.6 (2)
C5—C4—H1	118.4	C24—C19—C11	120.9 (2)
C4—C5—C6	118.8 (3)	C20—C19—C11	121.5 (2)
C4—C5—H2	120.6	C21—C20—C19	121.1 (2)
C6—C5—H2	120.6	C21—C20—H11	119.5
C7—C6—C5	118.6 (3)	C19—C20—H11	119.5
C7—C6—H3	120.7	C22—C21—C20	119.8 (3)
C5—C6—H3	120.7	C22—C21—H12	120.1
C6—C7—C8	119.7 (2)	C20—C21—H12	120.1
C6—C7—H4	120.2	C23—C22—C21	119.3 (2)
C8—C7—H4	120.2	C23—C22—H13	120.3
N1—C8—C7	121.7 (2)	C21—C22—H13	120.3
N1—C8—C9	114.5 (2)	C22—C23—C24	120.9 (3)
C7—C8—C9	123.7 (2)	C22—C23—H14	119.6
N2—C9—C10	122.9 (2)	C24—C23—H14	119.6
N2—C9—C8	115.1 (2)	C19—C24—C23	121.2 (3)
C10—C9—C8	122.0 (2)	C19—C24—H15	119.4
C9—C10—C11	120.0 (2)	C23—C24—H15	119.4

C8—N1—C4—C5	1.8 (4)	Mn1—N2—C13—C14	20.3 (3)
Mn1—N1—C4—C5	178.9 (2)	C11—C12—C13—N2	−1.1 (4)
N1—C4—C5—C6	−1.9 (5)	C11—C12—C13—C14	175.4 (2)
C4—C5—C6—C7	0.4 (4)	C18—N3—C14—C15	−0.3 (4)
C5—C6—C7—C8	1.0 (4)	C18—N3—C14—C13	177.8 (3)
C4—N1—C8—C7	−0.3 (4)	N2—C13—C14—N3	47.9 (3)
Mn1—N1—C8—C7	−177.7 (2)	C12—C13—C14—N3	−128.7 (3)
C4—N1—C8—C9	−177.3 (2)	N2—C13—C14—C15	−134.0 (3)
Mn1—N1—C8—C9	5.3 (3)	C12—C13—C14—C15	49.5 (4)
C6—C7—C8—N1	−1.1 (4)	N3—C14—C15—C16	−0.1 (4)
C6—C7—C8—C9	175.7 (2)	C13—C14—C15—C16	−178.1 (3)
C13—N2—C9—C10	−5.6 (3)	C14—C15—C16—C17	0.4 (5)
Mn1—N2—C9—C10	164.82 (19)	C15—C16—C17—C18	−0.3 (5)
C13—N2—C9—C8	173.0 (2)	C14—N3—C18—C17	0.5 (5)
Mn1—N2—C9—C8	−16.7 (3)	C16—C17—C18—N3	−0.2 (5)
N1—C8—C9—N2	7.9 (3)	C12—C11—C19—C24	−10.3 (4)
C7—C8—C9—N2	−169.1 (2)	C10—C11—C19—C24	170.7 (3)
N1—C8—C9—C10	−173.6 (2)	C12—C11—C19—C20	169.1 (2)
C7—C8—C9—C10	9.4 (4)	C10—C11—C19—C20	−9.9 (4)
N2—C9—C10—C11	1.4 (4)	C24—C19—C20—C21	−1.8 (4)
C8—C9—C10—C11	−177.0 (2)	C11—C19—C20—C21	178.7 (3)
C9—C10—C11—C12	2.9 (3)	C19—C20—C21—C22	−0.2 (5)

C9—C10—C11—C19	−178.0 (2)	C20—C21—C22—C23	2.7 (5)
C10—C11—C12—C13	−3.1 (4)	C21—C22—C23—C24	−3.1 (5)
C19—C11—C12—C13	177.8 (2)	C20—C19—C24—C23	1.4 (5)
C9—N2—C13—C12	5.3 (3)	C11—C19—C24—C23	−179.1 (3)
Mn1—N2—C13—C12	−163.30 (18)	C22—C23—C24—C19	1.0 (6)
C9—N2—C13—C14	−171.0 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H4···Br1^{i}	0.95	2.83	3.754 (3)	165
C16—H8···Br1^{ii}	0.95	2.88	3.612 (4)	135
C20—H11···Br1^{i}	0.95	2.92	3.844 (2)	163

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

cis-Bromidodicarbonyl(4′-phenyl-2,2′:6′,2′′-terpyridine-κ^3N,N',N'')manganese(I) (II)

Crystal data

$[MnBr(C_{21}H_{15}N_3)(CO)_2]$
M_r = 500.23
Monoclinic, $P2_1/c$
a = 10.497 (3) Å
b = 14.123 (5) Å
c = 13.504 (4) Å
β = 96.767 (3)°
V = 1988.0 (11) Å^3
Z = 4
$F(000)$ = 1000.00
D_x = 1.671 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 5160 reflections
θ = 3.0–27.5°
μ = 2.71 mm^{-1}
T = 93 K
Block, red
0.20 × 0.08 × 0.05 mm

Data collection

Rigaku Saturn70 diffractometer
Detector resolution: 28.626 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*, Rigaku, 1998)
T_{min} = 0.795, T_{max} = 0.873
19872 measured reflections
4518 independent reflections
4016 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.028
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −13→13
k = −18→18
l = −17→17

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.096
S = 1.27
4518 reflections
289 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0039P)^2 + 5.6867P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 e Å^{-3}

Special details

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)
Br1	0.39194 (6)	0.11344 (3)	0.73710 (4)	0.02535 (17)	0.807 (2)
O2	−0.0653 (5)	0.0445 (4)	0.8859 (4)	0.0351 (15)	0.807 (2)
C2	0.0332 (9)	0.0641 (9)	0.8536 (10)	0.037 (3)	0.807 (2)
Br2	−0.0197 (5)	0.0661 (4)	0.8657 (4)	0.0403 (14)	0.193 (2)
O3	0.4377 (18)	0.1006 (12)	0.7111 (13)	0.033 (4)*	0.193 (2)
C3	0.339 (3)	0.092 (3)	0.746 (3)	0.076 (12)*	0.193 (2)
Mn1	0.18158 (5)	0.08786 (4)	0.80533 (4)	0.02451 (14)	
O1	0.1797 (3)	−0.10749 (19)	0.7376 (2)	0.0359 (6)	
N1	0.2796 (3)	0.0760 (2)	0.9421 (2)	0.0224 (6)	
N2	0.2005 (3)	0.22091 (19)	0.8440 (2)	0.0202 (6)	
N3	0.0937 (3)	0.1521 (2)	0.6822 (2)	0.0219 (6)	
C1	0.1807 (4)	−0.0334 (3)	0.7637 (3)	0.0310 (8)	
C4	0.3125 (3)	−0.0050 (3)	0.9917 (3)	0.0275 (8)	
H1	0.288826	−0.063547	0.960043	0.033*	
C5	0.3784 (4)	−0.0070 (3)	1.0856 (3)	0.0298 (8)	
H2	0.400366	−0.065698	1.117441	0.036*	
C6	0.4125 (4)	0.0773 (3)	1.1335 (3)	0.0301 (8)	
H3	0.458098	0.077281	1.198549	0.036*	
C7	0.3789 (3)	0.1623 (3)	1.0847 (3)	0.0257 (7)	
H4	0.400583	0.221221	1.116233	0.031*	
C8	0.3132 (3)	0.1592 (2)	0.9894 (3)	0.0217 (7)	
C9	0.2711 (3)	0.2443 (2)	0.9303 (3)	0.0212 (7)	
C10	0.3006 (3)	0.3376 (2)	0.9548 (3)	0.0227 (7)	
H5	0.351261	0.352547	1.015754	0.027*	
C11	0.2548 (3)	0.4096 (2)	0.8886 (3)	0.0223 (7)	
C12	0.1818 (3)	0.3838 (2)	0.7994 (3)	0.0225 (7)	
H6	0.149023	0.431227	0.753384	0.027*	
C13	0.1572 (3)	0.2887 (2)	0.7779 (3)	0.0208 (7)	
C14	0.0918 (3)	0.2483 (2)	0.6854 (3)	0.0210 (7)	
C15	0.0335 (3)	0.3016 (3)	0.6061 (3)	0.0251 (7)	
H7	0.033795	0.368774	0.609582	0.030*	
C16	−0.0251 (3)	0.2560 (3)	0.5220 (3)	0.0274 (8)	
H8	−0.066553	0.291366	0.467603	0.033*	
C17	−0.0223 (3)	0.1587 (3)	0.5187 (3)	0.0277 (8)	
H9	−0.060962	0.125743	0.461531	0.033*	
C18	0.0376 (3)	0.1095 (3)	0.5994 (3)	0.0262 (7)	
H10	0.039210	0.042307	0.596314	0.031*	
C19	0.2863 (3)	0.5109 (2)	0.9128 (3)	0.0247 (7)	
C20	0.3268 (4)	0.5390 (3)	1.0100 (3)	0.0316 (8)	
H11	0.333688	0.493598	1.062254	0.038*	

C21	0.3573 (4)	0.6332 (3)	1.0315 (3)	0.0385 (10)
H12	0.385755	0.651422	1.098118	0.046*
C22	0.3466 (4)	0.7000 (3)	0.9572 (4)	0.0379 (10)
H13	0.367454	0.764157	0.972651	0.045*
C23	0.3056 (4)	0.6739 (3)	0.8598 (3)	0.0376 (10)
H14	0.297827	0.720240	0.808386	0.045*
C24	0.2757 (4)	0.5797 (3)	0.8373 (3)	0.0299 (8)
H15	0.247979	0.561819	0.770438	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0222 (3)	0.0293 (3)	0.0246 (3)	0.0054 (2)	0.0032 (2)	0.00736 (19)
O2	0.038 (3)	0.028 (3)	0.041 (3)	−0.0170 (18)	0.012 (2)	0.000 (2)
C2	0.055 (7)	0.023 (3)	0.031 (4)	0.009 (5)	−0.006 (5)	−0.006 (3)
Br2	0.060 (4)	0.0228 (17)	0.035 (2)	0.001 (3)	−0.005 (3)	−0.0077 (14)
Mn1	0.0276 (3)	0.0170 (3)	0.0275 (3)	0.0001 (2)	−0.0027 (2)	0.0030 (2)
O1	0.0504 (18)	0.0244 (14)	0.0342 (15)	0.0084 (12)	0.0102 (13)	0.0043 (12)
N1	0.0202 (14)	0.0197 (14)	0.0276 (15)	0.0010 (11)	0.0042 (12)	0.0048 (12)
N2	0.0176 (13)	0.0179 (13)	0.0250 (15)	0.0001 (10)	0.0017 (11)	0.0029 (11)
N3	0.0191 (14)	0.0215 (14)	0.0249 (15)	0.0006 (11)	0.0016 (12)	0.0015 (12)
C1	0.0266 (19)	0.037 (2)	0.029 (2)	−0.0021 (16)	0.0024 (15)	0.0106 (17)
C4	0.0248 (18)	0.0231 (17)	0.035 (2)	0.0036 (14)	0.0064 (15)	0.0077 (15)
C5	0.0276 (19)	0.0283 (19)	0.034 (2)	0.0070 (15)	0.0064 (16)	0.0115 (16)
C6	0.0286 (19)	0.039 (2)	0.0235 (18)	0.0076 (16)	0.0040 (15)	0.0082 (16)
C7	0.0239 (17)	0.0283 (18)	0.0252 (18)	0.0022 (14)	0.0041 (14)	0.0017 (14)
C8	0.0182 (16)	0.0240 (17)	0.0236 (17)	0.0012 (13)	0.0059 (13)	0.0031 (14)
C9	0.0177 (16)	0.0214 (16)	0.0249 (17)	0.0006 (13)	0.0042 (13)	0.0030 (13)
C10	0.0192 (16)	0.0247 (17)	0.0244 (18)	0.0003 (13)	0.0028 (13)	−0.0012 (14)
C11	0.0180 (16)	0.0202 (16)	0.0297 (18)	0.0012 (12)	0.0064 (14)	0.0008 (14)
C12	0.0208 (16)	0.0196 (16)	0.0270 (18)	0.0014 (13)	0.0028 (13)	0.0027 (14)
C13	0.0172 (15)	0.0224 (17)	0.0232 (17)	0.0012 (12)	0.0036 (13)	0.0041 (13)
C14	0.0173 (15)	0.0209 (16)	0.0251 (17)	0.0000 (12)	0.0037 (13)	0.0018 (13)
C15	0.0221 (17)	0.0243 (17)	0.0289 (19)	0.0016 (14)	0.0023 (14)	0.0057 (14)
C16	0.0225 (17)	0.0333 (19)	0.0261 (19)	0.0011 (15)	0.0016 (14)	0.0059 (15)
C17	0.0227 (18)	0.036 (2)	0.0241 (18)	−0.0009 (15)	0.0013 (14)	−0.0016 (15)
C18	0.0224 (17)	0.0247 (17)	0.0311 (19)	−0.0016 (14)	0.0020 (14)	−0.0005 (15)
C19	0.0181 (16)	0.0208 (17)	0.036 (2)	−0.0005 (13)	0.0065 (14)	−0.0015 (14)
C20	0.0290 (19)	0.0240 (18)	0.042 (2)	0.0000 (15)	0.0027 (17)	−0.0041 (16)
C21	0.031 (2)	0.031 (2)	0.053 (3)	−0.0024 (16)	0.0019 (19)	−0.0145 (19)
C22	0.030 (2)	0.0206 (18)	0.065 (3)	−0.0047 (15)	0.014 (2)	−0.0097 (19)
C23	0.038 (2)	0.0211 (18)	0.057 (3)	−0.0022 (16)	0.018 (2)	0.0041 (18)
C24	0.0288 (19)	0.0221 (17)	0.040 (2)	0.0013 (14)	0.0081 (16)	0.0006 (16)

Geometric parameters (Å, º)

Br1—O3	0.65 (2)	C9—C10	1.384 (5)
Br1—C3	0.66 (3)	C10—C11	1.401 (5)

Br1—Mn1	2.5170 (11)	C10—H5	0.9500
O2—Br2	0.654 (5)	C11—C12	1.398 (5)
O2—C2	1.201 (11)	C11—C19	1.496 (5)
C2—Br2	0.597 (8)	C12—C13	1.392 (5)
C2—Mn1	1.790 (9)	C12—H6	0.9500
O3—C3	1.194 (18)	C13—C14	1.468 (5)
Mn1—C1	1.803 (4)	C14—C15	1.390 (5)
Mn1—N2	1.954 (3)	C15—C16	1.384 (5)
Mn1—N1	2.012 (3)	C15—H7	0.9500
Mn1—N3	2.019 (3)	C16—C17	1.376 (5)
O1—C1	1.103 (5)	C16—H8	0.9500
N1—C4	1.350 (4)	C17—C18	1.380 (5)
N1—C8	1.364 (4)	C17—H9	0.9500
N2—C9	1.346 (4)	C18—H10	0.9500
N2—C13	1.351 (4)	C19—C20	1.390 (5)
N3—C18	1.343 (4)	C19—C24	1.402 (5)
N3—C14	1.360 (4)	C20—C21	1.390 (5)
C4—C5	1.371 (5)	C20—H11	0.9500
C4—H1	0.9500	C21—C22	1.371 (6)
C5—C6	1.381 (6)	C21—H12	0.9500
C5—H2	0.9500	C22—C23	1.385 (6)
C6—C7	1.395 (5)	C22—H13	0.9500
C6—H3	0.9500	C23—C24	1.393 (5)
C7—C8	1.387 (5)	C23—H14	0.9500
C7—H4	0.9500	C24—H15	0.9500
C8—C9	1.481 (5)		

O3—Br1—C3	131 (4)	N2—C9—C8	111.5 (3)
Br2—O2—C2	15.7 (10)	C10—C9—C8	126.8 (3)
Br2—C2—O2	17.2 (12)	C9—C10—C11	119.2 (3)
O2—C2—Mn1	177.5 (10)	C9—C10—H5	120.4
C2—Br2—O2	147 (2)	C11—C10—H5	120.4
Br1—O3—C3	24 (2)	C12—C11—C10	118.2 (3)
Br1—C3—O3	24.3 (19)	C12—C11—C19	121.5 (3)
C2—Mn1—C1	87.9 (4)	C10—C11—C19	120.3 (3)
C2—Mn1—N2	98.6 (4)	C13—C12—C11	120.0 (3)
C1—Mn1—N2	173.57 (15)	C13—C12—H6	120.0
C2—Mn1—N1	91.3 (4)	C11—C12—H6	120.0
C1—Mn1—N1	100.98 (14)	N2—C13—C12	120.4 (3)
N2—Mn1—N1	79.05 (12)	N2—C13—C14	112.0 (3)
C2—Mn1—N3	93.0 (4)	C12—C13—C14	127.5 (3)
C1—Mn1—N3	100.66 (15)	N3—C14—C15	121.5 (3)
N2—Mn1—N3	79.05 (12)	N3—C14—C13	114.1 (3)
N1—Mn1—N3	158.08 (12)	C15—C14—C13	124.4 (3)
C2—Mn1—Br1	177.4 (4)	C16—C15—C14	119.6 (3)
C1—Mn1—Br1	89.68 (12)	C16—C15—H7	120.2
N2—Mn1—Br1	83.89 (8)	C14—C15—H7	120.2
N1—Mn1—Br1	88.42 (8)	C17—C16—C15	118.8 (3)

N3—Mn1—Br1	88.26 (8)	C17—C16—H8	120.6
C4—N1—C8	117.4 (3)	C15—C16—H8	120.6
C4—N1—Mn1	126.8 (3)	C16—C17—C18	119.1 (3)
C8—N1—Mn1	115.8 (2)	C16—C17—H9	120.4
C9—N2—C13	120.4 (3)	C18—C17—H9	120.4
C9—N2—Mn1	119.7 (2)	N3—C18—C17	123.1 (3)
C13—N2—Mn1	119.3 (2)	N3—C18—H10	118.4
C18—N3—C14	117.9 (3)	C17—C18—H10	118.4
C18—N3—Mn1	126.7 (2)	C20—C19—C24	118.5 (3)
C14—N3—Mn1	115.5 (2)	C20—C19—C11	121.0 (3)
O1—C1—Mn1	179.5 (4)	C24—C19—C11	120.5 (3)
N1—C4—C5	123.2 (4)	C21—C20—C19	120.5 (4)
N1—C4—H1	118.4	C21—C20—H11	119.8
C5—C4—H1	118.4	C19—C20—H11	119.8
C4—C5—C6	119.4 (3)	C22—C21—C20	120.6 (4)
C4—C5—H2	120.3	C22—C21—H12	119.7
C6—C5—H2	120.3	C20—C21—H12	119.7
C5—C6—C7	118.9 (3)	C21—C22—C23	120.1 (4)
C5—C6—H3	120.5	C21—C22—H13	120.0
C7—C6—H3	120.5	C23—C22—H13	120.0
C8—C7—C6	118.8 (3)	C22—C23—C24	119.8 (4)
C8—C7—H4	120.6	C22—C23—H14	120.1
C6—C7—H4	120.6	C24—C23—H14	120.1
N1—C8—C7	122.3 (3)	C23—C24—C19	120.5 (4)
N1—C8—C9	113.7 (3)	C23—C24—H15	119.8
C7—C8—C9	124.0 (3)	C19—C24—H15	119.8
N2—C9—C10	121.7 (3)		

C8—N1—C4—C5	−0.7 (5)	C11—C12—C13—N2	1.8 (5)
Mn1—N1—C4—C5	−179.2 (3)	C11—C12—C13—C14	−174.8 (3)
N1—C4—C5—C6	0.7 (6)	C18—N3—C14—C15	0.3 (5)
C4—C5—C6—C7	0.0 (5)	Mn1—N3—C14—C15	−179.4 (3)
C5—C6—C7—C8	−0.5 (5)	C18—N3—C14—C13	−179.0 (3)
C4—N1—C8—C7	0.1 (5)	Mn1—N3—C14—C13	1.3 (4)
Mn1—N1—C8—C7	178.8 (3)	N2—C13—C14—N3	−3.4 (4)
C4—N1—C8—C9	−178.9 (3)	C12—C13—C14—N3	173.5 (3)
Mn1—N1—C8—C9	−0.2 (4)	N2—C13—C14—C15	177.4 (3)
C6—C7—C8—N1	0.5 (5)	C12—C13—C14—C15	−5.7 (6)
C6—C7—C8—C9	179.4 (3)	N3—C14—C15—C16	0.5 (5)
C13—N2—C9—C10	0.7 (5)	C13—C14—C15—C16	179.7 (3)
Mn1—N2—C9—C10	171.8 (2)	C14—C15—C16—C17	−1.0 (5)
C13—N2—C9—C8	−177.5 (3)	C15—C16—C17—C18	0.7 (5)
Mn1—N2—C9—C8	−6.4 (4)	C14—N3—C18—C17	−0.6 (5)
N1—C8—C9—N2	4.1 (4)	Mn1—N3—C18—C17	179.1 (3)
C7—C8—C9—N2	−174.9 (3)	C16—C17—C18—N3	0.1 (6)
N1—C8—C9—C10	−174.0 (3)	C12—C11—C19—C20	162.1 (3)
C7—C8—C9—C10	7.0 (5)	C10—C11—C19—C20	−19.3 (5)
N2—C9—C10—C11	0.6 (5)	C12—C11—C19—C24	−18.0 (5)

C8—C9—C10—C11	178.5 (3)	C10—C11—C19—C24	160.6 (3)
C9—C10—C11—C12	−0.7 (5)	C24—C19—C20—C21	−0.7 (6)
C9—C10—C11—C19	−179.4 (3)	C11—C19—C20—C21	179.2 (3)
C10—C11—C12—C13	−0.5 (5)	C19—C20—C21—C22	0.7 (6)
C19—C11—C12—C13	178.2 (3)	C20—C21—C22—C23	−0.2 (6)
C9—N2—C13—C12	−1.9 (5)	C21—C22—C23—C24	−0.3 (6)
Mn1—N2—C13—C12	−173.0 (2)	C22—C23—C24—C19	0.3 (6)
C9—N2—C13—C14	175.2 (3)	C20—C19—C24—C23	0.2 (5)
Mn1—N2—C13—C14	4.1 (4)	C11—C19—C24—C23	−179.7 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H2···Br1^{i}	0.95	2.84	3.528 (4)	130
C7—H4···Br1^{ii}	0.95	2.86	3.771 (4)	162
C12—H6···Br2^{iii}	0.95	2.75	3.688 (7)	171
C12—H6···O2^{iii}	0.95	2.55	3.491 (7)	173
C15—H7···Br2^{iii}	0.95	2.81	3.759 (7)	175
C15—H7···O2^{iii}	0.95	2.50	3.447 (7)	172
C16—H8···Br2^{iv}	0.95	2.52	3.286 (7)	138
C16—H8···O2^{iv}	0.95	2.57	3.363 (7)	141
C20—H11···Br1^{ii}	0.95	2.81	3.743 (4)	168
C20—H11···O3^{ii}	0.95	2.55	3.446 (18)	158
C24—H15···Br2^{iii}	0.95	2.84	3.611 (7)	139

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