metal-organic papers

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Key indicators

Single-crystal X-ray study
$T = 292$ K
Mean σ(C–C) = 0.006 Å
R factor = 0.064
wR factor = 0.138
Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

A new dinuclear Mn[II] compound with intermolecular π–π interactions

In the title compound, bis(μ-pyridine-2,5-dicarboxylato)bis-[aqua(pyrazino[2,3-*f*][1,10]phenanthroline)manganese(II)] dihydrate, $[Mn_2(C_7H_3NO_4)_2(C_{14}H_8N_4)_2(H_2O)_2]\cdot2H_2O$, each Mn[II] atom is six-coordinated by three N atoms from one bidentate pyrazino[2,3-*f*][1,10]phenanthroline and one monodentate pyridine-2,5-dicarboxylate ligand, and three O atoms from two monodentate pyridine-2,5-dicarboxylate ligands and one water molecule. The two Mn[II] atoms are bridged by two pyridine-2,5-dicarboxylate ligands, forming a centrosymmetric dinuclear molecule. Neighboring molecules interact through π–π contacts, leading to a one-dimensional supramolecular structure, and O—H···O hydrogen bonds complete the structure.

Comment

1,10-Phenanthroline (phen) and its derivatives are important ligands with numerous uses in the construction of metal–organic complexes (Che, Liu *et al.*, 2006). Supramolecular architectures based on the pyrazino[2,3-*f*][1,10]phenanthroline (Pyphen) molecule have received considerably less attention (Che, Xu & Liu, 2006). We selected pyridine-2,5-dicarboxylic acid (2,5-H$_2$pdc) as a linker ligand and Pyphen as a secondary ligand, generating a new dinuclear coordination compound, $[Mn_2(2,5-pdc)_2(Pyphen)_2(H_2O)_2]\cdot2H_2O$, (I), which is reported here.

(I)
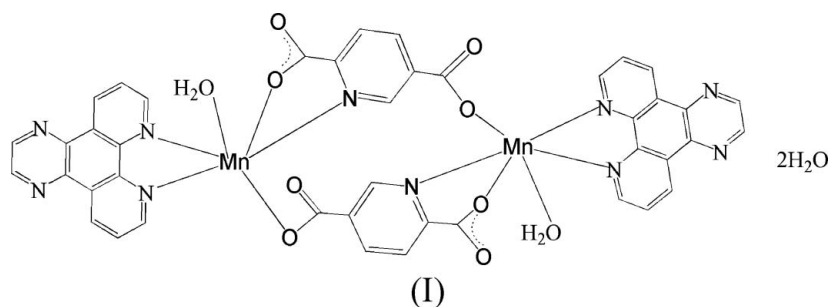
In (I), each Mn[II] atom is six-coordinated by three N atoms from one bidentate Pyphen molecule and one monodentate 2,5-pdc ligand, and three O atoms from two monodentate 2,5-pdc ligands and one water molecule. The Mn—N and Mn—O distances are normal (Table 1): a disorted octahedral *mer*-MnO$_3$N$_3$ arrangement is formed. The complete molecule contains two Mn[II] atoms bridged by two 2,5-pdc ligands, forming a dinuclear compound (Fig. 1), the complete assemblage being generated by inversion symmetry. The carboxylate C—O bond lengths suggest that the bonding of the C15/O1/O2 group is localized, but that of the C21/O3/O4 group is delo-
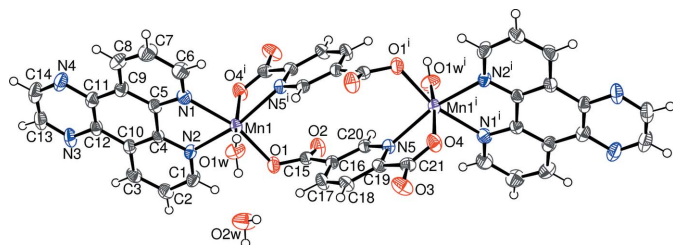
Figure 1
View of the structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (arbitrary spheres for the H atoms). [Symmetry code: (i) $1 - x, 1 - y, -z$.] The symmetry-related uncoordinated water molecule has been omitted.
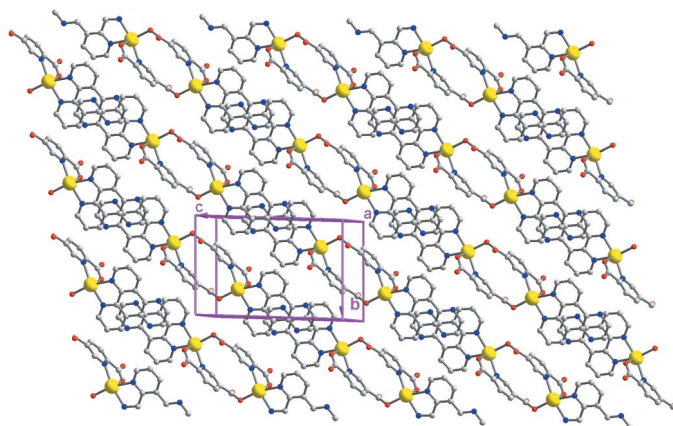

Figure 2
View of the one-dimensional supramolecular structure of (I), generated by $\pi-\pi$ interactions. H atoms and water molecules have been omitted.

calized. Despite this, the Mn1—O1 and Mn1—O4^i (see Table 1 for symmetry codes) bond lengths are very similar.

In the crystal structure, neighboring molecules are connected through $\pi-\pi$ interactions between Pyphen ligands with a stacking distance of 3.47 Å, resulting in a one-dimensional supramolecular structure (Fig. 2). Various O—H$\cdots$O hydrogen bonds involving the water molecules and carboxylate O-atom acceptors (Table 2) complete the structure of (I).

Experimental

The Pyphen ligand was synthesized according to the literature method of Dickeson & Summers (1970). A methanol solution (10 ml) of Pyphen (0.5 mmol) was added slowly to an aqueous solution (8 ml) of MnCl$_2$·H$_2$O (0.5 mmol) and 2,5-H$_2$pdc (0.5 mmol) with stirring. The resulting solution was filtered and the filtrate was allowed to stand in air at room temperature for several days, yielding pale-yellow crystals of (I) (39% yield based on Mn).

Crystal data

[Mn$_2$(C$_7$H$_3$NO$_4$)$_2$(C$_{14}$H$_8$N$_4$)$_2$-(H$_2$O)$_2$]·2H$_2$O	$\gamma = 109.47\ (3)°$
$M_r = 976.64$	$V = 970.6\ (4)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.3813\ (15)$ Å	$D_x = 1.671$ Mg m^{-3}
$b = 10.044\ (2)$ Å	Mo $K\alpha$ radiation
$c = 14.052\ (3)$ Å	$\mu = 0.73$ mm^{-1}
$\alpha = 95.71\ (3)°$	$T = 292\ (2)$ K
$\beta = 94.42\ (3)°$	Block, pale yellow
	$0.33 \times 0.27 \times 0.21$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	9612 measured reflections
ω scans	4413 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	2620 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.784$, $T_{\max} = 0.852$	$R_{\text{int}} = 0.081$
	$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.05P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.064$	$+ 0.1792P]$
$wR(F^2) = 0.138$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\max} < 0.001$
4413 reflections	$\Delta\rho_{\max} = 0.39$ e Å^{-3}
310 parameters	$\Delta\rho_{\min} = -0.54$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Mn1—O1W	2.110 (3)	Mn1—N1	2.324 (3)
Mn1—O1	2.156 (3)	C15—O2	1.236 (4)
Mn1—O4^i	2.143 (3)	C15—O1	1.280 (4)
Mn1—N2	2.241 (3)	C21—O4	1.248 (5)
Mn1—N5^i	2.278 (3)	C21—O3	1.252 (4)
O1W—Mn1—O4^i	166.72 (12)	O1—Mn1—N5^i	92.22 (11)
O1W—Mn1—O1	90.57 (11)	N2—Mn1—N5^i	161.67 (10)
O4^i—Mn1—O1	96.89 (11)	O1W—Mn1—N1	85.04 (12)
O1W—Mn1—N2	102.65 (12)	O4^i—Mn1—N1	90.46 (11)
O4^i—Mn1—N2	87.86 (11)	O1—Mn1—N1	164.46 (11)
O1—Mn1—N2	93.72 (11)	N2—Mn1—N1	72.82 (11)
O1W—Mn1—N5^i	94.60 (12)	N5^i—Mn1—N1	102.97 (12)
O4^i—Mn1—N5^i	74.22 (11)		

Symmetry code: (i) $-x + 1, -y + 1, -z$.

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

$D-$H$\cdots A$	$D-$H	H$\cdots A$	$D\cdots A$	$D-$H$\cdots A$
O1W—HW11$\cdots$O2W	0.83 (4)	1.89 (2)	2.704 (4)	166 (4)
O1W—HW12$\cdots$O3^{ii}	0.85 (2)	1.82 (2)	2.665 (4)	176 (4)
O2W—HW21$\cdots$O1^{iii}	0.85 (2)	2.04 (2)	2.874 (4)	165 (4)
O2W—HW22$\cdots$O2^{iv}	0.85 (2)	1.93 (2)	2.767 (4)	170 (4)

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

All H atoms on C atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of water molecules were located in difference Fourier maps and their positions and U_{iso} values were refined freely.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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