



Manganese(II) chloride complexes with pyridine *N*-oxide (PNO) derivatives and their solid-state structures

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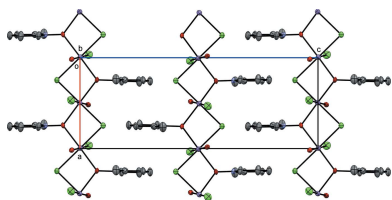
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Keywords: crystal structure; manganese; pyridine *N*-oxide ligand.**CCDC references:** 1570001; 1570000; 1569999**Supporting information:** this article has supporting information at journals.iucr.org/e

Three manganese(II) *N*-oxide complexes have been synthesized from the reaction of manganese(II) chloride with either pyridine *N*-oxide (PNO), 2-methylpyridine *N*-oxide (2MePNO) or 3-methylpyridine *N*-oxide (3MePNO). The compounds were synthesized from methanolic solutions of MnCl₂·4H₂O and the respective *N*-oxide, and subsequently characterized structurally by single-crystal X-ray diffraction. The compounds are *catena*-poly[[aquachloridomanganese(II)]-di- μ -chlorido-[aquachloridomanganese(II)]-bis(μ -pyridine *N*-oxide)], [MnCl₂(C₅H₅NO)(H₂O)]_n or [MnCl₂(PNO)(H₂O)]_n (**I**), *catena*-poly[[aquachloridomanganese(II)]-di- μ -chlorido-[aquachloridomanganese(II)]-bis(μ -2-methylpyridine *N*-oxide)], [MnCl₂(C₆H₇NO)(H₂O)]_n or [MnCl₂(2MePNO)(H₂O)]_n (**II**), and bis(μ -3-methylpyridine *N*-oxide)bis[diaquadichloridomanganese(II)], [Mn₂Cl₄(C₆H₇NO)₂(H₂O)₄] or [MnCl₂(3MePNO)(H₂O)]₂ (**III**). The Mn^{II} atoms are found in pseudo-octahedral environments for each of the three complexes. Compound **I** forms a coordination polymer with alternating pairs of bridging *N*-oxide and chloride ligands. The coordination environment is defined by two PNO bridging O atoms, two chloride bridging atoms, a terminal chloride, and a terminal water. Compound **II** also forms a coordination polymer with a similar metal cation; however, the coordination polymer is bridged between Mn^{II} atoms by both a single chloride and 2MePNO. The distorted octahedrally coordinated metal cation is defined by two bridging 2MePNO *trans* to each other, two chlorides, also *trans* to one another in the equatorial (polymeric) plane, and a terminal chloride and terminal water. Finally, complex **III** forms a dimer with two bridging 3MePNOs, two terminal chlorides and two terminal waters forming the six-coordinate metal environment. All three compounds exhibit hydrogen bonding between the coordinating water(s) and terminal chlorides.

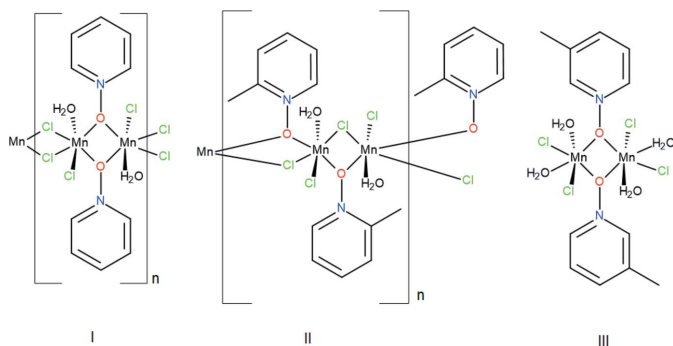
1. Chemical context

The utility of aromatic *N*-oxides to facilitate organic oxo-transfer reactions has been well documented over the years (see, for example, Eppenson, 2003). Many of these reactions are actually catalyzed by transition metal interactions with the *N*-oxide ligands (see, for example, Moustafa *et al.*, 2014). Furthermore, *N*-oxide metal interactions have recently attracted much interest in a variety of other areas, including metal organic frameworks (MOFs) (Hu *et al.*, 2014). These MOFs synthesized using *N*-oxide derivatives take advantage of the multiple binding modes of the *sp*³ O atom and the ease of modification of the organic backbone of the *N*-oxide. The utility of the MOFs has been examined in areas such as catalysis (Liu *et al.*, 2014) and sensors (Hu *et al.*, 2014). The constructs extend to the supramolecular study of coordination polymers that have been found in this type of complex



because of their incredible versatility as ligands (Sarma & Baruah, 2011).

In this context, we report the synthesis and solid-state structures of three pyridine *N*-oxide manganese(II) complexes. Notably, we used the ligands pyridine *N*-oxide, 2-methylpyridine *N*-oxide, and 3-methylpyridine *N*-oxide to study the impact of substitution of the pyridine on the two- and three-dimensional solid-state structures. The pyridine *N*-oxide (PNO) and 2-methylpyridine *N*-oxide (2MePNO) complexes form coordination polymers with subtle differences. The 3-methylpyridine *N*-oxide (3MePNO), however, forms a dimeric complex.



2. Structural commentary

Complex **I** exhibits the repeating motif of $[\text{MnCl}_2(\text{PNO})(\text{H}_2\text{O})]_n$ and crystallizes in the triclinic space group $P\bar{1}$, containing two formula units per unit cell (Fig. 1). The coordination sphere around each Mn^{II} atom is a distorted octahedron, with the equatorial atoms being two bridging chlorides alternating with two bridging pyridine *N*-oxide (PNO) molecules (Fig. 2). In the equatorial plane, the bridging chlorides and the bridging pyridine *N*-oxides are *cis* to one another. The axial positions are a terminal chloride and a water molecule. The $\text{Mn1}-\text{O1}$ bond length is 2.177 (3) Å, whereas the $\text{Mn1}-\text{O1}^{\text{vii}}$ bond length is slightly longer at 2.182 (3) Å for the bridging PNO [symmetry code (vii) $-x + 1, -y + 1, -z + 1$]. The bridging chlorides are found to have

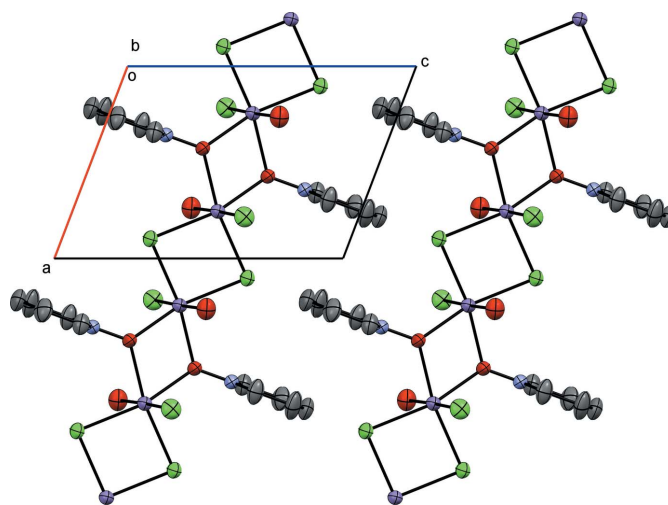
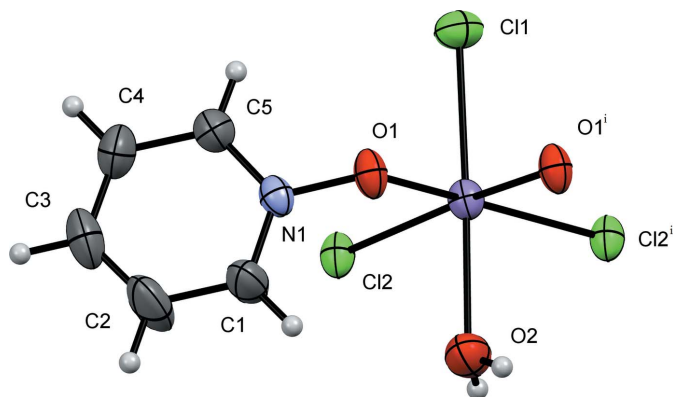


Figure 2
Crystal packing diagram of compound **I**, viewed along the *b* axis. H atoms have been omitted for clarity.

$\text{Mn}-\text{Cl2}$ distances of 2.5240 (19) and 2.532 (19) Å, respectively. Axially, the water is located 2.250 (3) Å from the Mn^{II} cation and the terminal chloride is at 2.479 (2) Å. The bond angles around the equator are severely compressed at the two bridging *N*-oxides, with the $\text{O1}-\text{Mn1}-\text{O1}^{\text{i}}$ angle observed at 72.03 (10)°. The remaining three angles are found to all be similar at 95.58 (7) (Cl2–Mn1–Cl2ⁱ), 96.80 (8) (O1–Mn1–Cl2), and 94.69 (9)° (O1^{vii}–Mn1–Cl2^{vii}). Axially, the bond angle from the water through manganese(II) and the terminal chloride (O2–Mn1–Cl1) is nearly linear at 177.36 (8)°.

Complex **II**, $[\text{MnCl}_2(2\text{MePNO})(\text{H}_2\text{O})]_n$, possesses a metal environment similar to complex **I** and crystallizes in the orthorhombic space group $P2_12_12_1$. The major difference in structure **II** is in the bridging network, where the chlorides and *N*-oxides are *trans* to one another rather than *cis* as in **I** (Figs. 3 and 4). The pseudo-octahedral environment includes an $\text{Mn1}-\text{Cl1}$ bond length of 2.516 (4) Å and an $\text{Mn1}-\text{O1}$ (*N*-

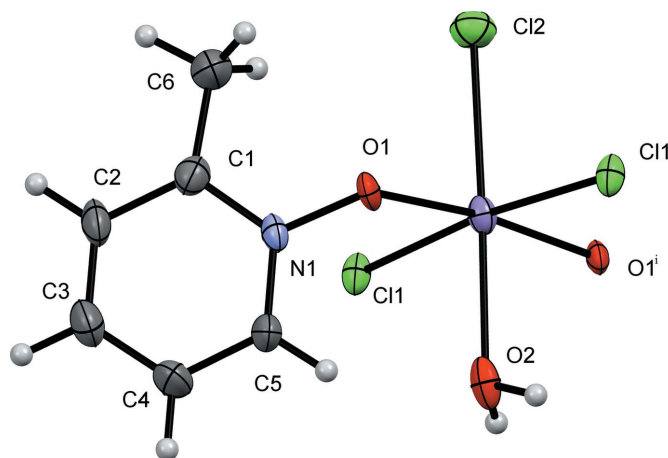


Figure 3
A view of compound **II**, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x - 1, y + \frac{3}{2}, -z + \frac{3}{2}$; (ii) $-x, y + \frac{3}{2}, -z + \frac{3}{2}$]

Figure 1
A view of compound **I**, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$]

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

| <i>D</i> –H··· <i>A</i> | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O2–H2A···Cl1 ⁱ | 0.83 (2) | 2.53 (2) | 3.348 (4) | 168 (4) |
| O2–H2B···Cl1 ⁱⁱ | 0.82 (2) | 2.52 (3) | 3.232 (4) | 147 (4) |

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

oxide) bond length of 2.170 (6) Å, with a Cl1–Mn1–O1 bond angle of 84.37 (19)°. The bond angle across the Cl atoms, Cl1–Mn1–Cl1^{viii}, is 174.02 (5)° and across the O atoms of 2MePNO, O1–Mn1–O1^{ix}, is 173.12 (6)°; a slight compression is observed across the bridges [symmetry codes: (viii) $-x - 1, y + \frac{3}{2}, -z + \frac{3}{2}$; (ix) $-x, y + \frac{3}{2}, -z + \frac{3}{2}$]. The axial (non-bridging) Mn1–Cl2 bond length is 2.503 (4) Å, while the axial water is found at a distance of 2.268 (6) Å from the metal center.

The dimeric complex **III**, [MnCl₂(3MePNO)(OH₂)₂]₂, crystallizes in the triclinic *P* $\bar{1}$ space group, with the inversion center sitting in the center of the dimer (Fig. 5). The 3-methyl derivative does not form a coordination polymer but discrete dimeric molecules. The structure possesses two bridging 3MePNO ligands, four terminal chlorides, and four terminal waters. Two waters and two chlorides are in the equatorial plane coincident with the *N*-oxide bridge, and the other equivalents are axial in the pseudo-octahedral geometry around the Mn^{II} atoms. The Mn1–Cl1 and Mn1–Cl2 bond lengths are 2.4601 (5) and 2.4903 (19) Å, respectively, with a Cl1–Mn1–Cl2 bond angle of 98.32 (4)°. The bridging *N*-oxide is at a distance of 2.1791 (18) Å from Mn1–O1, with an O1–Mn1–O1^{vii} bond angle of 71.86 (7)° [symmetry code: (vii) $-x + 1, -y + 1, -z + 1$]. The Mn1–O2(water) and Mn1–O3(water) bond lengths are 2.245 (2) and 2.1696 (17) Å, respectively, with an O2–Mn1–O3 bond angle of 85.83 (7)°.

The formation of the polymeric structure in **I** and **II** versus the dimer in **III** is likely due to the steric influence of the methyl group in the 3-position in 3MePNO and the core constituents. One can define the Mn₂ ‘*N*-oxide diamond core’ in each of the structures as follows: **I** is alternating Mn₂Cl₂ and Mn₂O₂ (oxygen bridges via PNO) cores, **II** is Mn₂ClO (oxygen bridge via 2MePNO) and **III** Mn₂O₂ (oxygen bridges via 3MePNO). In **I**, the unsubstituted pyridine *N*-oxide group

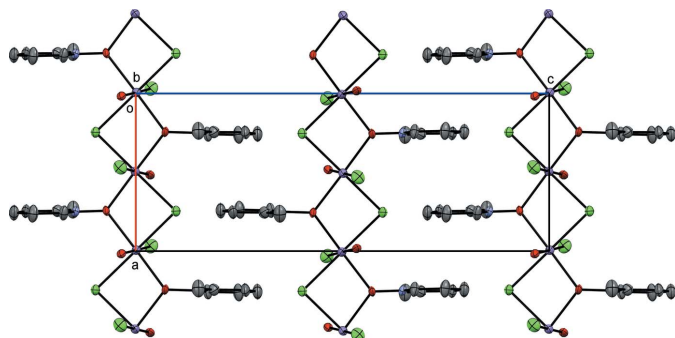


Figure 4
Crystal packing diagram of compound **II**, viewed along the *b* axis. H atoms have been omitted for clarity.

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

| <i>D</i> –H··· <i>A</i> | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O2–H2A···Cl2 ⁱⁱⁱ | 0.90 | 2.49 | 3.205 (7) | 137 |
| O2–H2B···Cl2 ^{iv} | 0.89 | 2.26 | 3.145 (7) | 169 |

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

does not generate as much steric strain, allowing for polymer formation. In **II**, the core is formed to permit alternating up and down pyridine *N*-oxides with the 2-methyl substituents also facing in opposite directions. This limits the steric interactions and the *N*-oxide slightly tilts out of the polymeric core line to allow the methyl group to effect less steric interactions. In **III**, the methyl group appears to inhibit polymer formation due to the position of this bulky substituent. Subsequently, when the polymer is not formed, an extra water molecule is required to fill the sixth coordination site on the metal cation occupied by a bridging atom in **I** and **II**.

3. Supramolecular features

The packing of **I** forms a coordination polymer of alternating bis-bridges of two chlorides and two pyridine *N*-oxides in the *a*-axis direction (Fig. 2). The aromatic rings stack at 6.860 (7) Å, outside of π -stacking distance due to the alternating chloride and pyridine *N*-oxide bridges. The single water molecule is locked into weak hydrogen-bonding interactions in two different modes. One hydrogen-bond interaction (H2A) is located down the bridge to the terminal chloride (Cl1), on the adjacent Mn^{II} atom, and the O2–H2A···Cl1ⁱ distance is 2.53 (2) Å. The other hydrogen-bond interaction (H2B) is across to the next polymeric chain with Cl1; the O2–H2B···Cl1ⁱⁱ distance is 2.52 (3) Å (see Table 1 for hydrogen-bond details and symmetry codes).

Complex **II** packs as a coordination polymer in the *a* direction similar to **I** (Fig. 4). However, as **I** has alternating pyridine *N*-oxide and chloride bridges (placing these ligands *cis* to one another), **II** has a single 2-methylpyridine *N*-oxide

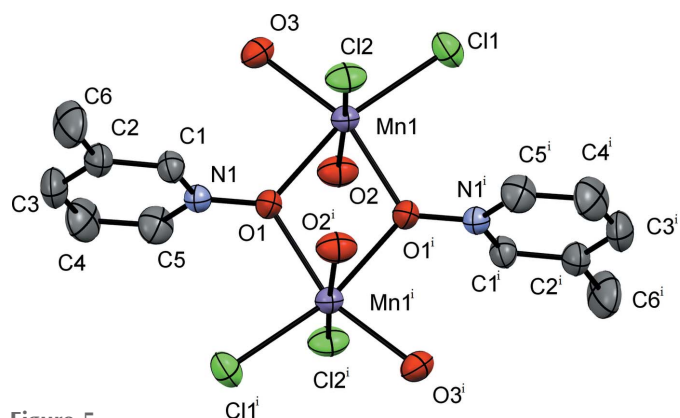


Figure 5
A view of the molecular structure of compound **III**, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x - 1, -y + 1, -z + 1$.]

Table 3
Hydrogen-bond geometry (Å, °) for **III**.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|----------|-------------|-------------|---------------|
| $O2-H2B\cdots Cl1^v$ | 0.80 (2) | 2.38 (2) | 3.147 (3) | 161 (2) |
| $O3-H3A\cdots Cl2^{vi}$ | 0.86 (2) | 2.28 (2) | 3.120 (2) | 167 (2) |

Symmetry codes: (v) $-x, -y + 1, -z + 1$; (vi) $-x, -y, -z + 1$.

and a single chloride in each bridge. Similar to **I**, the hydrogen-bonding interactions are to a terminal chloride (Cl2) on the adjacent Mn^{II} atom. There are two observed interactions, *viz.* $O2-H2A\cdots Cl2^{iii}$ with a distance of 2.49 Å and $O2-H2B\cdots Cl2^{iv}$ with a distance of 2.26 Å (see Table 2 for hydrogen-bond details and symmetry codes). The $H2A\cdots Cl2$ interaction is in the coordination polymer and the $H2B\cdots Cl2$ interaction is across the polymeric chains. Similar to **I**, the aromatic rings stack too far apart to be interacting in the *a* direction, at a distance of 6.862 (11) Å.

As noted above, compound **III** does not form a coordination polymer but is observed in the solid state as a dimer with two water molecules for each Mn^{II} atom (*versus* one aqua equivalent in **I** and **II**) (Fig. 5). The aromatic inter-centroid distance is longer than in the other two molecules, at 7.902 (7) Å. In compound **III**, a single water molecule

hydrogen bonds from the equatorial plane of one dimer to an axial chloride on another dimer. Conversely, the axial water hydrogen bonds to an equatorial chloride on a different dimer. These interactions are found to be $O2-H2B\cdots Cl1^v$ [distance 2.38 (2) Å] and $O3-H3A\cdots Cl2^{vi}$ [distance 2.28 (2) Å] (see Table 3 for hydrogen-bond details and symmetry codes).

4. Database survey

A search in the Cambridge Structural Database (CSD; Groom *et al.*, 2016) for aromatic *N*-oxides bound to manganese returned 87 entries. Similar *N*-oxides with simple counter-ions in the list include 4,4'-dipyridine *N,N'*-dioxide [FIVHAU (Ma *et al.*, 2005) and XOHQUH (Jiu *et al.*, 2008)], 1,2-bis(4-pyridyl)ethane *N,N'*-dioxide (TOJDAY and TOJDIG; Sun *et al.*, 2008), and 1,3-bis(4-pyridyl)propane *N,N'*-dioxide (Zhang *et al.*, 2003). Similarly, two derivatives of 3,5-dimethylpyridine *N*-oxide are found in the CSD (GIWQAF and GIWQEJ; Shi *et al.*, 2007).

5. Synthesis and crystallization

The title compounds were all synthesized in a similar manner. 0.200 g of $MnCl_2\cdot 4H_2O$ (1.01 mmol) was dissolved in a

Table 4
Experimental details.

| | I | II | III |
|--|--|---|--|
| Crystal data | | | |
| Chemical formula | $[MnCl_2(C_5H_5NO)(H_2O)]$ | $[MnCl_2(C_6H_7NO)(H_2O)]$ | $[Mn_2Cl_4(C_6H_7NO)_2(H_2O)_4]$ |
| M_r | 238.96 | 252.98 | 541.99 |
| Crystal system, space group | Triclinic, $P\bar{1}$ | Orthorhombic, $P2_12_12_1$ | Triclinic, $P\bar{1}$ |
| Temperature (K) | 173 | 173 | 173 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 6.897 (2), 7.050 (1), 9.853 (3) | 6.862 (2), 7.491 (2), 18.047 (5) | 7.902 (7), 8.026 (7), 9.893 (8) |
| α , β , γ (°) | 101.042 (7), 109.559 (10), 94.196 (6) | 90, 90, 90 | 98.033 (1), 99.272 (7), 113.634 (11) |
| <i>V</i> (Å ³) | 438.2 (2) | 927.7 (4) | 552.6 (8) |
| <i>Z</i> | 2 | 4 | 1 |
| Radiation type | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α |
| μ (mm ⁻¹) | 2.06 | 1.96 | 1.65 |
| Crystal size (mm) | 0.29 × 0.18 × 0.13 | 0.2 × 0.2 × 0.1 | 0.85 × 0.50 × 0.28 |
| Data collection | | | |
| Diffractometer | Rigaku XtalLab mini CCD | Rigaku XtalLab mini CCD | Rigaku XtalLab mini CCD |
| Absorption correction | Multi-scan (<i>REQAB</i> ; Rigaku, 1998) | Multi-scan (<i>REQAB</i> ; Rigaku, 1998) | Multi-scan (<i>REQAB</i> ; Rigaku, 1998) |
| T_{min} , T_{max} | 0.613, 0.765 | 0.563, 0.737 | 0.482, 0.630 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 4655, 2004, 1770 | 8438, 2109, 1800 | 5837, 2553, 2375 |
| R_{int} | 0.040 | 0.051 | 0.072 |
| $(\sin \theta/\lambda)_{max}$ (Å ⁻¹) | 0.651 | 0.649 | 0.652 |
| Refinement | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i> | 0.031, 0.080, 1.14 | 0.051, 0.100, 1.12 | 0.031, 0.087, 1.07 |
| No. of reflections | 2004 | 2109 | 2553 |
| No. of parameters | 108 | 112 | 135 |
| No. of restraints | 2 | 0 | 4 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³) | 0.40, -0.44 | 0.95, -0.73 | 0.56, -0.41 |
| Absolute structure | — | Refined as an inversion twin | — |
| Absolute structure parameter | — | 0.44 (8) | — |

Computer programs: *CrystalClearSM Expert* (Rigaku, 2011), *SHELXT* (Sheldrick, 2015a), *SHELXL2017* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

minimal amount of methanol, approximately 10 ml. Two stoichiometric equivalents of the appropriate *N*-oxide were also dissolved in approximately 20 ml of methanol (PNO: 0.191 g, 2.02 mmol; 2MePNO: 0.220 g, 2.02 mmol; 3MePNO: 0.220 g, 2.02 mmol). The solutions were stirred for approximately 10 min; during each reaction, a brown solution was observed upon mixing. The reaction solution was then allowed to sit and brown crystals were grown by slow evaporation in the near quantitative yields reported below based on the manganese(II) chloride starting material. The FT-IR spectra of the complexes all exhibit broad absorbances in the 3400–3000 cm⁻¹ region due to the $\nu(\text{O}-\text{H})$ of the coordinating water molecules, as well as the characteristic $\nu(\text{N}-\text{O})$ of the *N*-oxide pyridyl moiety in the 1250–1150 cm⁻¹ region noted previously (Mautner *et al.*, 2017).

Compound **I**, Mn(PNO)Cl₂·H₂O, yield 0.215 g (90.3%). Selected IR bands (ATR, FT-IR, KBr composite, cm⁻¹): 3364 (*m, br*), 3235 (*m, br*), 3068 (*m, br*), 1660 (*w*), 1471 (*w*), 1214 (*m*), 1205 (*m*), 1023 (*s*), 831 (*s*), 780 (*s*), 674 (*s*), 556 (*s*). Elemental analysis for MnCl₂C₅H₇NO₂, calculated (%): C 25.13, H 2.95, N 5.86; found (%): C 25.22, H 2.96, N 5.87.

Compound **II**, Mn(2MePNO)Cl₂·H₂O, yield 0.227 g (87.9%). Selected IR bands (ATR, FT-IR, KBr composite, cm⁻¹): 3410 (*m, br*), 3247(*m, br*), 3073(*m, br*), 1716 (*w*), 1619 (*w*), 1578 (*w*), 1421 (*m*), 1264 (*m*), 1154 (*m*), 1029 (*s*), 831 (*s*), 799 (*s*), 684 (*s*), 584 (*s*). Elemental analysis for MnCl₂·C₆H₉NO₂, calculated (%): C 28.48, H 3.59, N 5.53; found (%): C 28.75, H 3.53, N 5.28.

Compound **III**, Mn₂(3MePNO)₂Cl₄·4H₂O, yield 0.231 g (89.5%). Selected IR bands (ATR, FT-IR, KBr composite, cm⁻¹): 3374 (*m, br*), 3251 (*m, br*), 3094 (*m, br*), 1663 (*w*), 1614(*w*), 1492 (*m*), 1261 (*m*), 1164 (*m*), 1019 (*s*), 946 (*s*), 750 (*s*), 672 (*s*). Elemental analysis for Mn₂Cl₄C₁₂H₂₂N₂O₆, calculated (%): C 26.59, H 4.09, N 5.16; found (%): C 26.53, H 4.04, N 5.21.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All carbon-bound H atoms were positioned geometrically and refined as riding, with C–H = 0.95 or 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for C(H) and CH₃ groups, respectively. In order to ensure chemically meaningful O–H distances for the bound water molecules in compound **I**, the H2A–O2 and H2B–O2

distances were restrained to a target value of 0.84 (2) Å (using a DFIX command in *SHELXL2017*; Sheldrick, 2015b). In compound **II**, water H atoms were refined as riding, with the O–H distance constrained to 0.892 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ using an AFIX 7 command, and in compound **III**, H2A–O2, H2B–O2, H3A–O3, and H3B–O3 were restrained using DFIX as for compound **I**. A rotating-group model was applied for the methyl groups. Structure refinement of **II** exhibits inversion twinning. Several crystals were tried and the centrosymmetric space group *Pnma* was tested. In all cases, there was a significant reduction in the *R* value for the inversion twinning *P*2₁2₁2₁ solution.

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References

- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Eppenson, J. H. (2003). *Adv. Inorg. Chem.* **54**, 157–202.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hu, Z. C., Deibert, B. J. & Li, J. (2014). *Chem. Soc. Rev.* **43**, 5815–5840.
- Jiu, J., Blake, A. J., Champness, N. R., Hubberstey, P., Wilson, C. & Schröder, M. (2008). *Inorg. Chem.* **47**, 8652–8664.
- Liu, J., Chen, L., Cui, H., Zhang, Y., Zhang, L. & Su, C.-Y. (2014). *Chem. Soc. Rev.* **43**, 6011–6061.
- Ma, B.-Q., Sun, H.-L. & Gao, S. (2005). *Inorg. Chem.* **44**, 837–839.
- Mautner, F. A., Berger, C., Fischer, R. C., Massoud, S. S. & Vicente, R. (2017). *Polyhedron*, **134**, 126–134.
- Moustafa, M. E., Boyle, P. D. & Puddephatt, R. J. (2014). *Organometallics*, **33**, 5402–5413.
- Rigaku (1998). *REQAB*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2011). *CrystalClearSM Expert*. Rigaku Corporation, Tokyo, Japan.
- Sarma, R. & Baruah, J. B. (2011). *Solid State Sci.* **13**, 1692–1700.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shi, J.-M., Liu, Z., Li, W.-N., Zhao, H. Y. & Liu, L.-D. (2007). *J. Coord. Chem.* **60**, 1077–1082.
- Sun, H.-L., Wang, Z.-M., Gao, S. & Batten, S. R. (2008). *CrystEngComm*, **10**, 1796–1802.
- Zhang, L.-P., Lu, W.-J. & Mak, T. C. (2003). *Chem. Commun.* **22**, 2830–2831.

supporting information

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Computing details

For all structures, data collection: CrystalClearSM Expert (Rigaku, 2011); cell refinement: CrystalClearSM Expert (Rigaku, 2011); data reduction: CrystalClearSM Expert (Rigaku, 2011); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

catena-poly[[aquachloridomanganese(II)]-di- μ -chlorido-[aquachloridomanganese(II)]-bis(μ -pyridine *N*-oxide)] (I)

Crystal data

[MnCl₂(C₅H₅NO)(H₂O)]

$M_r = 238.96$

Triclinic, $P\bar{1}$

$a = 6.897$ (2) Å

$b = 7.050$ (1) Å

$c = 9.853$ (3) Å

$\alpha = 101.042$ (7)°

$\beta = 109.559$ (10)°

$\gamma = 94.196$ (6)°

$V = 438.2$ (2) Å³

$Z = 2$

$F(000) = 238$

$D_x = 1.811$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1189 reflections

$\theta = 2.3$ – 27.5 °

$\mu = 2.06$ mm⁻¹

$T = 173$ K

Prism, clear brown

$0.29 \times 0.18 \times 0.13$ mm

Data collection

Rigaku XtalLab mini CCD diffractometer

ω scans

Absorption correction: multi-scan (REQAB; Rigaku, 1998)

$T_{\min} = 0.613$, $T_{\max} = 0.765$

4655 measured reflections

2004 independent reflections

1770 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 2.3$ °

$h = -8 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.080$

$S = 1.14$

2004 reflections

108 parameters

2 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 0.444P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.40$ e Å⁻³

$\Delta\rho_{\min} = -0.44$ e Å⁻³

Special details

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

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Mn1 | 0.24478 (6) | 0.51944 (6) | 0.49588 (4) | 0.02748 (12) |
| Cl1 | 0.21608 (12) | 0.81797 (10) | 0.39668 (9) | 0.04150 (19) |
| O1 | 0.5727 (3) | 0.6094 (3) | 0.63106 (19) | 0.0327 (4) |
| N1 | 0.6425 (3) | 0.6894 (3) | 0.7767 (2) | 0.0283 (5) |
| C1 | 0.6940 (6) | 0.5762 (5) | 0.8731 (3) | 0.0493 (8) |
| H1 | 0.681940 | 0.441595 | 0.840110 | 0.059* |
| Cl2 | 0.10246 (10) | 0.65268 (10) | 0.69397 (7) | 0.03317 (16) |
| O2 | 0.2634 (4) | 0.2541 (3) | 0.5927 (3) | 0.0447 (5) |
| H2A | 0.146 (4) | 0.218 (6) | 0.594 (5) | 0.081 (16)* |
| H2B | 0.305 (7) | 0.162 (5) | 0.551 (5) | 0.087 (16)* |
| C2 | 0.7655 (7) | 0.6608 (6) | 1.0222 (4) | 0.0655 (11) |
| H2 | 0.802254 | 0.582800 | 1.090313 | 0.079* |
| C3 | 0.7826 (6) | 0.8564 (6) | 1.0704 (3) | 0.0543 (9) |
| H3 | 0.829678 | 0.913307 | 1.171227 | 0.065* |
| C4 | 0.7299 (6) | 0.9692 (5) | 0.9693 (4) | 0.0532 (9) |
| H4 | 0.742760 | 1.104037 | 1.001068 | 0.064* |
| C5 | 0.6577 (5) | 0.8836 (5) | 0.8203 (3) | 0.0421 (7) |
| H5 | 0.619974 | 0.959566 | 0.750808 | 0.051* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Mn1 | 0.0228 (2) | 0.0328 (2) | 0.0259 (2) | 0.00479 (16) | 0.00858 (16) | 0.00467 (16) |
| Cl1 | 0.0478 (4) | 0.0329 (4) | 0.0481 (4) | 0.0073 (3) | 0.0188 (4) | 0.0156 (3) |
| O1 | 0.0230 (9) | 0.0460 (12) | 0.0238 (9) | 0.0052 (8) | 0.0062 (8) | -0.0006 (8) |
| N1 | 0.0232 (11) | 0.0371 (12) | 0.0233 (10) | 0.0033 (9) | 0.0078 (9) | 0.0052 (9) |
| C1 | 0.076 (2) | 0.0386 (17) | 0.0325 (15) | 0.0152 (16) | 0.0152 (16) | 0.0124 (13) |
| Cl2 | 0.0307 (3) | 0.0377 (4) | 0.0267 (3) | 0.0016 (3) | 0.0102 (3) | -0.0016 (3) |
| O2 | 0.0553 (16) | 0.0394 (13) | 0.0420 (13) | 0.0117 (11) | 0.0186 (12) | 0.0115 (10) |
| C2 | 0.094 (3) | 0.073 (3) | 0.0290 (16) | 0.031 (2) | 0.0135 (19) | 0.0204 (17) |
| C3 | 0.057 (2) | 0.071 (3) | 0.0249 (15) | 0.0074 (18) | 0.0091 (15) | -0.0009 (15) |
| C4 | 0.067 (2) | 0.0425 (19) | 0.0391 (17) | -0.0022 (17) | 0.0151 (17) | -0.0064 (15) |
| C5 | 0.054 (2) | 0.0388 (17) | 0.0325 (15) | 0.0027 (14) | 0.0149 (14) | 0.0075 (13) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|---------------------|-----------|--------|------------|
| Mn1—Cl1 | 2.479 (2) | C1—C2 | 1.376 (5) |
| Mn1—O1 | 2.177 (3) | O2—H2A | 0.833 (19) |
| Mn1—O1 ⁱ | 2.182 (2) | O2—H2B | 0.819 (19) |

| | | | |
|--|-------------|---------------------------|-----------|
| Mn1—Cl2 ⁱⁱ | 2.5324 (19) | C2—H2 | 0.9300 |
| Mn1—Cl2 | 2.5240 (19) | C2—C3 | 1.353 (5) |
| Mn1—O2 | 2.250 (3) | C3—H3 | 0.9300 |
| O1—N1 | 1.341 (3) | C3—C4 | 1.364 (5) |
| N1—C1 | 1.331 (4) | C4—H4 | 0.9300 |
| N1—C5 | 1.339 (4) | C4—C5 | 1.377 (4) |
| C1—H1 | 0.9300 | C5—H5 | 0.9300 |
| | | | |
| Cl1—Mn1—Cl2 | 93.43 (6) | C5—N1—O1 | 118.0 (2) |
| Cl1—Mn1—Cl2 ⁱⁱ | 92.57 (6) | N1—C1—H1 | 120.4 |
| O1 ⁱ —Mn1—Cl1 | 95.12 (8) | N1—C1—C2 | 119.1 (3) |
| O1—Mn1—Cl1 | 93.65 (7) | C2—C1—H1 | 120.4 |
| O1—Mn1—O1 ⁱ | 72.02 (10) | Mn1—Cl2—Mn1 ⁱⁱ | 84.42 (7) |
| O1—Mn1—Cl2 ⁱⁱ | 165.77 (6) | Mn1—O2—H2A | 108 (3) |
| O1 ⁱ —Mn1—Cl2 ⁱⁱ | 94.69 (9) | Mn1—O2—H2B | 116 (3) |
| O1 ⁱ —Mn1—Cl2 | 166.32 (5) | H2A—O2—H2B | 110 (4) |
| O1—Mn1—Cl2 | 96.81 (8) | C1—C2—H2 | 119.7 |
| O1—Mn1—O2 | 86.96 (9) | C3—C2—C1 | 120.5 (3) |
| O1 ⁱ —Mn1—O2 | 87.46 (10) | C3—C2—H2 | 119.7 |
| Cl2—Mn1—Cl2 ⁱⁱ | 95.58 (7) | C2—C3—H3 | 120.4 |
| O2—Mn1—Cl1 | 177.42 (7) | C2—C3—C4 | 119.1 (3) |
| O2—Mn1—Cl2 ⁱⁱ | 87.40 (8) | C4—C3—H3 | 120.4 |
| O2—Mn1—Cl2 | 84.01 (9) | C3—C4—H4 | 120.0 |
| Mn1—O1—Mn1 ⁱ | 107.98 (10) | C3—C4—C5 | 120.1 (3) |
| N1—O1—Mn1 | 123.78 (14) | C5—C4—H4 | 120.0 |
| N1—O1—Mn1 ⁱ | 126.50 (16) | N1—C5—C4 | 119.1 (3) |
| C1—N1—O1 | 119.9 (2) | N1—C5—H5 | 120.5 |
| C1—N1—C5 | 122.0 (3) | C4—C5—H5 | 120.5 |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O2—H2A \cdots Cl1 ⁱⁱ | 0.83 (2) | 2.53 (2) | 3.348 (4) | 168 (4) |
| O2—H2B \cdots Cl1 ⁱⁱⁱ | 0.82 (2) | 2.52 (3) | 3.232 (4) | 147 (4) |

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

catena-Poly[[aquachloridomanganese(II)]-di- μ -chlorido-[aquachloridomanganese(II)]-bis(μ -2-methylpyridine *N*-oxide)] (II)

Crystal data

[MnCl₂(C₆H₇NO)(H₂O)]
M_r = 252.98
 Orthorhombic, *P*2₁2₁2₁
a = 6.862 (2) \AA
b = 7.491 (2) \AA
c = 18.047 (5) \AA
V = 927.7 (4) \AA^3

Z = 4
F(000) = 508
D_x = 1.811 Mg m⁻³
 Mo *K* α radiation, λ = 0.71075 \AA
 Cell parameters from 2686 reflections
 θ = 2.7–27.5 $^\circ$
 μ = 1.96 mm⁻¹

$T = 173$ K $0.2 \times 0.2 \times 0.1$ mm
Prism, colorless

Data collection

| | |
|---|--|
| Rigaku XtalLab mini CCD diffractometer | 2109 independent reflections |
| ω scans | 1800 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (REQAB; Rigaku, 1998) | $R_{\text{int}} = 0.051$ |
| $T_{\text{min}} = 0.563$, $T_{\text{max}} = 0.737$ | $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.3^\circ$ |
| 8438 measured reflections | $h = -8 \rightarrow 8$ |
| | $k = -9 \rightarrow 9$ |
| | $l = -23 \rightarrow 23$ |

Refinement

| | |
|----------------------------------|--|
| Refinement on F^2 | H-atom parameters constrained |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.004P)^2 + 2.3909P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.100$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 1.12$ | $\Delta\rho_{\text{max}} = 0.95 \text{ e } \text{\AA}^{-3}$ |
| 2109 reflections | $\Delta\rho_{\text{min}} = -0.73 \text{ e } \text{\AA}^{-3}$ |
| 112 parameters | Absolute structure: Refined as an inversion twin. |
| 0 restraints | Absolute structure parameter: 0.44 (8) |
| Primary atom site location: dual | |
| Hydrogen site location: mixed | |

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.

Refinement. Refined as a 2-component inversion twin.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|--------------|--------------|----------------------------------|
| Mn1 | 0.5059 (2) | 0.73290 (15) | 0.50137 (7) | 0.0197 (2) |
| Cl1 | 0.2537 (3) | 0.6800 (2) | 0.40260 (8) | 0.0226 (3) |
| O1 | 0.7561 (8) | 0.7085 (6) | 0.42855 (19) | 0.0179 (9) |
| N1 | 0.7503 (11) | 0.7249 (7) | 0.3544 (2) | 0.0199 (11) |
| C1 | 0.7553 (14) | 0.5782 (9) | 0.3112 (3) | 0.0276 (15) |
| Cl2 | 0.5309 (3) | 0.4110 (3) | 0.53742 (11) | 0.0325 (5) |
| O2 | 0.4833 (8) | 1.0223 (7) | 0.4655 (3) | 0.0265 (12) |
| H2A | 0.546895 | 1.093811 | 0.497004 | 0.040* |
| H2B | 0.358601 | 1.056880 | 0.464095 | 0.040* |
| C2 | 0.7532 (15) | 0.6041 (10) | 0.2345 (3) | 0.0321 (16) |
| H2 | 0.758660 | 0.503891 | 0.202342 | 0.038* |
| C3 | 0.7436 (16) | 0.7719 (11) | 0.2056 (4) | 0.0370 (18) |
| H3 | 0.740766 | 0.787849 | 0.153377 | 0.044* |
| C4 | 0.7378 (16) | 0.9180 (10) | 0.2515 (4) | 0.0371 (19) |
| H4 | 0.731159 | 1.035141 | 0.231495 | 0.044* |
| C5 | 0.7418 (15) | 0.8925 (9) | 0.3261 (3) | 0.0283 (16) |
| H5 | 0.738625 | 0.992359 | 0.358479 | 0.034* |
| C6 | 0.7629 (17) | 0.4059 (10) | 0.3484 (4) | 0.040 (2) |

| | | | | |
|-----|----------|----------|----------|--------|
| H6A | 0.757534 | 0.310158 | 0.311520 | 0.048* |
| H6B | 0.651845 | 0.395059 | 0.382265 | 0.048* |
| H6C | 0.884583 | 0.396660 | 0.376629 | 0.048* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|------------|--------------|
| Mn1 | 0.0171 (4) | 0.0266 (5) | 0.0154 (4) | −0.0028 (5) | 0.0017 (4) | −0.0008 (4) |
| Cl1 | 0.0212 (7) | 0.0300 (9) | 0.0167 (6) | 0.0003 (10) | 0.0004 (8) | −0.0069 (6) |
| O1 | 0.020 (2) | 0.025 (3) | 0.0089 (16) | −0.005 (3) | −0.002 (2) | −0.0013 (16) |
| N1 | 0.019 (2) | 0.029 (3) | 0.012 (2) | 0.002 (3) | 0.002 (3) | −0.001 (2) |
| C1 | 0.028 (4) | 0.028 (4) | 0.026 (3) | 0.003 (5) | −0.001 (4) | −0.005 (3) |
| Cl2 | 0.0377 (12) | 0.0234 (10) | 0.0365 (11) | −0.0021 (10) | 0.0037 (9) | 0.0050 (8) |
| O2 | 0.015 (3) | 0.048 (3) | 0.016 (2) | −0.009 (3) | 0.002 (2) | −0.003 (2) |
| C2 | 0.036 (4) | 0.046 (5) | 0.015 (3) | 0.007 (6) | 0.002 (4) | −0.004 (3) |
| C3 | 0.048 (5) | 0.046 (5) | 0.017 (3) | 0.004 (6) | 0.001 (4) | 0.001 (3) |
| C4 | 0.060 (5) | 0.027 (4) | 0.024 (4) | 0.002 (6) | 0.003 (5) | 0.005 (3) |
| C5 | 0.042 (4) | 0.026 (4) | 0.017 (3) | 0.007 (5) | 0.004 (4) | −0.002 (3) |
| C6 | 0.061 (6) | 0.029 (4) | 0.029 (4) | 0.007 (6) | 0.001 (5) | 0.000 (3) |

Geometric parameters (Å, °)

| | | | |
|--|------------|------------|------------|
| Mn1—Cl1 ⁱ | 2.514 (3) | O2—H2B | 0.8947 |
| Mn1—Cl1 | 2.516 (4) | C2—H2 | 0.9500 |
| Mn1—O1 ⁱⁱ | 2.174 (5) | C2—C3 | 1.363 (10) |
| Mn1—O1 | 2.171 (6) | C3—H3 | 0.9500 |
| Mn1—Cl2 | 2.503 (4) | C3—C4 | 1.374 (10) |
| Mn1—O2 | 2.268 (6) | C4—H4 | 0.9500 |
| O1—N1 | 1.345 (6) | C4—C5 | 1.360 (9) |
| N1—C1 | 1.348 (8) | C5—H5 | 0.9500 |
| N1—C5 | 1.357 (8) | C6—H6A | 0.9800 |
| C1—C2 | 1.397 (9) | C6—H6B | 0.9800 |
| C1—C6 | 1.456 (10) | C6—H6C | 0.9800 |
| O2—H2A | 0.8951 | | |
| Cl1 ⁱ —Mn1—Cl1 | 174.01 (5) | N1—C1—C6 | 117.1 (6) |
| O1 ⁱⁱ —Mn1—Cl1 | 84.38 (18) | C2—C1—C6 | 125.5 (7) |
| O1—Mn1—Cl1 ⁱ | 84.49 (18) | Mn1—O2—H2A | 110.9 |
| O1 ⁱⁱ —Mn1—Cl1 ⁱ | 94.57 (18) | Mn1—O2—H2B | 110.5 |
| O1—Mn1—Cl1 | 95.84 (18) | H2A—O2—H2B | 108.1 |
| O1—Mn1—O1 ⁱⁱ | 173.11 (6) | C1—C2—H2 | 119.7 |
| O1—Mn1—Cl2 | 91.26 (14) | C3—C2—C1 | 120.5 (7) |
| O1 ⁱⁱ —Mn1—Cl2 | 95.58 (14) | C3—C2—H2 | 119.7 |
| O1 ⁱⁱ —Mn1—O2 | 85.39 (19) | C2—C3—H3 | 119.8 |
| O1—Mn1—O2 | 87.78 (19) | C2—C3—C4 | 120.3 (6) |
| Cl2—Mn1—Cl1 ⁱ | 91.40 (9) | C4—C3—H3 | 119.8 |
| Cl2—Mn1—Cl1 | 94.57 (9) | C3—C4—H4 | 120.5 |
| O2—Mn1—Cl1 | 84.34 (16) | C5—C4—C3 | 119.0 (7) |

| | | | |
|----------------------------|-------------|-------------|-------------|
| O2—Mn1—C11 ⁱ | 89.71 (16) | C5—C4—H4 | 120.5 |
| O2—Mn1—C12 | 178.46 (15) | N1—C5—C4 | 120.3 (6) |
| Mn1 ⁱⁱ —C11—Mn1 | 86.32 (13) | N1—C5—H5 | 119.9 |
| Mn1—O1—Mn1 ⁱ | 104.73 (19) | C4—C5—H5 | 119.9 |
| N1—O1—Mn1 ⁱ | 125.7 (5) | C1—C6—H6A | 109.5 |
| N1—O1—Mn1 | 124.9 (5) | C1—C6—H6B | 109.5 |
| O1—N1—C1 | 120.1 (5) | C1—C6—H6C | 109.5 |
| O1—N1—C5 | 117.4 (5) | H6A—C6—H6B | 109.5 |
| C1—N1—C5 | 122.5 (5) | H6A—C6—H6C | 109.5 |
| N1—C1—C2 | 117.4 (7) | H6B—C6—H6C | 109.5 |
| Mn1—O1—N1—C1 | -102.4 (8) | C1—N1—C5—C4 | 0.0 (15) |
| Mn1 ⁱ —O1—N1—C1 | 105.6 (8) | C1—C2—C3—C4 | 0.7 (17) |
| Mn1—O1—N1—C5 | 78.4 (9) | C2—C3—C4—C5 | 0.0 (17) |
| Mn1 ⁱ —O1—N1—C5 | -73.7 (9) | C3—C4—C5—N1 | -0.3 (17) |
| O1—N1—C1—C2 | -178.6 (8) | C5—N1—C1—C2 | 0.6 (14) |
| O1—N1—C1—C6 | 1.2 (13) | C5—N1—C1—C6 | -179.6 (10) |
| O1—N1—C5—C4 | 179.3 (9) | C6—C1—C2—C3 | 179.2 (11) |
| N1—C1—C2—C3 | -1.0 (16) | | |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| O2—H2A \cdots C12 ⁱⁱⁱ | 0.90 | 2.49 | 3.205 (7) | 137 |
| O2—H2B \cdots C12 ⁱⁱ | 0.89 | 2.26 | 3.145 (7) | 169 |

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

Bis(μ -3-methylpyridine *N*-oxide)bis[diaquadichloridomanganese(II)] (III)

Crystal data

$[\text{Mn}_2\text{Cl}_4(\text{C}_6\text{H}_7\text{NO})_2(\text{H}_2\text{O})_4]$

$M_r = 541.99$

Triclinic, $P\bar{1}$

$a = 7.902$ (7) \AA

$b = 8.026$ (7) \AA

$c = 9.893$ (8) \AA

$\alpha = 98.033$ (1) $^\circ$

$\beta = 99.272$ (7) $^\circ$

$\gamma = 113.634$ (11) $^\circ$

$V = 552.6$ (8) \AA^3

$Z = 1$

$F(000) = 274$

$D_x = 1.629$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 5886 reflections

$\theta = 2.8\text{--}27.5^\circ$

$\mu = 1.65$ mm^{-1}

$T = 173$ K

Prism, clear brown

$0.85 \times 0.5 \times 0.28$ mm

Data collection

Rigaku XtaLab mini CCD
diffractometer

ω scans

Absorption correction: multi-scan
(REQAB; Rigaku, 1998)

$T_{\min} = 0.482, T_{\max} = 0.630$

5837 measured reflections

2553 independent reflections

2375 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.072$

$\theta_{\max} = 27.6^\circ, \theta_{\min} = 2.8^\circ$

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.087$

$S = 1.07$

2553 reflections

135 parameters

4 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.023P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

Special details

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

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Mn1 | 0.27031 (3) | 0.40104 (3) | 0.53553 (2) | 0.02936 (11) |
| Cl1 | 0.14922 (6) | 0.48607 (7) | 0.73553 (4) | 0.04342 (14) |
| Cl2 | 0.32299 (6) | 0.13672 (6) | 0.60668 (6) | 0.04544 (15) |
| O1 | 0.56562 (15) | 0.60090 (16) | 0.62683 (12) | 0.0345 (3) |
| O2 | 0.2605 (2) | 0.6467 (2) | 0.45620 (16) | 0.0443 (3) |
| H2A | 0.355 (3) | 0.710 (3) | 0.436 (2) | 0.055 (7)* |
| H2B | 0.167 (3) | 0.639 (3) | 0.404 (2) | 0.062 (8)* |
| O3 | 0.00694 (17) | 0.23434 (18) | 0.37696 (14) | 0.0395 (3) |
| H3A | -0.069 (3) | 0.128 (2) | 0.390 (2) | 0.062 (7)* |
| H3B | -0.054 (4) | 0.288 (4) | 0.352 (3) | 0.081 (10)* |
| N1 | 0.62886 (17) | 0.71302 (18) | 0.75570 (13) | 0.0294 (3) |
| C1 | 0.6561 (2) | 0.8903 (2) | 0.77007 (17) | 0.0342 (4) |
| H1 | 0.631326 | 0.934009 | 0.690425 | 0.041* |
| C2 | 0.7204 (3) | 1.0102 (3) | 0.90084 (19) | 0.0415 (4) |
| C3 | 0.7538 (3) | 0.9400 (3) | 1.0169 (2) | 0.0568 (6) |
| H3 | 0.795802 | 1.016517 | 1.106619 | 0.068* |
| C4 | 0.7250 (4) | 0.7571 (4) | 0.9997 (2) | 0.0611 (6) |
| H4 | 0.748138 | 0.710090 | 1.077885 | 0.073* |
| C5 | 0.6620 (3) | 0.6431 (3) | 0.8670 (2) | 0.0472 (5) |
| H5 | 0.642729 | 0.519251 | 0.854911 | 0.057* |
| C6 | 0.7494 (4) | 1.2087 (3) | 0.9131 (3) | 0.0701 (7) |
| H6A | 0.873126 | 1.282752 | 0.900126 | 0.105* |
| H6B | 0.739622 | 1.256760 | 1.004510 | 0.105* |
| H6C | 0.653880 | 1.213706 | 0.842403 | 0.105* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Mn1 | 0.02821 (16) | 0.02780 (17) | 0.03004 (17) | 0.00959 (12) | 0.00843 (11) | 0.00651 (12) |
| Cl1 | 0.0471 (3) | 0.0617 (3) | 0.0309 (2) | 0.0299 (2) | 0.01431 (18) | 0.0142 (2) |

| | | | | | | |
|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| C12 | 0.0436 (3) | 0.0349 (3) | 0.0596 (3) | 0.0137 (2) | 0.0151 (2) | 0.0236 (2) |
| O1 | 0.0326 (6) | 0.0310 (6) | 0.0313 (6) | 0.0074 (5) | 0.0091 (5) | -0.0010 (5) |
| O2 | 0.0389 (7) | 0.0414 (7) | 0.0584 (9) | 0.0185 (6) | 0.0137 (6) | 0.0231 (7) |
| O3 | 0.0339 (6) | 0.0322 (7) | 0.0438 (7) | 0.0079 (5) | 0.0039 (5) | 0.0080 (6) |
| N1 | 0.0295 (6) | 0.0293 (7) | 0.0271 (6) | 0.0107 (5) | 0.0061 (5) | 0.0062 (5) |
| C1 | 0.0443 (9) | 0.0307 (8) | 0.0273 (7) | 0.0159 (7) | 0.0082 (6) | 0.0067 (6) |
| C2 | 0.0484 (10) | 0.0363 (9) | 0.0336 (8) | 0.0138 (8) | 0.0112 (7) | 0.0016 (7) |
| C3 | 0.0674 (13) | 0.0598 (13) | 0.0262 (9) | 0.0158 (11) | 0.0049 (9) | 0.0014 (9) |
| C4 | 0.0766 (14) | 0.0687 (15) | 0.0355 (10) | 0.0289 (12) | 0.0028 (10) | 0.0246 (10) |
| C5 | 0.0591 (11) | 0.0424 (10) | 0.0425 (10) | 0.0236 (9) | 0.0064 (9) | 0.0186 (9) |
| C6 | 0.105 (2) | 0.0393 (11) | 0.0571 (14) | 0.0257 (13) | 0.0237 (14) | -0.0048 (10) |

Geometric parameters (Å, °)

| | | | |
|--------------------------|-------------|-----------|-------------|
| Mn1—Cl1 | 2.4602 (15) | C1—H1 | 0.9300 |
| Mn1—Cl2 | 2.4900 (19) | C1—C2 | 1.381 (2) |
| Mn1—O1 ⁱ | 2.2228 (17) | C2—C3 | 1.381 (3) |
| Mn1—O1 | 2.1792 (18) | C2—C6 | 1.500 (3) |
| Mn1—O2 | 2.246 (2) | C3—H3 | 0.9300 |
| Mn1—O3 | 2.1704 (17) | C3—C4 | 1.373 (4) |
| O1—N1 | 1.3411 (19) | C4—H4 | 0.9300 |
| O2—H2A | 0.791 (15) | C4—C5 | 1.377 (3) |
| O2—H2B | 0.802 (16) | C5—H5 | 0.9300 |
| O3—H3A | 0.863 (16) | C6—H6A | 0.9600 |
| O3—H3B | 0.795 (17) | C6—H6B | 0.9600 |
| N1—C1 | 1.334 (2) | C6—H6C | 0.9600 |
| N1—C5 | 1.340 (2) | | |
| Cl1—Mn1—Cl2 | 98.31 (4) | C1—N1—O1 | 119.45 (13) |
| O1—Mn1—Cl1 | 95.44 (6) | C1—N1—C5 | 121.69 (16) |
| O1 ⁱ —Mn1—Cl1 | 165.45 (4) | C5—N1—O1 | 118.86 (16) |
| O1 ⁱ —Mn1—Cl2 | 89.66 (5) | N1—C1—H1 | 119.3 |
| O1—Mn1—Cl2 | 93.11 (7) | N1—C1—C2 | 121.31 (16) |
| O1—Mn1—O1 ⁱ | 71.87 (7) | C2—C1—H1 | 119.3 |
| O1 ⁱ —Mn1—O2 | 82.07 (6) | C1—C2—C3 | 117.8 (2) |
| O1—Mn1—O2 | 81.64 (7) | C1—C2—C6 | 119.87 (19) |
| O2—Mn1—Cl1 | 89.20 (6) | C3—C2—C6 | 122.4 (2) |
| O2—Mn1—Cl2 | 171.24 (4) | C2—C3—H3 | 120.0 |
| O3—Mn1—Cl1 | 101.10 (7) | C4—C3—C2 | 119.99 (19) |
| O3—Mn1—Cl2 | 97.13 (6) | C4—C3—H3 | 120.0 |
| O3—Mn1—O1 ⁱ | 89.88 (8) | C3—C4—H4 | 119.9 |
| O3—Mn1—O1 | 159.02 (5) | C3—C4—C5 | 120.16 (18) |
| O3—Mn1—O2 | 85.76 (7) | C5—C4—H4 | 119.9 |
| Mn1—O1—Mn1 ⁱ | 108.13 (7) | N1—C5—C4 | 119.10 (19) |
| N1—O1—Mn1 | 124.29 (9) | N1—C5—H5 | 120.5 |
| N1—O1—Mn1 ⁱ | 127.41 (10) | C4—C5—H5 | 120.5 |
| Mn1—O2—H2A | 114.4 (17) | C2—C6—H6A | 109.5 |
| Mn1—O2—H2B | 121.9 (18) | C2—C6—H6B | 109.5 |

| | | | |
|------------|------------|------------|-------|
| H2A—O2—H2B | 112 (2) | C2—C6—H6C | 109.5 |
| Mn1—O3—H3A | 118.3 (16) | H6A—C6—H6B | 109.5 |
| Mn1—O3—H3B | 116 (2) | H6A—C6—H6C | 109.5 |
| H3A—O3—H3B | 109 (3) | H6B—C6—H6C | 109.5 |

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D—H</i> ⋯ <i>A</i> | <i>D—H</i> | <i>H</i> ⋯ <i>A</i> | <i>D</i> ⋯ <i>A</i> | <i>D—H</i> ⋯ <i>A</i> |
|---------------------------|------------|---------------------|---------------------|-----------------------|
| O2—H2B⋯C11 ⁱⁱ | 0.80 (2) | 2.38 (2) | 3.147 (3) | 161 (2) |
| O3—H3A⋯C12 ⁱⁱⁱ | 0.86 (2) | 2.28 (2) | 3.120 (2) | 167 (2) |

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