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**Key indicators**

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
 R factor = 0.045  
 wR factor = 0.096  
 Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

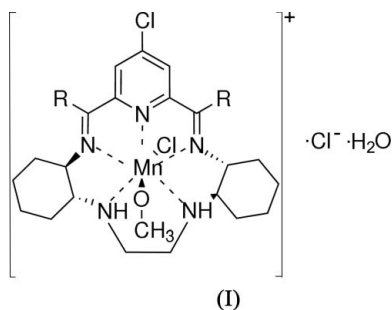
**Chloro[(4*R*,9*R*,14*R*,19*R*)-24-chloro-2,21-dimethyl-3,10,13,20,26-pentaazatetracyclo[20.3.1.0<sup>4,9</sup>.0<sup>14,19</sup>]-hexacos-1(26),2(3),20(21),22(23),24-pentaene]- (methoxo)manganese(II) chloride monohydrate**

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In the title compound,  $[\text{Mn}(\text{CH}_3\text{O})\text{Cl}(\text{C}_{23}\text{H}_{34}\text{ClN}_5)]\text{Cl}\cdot\text{H}_2\text{O}$ , the Mn atom is coordinated by five N atoms from the macrocyclic ligand in an approximately planar pentagonal configuration. In addition, the Mn atom is axially coordinated by a methoxy group and a Cl atom, one on each side of the plane.

**Comment**

Recently, synthetic metal complexes acting as model compounds for hydrolytic metalloenzymes have attracted much attention (Williams *et al.*, 1999). There has been growing interest in the study of the macrocyclic polyamine metal complexes since they appear to be efficient catalysts for the hydrolysis of phosphate esters (Li *et al.*, 2002). In addition, Aston *et al.* (2001) designed and synthesized a manganese(II) complex with a bis(cyclohexylpyridine)-substituted macrocyclic ligand to be a functional mimic of the superoxide dismutase (SOD) enzymes. Their manganese(II) complex with a bis(cyclohexylpyridine)-substituted macrocyclic ligand showed high catalytic activity. In order to study the catalytic activity, we synthesized the title manganese(II) complex with a single exchangeable substituent. Finally a model compound was self-assembled on a gold surface for studies of the bioactivity of the title compound.



Each macrocycle binds on one  $\text{Mn}^{\text{II}}$  atom. The manganese(II) coordination geometry can be best described as distorted pentagonal bipyramidal. The macrocyclic polyamine, which provides five N atoms to the  $\text{Mn}^{\text{II}}$  ion, defines the basal plane, while the chloride anion and the O atom occupy the apical positions.

**Experimental**

The title compound was synthesized according to the literature procedure (Aston *et al.*, 2001) in 84% yield. Crystals appropriate for data collection were obtained by slow evaporation of a methanol–1,2-dichloroethane solution (1:1) at 293 K.

## Crystal data

[Mn(CH<sub>3</sub>O)Cl(C<sub>23</sub>H<sub>34</sub>ClN<sub>5</sub>)]Cl·  
H<sub>2</sub>O  
M<sub>r</sub> = 590.89  
Orthorhombic, *P*<sub>2</sub><sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 8.3175 (7) Å  
*b* = 18.0065 (14) Å  
*c* = 19.0503 (15) Å  
*V* = 2853.1 (4) Å<sup>3</sup>  
*Z* = 4

*D*<sub>x</sub> = 1.376 Mg m<sup>-3</sup>  
Mo *K*α radiation  
Cell parameters from 4132  
reflections  
*θ* = 2.3–21.9°  
*μ* = 0.77 mm<sup>-1</sup>  
*T* = 293 (2) K  
Block, red  
0.30 × 0.20 × 0.10 mm

## Data collection

Bruker SMART 4K CCD area-  
detector diffractometer  
*φ* and *ω* scans  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2002)  
*T*<sub>min</sub> = 0.801, *T*<sub>max</sub> = 0.927  
16877 measured reflections

6158 independent reflections  
5039 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.041  
*θ*<sub>max</sub> = 27.0°  
*h* = −10 → 10  
*k* = −22 → 23  
*l* = −24 → 21

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.045  
*wR* (*F*<sup>2</sup>) = 0.096  
*S* = 1.00  
6158 reflections  
335 parameters  
H atoms treated by a mixture of  
independent and constrained  
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
(*Δ*/*σ*)<sub>max</sub> < 0.001  
*Δρ*<sub>max</sub> = 0.39 e Å<sup>-3</sup>  
*Δρ*<sub>min</sub> = −0.20 e Å<sup>-3</sup>  
Absolute structure: (Flack, 1983),  
2638 Friedel pairs  
Flack parameter: 0.004 (18)

Table 1

Selected geometric parameters (Å, °).

|           |           |            |            |
|-----------|-----------|------------|------------|
| Mn1—N4    | 2.232 (2) | Mn1—Cl1    | 2.4879 (9) |
| Mn1—N2    | 2.285 (2) | N3—C15     | 1.268 (4)  |
| Mn1—N1    | 2.306 (2) | N3—C14     | 1.470 (3)  |
| Mn1—O1    | 2.317 (2) | N5—C22     | 1.258 (4)  |
| Mn1—N5    | 2.333 (2) | N5—C1      | 1.476 (4)  |
| Mn1—N3    | 2.412 (2) |            |            |
| N2—Mn1—N1 | 77.69 (9) | N2—Mn1—N3  | 72.53 (8)  |
| N4—Mn1—O1 | 86.71 (8) | O1—Mn1—N3  | 85.04 (8)  |
| N2—Mn1—O1 | 91.95 (9) | N4—Mn1—Cl1 | 89.36 (6)  |
| N1—Mn1—O1 | 81.33 (8) | N2—Mn1—Cl1 | 88.60 (7)  |
| N4—Mn1—N5 | 69.55 (9) | N1—Mn1—Cl1 | 104.22 (7) |
| N1—Mn1—N5 | 72.48 (8) | O1—Mn1—Cl1 | 174.40 (6) |
| O1—Mn1—N5 | 90.02 (9) | N5—Mn1—Cl1 | 92.34 (6)  |
| N4—Mn1—N3 | 68.53 (8) | N3—Mn1—Cl1 | 89.81 (6)  |

Table 2

Hydrogen-bond geometry (Å, °).

| <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—H2 <i>D</i> ...Cl1 <sup>i</sup>   | 0.84 (4)    | 2.43 (5)      | 3.233 (4)             | 160 (4)                 |
| O2—H2 <i>C</i> ...Cl3 <sup>ii</sup>  | 0.93 (3)    | 2.29 (3)      | 3.208 (5)             | 169 (4)                 |
| N1—H1 <i>A</i> ...Cl3 <sup>iii</sup> | 0.92 (3)    | 2.59 (3)      | 3.496 (3)             | 169 (2)                 |
| N2—H2...Cl3 <sup>i</sup>             | 0.92 (3)    | 2.87 (3)      | 3.717 (3)             | 154 (2)                 |

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

All H atoms were initially located in a difference Fourier map. The methyl H atoms were constrained to an ideal geometry with C—H

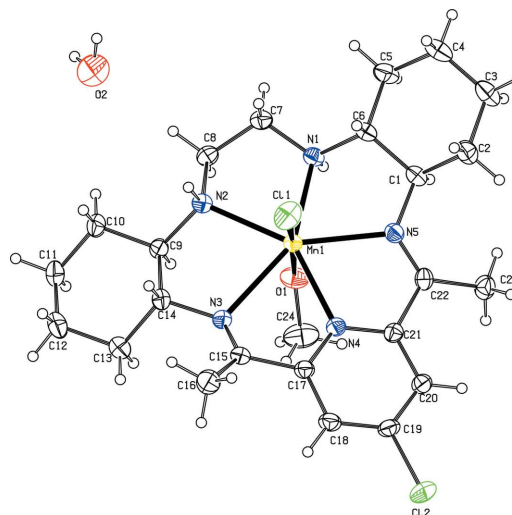


Figure 1

View of the asymmetric unit of (I) showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

distances of 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , but each group was allowed to rotate freely about its C—C bond. The position of the amine H atom was refined freely with an isotropic displacement parameter. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.93–0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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