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## Structure Reports

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# $(\mu$ -Ethane-1,1,2,2-tetracarboxylato)-bis[tetraaquamanganese(II)]

Meng-Wei Xue and Chang-Yun Chen\*

 School of Biochemical and Environmental Engineering, Nanjing Xiaozhuang College, Nanjing 210017, People's Republic of China  
 Correspondence e-mail: cychen@njzxc.edu.cn

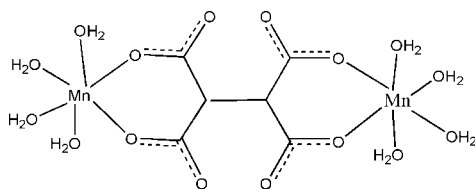
Received 26 February 2011; accepted 3 March 2011

 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.026;  $wR$  factor = 0.069; data-to-parameter ratio = 9.6.

In the centrosymmetric title molecule,  $[\text{Mn}_2(\text{C}_6\text{H}_2\text{O}_8)(\text{H}_2\text{O})_8]$ , the  $\text{Mn}^{\text{II}}$  atom is in an octahedral environment coordinated by six O-atom donors from water molecules and ethane-1,1,2,2-tetracarboxylate ligands. The crystal structure features a three-dimensional hydrogen-bonding network based on a strong and distinctive pattern of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions.

## Related literature

For related literature on metal-organic frameworks, see: Chen *et al.* (2007); Fan & Zhu (2006); Li & Yang (2006). For related literature on hydrogen bonding, see: Forster & Cheetham (2002); Kim & Jung (2000).



## Experimental

## Crystal data

 $[\text{Mn}_2(\text{C}_6\text{H}_2\text{O}_8)(\text{H}_2\text{O})_8]$   
 $M_r = 456.08$   
 Triclinic,  $P\bar{1}$   
 $a = 6.2901$  (12) Å  
 $b = 8.0212$  (15) Å  
 $c = 8.0769$  (15) Å  
 $\alpha = 108.522$  (3)°  
 $\beta = 95.068$  (3)°

 $\gamma = 97.086$  (3)°  
 $V = 379.92$  (12) Å<sup>3</sup>  
 $Z = 1$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.75$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.30 \times 0.26 \times 0.24$  mm

## Data collection

 Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (*SADABS*; Bruker, 2000)  
 $T_{\text{min}} = 0.785$ ,  $T_{\text{max}} = 0.823$ 

 1956 measured reflections  
 1379 independent reflections  
 1309 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.044$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.069$   
 $S = 1.05$   
 1379 reflections  
 144 parameters

 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.30$  e Å<sup>-3</sup>

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PB2059).

## References

- Bruker (2000). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, X. N., Zhang, W. X. & Chen, X. M. (2007). *J. Am. Chem. Soc.* **129**, 15738–15739.
- Fan, S. R. & Zhu, L. G. (2006). *Inorg. Chem.* **45**, 7935–7942.
- Forster, P. M. & Cheetham, A. K. (2002). *Angew. Chem. Int. Ed.* **41**, 457–459.
- Kim, Y. J. & Jung, D. Y. (2000). *Inorg. Chem.* **39**, 1470–1475.
- Li, Y. N. & Yang, R. T. (2006). *J. Am. Chem. Soc.* **128**, 726–727.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2011). E67, m449 [doi:10.1107/S1600536811008063]

**( $\mu$ -Ethane-1,1,2,2-tetracarboxylato)bis[tetraaquamanganese(II)]****Meng-Wei Xue and Chang-Yun Chen****S1. Comment**

The design and synthesis of metal-organic frameworks(MOFs) has become a very interesting research field. This not only stems from their potential application as functional materials but also from their intriguing structural topologies(Chen *et al.*, 2007; Fan & Zhu, 2006; Li & Yang, 2006). However, frankly speaking, the designed synthesis of coordination networks and supramolecular architectures is still a difficult challenge. The formation of coordination polymers is not only influenced by the geometrical and electronic properties of metal ions but also relying on other factors such as the rigidity or flexibility of the ligands and diversity of metal ions and organic ligands in coordination and noncovalent interactions such as hydrogen bonding (Kim & Jung, 2000; Forster *et al.*, 2002). Therefore, the rational design and construction of coordination polymers based upon assembly of metal ions and multifunctional organic ligands is an interesting research field. Herein we report the crystal structure of the title compound (I).

The molecular structure of (I) is illustrated in Fig. 1., where selected bond distances and bond angles are given in Table 1.

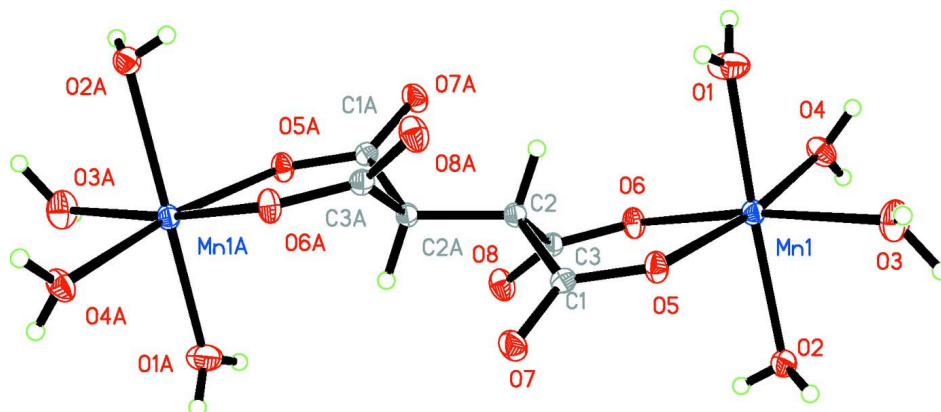
Single-crystal X-ray analysis reveals that 1 crystallizes in the triclinic space group P-1, The structure of 1 is a single molecule in which the asymmetric unit contains one Mn atom, half tce anion, four coordinated water molecules. In complex 1, there is one kind of crystallographically independent Mn<sup>II</sup> center. 1 features a 3-D hydrogen bonding network based on a strong and distinctive pattern of hydrogen bonding interactions. As show in Fig. 2., a one-dimensional chain is formed by bond generated by coordinated water molecule and uncoordinated oxygen atom of ligand tce, Further, one-dimensional chains are linked by bonds to form two-dimensional layers, and two-dimensional layers are also jointed by hydrogen bonds to give rise to three-dimensional structure.

**S2. Experimental**

A H<sub>2</sub>O solution (10 ml) of sodium 1,1,2,2-tetracarboxyl-ethylene (29.4 mg, 1 mmol) was added to a CH<sub>3</sub>OH solution (10 ml) of Mn(OAc)<sub>2</sub>·5H<sub>2</sub>O (17.3 mg, 1 mmol). The pH of the mixture was adjusted to about 7. The mixture was stirred for 2 h and then filtered. Single crystals appeared after the filtered solution was allowed to stand at room temperature for 2 days.

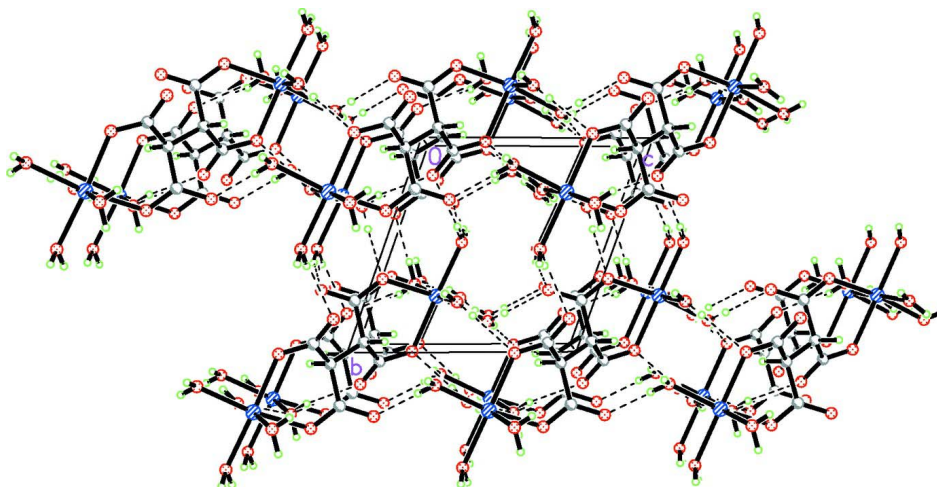
**S3. Refinement**

The C-bound H atoms were placed to the bonded parent atoms in geometrically idealized positions (C—H = 0.93, and 0.98 Å) and refined as riding atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The O-bound H atoms were located in difference Fourier maps and refined as riding in their as-found relative positions(O—H = 0.96 Å) with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ .



**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.



**Figure 2**

Crystal packing diagram of 1.

**( $\mu$ -Ethane-1,1,2,2-tetracarboxylato)bis[tetraquamanganese(II)]**

*Crystal data*

$[\text{Mn}_2(\text{C}_6\text{H}_2\text{O}_8)(\text{H}_2\text{O})_8]$

$M_r = 456.08$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 6.2901$  (12) Å

$b = 8.0212$  (15) Å

$c = 8.0769$  (15) Å

$\alpha = 108.522$  (3)°

$\beta = 95.068$  (3)°

$\gamma = 97.086$  (3)°

$V = 379.92$  (12) Å<sup>3</sup>

$Z = 1$

$F(000) = 232.0$

$D_x = 1.993$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 924 reflections

$\theta = 2.2$ – $20.2$ °

$\mu = 1.75$  mm<sup>-1</sup>

$T = 293$  K

Block, brown

$0.30 \times 0.26 \times 0.24$  mm

*Data collection*

Bruker SMART CCD area-detector  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan  
(SADABS; Bruker, 2000)  
 $T_{\min} = 0.785$ ,  $T_{\max} = 0.823$

1956 measured reflections  
1379 independent reflections  
1309 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.044$   
 $\theta_{\max} = 25.5^\circ$ ,  $\theta_{\min} = 2.7^\circ$   
 $h = -6 \rightarrow 7$   
 $k = -9 \rightarrow 9$   
 $l = -9 \rightarrow 9$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.069$   
 $S = 1.05$   
1379 reflections  
144 parameters  
0 restraints  
Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map  
Hydrogen site location: inferred from  
neighbouring sites  
H atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.30762 (4)	0.25813 (4)	0.70315 (3)	0.02040 (14)
O1	-0.0280 (3)	0.2382 (3)	0.6000 (2)	0.0407 (4)
O2	0.6555 (2)	0.3118 (2)	0.8276 (2)	0.0249 (3)
O3	0.3825 (3)	0.5167 (2)	0.6758 (2)	0.0388 (4)
O4	0.3632 (3)	0.1354 (2)	0.43505 (19)	0.0293 (3)
O5	0.2172 (2)	0.34158 (18)	0.96515 (17)	0.0238 (3)
O6	0.2933 (2)	-0.00729 (18)	0.72542 (18)	0.0246 (3)
O7	0.1900 (2)	0.28929 (19)	1.21579 (17)	0.0282 (3)
O8	0.3028 (2)	-0.1656 (2)	0.90616 (19)	0.0297 (3)
C1	0.1621 (3)	0.2406 (2)	1.0530 (2)	0.0186 (4)
C2	0.0577 (3)	0.0477 (2)	0.9454 (2)	0.0184 (4)
H9	-0.050 (3)	0.053 (3)	0.853 (3)	0.022*
C3	0.2319 (3)	-0.0512 (2)	0.8542 (2)	0.0192 (4)
H3	0.685 (4)	0.421 (5)	0.890 (4)	0.046 (8)*
H4	0.669 (4)	0.260 (4)	0.883 (4)	0.036 (8)*

H7	0.292 (4)	0.177 (4)	0.373 (3)	0.034 (7)*
H8	0.475 (6)	0.111 (5)	0.400 (5)	0.077 (12)*
H5	0.519 (9)	0.581 (8)	0.691 (7)	0.15 (2)*
H1	-0.108 (7)	0.278 (6)	0.663 (6)	0.100 (15)*
H2	-0.092 (6)	0.175 (5)	0.510 (5)	0.067 (11)*
H6	0.332 (6)	0.591 (6)	0.719 (5)	0.077 (13)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.0220 (2)	0.02101 (19)	0.01841 (19)	0.00202 (12)	0.00384 (12)	0.00706 (13)
O1	0.0267 (9)	0.0621 (12)	0.0257 (9)	0.0078 (8)	0.0007 (7)	0.0045 (8)
O2	0.0274 (8)	0.0220 (8)	0.0251 (8)	0.0022 (6)	0.0024 (6)	0.0086 (7)
O3	0.0508 (11)	0.0237 (8)	0.0427 (10)	0.0047 (8)	0.0128 (8)	0.0110 (7)
O4	0.0338 (9)	0.0375 (9)	0.0210 (7)	0.0145 (7)	0.0088 (7)	0.0114 (7)
O5	0.0331 (8)	0.0176 (7)	0.0200 (7)	0.0006 (6)	0.0069 (6)	0.0059 (5)
O6	0.0310 (8)	0.0234 (7)	0.0234 (7)	0.0073 (6)	0.0126 (6)	0.0098 (6)
O7	0.0389 (8)	0.0245 (7)	0.0180 (7)	-0.0011 (6)	0.0012 (6)	0.0057 (6)
O8	0.0345 (8)	0.0312 (8)	0.0317 (8)	0.0145 (6)	0.0116 (6)	0.0168 (6)
C1	0.0167 (9)	0.0192 (9)	0.0200 (9)	0.0048 (7)	0.0041 (7)	0.0056 (7)
C2	0.0196 (9)	0.0184 (9)	0.0177 (9)	0.0023 (7)	0.0031 (7)	0.0067 (7)
C3	0.0216 (9)	0.0163 (9)	0.0173 (9)	0.0006 (7)	0.0024 (7)	0.0032 (7)

*Geometric parameters (Å, °)*

Mn1—O3	2.1541 (18)	O3—H6	0.71 (4)
Mn1—O4	2.1552 (15)	O4—H7	0.82 (3)
Mn1—O5	2.1578 (13)	O4—H8	0.80 (4)
Mn1—O1	2.1674 (18)	O5—C1	1.273 (2)
Mn1—O6	2.1845 (14)	O6—C3	1.275 (2)
Mn1—O2	2.2557 (16)	O7—C1	1.236 (2)
O1—H1	0.77 (4)	O8—C3	1.237 (2)
O1—H2	0.78 (4)	C1—C2	1.541 (3)
O2—H3	0.85 (3)	C2—C2 <sup>i</sup>	1.515 (3)
O2—H4	0.71 (3)	C2—C3	1.536 (2)
O3—H5	0.92 (6)	C2—H9	0.98 (2)
O3—Mn1—O4	89.71 (7)	Mn1—O3—H5	126 (3)
O3—Mn1—O5	98.50 (6)	Mn1—O3—H6	123 (3)
O4—Mn1—O5	170.75 (6)	H5—O3—H6	96 (4)
O3—Mn1—O1	90.76 (8)	Mn1—O4—H7	107.7 (18)
O4—Mn1—O1	87.24 (7)	Mn1—O4—H8	128 (3)
O5—Mn1—O1	88.40 (6)	H7—O4—H8	113 (3)
O3—Mn1—O6	169.57 (7)	C1—O5—Mn1	126.22 (12)
O4—Mn1—O6	86.03 (6)	C3—O6—Mn1	125.18 (11)
O5—Mn1—O6	86.55 (5)	O7—C1—O5	123.56 (17)
O1—Mn1—O6	98.54 (7)	O7—C1—C2	120.04 (16)
O3—Mn1—O2	84.27 (8)	O5—C1—C2	116.39 (16)

O4—Mn1—O2	96.98 (6)	C2 <sup>i</sup> —C2—C3	112.65 (19)
O5—Mn1—O2	88.12 (6)	C2 <sup>i</sup> —C2—C1	112.95 (19)
O1—Mn1—O2	173.45 (7)	C3—C2—C1	108.56 (14)
O6—Mn1—O2	86.79 (6)	C2 <sup>i</sup> —C2—H9	107.6 (13)
Mn1—O1—H1	120 (3)	C3—C2—H9	107.4 (13)
Mn1—O1—H2	129 (3)	C1—C2—H9	107.4 (15)
H1—O1—H2	109 (4)	O8—C3—O6	124.24 (16)
Mn1—O2—H3	107.8 (18)	O8—C3—C2	120.15 (16)
Mn1—O2—H4	110 (2)	O6—C3—C2	115.61 (16)
H3—O2—H4	109 (3)		

Symmetry code: (i)  $-x, -y, -z+2$ .

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H3...O5 <sup>ii</sup>	0.85 (3)	1.88 (3)	2.726 (2)	174 (3)
O2—H4...O8 <sup>iii</sup>	0.71 (3)	2.07 (3)	2.765 (2)	166 (3)
O4—H7...O7 <sup>iv</sup>	0.82 (3)	1.89 (3)	2.689 (2)	167 (2)
O4—H8...O6 <sup>v</sup>	0.80 (4)	1.97 (4)	2.757 (2)	167 (4)
O3—H5...O7 <sup>ii</sup>	0.92 (6)	1.95 (6)	2.847 (2)	165 (5)
O1—H1...O2 <sup>vi</sup>	0.77 (4)	2.07 (4)	2.818 (2)	164 (5)
O1—H2...O6 <sup>vii</sup>	0.78 (4)	2.14 (4)	2.914 (2)	175 (4)
O3—H6...O8 <sup>viii</sup>	0.71 (4)	2.10 (4)	2.771 (2)	158 (4)

Symmetry codes: (ii)  $-x+1, -y+1, -z+2$ ; (iii)  $-x+1, -y, -z+2$ ; (iv)  $x, y, z-1$ ; (v)  $-x+1, -y, -z+1$ ; (vi)  $x-1, y, z$ ; (vii)  $-x, -y, -z+1$ ; (viii)  $x, y+1, z$ .