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# Chlorido[2,15-dimethyl-3,7,10,14,20-pentaazabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene]manganese(II) perchlorate acetonitrile solvate

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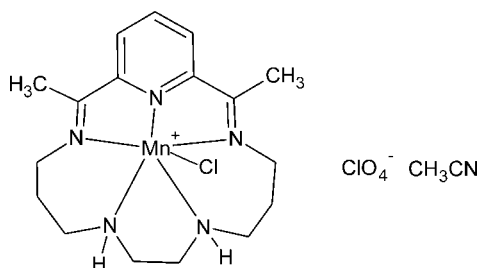
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å; disorder in solvent or counterion;  $R$  factor = 0.042;  $wR$  factor = 0.132; data-to-parameter ratio = 13.1.

The Mn ion in the title complex,  $[\text{MnCl}(\text{C}_{17}\text{H}_{27}\text{N}_5)]\text{ClO}_4 \cdot \text{CH}_3\text{CN}$ , is six-coordinated with a geometry intermediate between pentagonal pyramidal and heavily distorted octahedral. In the macrocycle, the pyridinium ring makes a large dihedral angle of  $63.70$  ( $9$ ) $^\circ$  with the best plane through the remaining four N atoms. This feature is common for 17-membered  $\text{N}_5$  rings, in contrast to their 16- and 15-membered analogues which often form planar  $\text{N}_5$  systems. In the crystal,  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{C}-\text{H} \cdots \text{O}$  interactions help to establish the packing. The perchlorate counter-ion is rotationally disordered around the chlorine centre, with occupation factors of 0.74 (1) and 0.26 (1).

## Related literature

For manganese(II) metalloproteins and pentaaza macrocyclic complexes, see, for example: Riley (1999); Aston *et al.* (2001); Patroniak *et al.* (2004); Radecka-Paryzek *et al.* (2005); Isobe *et al.* (2005); Grabolle *et al.* (2006). For the crystal structures of similar 17-membered macrocycles, see: Drew *et al.* (1977, 1979); Nelson *et al.* (1977); Drew & Nelson (1979).



## Experimental

### Crystal data

$[\text{MnCl}(\text{C}_{17}\text{H}_{27}\text{N}_5)]\text{ClO}_4 \cdot \text{C}_2\text{H}_3\text{N}$   
 $M_r = 532.33$   
 Triclinic,  $P\bar{1}$   
 $a = 10.0583$  (7) Å  
 $b = 10.9118$  (7) Å  
 $c = 11.9591$  (8) Å  
 $\alpha = 89.492$  (5) $^\circ$   
 $\beta = 70.195$  (6) $^\circ$   
 $\gamma = 84.093$  (5) $^\circ$   
 $V = 1227.89$  (14) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.79$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.4 \times 0.2 \times 0.1$  mm

### Data collection

Kuma KM-4 CCD diffractometer  
 Absorption correction: multi-scan (*CrysAlis CCD*; Oxford Diffraction, 2007)  
 $T_{\min} = 0.842$ ,  $T_{\max} = 0.924$   
 9805 measured reflections  
 4301 independent reflections  
 3212 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.132$   
 $S = 1.12$   
 4301 reflections  
 329 parameters  
 68 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.43$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.43$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

|         |           |         |            |
|---------|-----------|---------|------------|
| Mn1—N20 | 2.234 (2) | Mn1—N10 | 2.336 (3)  |
| Mn1—N3  | 2.326 (3) | Mn1—N14 | 2.350 (3)  |
| Mn1—N7  | 2.327 (3) | Mn1—Cl1 | 2.3934 (9) |

Table 2

Hydrogen-bond geometry (Å,  $^\circ$ ).

| $D-\text{H} \cdots A$                       | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|---|--------------|---------------------|--------------|-----------------------|
| $\text{C}25-\text{H}252 \cdots \text{O}2^i$ | 0.96         | 2.27                | 3.168 (6)    | 156                   |
| $\text{N}7-\text{H}7 \cdots \text{O}1$      | 0.91         | 2.16                | 3.050 (6)    | 165                   |
| $\text{N}10-\text{H}10 \cdots \text{O}3A^i$ | 0.91         | 2.23                | 3.13 (2)     | 169                   |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2236).

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**supplementary materials**

*Acta Cryst.* (2009). E65, m290-m291 [ doi:10.1107/S1600536809005595 ]

**Chlorido[2,15-dimethyl-3,7,10,14,20-pentaazabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene]manganese(II) perchlorate acetonitrile solvate**

**A. Glowinska, V. Patroniak, W. Radecka-Paryzek and M. Kubicki**

**Comment**

The significance of metal complexes containing synthetic macrocyclic ligands is most obvious as it relates to naturally occurring macrocyclic systems such as the porphyrin core in hemoglobin or chlorophylls, the corrin in vitamin B<sub>12</sub>, cyclic polyether antibiotics. Many of the recent advances in the coordination chemistry of manganese have arisen from the desire to understand and mimic the mechanism of water oxidation and dioxygen evolution during photosynthesis catalyzed by manganese metalloproteins (Grabolle *et al.*, 2006; Isobe *et al.*, 2005). The manganese(II) pentaaza macrocyclic complexes have been considered as synzymes (low molecular weight catalysts which mimic a natural enzymatic function) for superoxide anion dismutation and activity with the goal to design and synthesis better human pharmaceutical agents (Riley, 1999; Aston *et al.*, 2001). The effective method for the synthesis of macrocyclic complexes involves the coordination template effect. It consists of a metal ion being used to orient the reacting groups of linear substrates in the desired conformation for the condensation process which ultimately ends with ring closure (Radecka-Paryzek *et al.*, 2005). We have recently reported the first examples of 16-membered macrocyclic lanthanide complexes which are able to activate molecular oxygen (Patroniak *et al.*, 2004). Here we present the template action of manganese(II) in the synthesis of 17-membered pentaaza macrocycle. The crystal structure of the perchlorate salt of the resulting complex, chloro-(2,15-dimethyl-3,7,10,14,20-pentaazabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene)-manganese(ii), **1**, which crystallizes as the acetonitrile solvate, reveals that this metal ion which has no crystal-field stabilization energy in the high-spin state, can be accommodated by the particular stereochemical constraints enforced by the template process and adopt rare coordination geometry.

The N<sub>5</sub>-system in the 17-membered quinquedentate macrocyclic ligand does not form a plane, as it is often a case for 15- and 16-membered analogues (*e.g.* Patroniak *et al.*, 2004). Four non-pyridine nitrogen atoms N3, N7, N10 and N14 are approximately coplanar - however even for these four atoms the maximum deviation from the least-squares plane is as high as 0.207 (2) Å - and the pyridine nitrogen N20 is 1.369 (3) Å out of this plane (Fig. 1). The pyridine ring makes a dihedral angle of 63.70 (9)° with the mean plane of the remaining N<sub>4</sub>-system; a similar value was found in the thiocyanato-lead complex (63.1°, Drew & Nelson, 1979), while it was smaller, but still significant, in other complexes: 48.8° for bromo-mercury (Drew *et al.*, 1979), 49.7° for bromo-cadmium (Drew *et al.*, 1979), and 41.8° for bis-isothiocyanato-manganese (Drew *et al.*, 1977).

This non-planar disposition of five nitrogen atoms results also in an uncommon coordination of the Mn ion, which can be described as intermediate between a heavily distorted pentagonal pyramid (with the Cl atom at the apex and the N<sub>5</sub> system as the base) and a distorted octahedron (*cf.* Table 1).

The perchlorate counterions are disordered over two positions with site occupation factors of 0.74 (1) and 0.26 (1).

Through very weak interactions between cation and anions (See Table 2 for the most relevant ones), a centrosymmetric tetramer is formed around the cell centre, which appears as the building block on which the crystal architecture is based. Two solvent - acetonitrile molecules join to these tetramers by means of a rather linear C—H···O hydrogen bond. These cation-anion groups further organize into columns along the [001] direction, probably through second order contacts involving the

## supplementary materials

Chlorine atoms ( $\text{H}\cdots\text{Cl} \sim 2.90\text{\AA}$ ) which might impose some directionality to the main driving force of the crystal packing, the coulombic interaction between charged fragments.

### Experimental

To a mixture of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.065 g, 0.32 mmol) and  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.059 g, 0.16 mmol) in methanol (5 ml), 4,7-diazadecane-1,10-diamine (0.090 ml, 0.48 mmol) in methanol (5 ml) and 1,2-diacetylpyridine (0.081 g, 0.048 mmol) in methanol (5 ml) was added dropwise with stirring. The reaction was carried out for 24 h under reflux at argon atmosphere. The reaction mixture was evaporated to dryness and the remaining solid dissolved in boiling acetonitrile (15 ml), filtered under gravity, and left to stand overnight. Crystals suitable for X-ray diffraction analysis were formed.

ESI-MS  $m/z$  (%) = 171 (100  $\{[\text{MnL}^2]\}^{2+}$ ); 377 (33  $\{[\text{MnL}^2](\text{Cl})\}^+$ ); 441 (39  $\{[\text{MnL}^2](\text{ClO}_4)\}^+$ ).

Elemental analysis calculated for  $[\text{MnL}^2\text{Cl}](\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ : C, 32.83; H, 6.37; N, 11.96; found: C, 33.29; H, 4.72; N, 6.7.

### Refinement

Hydrogen atoms were located geometrically and refined in the 'riding model', with  $U_{\text{iso}}$ 's set at 1.2 (1.5 for methyl groups) times  $U_{\text{eq}}$ 's of their appropriate carrier atoms. Weak restraints were applied to both the geometry (*DFIX* for Cl—O bond lengths and O $\cdots$ O 1,3-distances) and displacement parameters (*ISOR*) of O atoms from the disordered perchlorate group.

### Figures

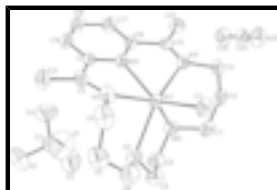


Fig. 1. Anisotropic displacement ellipsoid representation (at the 50% probability level) of the asymmetric unit content. Only the larger fraction of the disordered perchlorate is shown.

### Chlorido[2,15-dimethyl-3,7,10,14,20-pentaazabicyclo[14.3.1]eicosa- 1(20),2,14,16,18-pentaene]manganese(II) perchlorate acetonitrile solvate

#### Crystal data

$[\text{MnCl}(\text{C}_{17}\text{H}_{27}\text{N}_5)]\text{ClO}_4 \cdot \text{C}_2\text{H}_3\text{N}$

$M_r = 532.33$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 10.0583$  (7)  $\text{\AA}$

$b = 10.9118$  (7)  $\text{\AA}$

$c = 11.9591$  (8)  $\text{\AA}$

$\alpha = 89.492$  (5) $^\circ$

$\beta = 70.195$  (6) $^\circ$

$\gamma = 84.093$  (5) $^\circ$

$Z = 2$

$F_{000} = 554$

$D_x = 1.440$   $\text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073$   $\text{\AA}$

Cell parameters from 5931 reflections

$\theta = 3\text{--}24^\circ$

$\mu = 0.79$   $\text{mm}^{-1}$

$T = 293$  K

Block, colourless

$0.4 \times 0.2 \times 0.1$  mm

$$V = 1227.89 (14) \text{ \AA}^3$$

### Data collection

|  |  |
|--|--|
| Kuma KM-4 CCD diffractometer   | 4301 independent reflections           |
| Radiation source: fine-focus sealed tube                                   | 3212 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite  | $R_{\text{int}} = 0.018$               |
| $T = 293 \text{ K}$  | $\theta_{\text{max}} = 25.0^\circ$     |
| $\omega$ scans   | $\theta_{\text{min}} = 2.7^\circ$      |
| Absorption correction: multi-scan (CrysAlis CCD; Oxford Diffraction, 2007) | $h = -11 \rightarrow 8$                |
| $T_{\text{min}} = 0.842$ , $T_{\text{max}} = 0.924$                        | $k = -12 \rightarrow 12$               |
| 9805 measured reflections  | $l = -14 \rightarrow 12$               |

### Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.042$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.132$  | $w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$                    |
| $S = 1.12$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 4301 reflections   | $(\Delta/\sigma)_{\text{max}} < 0.001$                   |
| 329 parameters   | $\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$      |
| 68 restraints  | $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$     |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none                              |

### Special details

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|     | $x$          | $y$         | $z$         | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|--------------|-------------|-------------|----------------------------------|-----------|
| Mn1 | 0.44426 (5)  | 0.28963 (4) | 0.20642 (4) | 0.04702 (19)                     |           |
| Cl1 | 0.31564 (10) | 0.17792 (9) | 0.11320 (8) | 0.0692 (3)                       |           |
| C1  | 0.7488 (3)   | 0.3700 (3)  | 0.1391 (2)  | 0.0476 (7)                       |           |

## supplementary materials

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|      |             |             |            |             |
|------|-------------|-------------|------------|-------------|
| C2   | 0.7747 (3)  | 0.2331 (3)  | 0.1285 (3) | 0.0544 (8)  |
| C21  | 0.9208 (4)  | 0.1739 (4)  | 0.1132 (4) | 0.0838 (12) |
| H21A | 0.9209      | 0.0859      | 0.1134     | 0.109*      |
| H21B | 0.9492      | 0.2002      | 0.1774     | 0.109*      |
| H21C | 0.9862      | 0.1976      | 0.0390     | 0.109*      |
| N3   | 0.6681 (3)  | 0.1794 (2)  | 0.1317 (2) | 0.0579 (7)  |
| C4   | 0.6780 (5)  | 0.0432 (4)  | 0.1191 (4) | 0.0882 (13) |
| H4A  | 0.7750      | 0.0114      | 0.0738     | 0.106*      |
| H4B  | 0.6173      | 0.0215      | 0.0759     | 0.106*      |
| C5   | 0.6331 (5)  | -0.0152 (3) | 0.2403 (5) | 0.0938 (14) |
| H5A  | 0.6526      | -0.1040     | 0.2289     | 0.113*      |
| H5B  | 0.6910      | 0.0110      | 0.2842     | 0.113*      |
| C6   | 0.4797 (5)  | 0.0153 (4)  | 0.3139 (5) | 0.0972 (15) |
| H6A  | 0.4210      | -0.0044     | 0.2682     | 0.117*      |
| H6B  | 0.4571      | -0.0350     | 0.3838     | 0.117*      |
| N7   | 0.4460 (3)  | 0.1468 (3)  | 0.3517 (3) | 0.0682 (8)  |
| H7   | 0.5139      | 0.1655      | 0.3813     | 0.082*      |
| C8   | 0.3099 (4)  | 0.1695 (4)  | 0.4485 (4) | 0.0905 (13) |
| H8A  | 0.3115      | 0.1198      | 0.5158     | 0.109*      |
| H8B  | 0.2339      | 0.1468      | 0.4227     | 0.109*      |
| C9   | 0.2845 (5)  | 0.3013 (4)  | 0.4839 (3) | 0.0799 (11) |
| H9A  | 0.3599      | 0.3232      | 0.5109     | 0.096*      |
| H9B  | 0.1953      | 0.3167      | 0.5492     | 0.096*      |
| N10  | 0.2796 (3)  | 0.3788 (3)  | 0.3822 (2) | 0.0589 (7)  |
| H10  | 0.3047      | 0.4543      | 0.3933     | 0.071*      |
| C11  | 0.1369 (3)  | 0.3957 (4)  | 0.3697 (3) | 0.0662 (9)  |
| H11A | 0.0650      | 0.4035      | 0.4482     | 0.079*      |
| H11B | 0.1234      | 0.3230      | 0.3304     | 0.079*      |
| C12  | 0.1163 (3)  | 0.5084 (4)  | 0.2992 (3) | 0.0635 (9)  |
| H12A | 0.1351      | 0.5800      | 0.3367     | 0.076*      |
| H12B | 0.0175      | 0.5204      | 0.3045     | 0.076*      |
| C13  | 0.2087 (3)  | 0.5036 (4)  | 0.1681 (3) | 0.0592 (9)  |
| H13A | 0.1856      | 0.4369      | 0.1272     | 0.071*      |
| H13B | 0.1904      | 0.5802      | 0.1315     | 0.071*      |
| N14  | 0.3594 (2)  | 0.4841 (2)  | 0.1571 (2) | 0.0478 (6)  |
| C15  | 0.4326 (3)  | 0.5735 (3)  | 0.1512 (2) | 0.0469 (7)  |
| C22  | 0.3868 (4)  | 0.7083 (3)  | 0.1474 (3) | 0.0668 (10) |
| H22A | 0.2947      | 0.7186      | 0.1391     | 0.087*      |
| H22B | 0.4540      | 0.7437      | 0.0810     | 0.087*      |
| H22C | 0.3825      | 0.7487      | 0.2197     | 0.087*      |
| C16  | 0.5821 (3)  | 0.5369 (3)  | 0.1479 (3) | 0.0476 (7)  |
| C17  | 0.6801 (4)  | 0.6185 (3)  | 0.1400 (3) | 0.0631 (9)  |
| H17A | 0.6559      | 0.7028      | 0.1380     | 0.076*      |
| C18  | 0.8150 (4)  | 0.5727 (4)  | 0.1352 (3) | 0.0704 (10) |
| H18A | 0.8816      | 0.6263      | 0.1340     | 0.084*      |
| C19  | 0.8505 (3)  | 0.4478 (4)  | 0.1321 (3) | 0.0654 (10) |
| H19A | 0.9423      | 0.4160      | 0.1254     | 0.078*      |
| N20  | 0.6156 (2)  | 0.4155 (2)  | 0.1509 (2) | 0.0425 (5)  |
| N23  | -0.0126 (5) | 0.8132 (4)  | 0.1994 (4) | 0.1062 (13) |

|      |              |             |             |             |           |
|------|--------------|-------------|-------------|-------------|-----------|
| C24  | 0.0164 (4)   | 0.8829 (4)  | 0.2528 (4)  | 0.0760 (11) |           |
| C25  | 0.0549 (6)   | 0.9727 (4)  | 0.3213 (5)  | 0.1053 (16) |           |
| H251 | 0.1320       | 1.0136      | 0.2699      | 0.137*      |           |
| H252 | 0.0837       | 0.9318      | 0.3821      | 0.137*      |           |
| H253 | -0.0254      | 1.0322      | 0.3574      | 0.137*      |           |
| Cl2  | 0.72849 (11) | 0.28375 (9) | 0.48084 (8) | 0.0727 (3)  |           |
| O1   | 0.7114 (7)   | 0.2002 (6)  | 0.4036 (5)  | 0.155 (3)   | 0.744 (7) |
| O2   | 0.8302 (5)   | 0.2290 (5)  | 0.5320 (5)  | 0.136 (2)   | 0.744 (7) |
| O3   | 0.6031 (5)   | 0.3181 (7)  | 0.5761 (4)  | 0.156 (3)   | 0.744 (7) |
| O4   | 0.7887 (6)   | 0.3879 (5)  | 0.4240 (5)  | 0.149 (3)   | 0.744 (7) |
| O1A  | 0.6571 (17)  | 0.3333 (16) | 0.4029 (12) | 0.150 (8)   | 0.256 (7) |
| O2A  | 0.706 (2)    | 0.1585 (7)  | 0.491 (2)   | 0.194 (10)  | 0.256 (7) |
| O3A  | 0.668 (2)    | 0.3472 (18) | 0.5903 (10) | 0.202 (13)  | 0.256 (7) |
| O4A  | 0.8736 (8)   | 0.297 (2)   | 0.429 (2)   | 0.45 (4)    | 0.256 (7) |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Mn1 | 0.0438 (3)  | 0.0503 (3)  | 0.0490 (3)  | -0.0094 (2)  | -0.0170 (2)  | -0.0083 (2)  |
| Cl1 | 0.0697 (6)  | 0.0756 (6)  | 0.0717 (6)  | -0.0229 (5)  | -0.0314 (5)  | -0.0163 (5)  |
| C1  | 0.0384 (15) | 0.068 (2)   | 0.0364 (15) | -0.0069 (14) | -0.0123 (12) | -0.0001 (14) |
| C2  | 0.0488 (18) | 0.070 (2)   | 0.0444 (17) | 0.0035 (16)  | -0.0181 (14) | -0.0054 (15) |
| C21 | 0.053 (2)   | 0.102 (3)   | 0.093 (3)   | 0.014 (2)    | -0.027 (2)   | 0.005 (2)    |
| N3  | 0.0594 (17) | 0.0550 (16) | 0.0611 (17) | 0.0056 (13)  | -0.0254 (14) | -0.0202 (13) |
| C4  | 0.096 (3)   | 0.065 (2)   | 0.113 (4)   | 0.017 (2)    | -0.053 (3)   | -0.039 (2)   |
| C5  | 0.119 (4)   | 0.040 (2)   | 0.138 (4)   | -0.003 (2)   | -0.065 (3)   | -0.007 (2)   |
| C6  | 0.107 (4)   | 0.053 (2)   | 0.145 (4)   | -0.022 (2)   | -0.057 (3)   | 0.013 (3)    |
| N7  | 0.070 (2)   | 0.0633 (18) | 0.078 (2)   | -0.0174 (15) | -0.0311 (17) | 0.0106 (16)  |
| C8  | 0.080 (3)   | 0.098 (3)   | 0.089 (3)   | -0.020 (3)   | -0.021 (2)   | 0.037 (3)    |
| C9  | 0.084 (3)   | 0.098 (3)   | 0.048 (2)   | -0.009 (2)   | -0.0101 (19) | 0.002 (2)    |
| N10 | 0.0586 (16) | 0.0675 (18) | 0.0475 (15) | -0.0065 (14) | -0.0139 (13) | -0.0032 (13) |
| C11 | 0.0507 (19) | 0.084 (3)   | 0.053 (2)   | -0.0094 (18) | -0.0022 (16) | -0.0102 (18) |
| C12 | 0.0380 (17) | 0.090 (3)   | 0.056 (2)   | 0.0052 (17)  | -0.0099 (15) | -0.0180 (18) |
| C13 | 0.0404 (16) | 0.081 (2)   | 0.058 (2)   | 0.0041 (16)  | -0.0216 (15) | -0.0095 (17) |
| N14 | 0.0386 (13) | 0.0638 (17) | 0.0399 (13) | 0.0000 (12)  | -0.0133 (11) | -0.0075 (12) |
| C15 | 0.0493 (17) | 0.0554 (18) | 0.0340 (15) | -0.0048 (14) | -0.0118 (13) | -0.0024 (13) |
| C22 | 0.068 (2)   | 0.056 (2)   | 0.066 (2)   | 0.0073 (17)  | -0.0138 (18) | 0.0016 (17)  |
| C16 | 0.0473 (17) | 0.0570 (19) | 0.0406 (15) | -0.0078 (14) | -0.0169 (13) | -0.0062 (13) |
| C17 | 0.067 (2)   | 0.064 (2)   | 0.062 (2)   | -0.0224 (18) | -0.0226 (18) | -0.0012 (17) |
| C18 | 0.060 (2)   | 0.089 (3)   | 0.074 (2)   | -0.035 (2)   | -0.0295 (19) | -0.001 (2)   |
| C19 | 0.0417 (18) | 0.099 (3)   | 0.060 (2)   | -0.0172 (19) | -0.0211 (16) | 0.005 (2)    |
| N20 | 0.0366 (12) | 0.0502 (14) | 0.0414 (13) | -0.0061 (11) | -0.0134 (10) | -0.0028 (11) |
| N23 | 0.105 (3)   | 0.085 (3)   | 0.138 (4)   | -0.012 (2)   | -0.052 (3)   | -0.015 (3)   |
| C24 | 0.065 (2)   | 0.062 (2)   | 0.102 (3)   | -0.0037 (19) | -0.031 (2)   | 0.009 (2)    |
| C25 | 0.130 (4)   | 0.081 (3)   | 0.125 (4)   | -0.022 (3)   | -0.066 (4)   | 0.007 (3)    |
| Cl2 | 0.0845 (7)  | 0.0778 (6)  | 0.0613 (6)  | -0.0233 (5)  | -0.0277 (5)  | -0.0020 (5)  |
| O1  | 0.182 (5)   | 0.162 (5)   | 0.141 (5)   | -0.044 (4)   | -0.071 (4)   | -0.066 (4)   |
| O2  | 0.143 (4)   | 0.144 (4)   | 0.146 (5)   | 0.012 (3)    | -0.088 (4)   | 0.017 (3)    |

## supplementary materials

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|     |            |            |            |             |             |            |
|-----|------------|------------|------------|-------------|-------------|------------|
| O3  | 0.107 (4)  | 0.252 (7)  | 0.081 (3)  | 0.034 (4)   | -0.012 (3)  | -0.019 (4) |
| O4  | 0.164 (5)  | 0.132 (4)  | 0.169 (5)  | -0.070 (4)  | -0.064 (4)  | 0.062 (4)  |
| O1A | 0.168 (11) | 0.172 (12) | 0.119 (9)  | -0.018 (8)  | -0.060 (8)  | 0.029 (8)  |
| O2A | 0.227 (14) | 0.160 (13) | 0.204 (14) | -0.056 (9)  | -0.074 (10) | 0.006 (9)  |
| O3A | 0.226 (16) | 0.211 (15) | 0.181 (15) | -0.026 (10) | -0.081 (10) | -0.055 (9) |
| O4A | 0.44 (4)   | 0.45 (4)   | 0.46 (4)   | -0.054 (12) | -0.142 (16) | 0.024 (11) |

### *Geometric parameters (Å, °)*

|             |            |             |           |
|-------------|------------|-------------|-----------|
| Mn1—N20     | 2.234 (2)  | C11—H11A    | 0.9700    |
| Mn1—N3      | 2.326 (3)  | C11—H11B    | 0.9700    |
| Mn1—N7      | 2.327 (3)  | C12—C13     | 1.526 (4) |
| Mn1—N10     | 2.336 (3)  | C12—H12A    | 0.9700    |
| Mn1—N14     | 2.350 (3)  | C12—H12B    | 0.9700    |
| Mn1—C11     | 2.3934 (9) | C13—N14     | 1.469 (3) |
| C1—N20      | 1.341 (4)  | C13—H13A    | 0.9700    |
| C1—C19      | 1.376 (4)  | C13—H13B    | 0.9700    |
| C1—C2       | 1.489 (5)  | N14—C15     | 1.269 (4) |
| C2—N3       | 1.263 (4)  | C15—C22     | 1.500 (4) |
| C2—C21      | 1.496 (4)  | C15—C16     | 1.502 (4) |
| C21—H21A    | 0.9600     | C22—H22A    | 0.9600    |
| C21—H21B    | 0.9600     | C22—H22B    | 0.9600    |
| C21—H21C    | 0.9600     | C22—H22C    | 0.9600    |
| N3—C4       | 1.485 (5)  | C16—N20     | 1.337 (4) |
| C4—C5       | 1.520 (6)  | C16—C17     | 1.374 (4) |
| C4—H4A      | 0.9700     | C17—C18     | 1.379 (5) |
| C4—H4B      | 0.9700     | C17—H17A    | 0.9300    |
| C5—C6       | 1.498 (6)  | C18—C19     | 1.370 (5) |
| C5—H5A      | 0.9700     | C18—H18A    | 0.9300    |
| C5—H5B      | 0.9700     | C19—H19A    | 0.9300    |
| C6—N7       | 1.478 (5)  | N23—C24     | 1.118 (5) |
| C6—H6A      | 0.9700     | C24—C25     | 1.446 (7) |
| C6—H6B      | 0.9700     | C25—H251    | 0.9600    |
| N7—C8       | 1.463 (5)  | C25—H252    | 0.9600    |
| N7—H7       | 0.9100     | C25—H253    | 0.9600    |
| C8—C9       | 1.475 (6)  | C12—O1      | 1.367 (3) |
| C8—H8A      | 0.9700     | C12—O2      | 1.438 (3) |
| C8—H8B      | 0.9700     | C12—O3      | 1.403 (4) |
| C9—N10      | 1.487 (4)  | C12—O4      | 1.403 (3) |
| C9—H9A      | 0.9700     | C12—O1A     | 1.429 (5) |
| C9—H9B      | 0.9700     | C12—O2A     | 1.406 (5) |
| N10—C11     | 1.485 (4)  | C12—O3A     | 1.398 (5) |
| N10—H10     | 0.9100     | C12—O4A     | 1.402 (5) |
| C11—C12     | 1.521 (5)  |             |           |
| N20—Mn1—N3  | 68.62 (9)  | C9—N10—Mn1  | 109.3 (2) |
| N20—Mn1—N7  | 118.71 (9) | C11—N10—H10 | 108.4     |
| N3—Mn1—N7   | 75.97 (10) | C9—N10—H10  | 108.4     |
| N20—Mn1—N10 | 105.07 (9) | Mn1—N10—H10 | 108.4     |
| N3—Mn1—N10  | 141.85 (9) | N10—C11—C12 | 113.0 (3) |

|               |             |               |             |
|---------------|-------------|---------------|-------------|
| N7—Mn1—N10    | 75.11 (10)  | N10—C11—H11A  | 109.0       |
| N20—Mn1—N14   | 68.58 (8)   | C12—C11—H11A  | 109.0       |
| N3—Mn1—N14    | 130.50 (9)  | N10—C11—H11B  | 109.0       |
| N7—Mn1—N14    | 148.65 (10) | C12—C11—H11B  | 109.0       |
| N10—Mn1—N14   | 73.60 (9)   | H11A—C11—H11B | 107.8       |
| N20—Mn1—C11   | 137.26 (7)  | C11—C12—C13   | 115.8 (3)   |
| N3—Mn1—C11    | 100.45 (7)  | C11—C12—H12A  | 108.3       |
| N7—Mn1—C11    | 96.45 (8)   | C13—C12—H12A  | 108.3       |
| N10—Mn1—C11   | 107.03 (7)  | C11—C12—H12B  | 108.3       |
| N14—Mn1—C11   | 94.43 (7)   | C13—C12—H12B  | 108.3       |
| N20—C1—C19    | 120.6 (3)   | H12A—C12—H12B | 107.4       |
| N20—C1—C2     | 114.3 (3)   | N14—C13—C12   | 109.6 (2)   |
| C19—C1—C2     | 125.1 (3)   | N14—C13—H13A  | 109.7       |
| N3—C2—C1      | 114.9 (3)   | C12—C13—H13A  | 109.7       |
| N3—C2—C21     | 127.0 (3)   | N14—C13—H13B  | 109.7       |
| C1—C2—C21     | 118.2 (3)   | C12—C13—H13B  | 109.7       |
| C2—C21—H21A   | 109.5       | H13A—C13—H13B | 108.2       |
| C2—C21—H21B   | 109.5       | C15—N14—C13   | 121.8 (3)   |
| H21A—C21—H21B | 109.5       | C15—N14—Mn1   | 118.56 (19) |
| C2—C21—H21C   | 109.5       | C13—N14—Mn1   | 117.3 (2)   |
| H21A—C21—H21C | 109.5       | N14—C15—C22   | 127.6 (3)   |
| H21B—C21—H21C | 109.5       | N14—C15—C16   | 114.6 (3)   |
| C2—N3—C4      | 121.2 (3)   | C22—C15—C16   | 117.7 (3)   |
| C2—N3—Mn1     | 118.2 (2)   | C15—C22—H22A  | 109.5       |
| C4—N3—Mn1     | 118.7 (2)   | C15—C22—H22B  | 109.5       |
| N3—C4—C5      | 110.8 (3)   | H22A—C22—H22B | 109.5       |
| N3—C4—H4A     | 109.5       | C15—C22—H22C  | 109.5       |
| C5—C4—H4A     | 109.5       | H22A—C22—H22C | 109.5       |
| N3—C4—H4B     | 109.5       | H22B—C22—H22C | 109.5       |
| C5—C4—H4B     | 109.5       | N20—C16—C17   | 121.2 (3)   |
| H4A—C4—H4B    | 108.1       | N20—C16—C15   | 114.4 (3)   |
| C6—C5—C4      | 114.7 (4)   | C17—C16—C15   | 124.4 (3)   |
| C6—C5—H5A     | 108.6       | C16—C17—C18   | 118.7 (3)   |
| C4—C5—H5A     | 108.6       | C16—C17—H17A  | 120.7       |
| C6—C5—H5B     | 108.6       | C18—C17—H17A  | 120.7       |
| C4—C5—H5B     | 108.6       | C19—C18—C17   | 119.7 (3)   |
| H5A—C5—H5B    | 107.6       | C19—C18—H18A  | 120.2       |
| N7—C6—C5      | 112.2 (3)   | C17—C18—H18A  | 120.2       |
| N7—C6—H6A     | 109.2       | C18—C19—C1    | 119.3 (3)   |
| C5—C6—H6A     | 109.2       | C18—C19—H19A  | 120.3       |
| N7—C6—H6B     | 109.2       | C1—C19—H19A   | 120.3       |
| C5—C6—H6B     | 109.2       | C16—N20—C1    | 120.3 (2)   |
| H6A—C6—H6B    | 107.9       | C16—N20—Mn1   | 120.06 (18) |
| C8—N7—C6      | 111.9 (3)   | C1—N20—Mn1    | 118.8 (2)   |
| C8—N7—Mn1     | 107.3 (2)   | N23—C24—C25   | 179.6 (6)   |
| C6—N7—Mn1     | 117.4 (3)   | C24—C25—H251  | 109.5       |
| C8—N7—H7      | 106.6       | C24—C25—H252  | 109.5       |
| C6—N7—H7      | 106.6       | H251—C25—H252 | 109.5       |
| Mn1—N7—H7     | 106.6       | C24—C25—H253  | 109.5       |

## supplementary materials

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|               |             |                 |             |
|---------------|-------------|-----------------|-------------|
| N7—C8—C9      | 109.1 (3)   | H251—C25—H253   | 109.5       |
| N7—C8—H8A     | 109.9       | H252—C25—H253   | 109.5       |
| C9—C8—H8A     | 109.9       | O3A—C12—O4A     | 112.0 (8)   |
| N7—C8—H8B     | 109.9       | O1—C12—O3       | 113.0 (4)   |
| C9—C8—H8B     | 109.9       | O1—C12—O4       | 112.7 (4)   |
| H8A—C8—H8B    | 108.3       | O3—C12—O4       | 111.0 (4)   |
| C8—C9—N10     | 110.6 (3)   | O3A—C12—O2A     | 111.6 (7)   |
| C8—C9—H9A     | 109.5       | O4A—C12—O2A     | 110.8 (8)   |
| N10—C9—H9A    | 109.5       | O3A—C12—O1A     | 108.0 (7)   |
| C8—C9—H9B     | 109.5       | O4A—C12—O1A     | 108.5 (7)   |
| N10—C9—H9B    | 109.5       | O2A—C12—O1A     | 105.7 (7)   |
| H9A—C9—H9B    | 108.1       | O1—C12—O2       | 108.9 (4)   |
| C11—N10—C9    | 113.3 (3)   | O3—C12—O2       | 106.4 (3)   |
| C11—N10—Mn1   | 109.01 (19) | O4—C12—O2       | 104.1 (3)   |
| N20—C1—C2—N3  | 0.2 (4)     | C9—N10—C11—C12  | 158.7 (3)   |
| C19—C1—C2—N3  | -176.7 (3)  | Mn1—N10—C11—C12 | -79.3 (3)   |
| N20—C1—C2—C21 | 179.2 (3)   | N10—C11—C12—C13 | 66.3 (4)    |
| C19—C1—C2—C21 | 2.2 (5)     | C11—C12—C13—N14 | -57.5 (4)   |
| C1—C2—N3—C4   | 178.4 (3)   | C12—C13—N14—C15 | -92.3 (4)   |
| C21—C2—N3—C4  | -0.5 (5)    | C12—C13—N14—Mn1 | 70.2 (3)    |
| C1—C2—N3—Mn1  | -17.4 (4)   | N20—Mn1—N14—C15 | -16.4 (2)   |
| C21—C2—N3—Mn1 | 163.8 (3)   | N3—Mn1—N14—C15  | -48.2 (2)   |
| N20—Mn1—N3—C2 | 19.7 (2)    | N7—Mn1—N14—C15  | 94.0 (3)    |
| N7—Mn1—N3—C2  | -109.3 (2)  | N10—Mn1—N14—C15 | 97.6 (2)    |
| N10—Mn1—N3—C2 | -67.6 (3)   | Cl1—Mn1—N14—C15 | -155.9 (2)  |
| N14—Mn1—N3—C2 | 51.5 (3)    | N20—Mn1—N14—C13 | -179.5 (2)  |
| Cl1—Mn1—N3—C2 | 156.6 (2)   | N3—Mn1—N14—C13  | 148.72 (19) |
| N20—Mn1—N3—C4 | -175.6 (3)  | N7—Mn1—N14—C13  | -69.2 (3)   |
| N7—Mn1—N3—C4  | 55.3 (3)    | N10—Mn1—N14—C13 | -65.5 (2)   |
| N10—Mn1—N3—C4 | 97.0 (3)    | Cl1—Mn1—N14—C13 | 40.94 (19)  |
| N14—Mn1—N3—C4 | -143.9 (2)  | C13—N14—C15—C22 | -3.5 (5)    |
| Cl1—Mn1—N3—C4 | -38.8 (3)   | Mn1—N14—C15—C22 | -165.8 (2)  |
| C2—N3—C4—C5   | 94.4 (4)    | C13—N14—C15—C16 | 176.4 (2)   |
| Mn1—N3—C4—C5  | -69.7 (4)   | Mn1—N14—C15—C16 | 14.0 (3)    |
| N3—C4—C5—C6   | 65.7 (5)    | N14—C15—C16—N20 | 0.5 (4)     |
| C4—C5—C6—N7   | -67.4 (5)   | C22—C15—C16—N20 | -179.6 (3)  |
| C5—C6—N7—C8   | -164.2 (4)  | N14—C15—C16—C17 | 179.1 (3)   |
| C5—C6—N7—Mn1  | 71.1 (4)    | C22—C15—C16—C17 | -1.0 (4)    |
| N20—Mn1—N7—C8 | 122.6 (3)   | N20—C16—C17—C18 | -0.1 (5)    |
| N3—Mn1—N7—C8  | 178.2 (3)   | C15—C16—C17—C18 | -178.6 (3)  |
| N10—Mn1—N7—C8 | 23.4 (3)    | C16—C17—C18—C19 | 3.4 (5)     |
| N14—Mn1—N7—C8 | 27.0 (4)    | C17—C18—C19—C1  | -2.7 (5)    |
| Cl1—Mn1—N7—C8 | -82.6 (3)   | N20—C1—C19—C18  | -1.2 (5)    |
| N20—Mn1—N7—C6 | -110.5 (3)  | C2—C1—C19—C18   | 175.5 (3)   |
| N3—Mn1—N7—C6  | -54.9 (3)   | C17—C16—N20—C1  | -3.9 (4)    |
| N10—Mn1—N7—C6 | 150.3 (3)   | C15—C16—N20—C1  | 174.8 (2)   |
| N14—Mn1—N7—C6 | 153.9 (3)   | C17—C16—N20—Mn1 | 165.5 (2)   |
| Cl1—Mn1—N7—C6 | 44.3 (3)    | C15—C16—N20—Mn1 | -15.8 (3)   |
| C6—N7—C8—C9   | 178.6 (3)   | C19—C1—N20—C16  | 4.5 (4)     |

|                 |            |                 |             |
|-----------------|------------|-----------------|-------------|
| Mn1—N7—C8—C9    | -51.3 (4)  | C2—C1—N20—C16   | -172.5 (3)  |
| N7—C8—C9—N10    | 60.4 (4)   | C19—C1—N20—Mn1  | -165.0 (2)  |
| C8—C9—N10—C11   | 85.5 (4)   | C2—C1—N20—Mn1   | 17.9 (3)    |
| C8—C9—N10—Mn1   | -36.3 (4)  | N3—Mn1—N20—C16  | 171.1 (2)   |
| N20—Mn1—N10—C11 | 125.9 (2)  | N7—Mn1—N20—C16  | -129.6 (2)  |
| N3—Mn1—N10—C11  | -159.6 (2) | N10—Mn1—N20—C16 | -48.6 (2)   |
| N7—Mn1—N10—C11  | -117.8 (2) | N14—Mn1—N20—C16 | 16.6 (2)    |
| N14—Mn1—N10—C11 | 64.2 (2)   | Cl1—Mn1—N20—C16 | 89.0 (2)    |
| Cl1—Mn1—N10—C11 | -25.5 (2)  | N3—Mn1—N20—C1   | -19.29 (19) |
| N20—Mn1—N10—C9  | -109.7 (2) | N7—Mn1—N20—C1   | 40.0 (2)    |
| N3—Mn1—N10—C9   | -35.3 (3)  | N10—Mn1—N20—C1  | 121.0 (2)   |
| N7—Mn1—N10—C9   | 6.6 (2)    | N14—Mn1—N20—C1  | -173.8 (2)  |
| N14—Mn1—N10—C9  | -171.5 (2) | Cl1—Mn1—N20—C1  | -101.4 (2)  |
| Cl1—Mn1—N10—C9  | 98.9 (2)   |                 |             |

*Hydrogen-bond geometry (Å, °)*

| <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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C25—H252 $\cdots$ O2 <sup>i</sup> | 0.96        | 2.27                | 3.168 (6)                  | 156                           |
| N7—H7 $\cdots$ O1                 | 0.91        | 2.16                | 3.050 (6)                  | 165                           |
| N10—H10 $\cdots$ O3A <sup>i</sup> | 0.91        | 2.23                | 3.13 (2)                   | 169                           |

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

