metal-organic compounds

Poly[[diaquamanganese(II)]-μ3-4-oxido-2-oxo-1,2-dihydropyrimidine-5-carboxylato-$\kappa^4O^4,O^5:O^2:O^2$]

Zilu Chen,* Huihui Xing and Fupei Liang

College of Chemistry and Chemical Engineering, Guangxi Normal University, Yucai Road 15, Guilin 541004, People's Republic of China
Correspondence e-mail: chenziluczl@yahoo.co.uk

In the title compound, $[Mn(C_5H_2N_2O_4)(H_2O)_2]_n$, the Mn^{II} ion has a distorted octahedral geometry and the 4-oxido-2-oxo-1,2-dihydropyrimidine-5-carboxylate ($Hiso^{2-}$) anion acts as a $\mu_3:\eta^4$-bridging ligand. Two oxo O atoms from different $Hiso^{2-}$ ligands bridge two Mn^{II} ions, forming centrosymmetric dinuclear building blocks. Each dinuclear building block interacts with another four by the coordination of the oxide groups and carboxylate O atoms, producing a two-dimensional framework in the *ab* plane. Hydrogen bonds further extend the two-dimensional sheets into a three-dimensional supramolecular framework.

Comment

Construction of porous metal–organic frameworks (MOFs) for hydrogen storage has been intensively studied in recent years, with the aim of meeting targets of safe commercial application of hydrogen gas fuel in all kinds of vehicles (Zhao *et al.*, 2004; Kesanli *et al.*, 2005; Rosi *et al.*, 2003; Li & Yang, 2006; Han & Goddard, 2007). To achieve this goal, the designed MOFs must have both enough space to hold hydrogen gas and large surface areas and some special functional groups to bind hydrogen molecules. However, the reported MOFs at present undergo a relatively low enthalpy of adsorption change associated with the H_2 uptake, which is significantly lower than that required for fuel cells under operating temperatures and pressures (Dincă *et al.*, 2006). One strategy for solving this problem is to select appropriate organic linkers to increase the H_2 binding energy. The linkers used at present are usually organic carboxylic acids bearing aromatic rings, such as benzendicarboxylic acid, benzenetricarboxylic acid, biphenyl-3,3′,5,5′-tetracarboxylic acid and naphthalene-1,4,5,8-tetracarboxylic acid (Han & Goddard, 2007; Wong-Foy *et al.*, 2006; Surblé *et al.*, 2006; Sun *et al.*, 2006; Lin *et al.*, 2006). Organic acids with heteroatomic rings bearing other groups, such as hydroxy and amine groups, are used

(I)
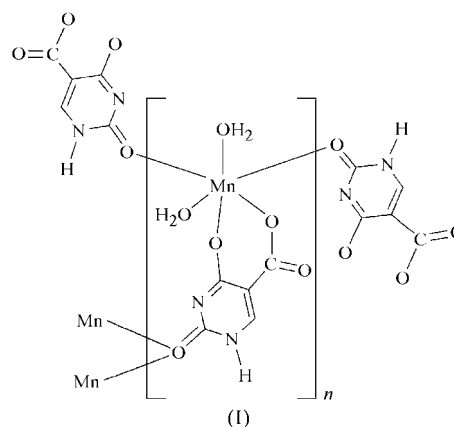
much less frequently. This encouraged us to use 2,4-dihydroxypyrimidine-5-carboxylic acid as the linker to build MOFs. We report here the synthesis and X-ray structure determination of the title complex, $[Mn(Hiso)(H_2O)_2]_n$ ($Hiso^{2-}$ is 4-oxido-2-oxo-1,2-dihydropyrimidine-5-carboxylate), which exhibits a two-dimensional coordination framework structure assembled by Mn^{II} and $Hiso^{2-}$ ions.
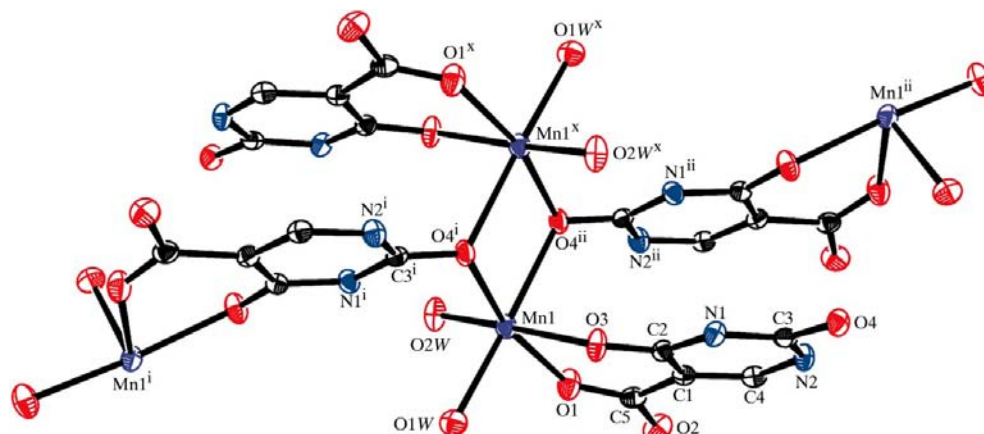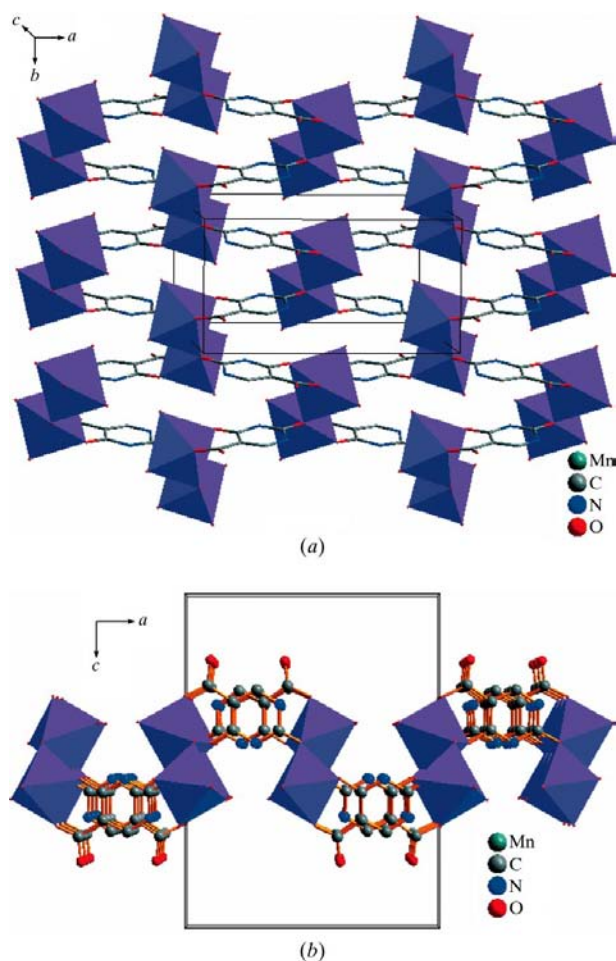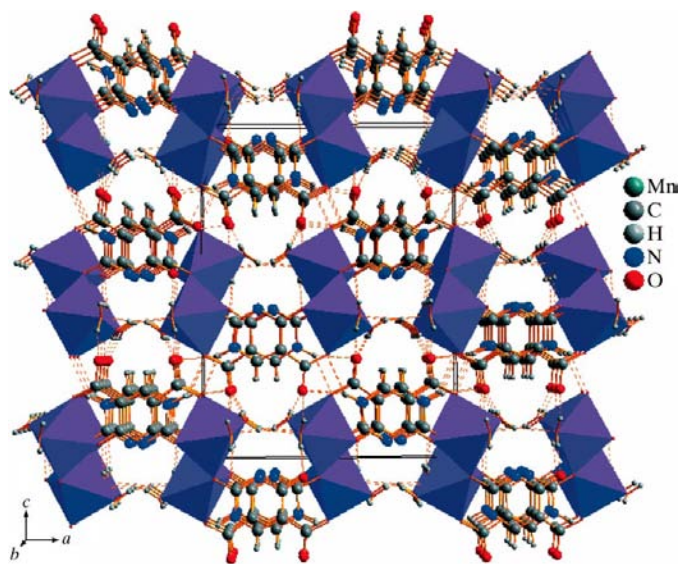

Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. For clarity, H atoms have been omitted. [Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{3}{2}, -z + 1$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (x) $-x + 1, -y + 1, -z + 1$.]

As shown in Fig. 1, the Mn^{II} ion is coordinated in a distorted octahedral geometry by two water molecules, two oxo O atoms from two different $Hiso^{2-}$ anions, and one carboxylate O atom and one oxide O atom from a third $Hiso^{2-}$ anion. The Mn—O bond lengths range from 2.1271 (16) to 2.3392 (16) Å, and the O—Mn—O angles are in the ranges 79.77 (6)– 104.37 (6) and 165.32 (6)–175.33 (6)° (Table 1). Thus, each Mn^{II} ion is coordinated to three $Hiso^{2-}$ anions, and each $Hiso^{2-}$ anion acts as a $\mu_3:\eta^4$-bridge using the oxo O atom to bridge two Mn^{II} ions, with an Mn—O—Mn angle of 100.23 (6)°, and the oxide O atom and one carboxylate O atom to chelate to another Mn^{II} ion. To the best of our knowledge, this coordination mode for the $Hiso^{2-}$ ion is unprecedented. The only reported tetradentate case is $[Pr_2(Hiso)(H_2iso)_4-(phen)_2(H_2O)_2]\cdot 5H_2O$, in which the $Hiso^{2-}$ anion bridges only two metal ions (Sun & Jin, 2004a).

Two Mn^{II} ions are bridged by the oxo groups of two $Hiso^{2-}$ ions, constructing a centrosymmetric dinuclear $[Mn_2(Hiso)_2-(H_2O)_4]$ building block with an Mn···Mn separation of 3.4697 (3) Å. Each dinuclear building block acts as a four-connected node to connect another four dinuclear building

Figure 3
The packing of (I). Broken lines indicate hydrogen bonds.

blocks by the coordination of the oxide groups and carboxylate O atoms to the Mn^{II} ions from the adjacent dinuclear building blocks. The Mn^{II} ions bridged by $Hiso^{2-}$ ions have Mn···Mn separations of 6.9978 (8) and 8.1870 (9) Å. This leads to the construction of a two-dimensional framework (Fig. 2a) parallel to the ab plane, which presents an s-like appearance viewed down the b axis (Fig. 2b). The pyrimidine rings aligned along the b axis are almost parallel to each other, with a dihedral angle of 5.546° and a center-to-center distance of 3.4617 (4) Å between adjacent pyrimidine rings. The center-to-plane distances are 3.194 and 3.273 Å, with offset angles of 22.67 and 19.03°, respectively. This indicates the presence of significant π–π interactions between adjacent pyrimidine rings. The two-dimensional framework also contains O2W—H2WA···O1W[viii], O2W—H2WA···N1[i] and O1W—H1WB···O3[vii] hydrogen bonds (details are given in Table 2). These π–π interactions and hydrogen bonds further stabilize the two-dimensional network. The construction of a two-dimensional framework from transition metal ions and 2,4-dihydroxypyrimidine-5-carboxylic acid is unprecedented. The reported cases are usually mononuclear compounds (Luo et al., 2002; Baran et al., 1996). Only a few were obtained as polynuclear complexes (Hueso-Ureña et al., 1996) or one-dimensional coordination polymers (Sun & Jin, 2004b).

The two-dimensional sheets pack along the c axis by the propagation of O1W—H1WA···O2[vi], O2W—H2WB···O2[ix], N2—H2···O1[v] and N2—H2···O2[v] hydrogen bonds between two adjacent sheets (Table 2), constructing a three-dimensional supramolecular framework (Fig. 3).

Figure 2
(a) The two-dimensional framework of (I), parallel to the ab plane. (b) The two-dimensional framework of (I), viewed along the b axis. H atoms have been omitted for clarity.

Experimental

A mixture of 2,4-dihydroxypyrimidine-5-carboxylic acid (0.0870 g, 0.5 mmol), $Mn(ClO_4)_2\cdot 6H_2O$ (0.0905 g, 0.25 mmol), NaOH (0.0200 g,

metal-organic compounds

0.5 mmol) and water (15 ml) was placed in a 22 ml Teflon-lined stainless steel reactor and heated at 383 K for 144 h. The mixture was cooled over a period of 48 h, giving yellow crystals in 30% yield. Analysis calculated for $C_5H_6MnN_2O_6$: C 24.51, H 2.47, N 11.43%; found: C 24.66, H 2.41, N 11.33%. IR (KBr): 3452 (s), 3321 (s), 3177 (s), 3060 (s), 2509 (w), 2455 (w), 2263 (w), 1987 (w), 1666 (s), 1639 (s), 1574 (s), 1493 (s), 1456 (s), 1392 (s), 1360 (s), 1182 (s), 1131 (m), 1013 (w), 1002 (w), 849 (m), 818 (s), 801 (m), 720 (m), 677 (m), 641 (s), 595 (m), 490 (m) cm^{-1}.

Crystal data

[Mn(C$_5$H$_2$N$_2$O$_4$)(H$_2$O)$_2$]
$M_r = 245.06$
Orthorhombic, $Pbca$
$a = 12.9325 (17)$ Å
$b = 6.7317 (9)$ Å
$c = 17.018 (2)$ Å

$V = 1481.5 (3)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.79$ mm^{-1}
$T = 273 (2)$ K
$0.20 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1998)
$T_{min} = 0.716$, $T_{max} = 0.841$

7030 measured reflections
1303 independent reflections
1132 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.063$
$S = 1.07$
1303 reflections

127 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O2W	2.1271 (16)	Mn1—O1W	2.1748 (17)
Mn1—O1	2.1278 (16)	Mn1—O4^i	2.1804 (16)
Mn1—O3	2.1437 (16)	Mn1—O4^{ii}	2.3392 (16)
O2W—Mn1—O1	86.77 (6)	O3—Mn1—O4^i	86.28 (6)
O2W—Mn1—O3	168.07 (6)	O1W—Mn1—O4^i	95.67 (6)
O1—Mn1—O3	81.86 (6)	O2W—Mn1—O4^{ii}	87.87 (6)
O2W—Mn1—O1W	94.27 (6)	O1—Mn1—O4^{ii}	91.32 (6)
O1—Mn1—O1W	92.94 (6)	O3—Mn1—O4^{ii}	88.77 (6)
O3—Mn1—O1W	89.94 (6)	O1W—Mn1—O4^{ii}	175.33 (6)
O2W—Mn1—O4^i	104.37 (6)	O4^i—Mn1—O4^{ii}	79.77 (6)
O1—Mn1—O4^i	165.32 (6)	Mn1^{iii}—O4—Mn1^{iv}	100.23 (6)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O2^v	0.86	2.30	3.121 (2)	160
N2—H2$\cdots$O1^v	0.86	2.31	3.039 (2)	143
O1W—H1WA$\cdots$O2^{vi}	0.85	1.91	2.741 (2)	165
O1W—H1WB$\cdots$O3^{vii}	0.85	1.84	2.690 (2)	178
O2W—H2WA$\cdots$O1W^{viii}	0.84	2.12	2.874 (2)	149
O2W—H2WA$\cdots$N1^i	0.84	2.64	3.094 (2)	115
O2W—H2WB$\cdots$O2^{ix}	0.85	1.85	2.687 (2)	167

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (v) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (vi) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + 1, -y + 2, -z + 1$; (viii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (ix) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

H atoms on C and N atoms were placed in calculated positions (C—H = 0.93 Å and N—H = 0.86 Å) and allowed for as riding [$U_{iso}(H) = 1.2U_{eq}(C,N)$]. H atoms in water molecules were located in a difference Fourier map and allowed for as riding on their parent atoms [$U_{iso}(H) = 1.5U_{eq}(O)$].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXTL* (Bruker, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3069). Services for accessing these data are described at the back of the journal.

References

Baran, E. J., Mercader, R. C., Hueso-Ureña, F., Moreno-Carretero, M. N., Quiros-Olozabal, M. & Salas-Peregrin, J. M. (1996). *Polyhedron*, **15**, 1717–1721.

Brandenburg, K. & Putz, H. (2004). *DIAMOND*. Version 3.0. Crystal Impact GbR, Bonn, Germany.

Bruker (1998). *SMART* (Version 5.051), *SAINT* (Version 5.01), *SADABS* (Version 2.0) and *SHELXTL* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Dincă, M., Yu, A. F. & Long, J. R. (2006). *J. Am. Chem. Soc.* **128**, 8904–8913.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Han, S. S. & Goddard, W. A. III (2007). *J. Am. Chem. Soc.* **129**, 8422–8423.

Hueso-Ureña, F., Moreno-Carretero, M. N., Quirós-Olozábal, M., Salas-Peregrín, J. M., Faure, R. & Cienfuegos-López, G. A. (1996). *Inorg. Chim. Acta*, **241**, 61–69.

Kesanli, B., Cui, Y., Smith, M. R., Bittner, E. W., Bockrath, B. C. & Lin, W. (2005). *Angew. Chem. Int. Ed.* **44**, 72–75.

Li, Y. W. & Yang, R. T. (2006). *J. Am. Chem. Soc.* **128**, 8136–8137.

Lin, X., Jia, J. H., Zhao, X. B., Thomas, K. M., Blake, A. J., Walker, G. S., Champness, N. R., Hubberstey, P. & Schröder, M. (2006). *Angew. Chem. Int. Ed.* **45**, 7358–7364.

Luo, J.-H., Hong, M.-C., Zhao, Y.-J., Cao, R. & Weng, J.-B. (2002). *Chin. J. Struct. Chem.* **21**, 392–395.

Rosi, N. L., Eckert, J., Eddaoudi, M., Vodak, D. T., Kim, J., O'Keeffe, M. & Yagi, O. M. (2003). *Science*, **300**, 1127–1129.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sun, C.-Y. & Jin, L.-P. (2004a). *Polyhedron*, **23**, 2085–2093.

Sun, C.-Y. & Jin, L.-P. (2004b). *Polyhedron*, **23**, 2227–2233.

Sun, D. F., Ma, S. Q., Ke, Y. X., Collins, D. J. & Zhou, H.-C. (2006). *J. Am. Chem. Soc.* **128**, 3896–3897.

Surblé, S., Millange, F., Serre, C., Düren, T., Latroche, M., Bourrelly, S., Llewellyn, P. L. & Férey, G. (2006). *J. Am. Chem. Soc.* **128**, 14889–14896.

Wong-Foy, A. G., Matzger, A. J. & Yaghi, O. M. (2006). *J. Am. Chem. Soc.* **128**, 3494–3495.

Zhao, X. B., Xiao, B., Fletcher, A. J., Thomas, K. M., Bradshaw, D. & Rosseinsky, M. J. (2004). *Science*, **306**, 1012–1015.