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Bond length of perchlorate at different temperatures: X-ray and neutron comparison

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The averages (average deviations from the mean are given in square brackets) of uncorrected Cl—O bond distances in a perchlorate anion from an X-ray diffraction analysis of (*N*-{2-[bis(pyridin-2-ylmethyl)amino]ethyl}-pyridine-2-carboxamidato)(nitric oxide)manganese perchlorate acetonitrile disolvate, $[Mn(C_{20}H_{20}N_5O)(NO)]ClO_4{\cdot}2CH_3CN$ or $[Mn(PaPy_3)(NO)]ClO_4{\cdot}\cdot 2CH_3CN$, decrease from 1.447 [4] Å at 10 K to 1.428 [4] Å at 170 K. The 10 K value is close to the neutron value (1.441 [1] Å) at 18 K. Comparisons are made with a second X-ray study at 30 K [1.444 (8) Å] and to libration-corrected, density functional theory (DFT), and Cambridge Structural Database (CSD) values.

1. Introduction

Many students erroneously assume that bond distances from X-ray diffraction structure determinations will shorten if the temperature of the data collection is lowered. This would seem to follow due to a shrinkage of the unit-cell volume and an increase in density. Neutron diffraction studies and high-pressure structure determinations reveal that, excepting a chemical reaction or phase change, the first effect of lowering the temperature is in compression of the void space rather than a change in intramolecular bond distances. X-ray diffraction bond distances differ because the measurement is not based on internuclear distances but is based on an electron density around the nucleus that is sensitive to the thermal motion of the atoms in question. This is not a new idea (Cox *et al.*, 1955; Busing & Levy, 1964). There is a large body of work on how to best deal with the fact that rigid-body motion around a fixed axis, termed libration, *i.e.* a kind of dynamic disorder, is particularly prone to yield foreshortened intramolecular distances. As an illustration, we have selected a transition-metal complex with a perchlorate anion that forms a stable crystal over a temperature range. Data was collected at 10, 90, and 170 K with the use of He and N_2 cryostats. It is important to point out that the structure does not undergo a structural phase transition over this temperature range and the perchlorate anion is free of any strong intermolecular interactions, *e.g.* hydrogen bonding. There is no evidence of the usual perchlorate disorder. Consequently, the crystal is a good candidate for this study. The 90 K crystal structure of this complex, namely (*N*-{2-[bis(pyridin-2-ylmethyl)amino]-ethyl}pyridine-2-carboxamidato)(nitric oxide)manganese perchlorate acetonitrile disolvate, $[Mn(PaPy_3)(NO)]ClO_4{\cdot}2CH_3CN$, (I), as an acetonitrile solvate was previously reported by the Mascharak group and was of interest in that study due to NO photolability (Ghosh *et al.*, 2004).

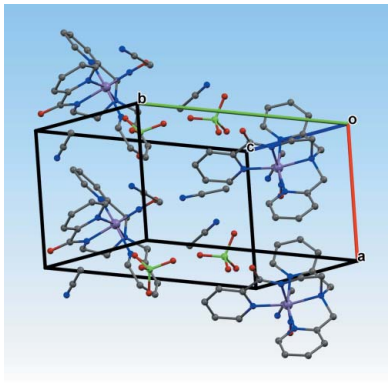


Table 1
Experimental details.

For all determinations: $[Mn(C_{20}H_{20}N_5O)(NO)]ClO_4{\cdot}2C_2H_3N$, M_r = 612.92, monoclinic, $P2_1$, Z = 2. Experiments were carried out with Mo $K\alpha$ radiation using a Bruker SMART 1000 diffractometer. Absorption was corrected for by multi-scan methods (*SADABS*; Sheldrick, 2016). Refinement was on 449 parameters with 1 restraint. Only H-atom displacement parameters were refined.

	(I) at 10 K	(I) at 90 K	(I) at 170 K
Crystal data			
Temperature (K)	10	90	170
a, b, c (Å)	8.2608 (8), 14.0676 (13), 11.5967 (11)	8.2788 (3), 14.0816 (6), 11.6343 (5)	8.3188 (4), 14.1117 (6), 11.6994 (5)
β (°)	97.9839 (16)	98.0814 (7)	98.3222 (7)
V (Å^3)	1334.6 (2)	1342.84 (9)	1358.96 (10)
μ (mm^{-1})	0.65	0.65	0.64
Crystal size (mm)	0.31 × 0.20 × 0.08	0.31 × 0.20 × 0.08	0.31 × 0.20 × 0.08
Data collection			
T_{min}, T_{max}	0.619, 0.746	0.662, 0.746	0.657, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8724, 5857, 5599	15371, 6074, 5824	15578, 6155, 5730
R_{int}	0.022	0.022	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650	0.649	0.650
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.087, 1.04	0.025, 0.061, 1.03	0.030, 0.072, 1.04
No. of reflections	5857	6074	6155
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.42	0.29, −0.24	0.37, −0.26
Absolute structure	Flack x determined using 2435 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)	Flack x determined using 2614 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)	Flack x determined using 2534 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.025 (13)	−0.022 (7)	−0.015 (8)

Computer programs: *SMART* (Bruker, 2003), *SAINT* (Bruker, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *XP* (Sheldrick, 1998) and *Mercury* (Macrae *et al.*, 2020).

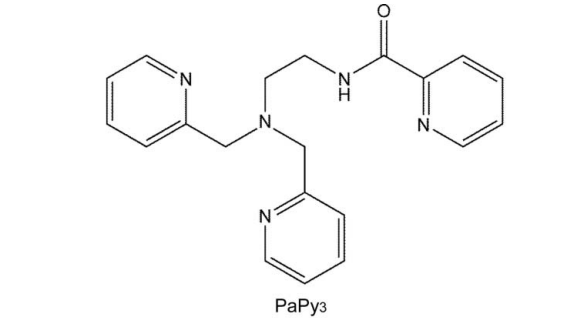
2. Experimental

2.1. Synthesis and crystallization

Details of the synthesis and crystallization of (I) were reported in a prior publication (Ghosh *et al.*, 2004). In a typical synthesis, the high-spin Mn^{II} complex $[Mn(PaPy_3)(H_2O)]ClO_4$ was reacted with NO in the dark in degassed MeCN to produce the low-spin Mn^{II}–NO complex (I) (Scheme 1) that was crystallized from MeCN/Et_2O at 277 K. The pale-green–brown plates of (I) rapidly lose NO in the presence of light and are oxygen-sensitive. They were coated with Paratone oil and a suitable crystal was selected under low room light. Initially, a suitable crystal was cooled to 10 K to assess its stability under a He(g) atmosphere.

2.2. Solution and refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The structures were solved and refined in the monoclinic space group $P2_1$ by standard techniques. H atoms were assigned by a combination of geometric and difference Fourier techniques, and refined with the use of isotropic displacement parameters. The structure at 10 K was well behaved and refined to an R_1 value of 0.034 for 5599 $F_o > 4\sigma(F_o)$. Subsequently, the cryostat was switched to N_2(g) and the data collected at 90 and 170 K. Refinement converged to R_1 = 0.025 (5824) and 0.030 (5730) at the higher temperatures, respectively. The higher R_1 value at 10 K may be related to lower redundancy [to save on He(g) use] and/or to imperfections due to static disorder caused by the cooling. Acetonitrile methyl H atoms were refined as riding on the parent C atom as a rigid group.



(I)
Scheme 1

3. Results and discussion

3.1. Crystal structure results

Views of the structure of (I) at the same perspective at the three different temperatures are presented in Fig. 1. Although

Table 2
Observed distances (Å).

	10 K	90 K	170 K
N6—O2	1.198 (4)	1.194 (3)	1.188 (3)
N7—C21	1.142 (5)	1.139 (4)	1.122 (5)
C21—C22	1.466 (5)	1.460 (4)	1.453 (6)
N8—C23	1.139 (5)	1.131 (4)	1.130 (5)
C23—C24	1.464 (5)	1.456 (4)	1.448 (6)
Cl—O3	1.451 (3)	1.442 (2)	1.427 (3)
Cl—O4	1.450 (3)	1.439 (2)	1.431 (3)
Cl—O5	1.442 (3)	1.433 (2)	1.420 (3)
Cl—O6	1.443 (3)	1.437 (2)	1.432 (3)
Aromatic CH (ave)	0.939	0.916	0.918
Secondary CH_2 (ave)	0.957	0.956	0.952
Methyl CH_3 (ave)	0.939	0.932	0.911

it is unusual for the perchlorate anion, there is no indication of split positions. Also, there are no strong intermolecular interactions. A packing diagram is given in Fig. 2. The four species in the asymmetric unit are the complex cation, the perchlorate anion, and two molecules of acetonitrile. At 10 K, the shortest intermolecular distance in the structure is a 2.29 Å nonclassical hydrogen bond between the keto O1 atom of the ligand and a secondary H atom on a neigboring complex. The shortest intermolecular contact to perchlorate is 2.47 Å from aromatic atom H13 of the complex to perchlorate atom O3.

As might be expected, the unit-cell volume increases as the temperature increases, specifically from 1334.6 (2) to 1342.84 (9) $Å^3$ between 10 and 90 K, and to 1358.96 (10) $Å^3$ at 170 K. At the same time, the percent filled space decreases from 70.7 to 70.0 to 68.9% over the same intervals in temperature (van der Sluis & Spek, 1990). The percent filled space ('packing index') assumes a set of standard temperature-independent covalent radii (Hofmann, 2002) and a default probe radius of 1.20 Å.

A selection of observed bond distances at the three temperatures are collected in Table 2.

Distances obtained from the X-ray measurements for the two acetonitrile solvent molecules and the terminal NO group of the magnesium complex are given in Table 2, along with those for the perchlorate anion. The remaining distances of the manganese complex have less variation than these, being core atoms, and fall within the commonly accepted limit of 3σ over the entire temperature range. The distances for the perchlorate anion change the most. In every case, however, the distances tend to decrease as the temperature increases. Even the C—H bond distances coincide with this trend.

It is also of potential interest to examine the anisotropic displacement parameters (ADPs) as a function of temperature. Table 3 gives the equivalent isotropic values. U_{eq} values are equal to one-third the trace of the diagonalized tensor in orthogonal coordinates, as required by the IUCr (Trueblood *et al.*, 1996).

3.2. Discussion

We were particularly interested to see the effect of temperature on the perchlorate anion, which is often disordered and tends to exhibit large librational motion due to its

Table 3
Equivalent isotropic atomic displacement parameters (U_{eq}, $Å^2$) for the perchlorate anion at three temperatures.

	10 K	90 K	170 K
Cl1	0.00811 (16)	0.01611 (13)	0.02949 (18)
O3	0.0148 (5)	0.0312 (5)	0.0592 (9)
O4	0.0139 (5)	0.0299 (5)	0.0592 (9)
O5	0.0145 (5)	0.0314 (5)	0.0605 (9)
O6	0.0145 (5)	0.0336 (5)	0.0677 (9)

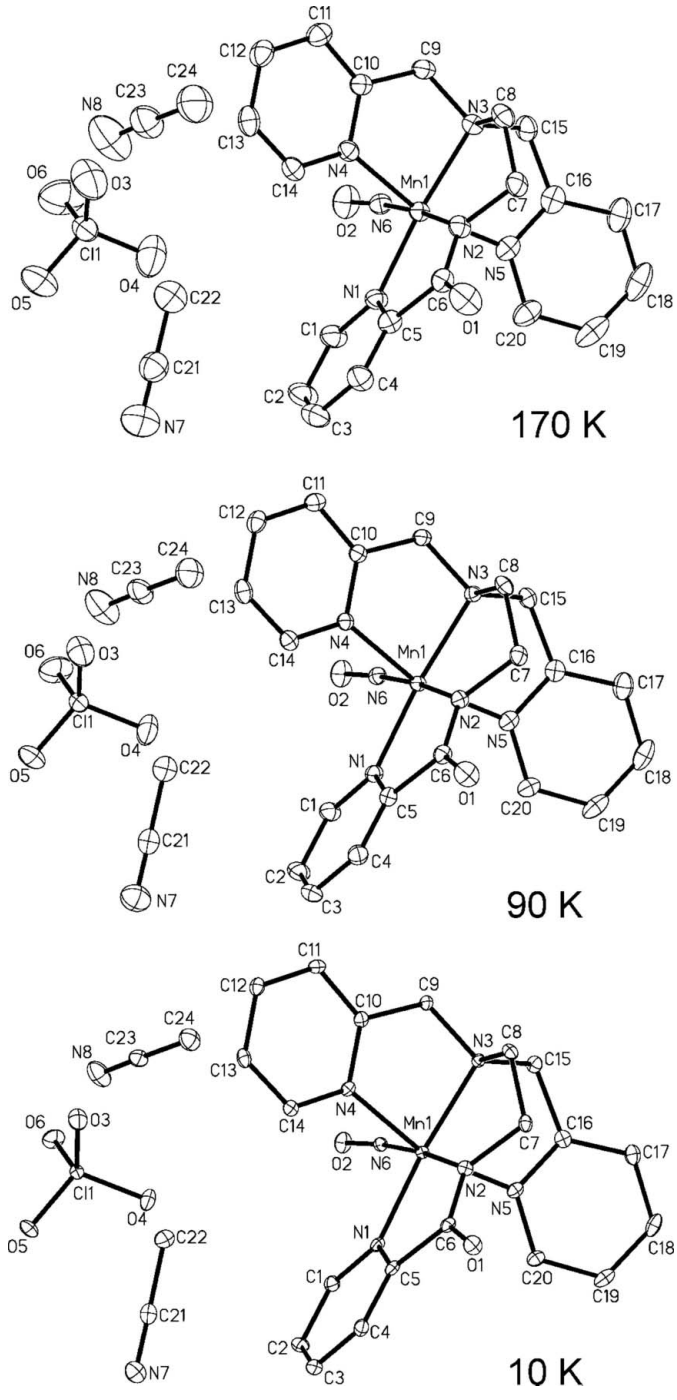


Figure 1
The crystal structure of $[Mn(PaPy_3)(NO)]ClO_4{\cdot}2CH_3CN$, (I), at three temperatures. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

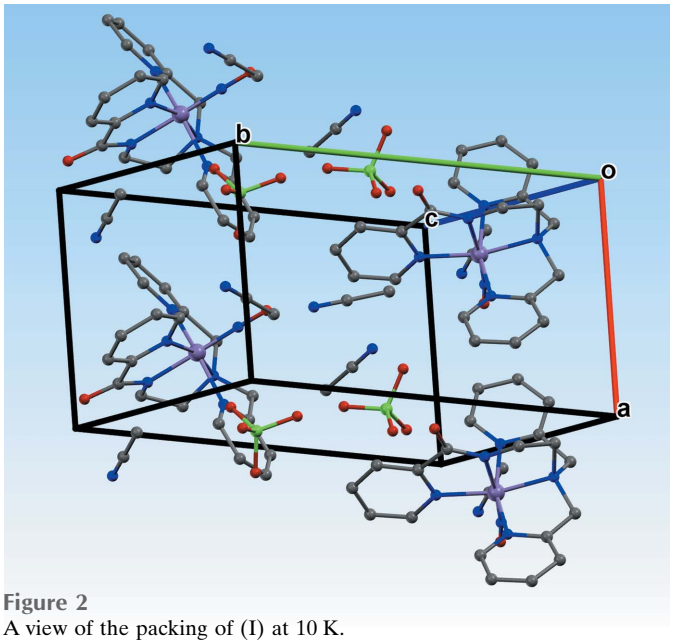


Figure 2
A view of the packing of (I) at 10 K.

rigidity and symmetrical shape. Uncorrected X-ray perchlorate distances are depicted as black circles in Fig. 3. As shown in the figure, the X-ray perchlorate Cl—O distances display a strong dependence on temperature, and the average of 1.447 Å at 10 K is almost 5σ larger than the average of 1.428 Å of the 170 K values. The displacement parameters given in Table 3 illustrate the dramatic reduction in the motion of the central Cl atom at 10 K as the symmetric group rotates around its center of mass.

Perchlorate is well known to form a Jahn–Teller type of interaction with copper(II) complexes and, in many cases, the O atom closest to copper is elongated relative to the other three, suggesting a resonance form that places a higher negative charge and greater single-bond character on the unique O atom. A significant proportion of these copper structures are disordered, however, and this observation is not conclusive. X-ray data alone, being time-averaged, cannot answer the question as to whether perchlorate has static or dynamic disorder. To further explore this issue, selected species could be examined with solid-state NMR, which has a far shorter measurement time scale (Facey *et al.*, 1996).

Two of the simplest methods to correct bond distances for libration are incorporated into crystallographic programs such as *XP* (Sheldrick, 1998) as the LIBR and RIDE commands. With the use of LIBR, librational analysis of rigid body motion is performed using the **TLS** method of Schomaker & Trueblood (1968). **TLS** analysis stands for Translation, Libration, and **S**. Translation and Libration are included as symmetric tensors. The **S** part is an additional nonsymmetric tensor that accounts for the correlation of **T** and **L**, and ensures that the corrections are independent of the assumed origin. The formalism works best when the molecule under study is a rigid body or group. Because the present crystal structure is uncomplicated by disorder and phase transitions, it provides a good case study for these effects. Results of the LIBR command are shown in Fig. 4 as red triangles. The second approach, called RIDE, is based on the method of Johnson (1970). Nearly identical results to the LIBR method are obtained with the RIDE method. Therefore, the possibility exists that the librational methods tend to over-correct in this case.

For completeness, some data for C—H bond distances are given in Table 2. The *SHELX* riding model assumes values of 0.96 Å for aromatic groups, 0.99 Å for secondary groups, and 0.98 Å for methyl groups at all of these temperatures. I quote from the *SHELX* listing file: 'Note that these distances are chosen to give the best fit to the X-ray data and so avoid the introduction of systematic error. The true internuclear distances are longer and do not vary with temperature! The apparent variation with temperature is caused by libration.'

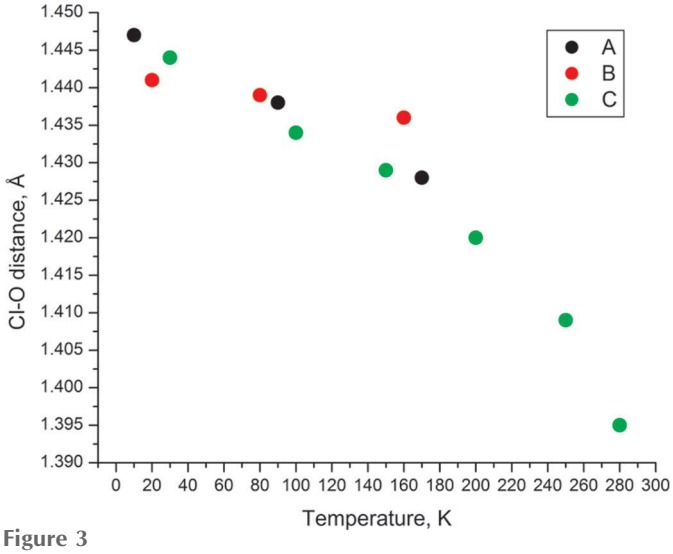


Figure 3
A comparison of uncorrected Cl—O distances in this work (**A**), neutron distances (McMullan *et al.*, 1997) (**B**), and X-ray distances (Bartual-Murgui *et al.*, 2018) (**C**).

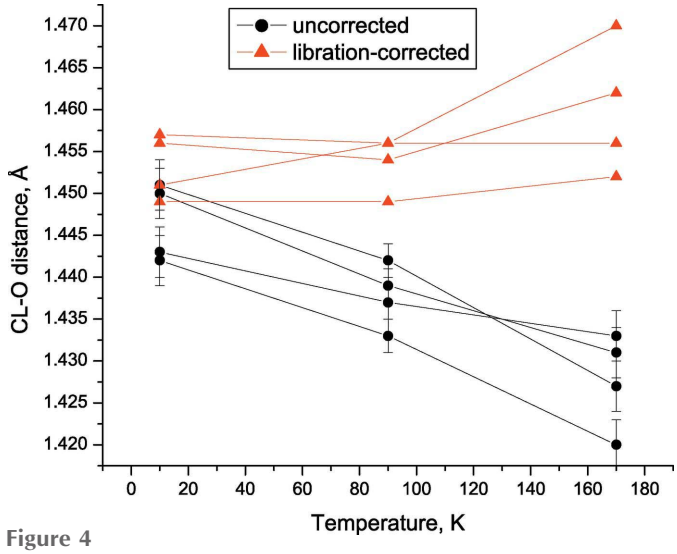


Figure 4
Changes in the four Cl—O distances of the perchlorate anion at different temperatures, as observed by X-ray and by use of the **TLS** method (Schomaker & Trueblood, 1968).

The neutron diffraction results for perchlorate display a weaker temperature dependence than the X-ray results, although we could only find one similar neutron temperature study (McMullan *et al.*, 1997). In this study, one of the O atoms is in closer proximity to a silver ion, and the more distant O atom is quoted here. Results for this variable-temperature study are: 1.441 (1) at 18 K, 1.439 (1) at 78 K, and 1.436 (1) Å at 158 K. A search of the Cambridge Structural Database (Groom *et al.*, 2016*; Conquest*, Version 2.0.1) for X-ray diffraction studies of perchlorate distances in the temperature range 283–303 K having no disorder or errors, powder data excluded, and with an R_1 value < 5%, yielded 3138 hits and a mean distance of 1.405 Å; in the range 160–180 K, gave 845 entries with a mean value of 1.426 Å; and in the range 80–100 K, gave 1217 entries with a mean value of 1.436 Å. An extensive synchrotron X-ray investigation into a spin-crossover solid produced data at temperatures ranging between 30 and 360 K with four perchlorate anions (Bartual-Murgui *et al.*, 2018). The two iron complexes in the crystal have H-atom donors and it is apparent that the O-atom acceptors have slightly longer Cl—O bonds. In addition, there is a loss of acetone solvent and an irreversible phase transition at higher temperatures. With the omission of the hydrogen-bonded Cl—O groups, comparative data for the available range are plotted in Fig. 3. A density functional theory (DFT) (*GAUSSIAN03*; Frisch *et al.*, 2009) value of 1.442 Å is computed for the Cl—O bond distance (Guzei, 2019).

4. Conclusions

In many crystal structure determinations, the most difficult and annoying challenges for the crystallographer pertain to complex disorder, especially in anions and solvent molecules. Treatment of these challenges relies on various tools, such as constraints, restraints, and rigid-group assignments in the refinement (Müller *et al.*, 2006). In order to apply these tools, assumptions are made about the expected values for bond distances based on the sums of covalent radii, statistics obtained from the CSD or other compendiums, or computational results. How important are these assumptions to the outcome of the crystallographic work? In fact, in *SHELXL*, assumptions about the distances for H atoms connected to their parent main group atom are adjusted to the temperature of the data collection but are far from the neutron values. The reason this is adopted is that it represents X-ray-obtained values and leads to convergence of the refinement without any adverse effects. It might also be argued that the exact choice of initial bond distance for the bonds involving non-H atoms in disordered groups is irrelevant. In many cases, this is true. But it is also true that 'short cuts make long delays' (J. R. R. Tolkien). Thus, the decision should consider the usefulness of the bond-distance information, its compatibility with X-ray data, and not necessarily what is 'real.' That is, we must be cognizant of the relationship between internuclear distances, temperature, and X-ray-obtained bond distances. By extrapolation of the information given in Table 2 and Fig. 4, useful starting parameters for the modeling of the disorder of the perchlorate group may be obtained.

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supporting information

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Bond length of perchlorate at different temperatures: X-ray and neutron comparison

Marilyn M. Olmstead

Computing details

For all structures, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: **[Program(s) used to create the graphics?]**; software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015).

(*N*-{2-[Bis(pyridin-2-ylmethyl)amino]ethyl}pyridine-2-carboxamidato)(nitric oxide)manganese perchlorate acetonitrile disolvate (mn1484)

Crystal data

$[Mn(C_{20}H_{20}N_5O)(NO)]ClO_4 \cdot 2C_2H_3N$
$M_r = 612.92$
Monoclinic, $P2_1$
$a = 8.2608$ (8) Å
$b = 14.0676$ (13) Å
$c = 11.5967$ (11) Å
$\beta = 97.9839$ (16)°
$V = 1334.6$ (2) Å^3
$Z = 2$
$F(000) = 632$
$D_x = 1.525$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5593 reflections
$\theta = 2.3$–27.5°
$\mu = 0.65$ mm^{-1}
$T = 10$ K
Plate, brown
0.31 × 0.20 × 0.08 mm

Data collection

Bruker SMART 1000 diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2016)
$T_{min} = 0.619$, $T_{max} = 0.746$
8724 measured reflections
5857 independent reflections
5599 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
$h = -10 \rightarrow 8$
$k = -18 \rightarrow 16$
$l = -15 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 1.04$
5857 reflections
449 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Absolute structure: Flack *x* determined using 2435 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.025 (13)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.68327 (5)	0.74947 (3)	0.80016 (4)	0.00573 (12)
O2	0.5315 (3)	0.64825 (18)	0.6012 (2)	0.0116 (5)
N6	0.5891 (3)	0.6863 (2)	0.6898 (2)	0.0075 (5)
O1	0.8821 (3)	0.98745 (18)	0.9641 (2)	0.0124 (5)
N1	0.6714 (3)	0.8728 (2)	0.7142 (2)	0.0077 (5)
N2	0.7970 (3)	0.8328 (2)	0.9199 (2)	0.0081 (6)
N3	0.7398 (3)	0.6480 (2)	0.9234 (2)	0.0066 (5)
N4	0.9030 (3)	0.7071 (2)	0.7575 (2)	0.0074 (5)
N5	0.4886 (3)	0.76819 (19)	0.8859 (2)	0.0083 (6)
C1	0.5980 (4)	0.8892 (2)	0.6042 (3)	0.0096 (6)
H1	0.542 (5)	0.837 (3)	0.566 (4)	0.014 (11)*
C2	0.6075 (4)	0.9767 (2)	0.5503 (3)	0.0113 (7)
H2	0.552 (5)	0.985 (3)	0.475 (4)	0.011 (10)*
C3	0.6961 (4)	1.0501 (3)	0.6090 (3)	0.0117 (7)
H3	0.696 (5)	1.113 (3)	0.571 (4)	0.010 (10)*
C4	0.7705 (4)	1.0338 (3)	0.7221 (3)	0.0098 (6)
H4	0.820 (5)	1.076 (3)	0.766 (4)	0.008 (10)*
C5	0.7546 (4)	0.9460 (2)	0.7722 (3)	0.0079 (6)
C6	0.8206 (4)	0.9239 (2)	0.8971 (3)	0.0083 (6)
C7	0.8236 (4)	0.7948 (2)	1.0374 (3)	0.0085 (6)
H7A	0.723 (5)	0.801 (3)	1.077 (4)	0.013 (10)*
H7B	0.907 (5)	0.827 (3)	1.084 (3)	0.006 (9)*
C8	0.8545 (4)	0.6892 (3)	1.0245 (3)	0.0087 (6)
H8A	0.959 (5)	0.679 (3)	1.007 (4)	0.014 (10)*
H8B	0.837 (5)	0.653 (3)	1.099 (4)	0.013 (10)*
C9	0.8255 (4)	0.5719 (2)	0.8670 (3)	0.0083 (7)
H9A	0.752 (5)	0.538 (3)	0.819 (3)	0.004 (9)*
H9B	0.876 (5)	0.530 (3)	0.926 (3)	0.001 (9)*
C10	0.9463 (4)	0.6198 (2)	0.7994 (3)	0.0082 (6)
C11	1.0924 (4)	0.5772 (2)	0.7805 (3)	0.0088 (6)
H11	1.128 (6)	0.516 (4)	0.812 (4)	0.023 (12)*
C12	1.1944 (4)	0.6256 (2)	0.7149 (3)	0.0096 (6)
H12	1.296 (5)	0.599 (3)	0.696 (3)	0.003 (9)*
C13	1.1497 (4)	0.7152 (2)	0.6721 (3)	0.0101 (6)
H13	1.218 (5)	0.757 (4)	0.626 (4)	0.024 (12)*

C14	1.0036 (4)	0.7548 (3)	0.6958 (3)	0.0080 (6)
H14	0.964 (4)	0.813 (3)	0.665 (3)	0.003 (9)*
C15	0.5837 (4)	0.6148 (2)	0.9605 (3)	0.0089 (6)
H15A	0.601 (5)	0.583 (3)	1.033 (4)	0.007 (10)*
H15B	0.530 (5)	0.577 (3)	0.900 (3)	0.004 (9)*
C16	0.4721 (4)	0.6990 (2)	0.9647 (3)	0.0089 (6)
C17	0.3587 (4)	0.7060 (3)	1.0423 (3)	0.0117 (7)
H17	0.345 (5)	0.655 (3)	1.094 (4)	0.009 (10)*
C18	0.2589 (4)	0.7855 (3)	1.0384 (3)	0.0124 (7)
H18	0.191 (5)	0.788 (3)	1.099 (4)	0.018 (11)*
C19	0.2724 (4)	0.8551 (3)	0.9553 (3)	0.0121 (7)
H19	0.221 (6)	0.904 (4)	0.953 (4)	0.022 (13)*
C20	0.3893 (4)	0.8443 (2)	0.8812 (3)	0.0094 (6)
H20	0.405 (5)	0.889 (3)	0.829 (3)	0.004 (9)*
N7	0.5476 (4)	0.9372 (2)	0.2361 (3)	0.0161 (6)
C21	0.5790 (4)	0.8632 (3)	0.2731 (3)	0.0121 (7)
C22	0.6210 (4)	0.7681 (2)	0.3197 (3)	0.0149 (8)
H22A	0.530135	0.742934	0.356548	0.020 (11)*
H22B	0.719266	0.771933	0.377599	0.040 (15)*
H22C	0.641831	0.725819	0.256225	0.026 (13)*
N8	0.7443 (4)	0.5341 (2)	0.2575 (3)	0.0206 (7)
C23	0.8040 (4)	0.5465 (3)	0.3508 (3)	0.0137 (7)
C24	0.8792 (5)	0.5645 (3)	0.4709 (3)	0.0171 (8)
H24A	0.956298	0.513272	0.496513	0.042 (16)*
H24B	0.794035	0.566895	0.521810	0.014 (11)*
H24C	0.937575	0.625296	0.474599	0.052 (18)*
Cl1	1.11161 (9)	0.81806 (5)	0.36019 (6)	0.00814 (16)
O3	1.2703 (3)	0.79664 (19)	0.4254 (2)	0.0148 (5)
O4	0.9992 (3)	0.84442 (18)	0.4403 (2)	0.0140 (5)
O5	1.1270 (3)	0.89504 (17)	0.2803 (2)	0.0145 (5)
O6	1.0502 (3)	0.73482 (17)	0.2958 (2)	0.0146 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0054 (2)	0.0055 (2)	0.0061 (2)	−0.00028 (18)	0.00032 (15)	−0.00045 (19)
O2	0.0123 (11)	0.0133 (12)	0.0087 (11)	−0.0028 (10)	0.0002 (9)	−0.0046 (10)
N6	0.0073 (13)	0.0063 (13)	0.0096 (13)	−0.0006 (10)	0.0034 (10)	0.0015 (10)
O1	0.0152 (12)	0.0111 (12)	0.0104 (12)	−0.0025 (10)	0.0001 (9)	−0.0021 (10)
N1	0.0081 (12)	0.0074 (13)	0.0075 (13)	0.0014 (11)	0.0013 (10)	−0.0018 (10)
N2	0.0076 (13)	0.0083 (14)	0.0081 (13)	−0.0009 (11)	0.0000 (10)	−0.0004 (11)
N3	0.0065 (12)	0.0062 (13)	0.0072 (13)	−0.0001 (10)	0.0013 (10)	−0.0004 (10)
N4	0.0063 (12)	0.0078 (13)	0.0080 (13)	0.0002 (10)	0.0010 (10)	−0.0012 (11)
N5	0.0079 (12)	0.0079 (15)	0.0086 (12)	−0.0003 (10)	−0.0001 (10)	−0.0031 (10)
C1	0.0099 (15)	0.0105 (16)	0.0082 (15)	0.0016 (13)	0.0007 (12)	−0.0006 (13)
C2	0.0123 (15)	0.0120 (17)	0.0090 (15)	0.0039 (13)	−0.0005 (12)	0.0021 (13)
C3	0.0134 (16)	0.0100 (16)	0.0124 (16)	0.0025 (13)	0.0047 (13)	0.0025 (13)
C4	0.0101 (14)	0.0097 (16)	0.0101 (15)	−0.0007 (13)	0.0037 (12)	−0.0011 (12)

C5	0.0060 (14)	0.0093 (16)	0.0085 (15)	0.0015 (12)	0.0015 (12)	−0.0021 (12)
C6	0.0064 (14)	0.0094 (15)	0.0092 (16)	0.0013 (12)	0.0010 (12)	−0.0009 (12)
C7	0.0074 (15)	0.0117 (17)	0.0061 (15)	−0.0006 (13)	0.0005 (12)	−0.0005 (12)
C8	0.0066 (15)	0.0105 (16)	0.0087 (15)	−0.0005 (12)	0.0004 (12)	0.0023 (13)
C9	0.0086 (15)	0.0080 (16)	0.0090 (16)	0.0005 (13)	0.0036 (13)	0.0009 (13)
C10	0.0098 (15)	0.0072 (15)	0.0077 (15)	−0.0017 (12)	0.0016 (11)	−0.0014 (12)
C11	0.0091 (15)	0.0073 (16)	0.0094 (16)	0.0010 (12)	−0.0007 (12)	−0.0003 (12)
C12	0.0065 (14)	0.0130 (17)	0.0094 (15)	−0.0003 (13)	0.0017 (12)	−0.0010 (13)
C13	0.0085 (15)	0.0135 (16)	0.0089 (15)	−0.0023 (13)	0.0029 (12)	0.0012 (13)
C14	0.0083 (13)	0.0081 (14)	0.0071 (13)	−0.0009 (14)	−0.0004 (10)	−0.0011 (14)
C15	0.0075 (14)	0.0089 (16)	0.0105 (16)	−0.0020 (12)	0.0021 (12)	−0.0005 (13)
C16	0.0081 (15)	0.0092 (16)	0.0090 (15)	−0.0028 (13)	−0.0006 (12)	−0.0014 (12)
C17	0.0109 (15)	0.0141 (17)	0.0106 (16)	−0.0024 (13)	0.0032 (12)	0.0005 (13)
C18	0.0092 (15)	0.0155 (16)	0.0131 (16)	−0.0031 (13)	0.0039 (13)	−0.0077 (13)
C19	0.0085 (15)	0.0119 (17)	0.0155 (17)	0.0025 (13)	−0.0002 (13)	−0.0056 (13)
C20	0.0071 (15)	0.0100 (16)	0.0106 (15)	0.0007 (12)	−0.0005 (12)	−0.0018 (13)
N7	0.0177 (15)	0.0156 (16)	0.0148 (15)	−0.0019 (13)	0.0014 (12)	0.0010 (13)
C21	0.0107 (15)	0.0153 (18)	0.0103 (15)	−0.0019 (13)	0.0021 (12)	−0.0017 (13)
C22	0.0141 (16)	0.015 (2)	0.0162 (17)	0.0031 (13)	0.0038 (13)	0.0012 (13)
N8	0.0302 (18)	0.0160 (16)	0.0148 (16)	−0.0082 (15)	0.0005 (13)	0.0011 (13)
C23	0.0164 (17)	0.0097 (17)	0.0156 (18)	0.0006 (14)	0.0041 (14)	0.0018 (13)
C24	0.0192 (18)	0.019 (2)	0.0124 (17)	−0.0007 (15)	−0.0002 (14)	−0.0003 (14)
Cl1	0.0091 (3)	0.0080 (4)	0.0075 (3)	0.0003 (3)	0.0018 (3)	0.0004 (3)
O3	0.0104 (11)	0.0217 (14)	0.0118 (11)	0.0009 (10)	−0.0004 (9)	0.0013 (10)
O4	0.0127 (12)	0.0180 (13)	0.0123 (12)	0.0011 (10)	0.0056 (9)	−0.0024 (10)
O5	0.0184 (12)	0.0109 (12)	0.0153 (12)	0.0003 (10)	0.0062 (10)	0.0064 (10)
O6	0.0187 (12)	0.0084 (13)	0.0160 (12)	−0.0011 (10)	0.0004 (9)	−0.0049 (10)

Geometric parameters (Å, º)

Mn1—N6	1.660 (3)	C9—H9B	0.95 (4)
Mn1—N2	1.955 (3)	C10—C11	1.391 (5)
Mn1—N1	1.997 (3)	C11—C12	1.390 (5)
Mn1—N5	2.022 (3)	C11—H11	0.97 (5)
Mn1—N3	2.028 (3)	C12—C13	1.386 (5)
Mn1—N4	2.036 (3)	C12—H12	0.97 (4)
O2—N6	1.197 (4)	C13—C14	1.391 (4)
O1—C6	1.246 (4)	C13—H13	1.02 (5)
N1—C1	1.354 (4)	C14—H14	0.94 (4)
N1—C5	1.363 (4)	C15—C16	1.506 (5)
N2—C6	1.328 (5)	C15—H15A	0.95 (4)
N2—C7	1.453 (4)	C15—H15B	0.94 (4)
N3—C9	1.484 (4)	C16—C17	1.389 (5)
N3—C15	1.490 (4)	C17—C18	1.387 (5)
N3—C8	1.516 (4)	C17—H17	0.95 (4)
N4—C14	1.349 (4)	C18—C19	1.389 (5)
N4—C10	1.351 (4)	C18—H18	0.96 (5)
N5—C20	1.345 (4)	C19—C20	1.387 (5)

N5—C16	1.354 (4)	C19—H19	0.80 (5)
C1—C2	1.387 (5)	C20—H20	0.90 (4)
C1—H1	0.95 (4)	N7—C21	1.141 (5)
C2—C3	1.389 (5)	C21—C22	1.467 (5)
C2—H2	0.93 (4)	C22—H22A	0.9800
C3—C4	1.387 (5)	C22—H22B	0.9800
C3—H3	0.98 (4)	C22—H22C	0.9800
C4—C5	1.379 (5)	N8—C23	1.139 (5)
C4—H4	0.85 (4)	C23—C24	1.465 (5)
C5—C6	1.508 (5)	C24—H24A	0.9800
C7—C8	1.519 (5)	C24—H24B	0.9800
C7—H7A	1.01 (4)	C24—H24C	0.9800
C7—H7B	0.93 (4)	Cl1—O5	1.442 (2)
C8—H8A	0.93 (4)	Cl1—O6	1.442 (2)
C8—H8B	1.03 (4)	Cl1—O4	1.450 (2)
C9—C10	1.511 (5)	Cl1—O3	1.451 (2)
C9—H9A	0.90 (4)		

N6—Mn1—N2	174.82 (13)	H8A—C8—H8B	111 (3)
N6—Mn1—N1	95.45 (12)	N3—C9—C10	107.3 (3)
N2—Mn1—N1	79.57 (11)	N3—C9—H9A	109 (2)
N6—Mn1—N5	97.42 (12)	C10—C9—H9A	111 (2)
N2—Mn1—N5	84.79 (11)	N3—C9—H9B	109 (2)
N1—Mn1—N5	98.36 (11)	C10—C9—H9B	113 (2)
N6—Mn1—N3	101.77 (13)	H9A—C9—H9B	107 (3)
N2—Mn1—N3	83.15 (11)	N4—C10—C11	121.8 (3)
N1—Mn1—N3	162.56 (11)	N4—C10—C9	115.5 (3)
N5—Mn1—N3	82.31 (11)	C11—C10—C9	122.7 (3)
N6—Mn1—N4	89.66 (12)	C12—C11—C10	118.7 (3)
N2—Mn1—N4	89.52 (11)	C12—C11—H11	118 (3)
N1—Mn1—N4	96.69 (11)	C10—C11—H11	123 (3)
N5—Mn1—N4	162.66 (11)	C13—C12—C11	119.4 (3)
N3—Mn1—N4	80.76 (11)	C13—C12—H12	118 (2)
O2—N6—Mn1	171.4 (3)	C11—C12—H12	123 (2)
C1—N1—C5	117.7 (3)	C12—C13—C14	119.3 (3)
C1—N1—Mn1	127.1 (2)	C12—C13—H13	125 (3)
C5—N1—Mn1	115.1 (2)	C14—C13—H13	115 (3)
C6—N2—C7	122.3 (3)	N4—C14—C13	121.4 (3)
C6—N2—Mn1	120.5 (2)	N4—C14—H14	115 (2)
C7—N2—Mn1	116.2 (2)	C13—C14—H14	123 (2)
C9—N3—C15	112.7 (3)	N3—C15—C16	108.7 (3)
C9—N3—C8	109.3 (3)	N3—C15—H15A	112 (2)
C15—N3—C8	111.7 (3)	C16—C15—H15A	112 (2)
C9—N3—Mn1	105.9 (2)	N3—C15—H15B	107 (2)
C15—N3—Mn1	107.5 (2)	C16—C15—H15B	104 (2)
C8—N3—Mn1	109.5 (2)	H15A—C15—H15B	113 (3)
C14—N4—C10	119.4 (3)	N5—C16—C17	121.8 (3)
C14—N4—Mn1	128.3 (2)	N5—C16—C15	115.1 (3)

C10—N4—Mn1	112.3 (2)	C17—C16—C15	123.1 (3)
C20—N5—C16	118.8 (3)	C18—C17—C16	119.1 (3)
C20—N5—Mn1	127.3 (2)	C18—C17—H17	120 (2)
C16—N5—Mn1	113.6 (2)	C16—C17—H17	121 (2)
N1—C1—C2	122.0 (3)	C17—C18—C19	119.1 (3)
N1—C1—H1	115 (3)	C17—C18—H18	114 (3)
C2—C1—H1	123 (3)	C19—C18—H18	126 (3)
C1—C2—C3	119.8 (3)	C20—C19—C18	118.9 (3)
C1—C2—H2	118 (3)	C20—C19—H19	119 (4)
C3—C2—H2	122 (3)	C18—C19—H19	122 (3)
C4—C3—C2	118.3 (3)	N5—C20—C19	122.3 (3)
C4—C3—H3	123 (2)	N5—C20—H20	116 (3)
C2—C3—H3	119 (2)	C19—C20—H20	122 (3)
C5—C4—C3	119.4 (3)	N7—C21—C22	179.3 (4)
C5—C4—H4	116 (3)	C21—C22—H22A	109.5
C3—C4—H4	124 (3)	C21—C22—H22B	109.5
N1—C5—C4	122.6 (3)	H22A—C22—H22B	109.5
N1—C5—C6	114.1 (3)	C21—C22—H22C	109.5
C4—C5—C6	123.2 (3)	H22A—C22—H22C	109.5
O1—C6—N2	128.9 (3)	H22B—C22—H22C	109.5
O1—C6—C5	120.8 (3)	N8—C23—C24	178.8 (4)
N2—C6—C5	110.3 (3)	C23—C24—H24A	109.5
N2—C7—C8	105.8 (3)	C23—C24—H24B	109.5
N2—C7—H7A	112 (2)	H24A—C24—H24B	109.5
C8—C7—H7A	107 (2)	C23—C24—H24C	109.5
N2—C7—H7B	111 (2)	H24A—C24—H24C	109.5
C8—C7—H7B	114 (2)	H24B—C24—H24C	109.5
H7A—C7—H7B	107 (3)	O5—Cl1—O6	109.46 (15)
N3—C8—C7	110.8 (3)	O5—Cl1—O4	109.92 (15)
N3—C8—H8A	106 (3)	O6—Cl1—O4	109.19 (15)
C7—C8—H8A	110 (3)	O5—Cl1—O3	109.69 (16)
N3—C8—H8B	109 (2)	O6—Cl1—O3	109.18 (15)
C7—C8—H8B	111 (2)	O4—Cl1—O3	109.38 (15)

C5—N1—C1—C2	0.8 (5)	Mn1—N4—C10—C11	−179.8 (3)
Mn1—N1—C1—C2	−175.3 (2)	C14—N4—C10—C9	−179.9 (3)
N1—C1—C2—C3	0.8 (5)	Mn1—N4—C10—C9	0.5 (4)
C1—C2—C3—C4	−1.3 (5)	N3—C9—C10—N4	−30.3 (4)
C2—C3—C4—C5	0.0 (5)	N3—C9—C10—C11	150.0 (3)
C1—N1—C5—C4	−2.1 (5)	N4—C10—C11—C12	−1.2 (5)
Mn1—N1—C5—C4	174.5 (2)	C9—C10—C11—C12	178.5 (3)
C1—N1—C5—C6	175.3 (3)	C10—C11—C12—C13	1.3 (5)
Mn1—N1—C5—C6	−8.1 (3)	C11—C12—C13—C14	−0.1 (5)
C3—C4—C5—N1	1.7 (5)	C10—N4—C14—C13	1.4 (5)
C3—C4—C5—C6	−175.5 (3)	Mn1—N4—C14—C13	−178.9 (2)
C7—N2—C6—O1	8.1 (5)	C12—C13—C14—N4	−1.3 (5)
Mn1—N2—C6—O1	175.8 (3)	C9—N3—C15—C16	−154.6 (3)
C7—N2—C6—C5	−169.7 (3)	C8—N3—C15—C16	81.9 (3)

Mn1—N2—C6—C5	−2.0 (4)	Mn1—N3—C15—C16	−38.2 (3)
N1—C5—C6—O1	−171.5 (3)	C20—N5—C16—C17	−1.7 (5)
C4—C5—C6—O1	5.9 (5)	Mn1—N5—C16—C17	171.6 (3)
N1—C5—C6—N2	6.5 (4)	C20—N5—C16—C15	177.7 (3)
C4—C5—C6—N2	−176.1 (3)	Mn1—N5—C16—C15	−9.0 (3)
C6—N2—C7—C8	−156.8 (3)	N3—C15—C16—N5	31.9 (4)
Mn1—N2—C7—C8	35.1 (3)	N3—C15—C16—C17	−148.7 (3)
C9—N3—C8—C7	145.7 (3)	N5—C16—C17—C18	0.5 (5)
C15—N3—C8—C7	−88.9 (3)	C15—C16—C17—C18	−178.9 (3)
Mn1—N3—C8—C7	30.0 (3)	C16—C17—C18—C19	1.5 (5)
N2—C7—C8—N3	−41.0 (3)	C17—C18—C19—C20	−2.2 (5)
C15—N3—C9—C10	161.6 (3)	C16—N5—C20—C19	0.9 (5)
C8—N3—C9—C10	−73.6 (3)	Mn1—N5—C20—C19	−171.3 (2)
Mn1—N3—C9—C10	44.3 (3)	C18—C19—C20—N5	1.0 (5)
C14—N4—C10—C11	−0.1 (5)		

(*N*-{2-[Bis(pyridin-2-ylmethyl)amino]ethyl}pyridine-2-carboxamidato)(nitric oxide)manganese perchlorate acetonitrile disolvate (mn1485)

Crystal data

$[Mn(C_{20}H_{20}N_5O)(NO)]ClO_4·2C_2H_3N$
M_r = 612.92
Monoclinic, $P2_1$
a = 8.2788 (3) Å
b = 14.0816 (6) Å
c = 11.6343 (5) Å
β = 98.0814 (7)°
V = 1342.84 (9) Å^3
Z = 2
$F(000)$ = 632
D_x = 1.516 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7957 reflections
θ = 2.3–27.5°
μ = 0.65 mm^{-1}
T = 90 K
Plate, brown
0.31 × 0.20 × 0.08 mm

Data collection

Bruker SMART 1000 diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2016)
T_{min} = 0.662, T_{max} = 0.746
15371 measured reflections
6074 independent reflections
5824 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 27.5°, θ_{min} = 2.3°
h = −10→10
k = −17→18
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.061
S = 1.03
6074 reflections
449 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.2616P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack x determined using 2614 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.022 (7)

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}
Mn1	0.68276 (4)	0.74940 (2)	0.80043 (3)	0.00938 (8)
O2	0.5306 (2)	0.64769 (14)	0.60312 (16)	0.0193 (4)
N6	0.5883 (3)	0.68650 (15)	0.69055 (17)	0.0117 (4)
O1	0.8820 (3)	0.98685 (14)	0.96358 (16)	0.0213 (4)
N1	0.6709 (3)	0.87253 (15)	0.71482 (17)	0.0122 (4)
N2	0.7966 (3)	0.83284 (15)	0.91955 (17)	0.0116 (4)
N3	0.7397 (3)	0.64809 (15)	0.92347 (17)	0.0107 (4)
N4	0.9015 (3)	0.70720 (15)	0.75761 (17)	0.0111 (4)
N5	0.4881 (2)	0.76798 (14)	0.88584 (17)	0.0132 (5)
C1	0.5971 (3)	0.88918 (19)	0.6055 (2)	0.0158 (5)
H1	0.538 (4)	0.840 (2)	0.569 (3)	0.019 (8)*
C2	0.6060 (4)	0.9762 (2)	0.5515 (2)	0.0203 (6)
H2	0.555 (4)	0.983 (3)	0.477 (3)	0.029 (9)*
C3	0.6954 (4)	1.0495 (2)	0.6094 (2)	0.0200 (6)
H3	0.703 (4)	1.108 (2)	0.572 (3)	0.014 (7)*
C4	0.7694 (3)	1.0333 (2)	0.7222 (2)	0.0159 (5)
H4	0.822 (4)	1.075 (2)	0.764 (3)	0.020 (8)*
C5	0.7540 (3)	0.94599 (18)	0.7725 (2)	0.0128 (5)
C6	0.8201 (3)	0.92345 (19)	0.8969 (2)	0.0130 (5)
C7	0.8235 (3)	0.79473 (19)	1.0369 (2)	0.0137 (5)
H7A	0.727 (4)	0.803 (2)	1.072 (3)	0.015 (7)*
H7B	0.910 (4)	0.827 (2)	1.083 (3)	0.013 (7)*
C8	0.8536 (3)	0.6895 (2)	1.0246 (2)	0.0139 (5)
H8A	0.966 (4)	0.681 (3)	1.007 (3)	0.025 (8)*
H8B	0.850 (4)	0.655 (2)	1.098 (3)	0.019 (8)*
C9	0.8253 (3)	0.57213 (19)	0.8671 (2)	0.0135 (5)
H9A	0.754 (4)	0.539 (2)	0.817 (3)	0.016 (8)*
H9B	0.878 (3)	0.530 (2)	0.925 (2)	0.005 (6)*
C10	0.9456 (3)	0.61986 (18)	0.7992 (2)	0.0121 (5)
C11	1.0909 (3)	0.57742 (19)	0.7807 (2)	0.0151 (5)
H11	1.121 (4)	0.521 (3)	0.811 (3)	0.019 (8)*
C12	1.1917 (3)	0.6256 (2)	0.7150 (2)	0.0164 (5)
H12	1.290 (4)	0.600 (2)	0.698 (3)	0.019 (8)*
C13	1.1473 (3)	0.7149 (2)	0.6722 (2)	0.0164 (5)
H13	1.209 (4)	0.752 (3)	0.631 (3)	0.022 (7)*
C14	1.0017 (3)	0.7544 (2)	0.69555 (19)	0.0137 (4)
H14	0.962 (3)	0.814 (2)	0.665 (2)	0.008 (7)*
C15	0.5838 (3)	0.61521 (19)	0.9600 (2)	0.0143 (5)
H15A	0.602 (4)	0.584 (2)	1.033 (3)	0.017 (8)*

H15B	0.534 (4)	0.577 (2)	0.897 (3)	0.013 (7)*
C16	0.4719 (3)	0.69907 (19)	0.9638 (2)	0.0144 (5)
C17	0.3590 (3)	0.7055 (2)	1.0410 (2)	0.0205 (6)
H17	0.345 (4)	0.655 (2)	1.093 (3)	0.017 (8)*
C18	0.2595 (4)	0.7849 (2)	1.0370 (3)	0.0234 (6)
H18	0.191 (5)	0.793 (3)	1.092 (3)	0.037 (10)*
C19	0.2722 (3)	0.8545 (2)	0.9543 (2)	0.0206 (6)
H19	0.206 (4)	0.907 (3)	0.948 (3)	0.029 (9)*
C20	0.3889 (3)	0.84399 (19)	0.8811 (2)	0.0164 (5)
H20	0.404 (3)	0.889 (2)	0.831 (2)	0.008 (7)*
N7	0.5493 (3)	0.9375 (2)	0.2356 (2)	0.0305 (6)
C21	0.5796 (3)	0.8638 (2)	0.2724 (2)	0.0205 (6)
C22	0.6198 (4)	0.7690 (2)	0.3190 (3)	0.0270 (7)
H22A	0.529299	0.744881	0.356593	0.055 (11)*
H22B	0.718796	0.772250	0.375998	0.059 (13)*
H22C	0.638354	0.726260	0.255655	0.044 (11)*
N8	0.7420 (4)	0.5345 (2)	0.2587 (2)	0.0409 (8)
C23	0.8020 (4)	0.5464 (2)	0.3510 (3)	0.0257 (6)
C24	0.8780 (4)	0.5637 (2)	0.4698 (3)	0.0314 (7)
H24A	0.952593	0.511439	0.495528	0.067 (15)*
H24B	0.793476	0.567859	0.520732	0.067 (15)*
H24C	0.939142	0.623483	0.473203	0.061 (14)*
Cl1	1.11245 (8)	0.81844 (4)	0.36004 (5)	0.01615 (13)
O3	1.2691 (3)	0.79734 (17)	0.42600 (18)	0.0313 (5)
O4	0.9989 (3)	0.84429 (17)	0.43774 (18)	0.0299 (5)
O5	1.1274 (3)	0.89430 (16)	0.2802 (2)	0.0314 (5)
O6	1.0526 (3)	0.73529 (16)	0.29613 (19)	0.0337 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.00981 (16)	0.00902 (16)	0.00884 (15)	0.00002 (15)	−0.00028 (11)	−0.00059 (14)
O2	0.0210 (10)	0.0220 (10)	0.0143 (9)	−0.0059 (8)	0.0000 (7)	−0.0081 (8)
N6	0.0104 (10)	0.0112 (10)	0.0137 (10)	−0.0003 (8)	0.0026 (8)	0.0003 (8)
O1	0.0283 (11)	0.0168 (10)	0.0173 (9)	−0.0067 (8)	−0.0022 (8)	−0.0046 (8)
N1	0.0140 (10)	0.0118 (10)	0.0106 (9)	0.0014 (8)	0.0004 (7)	−0.0013 (8)
N2	0.0114 (10)	0.0122 (11)	0.0107 (10)	−0.0004 (8)	0.0000 (8)	−0.0011 (8)
N3	0.0102 (10)	0.0104 (10)	0.0116 (9)	0.0003 (8)	0.0015 (8)	0.0002 (8)
N4	0.0118 (10)	0.0116 (10)	0.0097 (9)	0.0000 (8)	0.0003 (7)	−0.0007 (8)
N5	0.0118 (10)	0.0140 (13)	0.0131 (9)	−0.0009 (8)	−0.0010 (7)	−0.0046 (8)
C1	0.0194 (13)	0.0141 (13)	0.0126 (12)	0.0018 (11)	−0.0020 (9)	−0.0009 (10)
C2	0.0290 (15)	0.0174 (14)	0.0134 (12)	0.0062 (11)	−0.0007 (11)	0.0022 (10)
C3	0.0283 (15)	0.0136 (13)	0.0189 (13)	0.0042 (11)	0.0059 (11)	0.0055 (10)
C4	0.0187 (13)	0.0130 (12)	0.0163 (11)	−0.0010 (10)	0.0032 (10)	−0.0017 (10)
C5	0.0126 (12)	0.0136 (12)	0.0123 (11)	−0.0003 (9)	0.0023 (9)	−0.0010 (9)
C6	0.0125 (12)	0.0142 (12)	0.0123 (12)	−0.0002 (10)	0.0011 (9)	−0.0014 (9)
C7	0.0127 (12)	0.0183 (14)	0.0096 (11)	0.0000 (10)	−0.0003 (9)	−0.0009 (9)
C8	0.0136 (13)	0.0165 (13)	0.0109 (12)	−0.0013 (10)	−0.0006 (9)	0.0032 (10)

C9	0.0136 (13)	0.0116 (13)	0.0156 (12)	0.0018 (10)	0.0039 (10)	0.0026 (10)
C10	0.0133 (12)	0.0115 (12)	0.0113 (11)	−0.0006 (9)	0.0010 (9)	−0.0006 (9)
C11	0.0148 (13)	0.0138 (13)	0.0159 (12)	0.0018 (10)	0.0000 (10)	−0.0005 (10)
C12	0.0110 (12)	0.0227 (14)	0.0154 (12)	0.0012 (10)	0.0019 (9)	−0.0024 (10)
C13	0.0151 (12)	0.0206 (13)	0.0142 (12)	−0.0055 (10)	0.0037 (10)	0.0003 (10)
C14	0.0158 (11)	0.0134 (11)	0.0117 (10)	−0.0021 (12)	0.0008 (8)	−0.0005 (11)
C15	0.0147 (12)	0.0148 (12)	0.0139 (12)	−0.0025 (10)	0.0034 (9)	0.0019 (10)
C16	0.0113 (12)	0.0166 (13)	0.0150 (12)	−0.0036 (10)	0.0001 (9)	−0.0023 (10)
C17	0.0178 (14)	0.0247 (15)	0.0200 (13)	−0.0061 (11)	0.0062 (10)	−0.0034 (11)
C18	0.0151 (13)	0.0300 (15)	0.0269 (14)	−0.0049 (11)	0.0088 (11)	−0.0131 (12)
C19	0.0133 (13)	0.0218 (14)	0.0257 (14)	0.0032 (11)	−0.0007 (10)	−0.0123 (11)
C20	0.0149 (13)	0.0151 (13)	0.0184 (12)	0.0024 (10)	−0.0004 (10)	−0.0036 (10)
N7	0.0330 (15)	0.0261 (15)	0.0312 (14)	−0.0018 (12)	0.0002 (11)	0.0009 (11)
C21	0.0192 (14)	0.0239 (15)	0.0189 (13)	−0.0025 (11)	0.0041 (10)	−0.0029 (11)
C22	0.0281 (15)	0.0280 (19)	0.0263 (14)	0.0035 (12)	0.0084 (12)	0.0022 (12)
N8	0.063 (2)	0.0290 (15)	0.0277 (15)	−0.0181 (15)	−0.0029 (14)	0.0007 (12)
C23	0.0359 (17)	0.0169 (14)	0.0243 (15)	−0.0041 (13)	0.0045 (13)	0.0018 (11)
C24	0.0365 (19)	0.0337 (19)	0.0228 (15)	−0.0005 (15)	−0.0005 (13)	−0.0036 (13)
Cl1	0.0193 (3)	0.0148 (3)	0.0146 (3)	0.0010 (2)	0.0032 (2)	0.0017 (2)
O3	0.0199 (11)	0.0460 (14)	0.0266 (11)	0.0000 (10)	−0.0009 (8)	0.0066 (10)
O4	0.0265 (11)	0.0401 (14)	0.0256 (11)	0.0025 (10)	0.0124 (9)	−0.0029 (9)
O5	0.0398 (13)	0.0232 (12)	0.0332 (12)	0.0039 (10)	0.0123 (10)	0.0139 (9)
O6	0.0419 (13)	0.0197 (13)	0.0374 (11)	0.0003 (10)	−0.0017 (10)	−0.0084 (9)

Geometric parameters (Å, º)

Mn1—N6	1.658 (2)	C9—H9B	0.95 (3)
Mn1—N2	1.955 (2)	C10—C11	1.387 (4)
Mn1—N1	1.995 (2)	C11—C12	1.385 (4)
Mn1—N5	2.026 (2)	C11—H11	0.89 (4)
Mn1—N3	2.029 (2)	C12—C13	1.383 (4)
Mn1—N4	2.033 (2)	C12—H12	0.94 (3)
O2—N6	1.193 (3)	C13—C14	1.389 (4)
O1—C6	1.245 (3)	C13—H13	0.91 (4)
N1—C1	1.352 (3)	C14—H14	0.95 (3)
N1—C5	1.365 (3)	C15—C16	1.505 (4)
N2—C6	1.323 (4)	C15—H15A	0.95 (3)
N2—C7	1.454 (3)	C15—H15B	0.96 (3)
N3—C9	1.486 (3)	C16—C17	1.387 (4)
N3—C15	1.488 (3)	C17—C18	1.385 (4)
N3—C8	1.517 (3)	C17—H17	0.95 (3)
N4—C14	1.349 (3)	C18—C19	1.387 (5)
N4—C10	1.353 (3)	C18—H18	0.92 (4)
N5—C20	1.345 (3)	C19—C20	1.383 (4)
N5—C16	1.348 (3)	C19—H19	0.92 (4)
C1—C2	1.383 (4)	C20—H20	0.89 (3)
C1—H1	0.92 (3)	N7—C21	1.138 (4)
C2—C3	1.389 (4)	C21—C22	1.462 (4)

C2—H2	0.91 (3)	C22—H22A	0.9800
C3—C4	1.387 (4)	C22—H22B	0.9800
C3—H3	0.93 (3)	C22—H22C	0.9800
C4—C5	1.375 (4)	N8—C23	1.130 (4)
C4—H4	0.85 (3)	C23—C24	1.457 (4)
C5—C6	1.507 (3)	C24—H24A	0.9800
C7—C8	1.513 (4)	C24—H24B	0.9800
C7—H7A	0.95 (3)	C24—H24C	0.9800
C7—H7B	0.95 (3)	Cl1—O5	1.432 (2)
C8—H8A	0.99 (4)	Cl1—O6	1.437 (2)
C8—H8B	0.99 (3)	Cl1—O4	1.439 (2)
C9—C10	1.513 (4)	Cl1—O3	1.442 (2)
C9—H9A	0.90 (3)		

N6—Mn1—N2	174.68 (10)	H8A—C8—H8B	105 (3)
N6—Mn1—N1	95.43 (9)	N3—C9—C10	107.5 (2)
N2—Mn1—N1	79.43 (9)	N3—C9—H9A	110 (2)
N6—Mn1—N5	97.22 (9)	C10—C9—H9A	108 (2)
N2—Mn1—N5	84.95 (9)	N3—C9—H9B	109.6 (16)
N1—Mn1—N5	98.40 (8)	C10—C9—H9B	112.0 (17)
N6—Mn1—N3	101.88 (10)	H9A—C9—H9B	109 (3)
N2—Mn1—N3	83.20 (9)	N4—C10—C11	122.2 (2)
N1—Mn1—N3	162.46 (8)	N4—C10—C9	115.2 (2)
N5—Mn1—N3	82.33 (8)	C11—C10—C9	122.6 (2)
N6—Mn1—N4	89.70 (9)	C12—C11—C10	118.5 (2)
N2—Mn1—N4	89.56 (9)	C12—C11—H11	120 (2)
N1—Mn1—N4	96.58 (8)	C10—C11—H11	122 (2)
N5—Mn1—N4	162.81 (8)	C13—C12—C11	119.6 (2)
N3—Mn1—N4	80.85 (8)	C13—C12—H12	118 (2)
O2—N6—Mn1	172.05 (19)	C11—C12—H12	123 (2)
C1—N1—C5	117.4 (2)	C12—C13—C14	119.1 (2)
C1—N1—Mn1	127.19 (18)	C12—C13—H13	125 (2)
C5—N1—Mn1	115.29 (16)	C14—C13—H13	116 (2)
C6—N2—C7	122.4 (2)	N4—C14—C13	121.6 (3)
C6—N2—Mn1	120.53 (17)	N4—C14—H14	115.5 (17)
C7—N2—Mn1	116.02 (16)	C13—C14—H14	122.7 (17)
C9—N3—C15	112.9 (2)	N3—C15—C16	109.0 (2)
C9—N3—C8	109.6 (2)	N3—C15—H15A	111.2 (19)
C15—N3—C8	111.58 (19)	C16—C15—H15A	111.1 (19)
C9—N3—Mn1	105.82 (15)	N3—C15—H15B	104.8 (18)
C15—N3—Mn1	107.19 (15)	C16—C15—H15B	105.4 (18)
C8—N3—Mn1	109.53 (16)	H15A—C15—H15B	115 (3)
C14—N4—C10	118.9 (2)	N5—C16—C17	121.9 (2)
C14—N4—Mn1	128.56 (18)	N5—C16—C15	115.2 (2)
C10—N4—Mn1	112.54 (16)	C17—C16—C15	123.0 (2)
C20—N5—C16	118.9 (2)	C18—C17—C16	118.9 (3)
C20—N5—Mn1	127.27 (18)	C18—C17—H17	119.9 (19)
C16—N5—Mn1	113.48 (17)	C16—C17—H17	121.1 (19)

N1—C1—C2	122.4 (3)	C17—C18—C19	119.4 (3)
N1—C1—H1	117 (2)	C17—C18—H18	120 (2)
C2—C1—H1	121 (2)	C19—C18—H18	121 (2)
C1—C2—C3	119.8 (2)	C20—C19—C18	118.6 (3)
C1—C2—H2	119 (2)	C20—C19—H19	120 (2)
C3—C2—H2	121 (2)	C18—C19—H19	121 (2)
C4—C3—C2	118.1 (3)	N5—C20—C19	122.3 (3)
C4—C3—H3	122.3 (19)	N5—C20—H20	117.5 (19)
C2—C3—H3	119.6 (19)	C19—C20—H20	120.1 (19)
C5—C4—C3	119.6 (3)	N7—C21—C22	179.4 (3)
C5—C4—H4	116 (2)	C21—C22—H22A	109.5
C3—C4—H4	124 (2)	C21—C22—H22B	109.5
N1—C5—C4	122.6 (2)	H22A—C22—H22B	109.5
N1—C5—C6	113.7 (2)	C21—C22—H22C	109.5
C4—C5—C6	123.6 (2)	H22A—C22—H22C	109.5
O1—C6—N2	128.8 (2)	H22B—C22—H22C	109.5
O1—C6—C5	120.6 (2)	N8—C23—C24	178.8 (4)
N2—C6—C5	110.5 (2)	C23—C24—H24A	109.5
N2—C7—C8	106.2 (2)	C23—C24—H24B	109.5
N2—C7—H7A	109.2 (18)	H24A—C24—H24B	109.5
C8—C7—H7A	109.0 (19)	C23—C24—H24C	109.5
N2—C7—H7B	111.1 (18)	H24A—C24—H24C	109.5
C8—C7—H7B	113.7 (19)	H24B—C24—H24C	109.5
H7A—C7—H7B	108 (3)	O5—Cl1—O6	109.09 (14)
C7—C8—N3	110.9 (2)	O5—Cl1—O4	110.02 (14)
C7—C8—H8A	108 (2)	O6—Cl1—O4	108.84 (14)
N3—C8—H8A	106.8 (19)	O5—Cl1—O3	110.21 (14)
C7—C8—H8B	112.3 (18)	O6—Cl1—O3	109.05 (14)
N3—C8—H8B	112.7 (19)	O4—Cl1—O3	109.61 (13)

C5—N1—C1—C2	1.1 (4)	Mn1—N4—C10—C11	−179.68 (19)
Mn1—N1—C1—C2	−175.4 (2)	C14—N4—C10—C9	−179.6 (2)
N1—C1—C2—C3	1.0 (4)	Mn1—N4—C10—C9	0.3 (3)
C1—C2—C3—C4	−1.9 (4)	N3—C9—C10—N4	−30.1 (3)
C2—C3—C4—C5	0.7 (4)	N3—C9—C10—C11	149.9 (2)
C1—N1—C5—C4	−2.4 (4)	N4—C10—C11—C12	−1.5 (4)
Mn1—N1—C5—C4	174.5 (2)	C9—C10—C11—C12	178.4 (2)
C1—N1—C5—C6	175.1 (2)	C10—C11—C12—C13	1.5 (4)
Mn1—N1—C5—C6	−8.0 (3)	C11—C12—C13—C14	−0.3 (4)
C3—C4—C5—N1	1.5 (4)	C10—N4—C14—C13	0.9 (3)
C3—C4—C5—C6	−175.7 (2)	Mn1—N4—C14—C13	−179.06 (18)
C7—N2—C6—O1	8.2 (4)	C12—C13—C14—N4	−0.9 (4)
Mn1—N2—C6—O1	176.0 (2)	C9—N3—C15—C16	−154.3 (2)
C7—N2—C6—C5	−169.7 (2)	C8—N3—C15—C16	81.7 (2)
Mn1—N2—C6—C5	−1.9 (3)	Mn1—N3—C15—C16	−38.2 (2)
N1—C5—C6—O1	−171.7 (2)	C20—N5—C16—C17	−1.6 (4)
C4—C5—C6—O1	5.8 (4)	Mn1—N5—C16—C17	171.7 (2)
N1—C5—C6—N2	6.4 (3)	C20—N5—C16—C15	177.9 (2)

C4—C5—C6—N2	−176.1 (2)	Mn1—N5—C16—C15	−8.8 (3)
C6—N2—C7—C8	−156.9 (2)	N3—C15—C16—N5	31.8 (3)
Mn1—N2—C7—C8	34.8 (3)	N3—C15—C16—C17	−148.7 (2)
N2—C7—C8—N3	−40.5 (3)	N5—C16—C17—C18	0.4 (4)
C9—N3—C8—C7	145.2 (2)	C15—C16—C17—C18	−179.1 (2)
C15—N3—C8—C7	−89.1 (3)	C16—C17—C18—C19	1.7 (4)
Mn1—N3—C8—C7	29.5 (2)	C17—C18—C19—C20	−2.5 (4)
C15—N3—C9—C10	161.1 (2)	C16—N5—C20—C19	0.8 (4)
C8—N3—C9—C10	−73.8 (2)	Mn1—N5—C20—C19	−171.51 (19)
Mn1—N3—C9—C10	44.2 (2)	C18—C19—C20—N5	1.3 (4)
C14—N4—C10—C11	0.3 (3)		

(*N*-{2-[Bis(pyridin-2-ylmethyl)amino]ethyl}pyridine-2-carboxamidato)(nitric oxide)manganese perchlorate acetonitrile disolvate (mn1486)

Crystal data

$[Mn(C_{20}H_{20}N_5O)(NO)]ClO_4·2C_2H_3N$
M_r = 612.92
Monoclinic, $P2_1$
a = 8.3188 (4) Å
b = 14.1117 (6) Å
c = 11.6994 (5) Å
β = 98.3222 (7)°
V = 1358.96 (10) Å^3
Z = 2
$F(000)$ = 632
D_x = 1.498 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6558 reflections
θ = 2.3–27.4°
μ = 0.64 mm^{-1}
T = 170 K
Plate, brown
0.31 × 0.20 × 0.08 mm

Data collection

Bruker SMART 1000 diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2016)
T_{min} = 0.657, T_{max} = 0.746
15578 measured reflections
6155 independent reflections
5730 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 27.5°, θ_{min} = 2.3°
h = −10→10
k = −18→18
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.072
S = 1.04
6155 reflections
449 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.1568P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Absolute structure: Flack x determined using 2534 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.015 (8)

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}
Mn1	0.68244 (4)	0.74936 (3)	0.80066 (3)	0.01561 (10)
O2	0.5287 (3)	0.64701 (18)	0.6063 (2)	0.0323 (5)
N6	0.5877 (3)	0.68599 (17)	0.6922 (2)	0.0181 (5)
O1	0.8822 (3)	0.98616 (17)	0.9620 (2)	0.0359 (6)
N1	0.6702 (3)	0.87232 (17)	0.7151 (2)	0.0196 (5)
N2	0.7964 (3)	0.83282 (18)	0.9191 (2)	0.0193 (5)
N3	0.7398 (3)	0.64869 (18)	0.9230 (2)	0.0180 (5)
N4	0.9000 (3)	0.70688 (17)	0.75820 (19)	0.0177 (5)
N5	0.4891 (3)	0.76810 (17)	0.8853 (2)	0.0211 (6)
C1	0.5957 (4)	0.8884 (2)	0.6067 (3)	0.0258 (7)
H1	0.536 (4)	0.837 (3)	0.570 (3)	0.028 (10)*
C2	0.6042 (5)	0.9756 (2)	0.5528 (3)	0.0325 (7)
H2	0.558 (5)	0.981 (3)	0.481 (4)	0.040 (11)*
C3	0.6925 (5)	1.0481 (3)	0.6102 (3)	0.0342 (8)
H3	0.702 (4)	1.108 (3)	0.571 (3)	0.031 (10)*
C4	0.7673 (4)	1.0324 (2)	0.7224 (3)	0.0266 (6)
H4	0.821 (5)	1.072 (3)	0.765 (3)	0.033 (10)*
C5	0.7527 (3)	0.9454 (2)	0.7723 (3)	0.0210 (6)
C6	0.8200 (4)	0.9233 (2)	0.8959 (3)	0.0203 (6)
C7	0.8241 (4)	0.7952 (2)	1.0355 (3)	0.0218 (6)
H7A	0.730 (4)	0.807 (3)	1.073 (3)	0.026 (9)*
H7B	0.911 (4)	0.829 (3)	1.080 (3)	0.023 (9)*
C8	0.8541 (4)	0.6897 (2)	1.0236 (3)	0.0227 (7)
H8A	0.958 (4)	0.684 (2)	1.006 (3)	0.019 (8)*
H8B	0.843 (4)	0.655 (3)	1.096 (3)	0.027 (9)*
C9	0.8247 (4)	0.5727 (2)	0.8675 (3)	0.0213 (6)
H9A	0.753 (4)	0.539 (3)	0.817 (3)	0.021 (9)*
H9B	0.879 (4)	0.530 (2)	0.923 (3)	0.012 (7)*
C10	0.9438 (3)	0.6199 (2)	0.7999 (2)	0.0187 (6)
C11	1.0879 (4)	0.5779 (2)	0.7814 (3)	0.0246 (6)
H11	1.121 (5)	0.520 (3)	0.816 (3)	0.034 (10)*
C12	1.1878 (4)	0.6254 (3)	0.7154 (3)	0.0274 (7)
H12	1.287 (5)	0.600 (3)	0.698 (3)	0.031 (10)*
C13	1.1431 (4)	0.7141 (2)	0.6728 (3)	0.0270 (7)
H13	1.204 (4)	0.751 (3)	0.632 (3)	0.033 (9)*
C14	0.9986 (3)	0.7537 (3)	0.6955 (2)	0.0211 (5)
H14	0.960 (4)	0.813 (3)	0.665 (3)	0.020 (8)*
C15	0.5855 (4)	0.6157 (2)	0.9598 (3)	0.0231 (6)
H15A	0.602 (4)	0.583 (2)	1.035 (3)	0.017 (8)*

H15B	0.539 (4)	0.577 (2)	0.899 (3)	0.017 (8)*
C16	0.4735 (4)	0.6993 (2)	0.9628 (3)	0.0238 (6)
C17	0.3602 (4)	0.7057 (3)	1.0391 (3)	0.0340 (8)
H17	0.346 (5)	0.654 (3)	1.087 (3)	0.036 (10)*
C18	0.2605 (4)	0.7843 (3)	1.0342 (3)	0.0392 (9)
H18	0.197 (5)	0.791 (3)	1.093 (4)	0.046 (12)*
C19	0.2743 (4)	0.8537 (3)	0.9531 (3)	0.0364 (8)
H19	0.215 (5)	0.906 (3)	0.944 (4)	0.041 (11)*
C20	0.3899 (4)	0.8437 (2)	0.8803 (3)	0.0281 (7)
H20	0.404 (4)	0.886 (3)	0.826 (3)	0.026 (9)*
N7	0.5514 (5)	0.9375 (3)	0.2336 (3)	0.0510 (9)
C21	0.5792 (4)	0.8650 (3)	0.2705 (3)	0.0357 (8)
C22	0.6172 (5)	0.7709 (3)	0.3179 (4)	0.0476 (10)
H22A	0.528763	0.749046	0.358285	0.082 (16)*
H22B	0.718521	0.773296	0.372190	0.10 (2)*
H22C	0.629887	0.726864	0.254968	0.086 (19)*
N8	0.7402 (6)	0.5355 (3)	0.2588 (3)	0.0711 (13)
C23	0.8010 (5)	0.5464 (3)	0.3506 (4)	0.0444 (9)
C24	0.8760 (6)	0.5636 (4)	0.4684 (4)	0.0562 (12)
H24A	0.951437	0.511906	0.493922	0.12 (2)*
H24B	0.791716	0.566735	0.518829	0.084 (19)*
H24C	0.935446	0.623703	0.472274	0.13 (3)*
Cl1	1.11518 (10)	0.81883 (5)	0.35973 (7)	0.02953 (18)
O3	1.2675 (3)	0.7980 (3)	0.4280 (3)	0.0593 (9)
O4	0.9991 (4)	0.8435 (3)	0.4339 (3)	0.0593 (9)
O5	1.1300 (4)	0.8934 (2)	0.2805 (3)	0.0606 (9)
O6	1.0572 (5)	0.7364 (2)	0.2950 (3)	0.0677 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01638 (18)	0.01521 (18)	0.01435 (17)	−0.00019 (18)	−0.00083 (13)	−0.00095 (18)
O2	0.0349 (13)	0.0359 (13)	0.0248 (12)	−0.0093 (11)	0.0003 (10)	−0.0134 (10)
N6	0.0177 (11)	0.0165 (11)	0.0197 (11)	0.0001 (9)	0.0016 (9)	−0.0006 (9)
O1	0.0479 (15)	0.0290 (13)	0.0272 (12)	−0.0134 (11)	−0.0070 (11)	−0.0064 (10)
N1	0.0236 (12)	0.0176 (12)	0.0164 (11)	0.0026 (10)	−0.0009 (9)	−0.0004 (9)
N2	0.0207 (12)	0.0208 (13)	0.0152 (11)	−0.0007 (10)	−0.0014 (10)	−0.0009 (10)
N3	0.0188 (12)	0.0169 (11)	0.0180 (11)	−0.0004 (10)	0.0018 (10)	0.0016 (9)
N4	0.0188 (11)	0.0175 (11)	0.0165 (11)	−0.0005 (9)	0.0015 (9)	0.0003 (9)
N5	0.0174 (11)	0.0229 (15)	0.0219 (11)	−0.0013 (10)	−0.0007 (9)	−0.0077 (10)
C1	0.0329 (17)	0.0218 (16)	0.0204 (14)	0.0035 (14)	−0.0037 (13)	−0.0015 (12)
C2	0.046 (2)	0.0263 (17)	0.0223 (16)	0.0063 (15)	−0.0047 (15)	0.0027 (13)
C3	0.047 (2)	0.0243 (17)	0.0312 (17)	0.0057 (15)	0.0062 (15)	0.0081 (14)
C4	0.0339 (16)	0.0197 (15)	0.0260 (15)	−0.0046 (13)	0.0034 (13)	−0.0011 (12)
C5	0.0208 (14)	0.0198 (14)	0.0219 (14)	−0.0017 (11)	0.0013 (12)	−0.0030 (11)
C6	0.0203 (14)	0.0211 (15)	0.0190 (14)	−0.0021 (12)	0.0010 (12)	−0.0035 (12)
C7	0.0222 (15)	0.0279 (17)	0.0142 (13)	0.0000 (13)	−0.0010 (12)	−0.0011 (12)
C8	0.0221 (16)	0.0264 (16)	0.0187 (14)	−0.0008 (13)	0.0003 (12)	0.0042 (12)

C9	0.0228 (15)	0.0174 (15)	0.0236 (15)	0.0027 (13)	0.0034 (13)	0.0040 (13)
C10	0.0202 (13)	0.0175 (14)	0.0176 (13)	−0.0001 (11)	0.0001 (11)	−0.0011 (11)
C11	0.0216 (15)	0.0256 (16)	0.0258 (15)	0.0038 (12)	0.0011 (12)	−0.0017 (13)
C12	0.0197 (15)	0.0357 (18)	0.0270 (16)	0.0036 (13)	0.0044 (12)	−0.0015 (13)
C13	0.0232 (15)	0.0348 (17)	0.0244 (15)	−0.0077 (13)	0.0088 (12)	0.0007 (13)
C14	0.0248 (12)	0.0208 (13)	0.0173 (11)	−0.0025 (15)	0.0011 (10)	0.0014 (14)
C15	0.0217 (14)	0.0244 (15)	0.0243 (15)	−0.0040 (12)	0.0073 (12)	0.0020 (13)
C16	0.0177 (14)	0.0279 (16)	0.0254 (15)	−0.0055 (12)	0.0020 (12)	−0.0056 (13)
C17	0.0264 (17)	0.043 (2)	0.0351 (18)	−0.0063 (15)	0.0139 (14)	−0.0059 (16)
C18	0.0228 (16)	0.051 (2)	0.047 (2)	−0.0079 (15)	0.0165 (16)	−0.0214 (17)
C19	0.0233 (16)	0.037 (2)	0.048 (2)	0.0053 (15)	0.0023 (15)	−0.0209 (17)
C20	0.0235 (15)	0.0287 (17)	0.0307 (17)	0.0033 (13)	−0.0009 (13)	−0.0104 (14)
N7	0.054 (2)	0.042 (2)	0.055 (2)	0.0000 (17)	0.0013 (18)	0.0042 (17)
C21	0.0353 (18)	0.038 (2)	0.0340 (18)	0.0000 (16)	0.0046 (15)	−0.0029 (16)
C22	0.053 (2)	0.044 (3)	0.047 (2)	0.0044 (19)	0.0132 (19)	0.0062 (18)
N8	0.110 (4)	0.051 (2)	0.048 (2)	−0.033 (3)	−0.003 (2)	0.001 (2)
C23	0.061 (3)	0.031 (2)	0.041 (2)	−0.0086 (19)	0.006 (2)	−0.0003 (17)
C24	0.067 (3)	0.060 (3)	0.039 (2)	0.003 (3)	−0.001 (2)	−0.003 (2)
Cl1	0.0355 (4)	0.0271 (4)	0.0260 (4)	0.0018 (3)	0.0043 (3)	0.0042 (3)
O3	0.0357 (15)	0.092 (3)	0.0475 (17)	0.0012 (15)	−0.0031 (13)	0.0180 (17)
O4	0.0516 (17)	0.079 (2)	0.0519 (18)	0.0017 (17)	0.0224 (14)	−0.0046 (17)
O5	0.079 (2)	0.0425 (18)	0.064 (2)	0.0072 (16)	0.0230 (17)	0.0258 (15)
O6	0.088 (2)	0.0376 (18)	0.072 (2)	0.0024 (18)	−0.0067 (18)	−0.0146 (17)

Geometric parameters (Å, º)

Mn1—N6	1.656 (2)	C9—H9B	0.95 (3)
Mn1—N2	1.956 (2)	C10—C11	1.382 (4)
Mn1—N1	1.998 (2)	C11—C12	1.386 (5)
Mn1—N3	2.024 (2)	C11—H11	0.93 (4)
Mn1—N5	2.025 (2)	C12—C13	1.378 (5)
Mn1—N4	2.035 (2)	C12—H12	0.95 (4)
O2—N6	1.188 (3)	C13—C14	1.385 (4)
O1—C6	1.239 (4)	C13—H13	0.91 (4)
N1—C1	1.348 (4)	C14—H14	0.95 (3)
N1—C5	1.360 (4)	C15—C16	1.506 (5)
N2—C6	1.326 (4)	C15—H15A	0.98 (3)
N2—C7	1.449 (4)	C15—H15B	0.94 (3)
N3—C9	1.484 (4)	C16—C17	1.392 (4)
N3—C15	1.487 (4)	C17—C18	1.382 (5)
N3—C8	1.517 (4)	C17—H17	0.94 (4)
N4—C14	1.350 (4)	C18—C19	1.380 (6)
N4—C10	1.351 (4)	C18—H18	0.93 (4)
N5—C20	1.345 (4)	C19—C20	1.381 (5)
N5—C16	1.347 (4)	C19—H19	0.89 (4)
C1—C2	1.389 (5)	C20—H20	0.89 (4)
C1—H1	0.94 (4)	N7—C21	1.121 (5)
C2—C3	1.376 (5)	C21—C22	1.457 (5)

C2—H2	0.87 (4)	C22—H22A	0.9800
C3—C4	1.386 (5)	C22—H22B	0.9800
C3—H3	0.97 (4)	C22—H22C	0.9800
C4—C5	1.372 (4)	N8—C23	1.129 (5)
C4—H4	0.83 (4)	C23—C24	1.449 (6)
C5—C6	1.506 (4)	C24—H24A	0.9800
C7—C8	1.519 (4)	C24—H24B	0.9800
C7—H7A	0.97 (4)	C24—H24C	0.9800
C7—H7B	0.96 (4)	Cl1—O5	1.420 (3)
C8—H8A	0.92 (3)	Cl1—O3	1.427 (3)
C8—H8B	0.99 (4)	Cl1—O4	1.431 (3)
C9—C10	1.510 (4)	Cl1—O6	1.433 (3)
C9—H9A	0.91 (4)		

N6—Mn1—N2	175.05 (12)	H8A—C8—H8B	111 (3)
N6—Mn1—N1	95.79 (11)	N3—C9—C10	107.5 (2)
N2—Mn1—N1	79.41 (10)	N3—C9—H9A	110 (2)
N6—Mn1—N3	101.57 (11)	C10—C9—H9A	108 (2)
N2—Mn1—N3	83.17 (10)	N3—C9—H9B	111.6 (19)
N1—Mn1—N3	162.41 (10)	C10—C9—H9B	110.5 (18)
N6—Mn1—N5	96.99 (10)	H9A—C9—H9B	109 (3)
N2—Mn1—N5	85.00 (10)	N4—C10—C11	121.8 (3)
N1—Mn1—N5	98.34 (10)	N4—C10—C9	115.3 (2)
N3—Mn1—N5	82.44 (10)	C11—C10—C9	122.9 (3)
N6—Mn1—N4	89.73 (11)	C10—C11—C12	118.9 (3)
N2—Mn1—N4	89.61 (10)	C10—C11—H11	121 (2)
N1—Mn1—N4	96.68 (10)	C12—C11—H11	120 (2)
N3—Mn1—N4	80.73 (9)	C13—C12—C11	119.3 (3)
N5—Mn1—N4	162.82 (9)	C13—C12—H12	118 (2)
O2—N6—Mn1	172.4 (2)	C11—C12—H12	123 (2)
C1—N1—C5	117.8 (3)	C12—C13—C14	119.5 (3)
C1—N1—Mn1	126.9 (2)	C12—C13—H13	125 (3)
C5—N1—Mn1	115.24 (19)	C14—C13—H13	116 (3)
C6—N2—C7	122.5 (3)	N4—C14—C13	121.3 (3)
C6—N2—Mn1	120.4 (2)	N4—C14—H14	116 (2)
C7—N2—Mn1	116.1 (2)	C13—C14—H14	123 (2)
C9—N3—C15	112.7 (2)	N3—C15—C16	108.9 (2)
C9—N3—C8	109.3 (2)	N3—C15—H15A	112.9 (19)
C15—N3—C8	111.4 (2)	C16—C15—H15A	110.5 (19)
C9—N3—Mn1	106.02 (18)	N3—C15—H15B	103.9 (19)
C15—N3—Mn1	107.40 (18)	C16—C15—H15B	107 (2)
C8—N3—Mn1	109.75 (18)	H15A—C15—H15B	114 (3)
C14—N4—C10	119.1 (3)	N5—C16—C17	121.7 (3)
C14—N4—Mn1	128.4 (2)	N5—C16—C15	115.4 (3)
C10—N4—Mn1	112.49 (18)	C17—C16—C15	122.9 (3)
C20—N5—C16	118.9 (3)	C18—C17—C16	118.9 (4)
C20—N5—Mn1	127.5 (2)	C18—C17—H17	121 (2)
C16—N5—Mn1	113.30 (19)	C16—C17—H17	119 (2)

N1—C1—C2	122.0 (3)	C19—C18—C17	119.3 (3)
N1—C1—H1	116 (2)	C19—C18—H18	124 (3)
C2—C1—H1	122 (2)	C17—C18—H18	117 (3)
C3—C2—C1	119.7 (3)	C18—C19—C20	119.2 (3)
C3—C2—H2	123 (3)	C18—C19—H19	125 (3)
C1—C2—H2	118 (3)	C20—C19—H19	116 (3)
C2—C3—C4	118.6 (3)	N5—C20—C19	122.1 (3)
C2—C3—H3	119 (2)	N5—C20—H20	115 (2)
C4—C3—H3	122 (2)	C19—C20—H20	123 (2)
C5—C4—C3	119.4 (3)	N7—C21—C22	179.3 (4)
C5—C4—H4	114 (3)	C21—C22—H22A	109.5
C3—C4—H4	126 (3)	C21—C22—H22B	109.5
N1—C5—C4	122.6 (3)	H22A—C22—H22B	109.5
N1—C5—C6	114.0 (3)	C21—C22—H22C	109.5
C4—C5—C6	123.4 (3)	H22A—C22—H22C	109.5
O1—C6—N2	128.5 (3)	H22B—C22—H22C	109.5
O1—C6—C5	120.9 (3)	N8—C23—C24	177.9 (5)
N2—C6—C5	110.5 (3)	C23—C24—H24A	109.5
N2—C7—C8	106.2 (3)	C23—C24—H24B	109.5
N2—C7—H7A	109 (2)	H24A—C24—H24B	109.5
C8—C7—H7A	112 (2)	C23—C24—H24C	109.5
N2—C7—H7B	110 (2)	H24A—C24—H24C	109.5
C8—C7—H7B	115 (2)	H24B—C24—H24C	109.5
H7A—C7—H7B	105 (3)	O5—Cl1—O3	111.3 (2)
N3—C8—C7	110.6 (3)	O5—Cl1—O4	110.2 (2)
N3—C8—H8A	107 (2)	O3—Cl1—O4	109.4 (2)
C7—C8—H8A	106 (2)	O5—Cl1—O6	108.2 (2)
N3—C8—H8B	110 (2)	O3—Cl1—O6	109.4 (2)
C7—C8—H8B	112 (2)	O4—Cl1—O6	108.2 (2)

C5—N1—C1—C2	1.3 (4)	Mn1—N4—C10—C11	−179.7 (2)
Mn1—N1—C1—C2	−175.5 (3)	C14—N4—C10—C9	−179.2 (3)
N1—C1—C2—C3	0.8 (5)	Mn1—N4—C10—C9	0.3 (3)
C1—C2—C3—C4	−1.7 (5)	N3—C9—C10—N4	−30.0 (4)
C2—C3—C4—C5	0.6 (5)	N3—C9—C10—C11	150.0 (3)
C1—N1—C5—C4	−2.5 (4)	N4—C10—C11—C12	−1.8 (5)
Mn1—N1—C5—C4	174.7 (2)	C9—C10—C11—C12	178.1 (3)
C1—N1—C5—C6	175.2 (3)	C10—C11—C12—C13	1.8 (5)
Mn1—N1—C5—C6	−7.6 (3)	C11—C12—C13—C14	−0.7 (5)
C3—C4—C5—N1	1.6 (5)	C10—N4—C14—C13	0.3 (4)
C3—C4—C5—C6	−175.9 (3)	Mn1—N4—C14—C13	−179.1 (2)
C7—N2—C6—O1	8.2 (5)	C12—C13—C14—N4	−0.3 (4)
Mn1—N2—C6—O1	176.2 (3)	C9—N3—C15—C16	−154.2 (3)
C7—N2—C6—C5	−169.5 (3)	C8—N3—C15—C16	82.5 (3)
Mn1—N2—C6—C5	−1.5 (3)	Mn1—N3—C15—C16	−37.8 (3)
N1—C5—C6—O1	−172.0 (3)	C20—N5—C16—C17	−1.5 (4)
C4—C5—C6—O1	5.6 (5)	Mn1—N5—C16—C17	172.1 (2)
N1—C5—C6—N2	5.9 (4)	C20—N5—C16—C15	178.0 (3)

C4—C5—C6—N2	−176.5 (3)	Mn1—N5—C16—C15	−8.4 (3)
C6—N2—C7—C8	−156.7 (3)	N3—C15—C16—N5	31.2 (4)
Mn1—N2—C7—C8	34.8 (3)	N3—C15—C16—C17	−149.3 (3)
C9—N3—C8—C7	145.3 (3)	N5—C16—C17—C18	0.6 (5)
C15—N3—C8—C7	−89.4 (3)	C15—C16—C17—C18	−178.9 (3)
Mn1—N3—C8—C7	29.4 (3)	C16—C17—C18—C19	0.9 (5)
N2—C7—C8—N3	−40.4 (3)	C17—C18—C19—C20	−1.4 (5)
C15—N3—C9—C10	161.4 (2)	C16—N5—C20—C19	1.0 (4)
C8—N3—C9—C10	−74.1 (3)	Mn1—N5—C20—C19	−171.6 (2)
Mn1—N3—C9—C10	44.2 (3)	C18—C19—C20—N5	0.5 (5)
C14—N4—C10—C11	0.8 (4)		