

## Diaqua(1,10-phenanthroline-5,6-dione- $\kappa^2N,N$ )(pyridine-2,6-dicarboxylato- $\kappa^3O,N,O'$ )manganese(II) dihydrate

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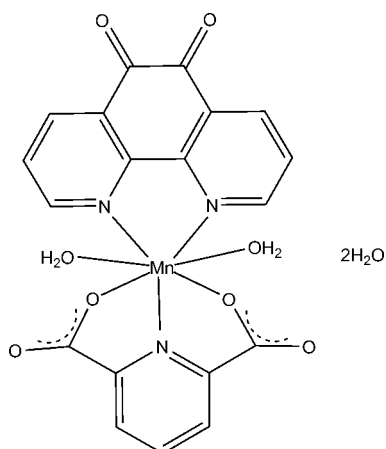
Received 8 April 2007; accepted 28 May 2007

Key indicators: single-crystal X-ray study;  $T = 273$  K; mean  $\sigma(C-C) = 0.003$  Å;  $R$  factor = 0.029;  $wR$  factor = 0.082; data-to-parameter ratio = 11.0.

The title compound,  $[Mn(C_7H_3NO_4)(C_{12}H_6N_2O_2)(H_2O)_2] \cdot 2H_2O$ , is a neutral mononuclear  $Mn^{II}$  complex. The  $Mn-N$  bond to the pyridine-2,6-dicarboxylate ligand lies along a crystallographic twofold rotation axis. The  $Mn^{2+}$  cation has a distorted pentagonal-bipyramidal configuration, coordinated by three N atoms, one from the pyridine-2,6-dicarboxylate ligand and two from the chelating 1,10-phenanthroline-5,6-dione ligand. The remaining four coordination sites are occupied by O atoms, two from the pyridine-2,6-dicarboxylate ligand and two from water molecules. The asymmetric unit also contains a solvent water molecule. The crystal structure is stabilized by a network of  $O-H \cdots O$  hydrogen-bonding interactions in a three-dimensional supramolecular structure.

### Related literature

For related literature, see: Calderazzo *et al.* (2002); Larsson & Öhrström (2004); Liu *et al.* (2006); Okabe & Oya (2000).



### Experimental

#### Crystal data

$[Mn(C_7H_3NO_4)(C_{12}H_6N_2O_2) \cdot (H_2O)_2] \cdot 2H_2O$   
 $M_r = 502.30$   
 Monoclinic,  $C2/c$   
 $a = 10.1751$  (11) Å  
 $b = 14.8325$  (11) Å  
 $c = 14.6121$  (13) Å

$\beta = 109.861$  (1)°  
 $V = 2074.1$  (3) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.70$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
 $0.16 \times 0.12 \times 0.10$  mm

#### Data collection

Bruker SMART APEX CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{min} = 0.896$ ,  $T_{max} = 0.933$

5144 measured reflections  
 1843 independent reflections  
 1637 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.018$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.082$   
 $S = 1.04$   
 1843 reflections  
 167 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{max} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.20$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4A $\cdots$ O3 <sup>i</sup>	0.79 (3)	2.15 (3)	2.936 (2)	175 (3)
O4—H4B $\cdots$ O5 <sup>ii</sup>	0.84 (3)	1.85 (3)	2.687 (2)	175 (3)
O5—H5B $\cdots$ O2 <sup>iii</sup>	0.87 (3)	1.93 (3)	2.795 (2)	171 (3)
O5—H5A $\cdots$ O2	0.81 (3)	2.03 (3)	2.793 (2)	156 (3)

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2058).

### References

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**supplementary materials**

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## **Diaqua(1,10-phenanthroline-5,6-dione- $\kappa^2N,N$ )(pyridine-2,6-dicarboxylato- $\kappa^3O,N,O'$ )manganese(II) dihydrate**

**H.-G. Ge, Q. Xu, X.-H. Guo, W.-J. Sun and C.-B. Zhao**

### **Comment**

Pyridine-2,6-dicarboxylic acid (pdc) is an excellent ligand because it combines the coordination properties of the pyridine and carboxylate group, which may bind metal ions in a variety of bonding modes (Liu *et al.*, 2006; Okabe & Oya, 2000). 1,10-Phenanthroline-5,6-dione (pdo) is a versatile ligand for the assembly of metal organic materials (Calderazzo *et al.*, 2002; Larsson & Öhrström, 2004). Here, we report the mononuclear  $Mn^{2+}$  complex, (I), formed from a dianionic pyridine-2,6-dicarboxylate ligand ( $pdc^{2-}$ ), the N-donor ligand 1,10-phenanthroline-5,6-dione (pdo) and water molecules and explore its supramolecular structure.

As can be seen from Fig. 1, the asymmetric unit comprises a  $Mn^{2+}$  cation, half a dianionic pdc ligand and half a bidentate chelating pdo ligand, all located on a twofold symmetry axis, as well as one coordinated water molecule and one crystal lattice water molecule. A ring nitrogen atom and two oxygen atoms of the carboxylate group belonging to the pdc ligand are involved in coordination to the  $Mn^{2+}$  cation. The pdo group acts as a chelating ligand through the N atoms. Coordination of two water molecules at the axial sites completes the distorted pentagonal dipyramid coordination geometry.

In the crystal structure, hydrogen bonding interactions are observed between the coordinated water molecules, the crystal lattice water molecules and the oxygen atoms of the carboxyl groups in a neighbouring unit to form a three-dimensional supramolecular structure (Figure 2).

### **Experimental**

The title compound was obtained as the main product from the hydrothermal reaction of manganese chloride (0.063 g, 0.5 mmol), 1,10-phenanthroline-5,6-dione (0.105 g, 0.5 mmol), pyridine-2,6-dicarboxylic acid (0.084 g, 0.5 mmol) and water (10 ml) in a 25 ml Teflon-lined stainless steel Parr bomb at 413 K over three days. After cooling slowly to room temperature, light yellow single crystals of (I) were obtained.

### **Refinement**

All H atoms attached to C atoms from the organic ligands were generated in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and  $U_{iso}=1.2U_{eq}$  for aromatic.

The water H atoms were located on a difference map and refined isotropically.

## Figures

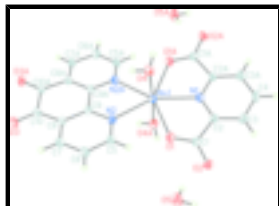


Fig. 1. A view of the molecular structure of title complex with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. (symmetry code for A:  $2 - x, y, 1.5 - z$ )

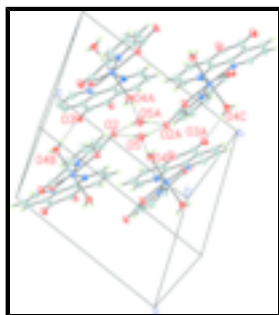


Fig. 2. A view of the three-dimensional supramolecular structure of the title complex. Hydrogen bonds are drawn as dashed lines.

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### Crystal data

$[\text{Mn}(\text{C}_7\text{H}_3\text{NO}_4)(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

$M_r = 502.30$

Monoclinic,  $C2/c$

Hall symbol:  $-C 2yc$

$a = 10.1751$  (11) Å

$b = 14.8325$  (11) Å

$c = 14.6121$  (13) Å

$\beta = 109.8610$  (10)°

$V = 2074.1$  (3) Å<sup>3</sup>

$Z = 4$

$F_{000} = 1028$

$D_x = 1.609$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 117 reflections

$\theta = 5\text{--}20^\circ$

$\mu = 0.70$  mm<sup>-1</sup>

$T = 273$  (2) K

Block, yellow

$0.16 \times 0.12 \times 0.10$  mm

### Data collection

Bruker SMART APEX CCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 273$ (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.896$ ,  $T_{\max} = 0.933$

5144 measured reflections

1843 independent reflections

1637 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 25.1^\circ$

$\theta_{\text{min}} = 2.5^\circ$

$h = -8 \rightarrow 12$

$k = -17 \rightarrow 16$

$l = -17 \rightarrow 16$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 1.3664P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
1843 reflections	$(\Delta/\sigma)_{\max} < 0.001$
167 parameters	$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
	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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	1.0000	0.79318 (2)	0.7500	0.03159 (16)
N1	1.0000	0.94747 (14)	0.7500	0.0297 (5)
N2	0.87516 (16)	0.66130 (10)	0.67750 (11)	0.0321 (4)
O1	0.78287 (14)	0.84912 (9)	0.66535 (11)	0.0420 (4)
O2	0.64025 (13)	0.96698 (9)	0.62159 (10)	0.0399 (3)
O3	0.87158 (15)	0.34079 (9)	0.68074 (11)	0.0442 (4)
O4	1.07694 (18)	0.78734 (11)	0.62489 (12)	0.0422 (4)
O5	0.44735 (19)	0.86864 (11)	0.47295 (14)	0.0526 (4)
C1	0.75793 (19)	0.93165 (12)	0.65935 (13)	0.0312 (4)
C2	0.88249 (18)	0.99259 (12)	0.70524 (13)	0.0312 (4)
C3	0.8784 (2)	1.08543 (13)	0.70317 (17)	0.0454 (5)
H3	0.7956	1.1158	0.6709	0.054*
C4	1.0000	1.1326 (2)	0.7500	0.0560 (9)
H4C	1.0000	1.1953	0.7500	0.067*
C5	0.7540 (2)	0.66263 (13)	0.60287 (14)	0.0382 (5)
H5	0.7134	0.7183	0.5808	0.046*
C6	0.6858 (2)	0.58587 (13)	0.55676 (15)	0.0408 (5)

## supplementary materials

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H6	0.6028	0.5901	0.5043	0.049*
C7	0.7432 (2)	0.50313 (13)	0.59014 (14)	0.0373 (5)
H7	0.6997	0.4503	0.5607	0.045*
C8	0.86766 (19)	0.49984 (12)	0.66870 (14)	0.0302 (4)
C9	0.93241 (18)	0.58054 (11)	0.70935 (13)	0.0284 (4)
C10	0.92846 (18)	0.41197 (12)	0.70854 (13)	0.0317 (4)
H4A	1.156 (3)	0.8007 (18)	0.6365 (19)	0.060 (9)*
H5A	0.507 (3)	0.8825 (19)	0.523 (2)	0.070 (9)*
H4B	1.064 (3)	0.738 (2)	0.594 (2)	0.078 (9)*
H5B	0.419 (3)	0.917 (2)	0.438 (2)	0.101 (12)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.0289 (2)	0.0216 (2)	0.0395 (3)	0.000	0.00533 (18)	0.000
N1	0.0268 (11)	0.0244 (11)	0.0341 (11)	0.000	0.0055 (9)	0.000
N2	0.0303 (8)	0.0246 (8)	0.0368 (8)	0.0005 (6)	0.0055 (7)	0.0019 (6)
O1	0.0332 (7)	0.0264 (7)	0.0570 (9)	0.0003 (6)	0.0031 (7)	-0.0033 (6)
O2	0.0281 (7)	0.0334 (7)	0.0477 (8)	0.0049 (6)	-0.0008 (6)	-0.0034 (6)
O3	0.0393 (8)	0.0243 (7)	0.0606 (9)	-0.0055 (6)	0.0061 (7)	-0.0048 (6)
O4	0.0392 (9)	0.0368 (9)	0.0489 (9)	-0.0059 (7)	0.0129 (7)	-0.0064 (7)
O5	0.0578 (11)	0.0388 (9)	0.0477 (10)	-0.0026 (8)	0.0003 (9)	-0.0084 (7)
C1	0.0293 (10)	0.0277 (9)	0.0337 (9)	0.0020 (8)	0.0071 (8)	-0.0020 (7)
C2	0.0269 (10)	0.0275 (9)	0.0352 (10)	0.0019 (8)	0.0054 (8)	-0.0011 (7)
C3	0.0341 (11)	0.0273 (10)	0.0620 (14)	0.0055 (8)	-0.0005 (10)	0.0010 (9)
C4	0.0481 (19)	0.0206 (14)	0.083 (2)	0.000	0.0011 (17)	0.000
C5	0.0348 (10)	0.0291 (10)	0.0422 (11)	0.0035 (8)	0.0022 (9)	0.0025 (8)
C6	0.0347 (11)	0.0361 (11)	0.0416 (11)	-0.0003 (9)	-0.0003 (9)	0.0006 (8)
C7	0.0352 (11)	0.0288 (10)	0.0423 (11)	-0.0052 (8)	0.0062 (9)	-0.0040 (8)
C8	0.0280 (9)	0.0248 (9)	0.0377 (10)	-0.0015 (7)	0.0111 (8)	-0.0015 (7)
C9	0.0280 (9)	0.0238 (9)	0.0339 (9)	0.0006 (7)	0.0113 (8)	0.0009 (7)
C10	0.0303 (10)	0.0245 (9)	0.0405 (10)	-0.0010 (8)	0.0121 (9)	-0.0010 (7)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Mn1—O4 <sup>i</sup>	2.2214 (16)	O5—H5B	0.87 (3)
Mn1—O4	2.2214 (16)	C1—C2	1.515 (2)
Mn1—N1	2.289 (2)	C2—C3	1.378 (3)
Mn1—O1 <sup>i</sup>	2.2897 (14)	C3—C4	1.384 (3)
Mn1—O1	2.2897 (14)	C3—H3	0.9300
Mn1—N2	2.3765 (15)	C4—C3 <sup>i</sup>	1.384 (3)
Mn1—N2 <sup>i</sup>	2.3765 (15)	C4—H4C	0.9300
N1—C2 <sup>i</sup>	1.332 (2)	C5—C6	1.383 (3)
N1—C2	1.332 (2)	C5—H5	0.9300
N2—C5	1.340 (2)	C6—C7	1.376 (3)
N2—C9	1.344 (2)	C6—H6	0.9300
O1—C1	1.247 (2)	C7—C8	1.391 (3)
O2—C1	1.251 (2)	C7—H7	0.9300

O3—C10	1.206 (2)	C8—C9	1.398 (2)
O4—H4A	0.79 (3)	C8—C10	1.475 (2)
O4—H4B	0.84 (3)	C9—C9 <sup>i</sup>	1.481 (3)
O5—H5A	0.81 (3)	C10—C10 <sup>i</sup>	1.546 (4)
O4 <sup>i</sup> —Mn1—O4	175.53 (8)	H5A—O5—H5B	109 (3)
O4 <sup>i</sup> —Mn1—N1	92.23 (4)	O1—C1—O2	125.72 (17)
O4—Mn1—N1	92.23 (4)	O1—C1—C2	115.77 (16)
O4 <sup>i</sup> —Mn1—O1 <sup>i</sup>	96.58 (6)	O2—C1—C2	118.48 (16)
O4—Mn1—O1 <sup>i</sup>	85.04 (6)	N1—C2—C3	121.89 (18)
N1—Mn1—O1 <sup>i</sup>	68.75 (3)	N1—C2—C1	113.20 (15)
O4 <sup>i</sup> —Mn1—O1	85.04 (6)	C3—C2—C1	124.90 (17)
O4—Mn1—O1	96.58 (6)	C2—C3—C4	118.7 (2)
N1—Mn1—O1	68.75 (3)	C2—C3—H3	120.7
O1 <sup>i</sup> —Mn1—O1	137.51 (7)	C4—C3—H3	120.7
O4 <sup>i</sup> —Mn1—N2	92.88 (6)	C3 <sup>i</sup> —C4—C3	119.2 (3)
O4—Mn1—N2	83.43 (6)	C3 <sup>i</sup> —C4—H4C	120.4
N1—Mn1—N2	145.40 (4)	C3—C4—H4C	120.4
O1 <sup>i</sup> —Mn1—N2	144.15 (5)	N2—C5—C6	123.68 (17)
O1—Mn1—N2	77.64 (5)	N2—C5—H5	118.2
O4 <sup>i</sup> —Mn1—N2 <sup>i</sup>	83.43 (6)	C6—C5—H5	118.2
O4—Mn1—N2 <sup>i</sup>	92.88 (5)	C7—C6—C5	118.63 (18)
N1—Mn1—N2 <sup>i</sup>	145.40 (4)	C7—C6—H6	120.7
O1 <sup>i</sup> —Mn1—N2 <sup>i</sup>	77.64 (5)	C5—C6—H6	120.7
O1—Mn1—N2 <sup>i</sup>	144.15 (5)	C6—C7—C8	118.81 (17)
N2—Mn1—N2 <sup>i</sup>	69.20 (7)	C6—C7—H7	120.6
C2 <sup>i</sup> —N1—C2	119.7 (2)	C8—C7—H7	120.6
C2 <sup>i</sup> —N1—Mn1	120.16 (11)	C7—C8—C9	119.08 (17)
C2—N1—Mn1	120.16 (11)	C7—C8—C10	119.91 (16)
C5—N2—C9	117.74 (16)	C9—C8—C10	121.00 (17)
C5—N2—Mn1	123.73 (12)	N2—C9—C8	121.99 (16)
C9—N2—Mn1	118.43 (12)	N2—C9—C9 <sup>i</sup>	116.93 (10)
C1—O1—Mn1	121.98 (12)	C8—C9—C9 <sup>i</sup>	121.08 (11)
Mn1—O4—H4A	116 (2)	O3—C10—C8	123.47 (17)
Mn1—O4—H4B	116 (2)	O3—C10—C10 <sup>i</sup>	118.71 (11)
H4A—O4—H4B	107 (3)	C8—C10—C10 <sup>i</sup>	117.80 (10)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4A $\cdots$ O3 <sup>ii</sup>	0.79 (3)	2.15 (3)	2.936 (2)	175 (3)
O4—H4B $\cdots$ O5 <sup>iii</sup>	0.84 (3)	1.85 (3)	2.687 (2)	175 (3)
O5—H5B $\cdots$ O2 <sup>iv</sup>	0.87 (3)	1.93 (3)	2.795 (2)	171 (3)

## supplementary materials

O5—H5A...O2 0.81 (3) 2.03 (3) 2.793 (2) 156 (3)  
Symmetry codes: (ii)  $x+1/2, y+1/2, z$ ; (iii)  $-x+3/2, -y+3/2, -z+1$ ; (iv)  $-x+1, -y+2, -z+1$ .

Fig. 1

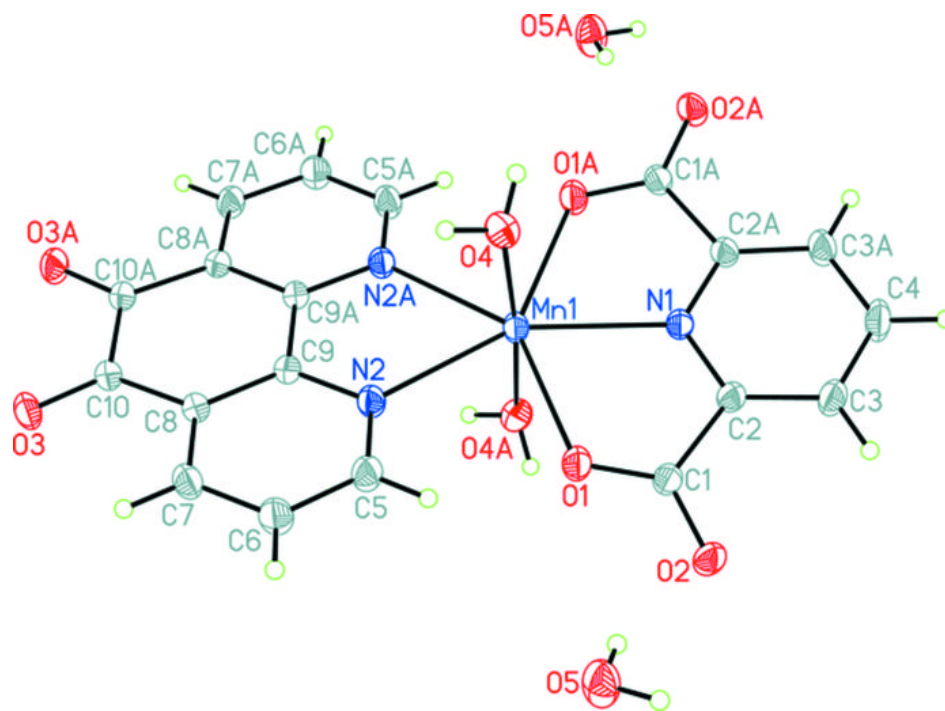




Fig. 2

