

Diaqua[*N,N'*-(*o*-phenylene)bis(pyridine-2-carboxamidato)- κ^4 *N*]manganese(III) perchlorate

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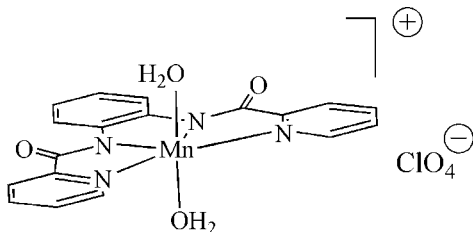
Received 4 October 2007; accepted 15 October 2007

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.034; wR factor = 0.081; data-to-parameter ratio = 13.6.

In the Mn^{III} complex of the title compound, $[\text{Mn}^{\text{III}}(\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_2]\text{ClO}_4$, the Mn^{III} atom is coordinated by four N atoms from the bpb^{2-} [1,2-bis(pyridine-2-carboxamido)benzene] ligand located in the equatorial plane and two O atoms of water molecules at axial positions, yielding a distorted MnN_4O_2 octahedral coordination geometry. The bpb^{2-} ligand is nearly planar, with a maximum deviation of 0.2311 (3) Å from the mean plane. The Mn^{III} complex cation and the perchlorate anion, both of which are located on twofold rotation axes, are connected by $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds into a three-dimensional supramolecular network structure.

Related literature

For iron and chromium monomeric complexes with the in-plane 1,2-bis(pyridine-2-carboxamido)benzene (bpb^{2-}) ligand, see: Ni *et al.* (2006); Ni (2007); Che *et al.* (1988); Dutta *et al.* (2000). For manganese monomeric compounds with the bpb^{2-} ligand and its derivatives, see: Liang *et al.* (2007); Lin *et al.* (2003); Havranek *et al.* (1999). For the synthesis of the H_2bpb ligand, see: Barnes *et al.* (1978).



Experimental

Crystal data

$[\text{Mn}(\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_2]\cdot\text{ClO}_4$	$a = 9.941$ (2) Å
$M_r = 506.74$	$b = 15.416$ (3) Å
Orthorhombic, <i>Pbcn</i>	$c = 13.357$ (3) Å

$V = 2047.0$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.83$ mm⁻¹
 $T = 293$ (2) K
 $0.12 \times 0.08 \times 0.06$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
 $T_{\text{min}} = 0.926$, $T_{\text{max}} = 0.954$
 13809 measured reflections
 1987 independent reflections
 1456 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.087$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.081$
 $S = 1.02$
 1987 reflections
 146 parameters
 H-atom parameters not refined
 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H1W}\cdots\text{O3}^{\text{i}}$	0.85	1.84	2.685 (2)	178
$\text{O1W}-\text{H2W}\cdots\text{O1}^{\text{ii}}$	0.85	1.99	2.812 (2)	163
$\text{C2}-\text{H2}\cdots\text{O2}^{\text{iii}}$	0.93	2.44	3.195 (2)	139
$\text{C5}-\text{H5}\cdots\text{O2}$	0.93	2.45	3.205 (2)	138

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

Data collection: *APEX2* (Bruker, 2004); 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: *XP* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97* and *XP*.

This work was supported by the Natural Science Foundation of China (grant No. 20701027).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2217).

References

- Barnes, D. J., Chapman, R. L., Vagg, R. S. & Watton, E. C. (1978). *J. Chem. Eng. Data*, **23**, 349–350.
 Bruker (2001). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Che, C.-M., Ma, J.-X., Wong, W.-T., Lai, T.-F. & Poon, C.-K. (1988). *Inorg. Chem.* **27**, 2547–2548.
 Dutta, S. K., Beckmann, U., Bill, E., Weyhermuller, T. & Wieghardt, K. (2000). *Inorg. Chem.* **39**, 3355–3364.
 Havranek, M., Singh, A. & Sames, D. (1999). *J. Am. Chem. Soc.* **121**, 8965–8966.
 Liang, L., Qu, Y.-Y., Yang, L. & Zhou, X.-G. (2007). *Acta Cryst.* **E63**, m1503–m1505.
 Lin, J., Tu, C., Lin, H., Jiang, P., Ding, J. & Guo, Z. (2003). *Inorg. Chem. Commun.* **39**, 262–265.
 Ni, Z.-H. (2007). *Acta Cryst.* **E63**, m2531–m2532.
 Ni, Z.-H., Kou, H.-Z., Zhang, L.-F., Ge, C., Wang, R.-J. & Cui, A.-L. (2006). *J. Chem. Crystallogr.* **6**, 465–472.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sheldrick, G. M. (1998). *XP*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E63, m2760 [doi:10.1107/S1600536807050453]

Diaqua[*N,N'*-(*o*-phenylene)bis(pyridine-2-carboxamidato)- κ^4N]manganese(III) perchlorate

L.-F. Zhang

Comment

To date, many iron and chromium coordination complexes containing a large in-plane pyridine carboxamide ligand [bpb²⁻: 1,2-bis(pyridine-2-carboxamido)benzenate], such as [Cr^{III}(bpb)(H₂O)(OH)], [Cr^{III}(bpb)(H₂O)(N₃)] (Ni *et al.*, 2006), [Cr^V(bpb)(N)] (Che *et al.*, 1988), Na[Fe^{III}(bpb)(N₃)₂], Na[Fe^{III}(bpb)(CN)₂] (Dutta *et al.*, 2000) and [Co^{III}(C₁₂H₈N₂)₂(CN)₂] [Cr^{III}(bpb)(N₃)₂·H₂O] (Ni, 2007), have been synthesized and structural characterized. However, the manganese(III) complexes with the bpb²⁻ ligand and its derivatives are relative scarce (Lin *et al.*, 2003; Liang *et al.*, 2007; Havranek *et al.*, 1999). Herein, we report a new Mn(III) complex [Mn^{III}(bpb)(H₂O)₂]ClO₄, (I).

The geometry and labeling scheme for the crystal structure of the title complex is depicted in Figure 1. The title compound comprises of a [Mn^{III}(bpb)(H₂O)₂]⁺ cation and a ClO₄⁻ balanced anion. The Mn^{III} atom is coordinated by four N atoms from the bpb²⁻ ligand located at the equatorial plane and two *trans* coordinated water molecule O atoms, yielding a distorted MnN₄O₂ octahedral coordination geometry.

The C—O, C_{pyridine}—N and C_{carboxy}—N bond distances of the bpb²⁻ ligand in the title complex are well agree with those reported for other complexes containing the bpb²⁻ ligand. The Mn—N_{pyridine} bond distance [2.0563 (18) Å] are significantly longer than that of Mn—N_{amide} bond length [1.9293 (18) Å], which is in agreement with the fact that the deprotonated amide group is a very strong σ -donor. The O_{water}—Mn—O_{water} bond angle is 158.42 (10)°, which is significantly deviated from 180°. The bpb²⁻ ligands is nearly planar with the largest deviation value of 0.2311 (3) Å from the mean plane.

There exist affluent hydrogen bonds involving coordinated water molecules, perchlorate anions and carboxamide oxygen atoms and pyridine carbon atoms (Table 1), which link the [Mn^{III}(bpb)(H₂O)₂]ClO₄ molecules into a three-dimensional supramolecular structure.

Experimental

The material H₂bpb was synthesized according to the literature method (Barnes *et al.*, 1978). Solid H₂bpb (320 mg, 1 mmol) was added into a methanol-water (20:1 *v/v*) solution (50 ml) of Mn^{II}(ClO₄)₂·6H₂O (360 mg, 1 mmol). Then, solid NaOH (80 mg, 2 mmol) was added into the above mixture. The resulting mixture was refluxed for about 2 d until the solution become dark brown. The mixture was then filtered and the resulting solution was kept at room temperature for about one week, giving rise to block brown crystals of the title compound (yield 50%). Elemental analysis [found(calculated)] for C₁₈H₁₆ClMnN₄O₈: C 42.54 (42.66), H 3.30 (3.18), N 11.52% (11.60%).

Refinement

H atoms of the water molecules were found in a difference Fourier map and refined as riding, with O—H = 0.85 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. C-bound H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

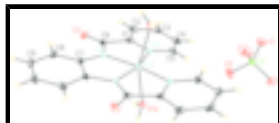


Fig. 1. The molecular structure of the title compound, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

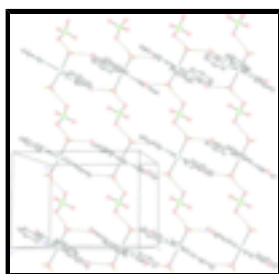


Fig. 2. A packing view of the title compound, viewed approximately down the *b* axis, showing two-dimensional network supramolecular structure through O—H...O hydrogen bonds. All H atoms bound to C atoms are omitted for clarity.

Diaqua[*N,N'*-(*o*-phenylene)bis(pyridine-2-carboxamidato)- κ^4N]manganese(III) perchlorate

Crystal data

[Mn(C₁₈H₁₂N₄O₂)(H₂O)₂] \cdot ClO₄

$M_r = 506.74$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 9.941(2)$ Å

$b = 15.416(3)$ Å

$c = 13.357(3)$ Å

$V = 2047.0(7)$ Å³

$Z = 4$

$F_{000} = 1032$

$D_x = 1.644$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1987 reflections

$\theta = 3.1\text{--}26.0^\circ$

$\mu = 0.83$ mm⁻¹

$T = 293(2)$ K

Block, brown

$0.12 \times 0.08 \times 0.06$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

1987 independent reflections

1456 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.087$

$\theta_{\text{max}} = 26.0^\circ$

$\theta_{\text{min}} = 3.1^\circ$

$h = -12 \rightarrow 12$

$T_{\min} = 0.926$, $T_{\max} = 0.954$
13809 measured reflections

$k = -18 \rightarrow 18$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters not refined
$wR(F^2) = 0.081$	$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.6P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
1987 reflections	$(\Delta/\sigma)_{\max} < 0.001$
146 parameters	$\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
	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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.0000	0.43209 (3)	0.7500	0.01226 (15)
C1	-0.1402 (2)	0.41304 (16)	0.93572 (16)	0.0158 (5)
C2	-0.2037 (2)	0.37831 (18)	1.01907 (17)	0.0229 (6)
H2	-0.2490	0.4140	1.0639	0.027*
C3	-0.1983 (2)	0.29012 (17)	1.03424 (18)	0.0264 (6)
H3	-0.2391	0.2657	1.0902	0.032*
C4	-0.1322 (2)	0.23801 (17)	0.96636 (17)	0.0246 (6)
H4	-0.1269	0.1784	0.9762	0.030*
C5	-0.0740 (2)	0.27627 (15)	0.88316 (17)	0.0200 (5)
H5	-0.0303	0.2412	0.8367	0.024*
C6	-0.1314 (2)	0.50845 (16)	0.91745 (16)	0.0162 (5)
C7	-0.0379 (2)	0.61090 (15)	0.79440 (16)	0.0149 (5)
C8	-0.0769 (2)	0.68901 (16)	0.83709 (17)	0.0216 (6)
H8	-0.1288	0.6895	0.8950	0.026*
C9	-0.0381 (3)	0.76609 (16)	0.79295 (18)	0.0263 (6)
H9	-0.0639	0.8185	0.8216	0.032*

supplementary materials

N1	-0.06538 (18)	0.52651 (12)	0.83139 (12)	0.0139 (4)
N2	-0.07841 (18)	0.36203 (12)	0.86726 (13)	0.0152 (4)
O1	-0.10420 (19)	-0.01530 (13)	0.79040 (13)	0.0386 (5)
O2	0.0547 (2)	0.09200 (15)	0.82695 (18)	0.0689 (8)
O3	-0.17778 (17)	0.56134 (11)	0.97762 (11)	0.0234 (4)
O1W	0.19449 (15)	0.40514 (10)	0.82552 (10)	0.0183 (4)
H1W	0.1914	0.4163	0.8878	0.027*
H2W	0.2651	0.4282	0.8015	0.027*
Cl1	0.0000	0.03896 (6)	0.7500	0.0297 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0141 (3)	0.0120 (3)	0.0107 (3)	0.000	0.0028 (2)	0.000
C1	0.0112 (11)	0.0252 (14)	0.0111 (12)	-0.0006 (10)	-0.0016 (9)	0.0027 (10)
C2	0.0170 (13)	0.0376 (16)	0.0141 (12)	-0.0032 (11)	0.0036 (10)	0.0033 (11)
C3	0.0206 (13)	0.0396 (17)	0.0191 (13)	-0.0117 (12)	0.0007 (11)	0.0096 (12)
C4	0.0260 (14)	0.0240 (14)	0.0238 (14)	-0.0102 (11)	-0.0067 (11)	0.0091 (12)
C5	0.0209 (13)	0.0202 (14)	0.0188 (13)	-0.0051 (11)	-0.0041 (10)	0.0009 (10)
C6	0.0116 (11)	0.0244 (14)	0.0127 (12)	0.0009 (10)	-0.0023 (9)	-0.0012 (10)
C7	0.0148 (11)	0.0149 (12)	0.0151 (12)	0.0017 (10)	-0.0035 (9)	0.0000 (10)
C8	0.0219 (13)	0.0209 (14)	0.0219 (13)	0.0049 (11)	-0.0020 (11)	-0.0043 (11)
C9	0.0334 (15)	0.0137 (12)	0.0320 (15)	0.0048 (11)	-0.0097 (11)	-0.0050 (11)
N1	0.0156 (10)	0.0162 (11)	0.0098 (10)	-0.0002 (8)	0.0025 (8)	-0.0006 (8)
N2	0.0147 (10)	0.0164 (11)	0.0144 (10)	-0.0017 (8)	-0.0008 (8)	0.0012 (8)
O1	0.0275 (11)	0.0486 (14)	0.0398 (11)	-0.0079 (10)	0.0009 (9)	-0.0066 (10)
O2	0.0526 (15)	0.0466 (15)	0.108 (2)	0.0080 (12)	-0.0470 (14)	-0.0416 (14)
O3	0.0284 (10)	0.0280 (10)	0.0139 (8)	0.0101 (8)	0.0034 (8)	-0.0041 (8)
O1W	0.0178 (9)	0.0267 (10)	0.0103 (8)	0.0004 (7)	0.0011 (6)	-0.0010 (7)
Cl1	0.0223 (5)	0.0172 (4)	0.0495 (6)	0.000	-0.0171 (4)	0.000

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

Mn1—N1 ⁱ	1.9295 (18)	C5—H5	0.9300
Mn1—N1	1.9295 (18)	C6—O3	1.234 (3)
Mn1—N2 ⁱ	2.0561 (18)	C6—N1	1.353 (3)
Mn1—N2	2.0561 (18)	C7—C8	1.387 (3)
Mn1—O1W ⁱ	2.2200 (15)	C7—C7 ⁱ	1.406 (4)
Mn1—O1W	2.2200 (15)	C7—N1	1.418 (3)
C1—N2	1.353 (3)	C8—C9	1.381 (3)
C1—C2	1.387 (3)	C8—H8	0.9300
C1—C6	1.493 (3)	C9—C9 ⁱ	1.375 (5)
C2—C3	1.376 (4)	C9—H9	0.9300
C2—H2	0.9300	O1—Cl1	1.4366 (19)
C3—C4	1.378 (3)	O2—Cl1	1.422 (2)
C3—H3	0.9300	O1W—H1W	0.8500
C4—C5	1.385 (3)	O1W—H2W	0.8500
C4—H4	0.9300	Cl1—O2 ⁱ	1.422 (2)

C5—N2	1.340 (3)	C11—O1 ⁱ	1.4366 (19)
N1 ⁱ —Mn1—N1	82.06 (11)	C4—C5—H5	118.9
N1 ⁱ —Mn1—N2 ⁱ	80.76 (8)	O3—C6—N1	126.8 (2)
N1—Mn1—N2 ⁱ	162.40 (8)	O3—C6—C1	121.5 (2)
N1 ⁱ —Mn1—N2	162.40 (8)	N1—C6—C1	111.70 (19)
N1—Mn1—N2	80.76 (8)	C8—C7—C7 ⁱ	119.78 (14)
N2 ⁱ —Mn1—N2	116.62 (11)	C8—C7—N1	126.8 (2)
N1 ⁱ —Mn1—O1W ⁱ	100.29 (7)	C7 ⁱ —C7—N1	113.41 (12)
N1—Mn1—O1W ⁱ	95.96 (7)	C9—C8—C7	119.5 (2)
N2 ⁱ —Mn1—O1W ⁱ	83.44 (6)	C9—C8—H8	120.2
N2—Mn1—O1W ⁱ	85.27 (6)	C7—C8—H8	120.2
N1 ⁱ —Mn1—O1W	95.96 (7)	C9 ⁱ —C9—C8	120.66 (15)
N1—Mn1—O1W	100.29 (7)	C9 ⁱ —C9—H9	119.7
N2 ⁱ —Mn1—O1W	85.27 (6)	C8—C9—H9	119.7
N2—Mn1—O1W	83.44 (6)	C6—N1—C7	125.33 (19)
O1W ⁱ —Mn1—O1W	158.42 (8)	C6—N1—Mn1	119.14 (16)
N2—C1—C2	121.6 (2)	C7—N1—Mn1	115.53 (14)
N2—C1—C6	115.82 (19)	C5—N2—C1	118.8 (2)
C2—C1—C6	122.5 (2)	C5—N2—Mn1	128.81 (16)
C3—C2—C1	118.8 (2)	C1—N2—Mn1	112.42 (15)
C3—C2—H2	120.6	Mn1—O1W—H1W	112.0
C1—C2—H2	120.6	Mn1—O1W—H2W	117.9
C2—C3—C4	119.9 (2)	H1W—O1W—H2W	108.4
C2—C3—H3	120.1	O2—C11—O2 ⁱ	109.8 (2)
C4—C3—H3	120.1	O2—C11—O1	109.83 (13)
C3—C4—C5	118.6 (2)	O2 ⁱ —C11—O1	109.31 (12)
C3—C4—H4	120.7	O2—C11—O1 ⁱ	109.31 (12)
C5—C4—H4	120.7	O2 ⁱ —C11—O1 ⁱ	109.83 (13)
N2—C5—C4	122.3 (2)	O1—C11—O1 ⁱ	108.78 (17)
N2—C5—H5	118.9		

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

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>
O1W—H1W \cdots O3 ⁱⁱ	0.85	1.84	2.685 (2)	178
O1W—H2W \cdots O1 ⁱⁱⁱ	0.85	1.99	2.812 (2)	163
C2—H2 \cdots O2 ^{iv}	0.93	2.44	3.195 (2)	139
C5—H5 \cdots O2	0.93	2.45	3.205 (2)	138

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

Fig. 1

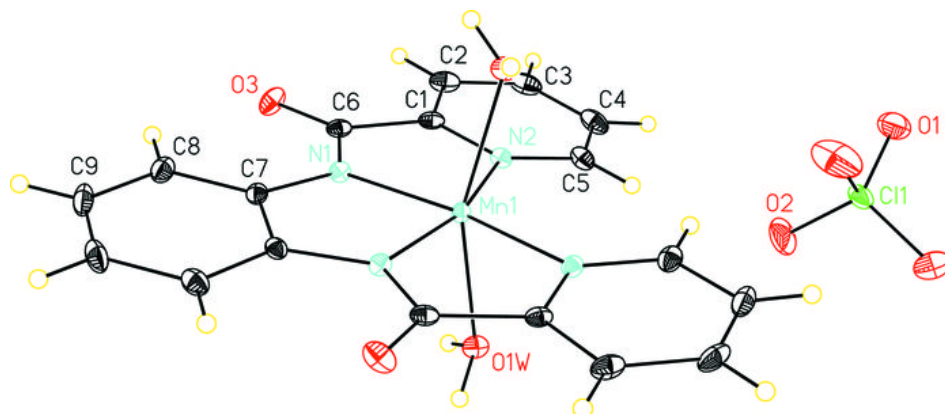


Fig. 2

