

Tetraaqua(1,10-phenanthroline-*N,N'*)-  
manganese(II) dinitrateWenguo Wang, Chengbing Ma,  
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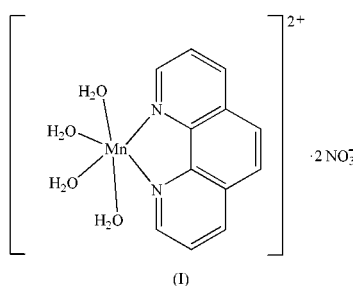
## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
 $R$  factor = 0.057  
 $wR$  factor = 0.131  
Data-to-parameter ratio = 11.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{NO}_3)_2$ , was obtained from the reaction of benzoic acid, 1,10-phenanthroline and manganese nitrate tetrahydrate. The Mn atom is coordinated in a distorted octahedral arrangement by four water molecules and two N atoms from the phenanthroline ligand.

## Comment

There are three manganese enzymes containing a mononuclear manganese site, *viz.* superoxide dismutase, peroxidase and dioxygenase, which participate in redox changes in the respective areas of biology (Law *et al.*, 1999). Carboxylato-bridged complexes containing 1,10-phenanthroline (phen) or bipyridine (bpy) are often employed to mimic the function and structure of these active sites, based on the knowledge that Mn centers in these enzymes are predominately coordinated by N,O donors from available amino acid side chains (Pecoraro & Butler, 1986). Recently, we have reported a new example of a mononuclear manganese complex,  $[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{SO}_4)$  (II), with only one phen ligand and sulfate as counterion (Ma *et al.*, 2002). A similar complex,  $[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3](\text{SO}_4)$ , has also been reported (Zheng *et al.*, 2000). The title complex, (I), contains the same cation as in complex (II) and two  $\text{NO}_3^-$  counter-ions, exhibiting similar structural features to (II).



The manganese atom is coordinated by four O atoms from four water molecules and two N atoms from one phenanthroline ligand, forming a distorted octahedron (Fig. 1). The Mn–O distances vary from 2.13 (1) to 2.21 (2) Å, the Mn–N bond lengths are 2.21 (2) and 2.29 (2) Å, in the normal range (Hauptmann *et al.*, 2000; Deng *et al.*, 2000; Ruiz *et al.*, 2000). The Mn–O and Mn–N distances are comparable to those of complex (II). The *o*-phenanthroline rings lie approximately planar. The phenanthroline rings lay alternately in a head-to-tail manner (Fig. 2), forming a layer structure with a layer separation of 4.42 Å, which is larger than the sum of the van

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der Waals radii of two C atoms (Bondi, 1964), implying that  $\pi$ - $\pi$  stacking interaction between the phen rings is not significant.

Hydrogen-bonding interactions were found between the water ligands and the nitrate ions (Table 1), with O...O distances ranging from 2.83 to 3.27 Å, linking interlayer and intralayer molecules to form two-dimensional sheets.

## Experimental

The title complex was synthesized by mixing manganese nitrate tetrahydrate, 1,10-phenanthroline and benzoic acid in an ethanol-water solution. The resulting solution was heated at 353 K. After cooling to room temperature, the solution was filtered and the filtrate allowed to evaporate in the air for a few weeks, depositing light yellow crystals of the title compound.

### Crystal data

$[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{NO}_3)_2$	$D_x = 1.587 \text{ Mg m}^{-3}$
$M_r = 431.23$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 974 reflections
$a = 14.144 (2) \text{ \AA}$	$\theta = 2.4\text{--}25.0^\circ$
$b = 10.6484 (15) \text{ \AA}$	$\mu = 0.79 \text{ mm}^{-1}$
$c = 12.2202 (19) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 101.356 (3)^\circ$	Block, light yellow
$V = 1804.5 (5) \text{ \AA}^3$	$0.16 \times 0.10 \times 0.08 \text{ mm}$
$Z = 4$	

### Data collection

Bruker SMART CCD area-detector diffractometer	1585 independent reflections
$\varphi$ and $\omega$ scans	953 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.045$
$T_{\text{min}} = 0.909$ , $T_{\text{max}} = 0.939$	$\theta_{\text{max}} = 25.0^\circ$
2675 measured reflections	$h = -16 \rightarrow 7$
	$k = -12 \rightarrow 10$
	$l = -12 \rightarrow 14$

### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.002$
1585 reflections	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
139 parameters	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$

**Table 1**

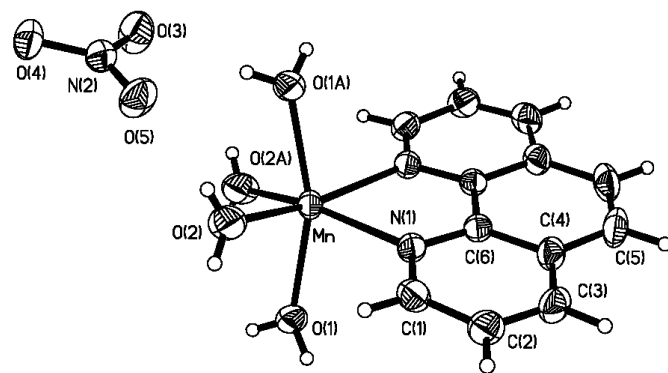
Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{O1--H1}\cdots\text{O3}^{\text{i}}$	0.81 (2)	2.05 (3)	2.842 (5)	168 (8)
$\text{O1--H2}\cdots\text{O4}^{\text{ii}}$	0.84 (6)	2.01 (6)	2.845 (5)	170 (5)
$\text{O1--H2}\cdots\text{O3}^{\text{ii}}$	0.84 (6)	2.65 (5)	3.250 (5)	129 (4)
$\text{O1--H2}\cdots\text{N2}^{\text{ii}}$	0.84 (6)	2.67 (6)	3.449 (6)	154 (5)
$\text{O2--H4}\cdots\text{O4}^{\text{iii}}$	0.81 (2)	2.44 (3)	3.192 (6)	155 (6)
$\text{O2--H4}\cdots\text{O5}^{\text{iii}}$	0.81 (2)	2.16 (4)	2.819 (6)	140 (5)

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

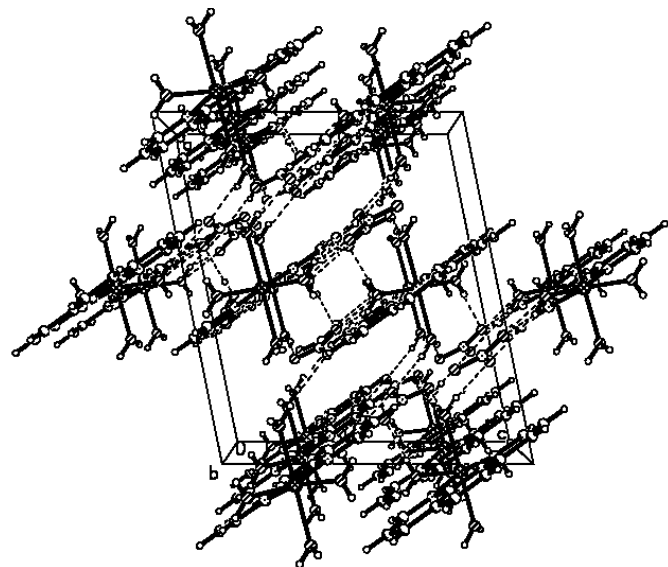
The C-bound H atoms were placed at geometrically calculated positions, with  $\text{C--H} = 0.93 \text{ \AA}$ , and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . The O-bound H atoms were located from difference Fourier syntheses refined freely with isotropic displacement parameters.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT* and *XPREP* in *SHELXTL*



**Figure 1**

Structure of (I), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 30% probability level.



**Figure 2**

A packing diagram of the title compound.

(Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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