catena-Poly[[diaqua(1,10-phenanthroline-κ^2N,N')-manganese(II)]-μ-acetylenedicarboxylato-$\kappa^2O:O'$]

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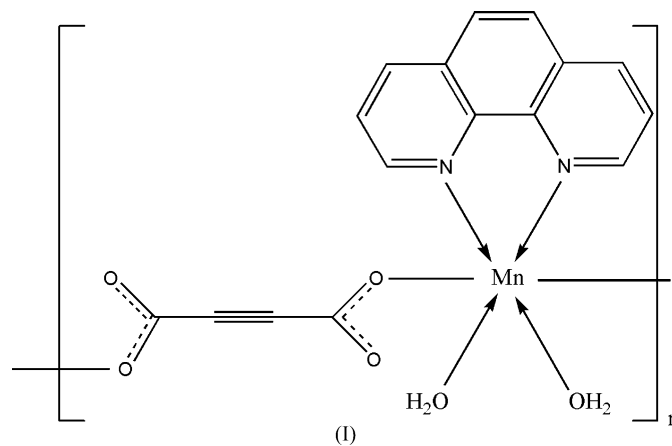
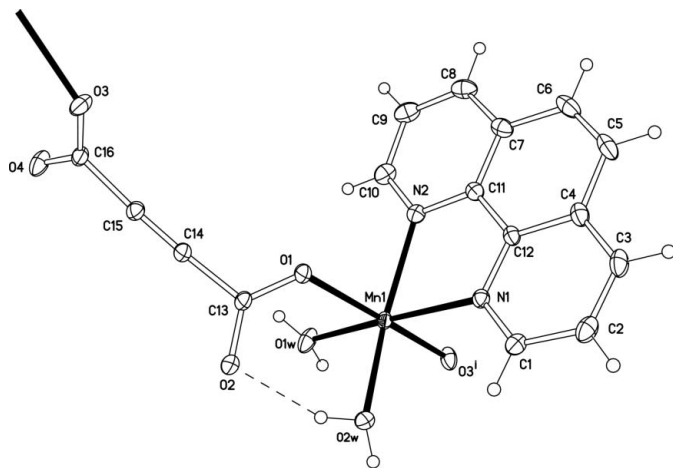Correspondence e-mail: shangao67@yahoo.com

In the title complex, $[Mn(C_4O_4)(C_{12}H_8N_2)(H_2O)_2]_n$, each Mn^{II} ion is octahedrally coordinated by two N atoms of a 1,10-phenanthroline ligand, two carboxylate O atoms of different acetylenedicarboxylate (ace^{2-}) ligands and two coordinated water molecules, and the octahedral units are connected by ace^{2-} bridges, which adopt a bis-monodentate coordination mode, to form a one-dimensional structure along the [101] direction. A three-dimensional supramolecular architecture is constructed *via* hydrogen-bond and π–π interactions.

Comment

The construction of coordination polymers and networks by the self-assembly of organic ligands and metal ions is a rapidly growing area of reaseach (Evans & Lin, 2002). Recently, many new complexes have been synthesized using acetylene-dicarboxylate to combine with specific transition metal ions (Stein & Ruschewitz, 2005), and hence this ligand can be regard as a good candidate to fabricate coordination polymers. To our knowledge, some transition metal complexes with one-dimensional chain structures of Co, Ni, Cu and Cd (Panten-burg & Ruschewitz, 2002; Hohn *et al.*, 2002; Billetter *et al.*, 2003; Ruschewitz & Pantenburg, 2002) have been reported to date. However, compared with the extensively investigated transition metal cordination polymers, there are relatively few reports of metal–organic frameworks constructed with acetylenedicarboxylate by introducing neutral *N*-heterocylic ligands. In order to explore further the behaviour of this ligand, we have obtained the title new manganese complex, $[Mn(ace)(phen)(H_2O)_2]_n$ (phen is 1,10-phenanthroline and ace^{2-} is acetylenedicarboxylate dianion), (I).

(I)

As shown in Fig. 1, complex (I) is an infinite one-dimensional chain polymer, with one Mn^{II} ion, one ace^{2-} ligand, one

Figure 1
The asymmetric unit, extended to complete the Mn coordination, of the title complex, with displacement ellipsoids drawn at the 30% probability level. The dashed line indicates a hydrogen bond. [Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.]
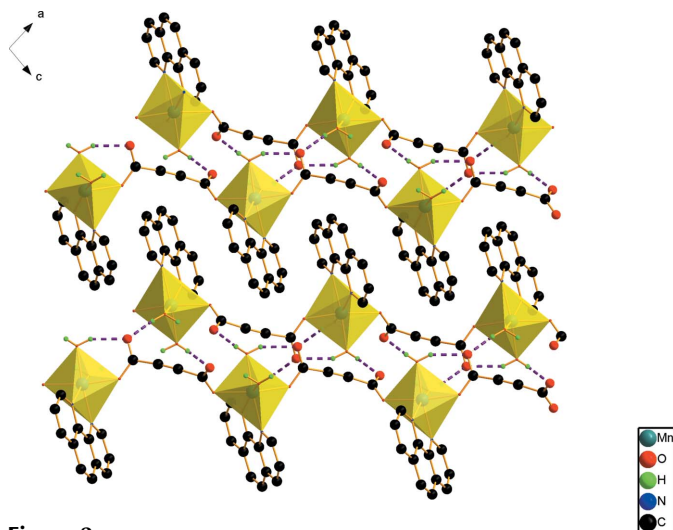
Figure 2
The packing of (I), projected along the a axis. Dashed lines indicate hydrogen bonds. H atoms not involved in these interactions have been omitted.

phen ligand and two coordinated water molecules in the asymmetric unit. The Mn^{II} ion is coordinated by two carboxylate O atoms of two ace^{2-} ligands [Mn1—O1 = 2.1647 (12) Å and Mn1—O3^i = 2.145 (12) Å; symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$], two N atoms of one phen ligand [Mn1—N1 = 2.2571 (13) Å and Mn1—N2 = 2.2792 (13) Å], and two coordinated water molecules [Mn1—O1W = 2.1485 (13) Å and Mn1—O2W = 2.2013 (12) Å], showing a distorted octahedral geometry. (Table 2 and Fig. 2). Each quasi-linear ace^{2-} anion coordinates to Mn^{II} ions in a bis-monodentate coordination mode, linking the Mn^{II} ions into a one-dimensional chain along the [101] direction. The dihedral angle between the two chelating phen ligands around two adjacent Mn^{II} ions is 40.94 (5)°.

The angle between the coordinated water molecules is 90.64 (5)°, and this orientation plays a crucial role in forming a

high-dimensional hydrogen-bond network. Thus, adjacent chains are connected by hydrogen bonds into a layer, with O···O distances in the range 2.6701 (17)–2.7890 (16) Å and O—H···O angles in the range 152 (2)–177 (2)°. In addition, the layers are connected via π–π interactions between one of the rings of the phen ligand (C7–C10/N2/C11) and a symmetry-related ring at $(-x, 1 - y, 1 - z)$, with a centroid-to-centroid distance of 3.6247 Å, thus forming a three-dimensional supramolecular network.

Experimental

Complex (I) was synthesized by the addition of $MnCl_2 \cdot 6H_2O$ (0.234 g, 1 mmol) and phen (0.198 g, 1 mmol) to an ethanol–water (1:1 v/v) solution (20 ml) of acetylenedicarboxylic acid (0.144 g, 1 mmol). The pH of the solution was adjusted to 7 with 1.0 M NaOH solution. After the mixture had been stirred for 30 min, the residue was filtered. The filtrate was allowed to evaporate at room temperature and yellow crystals of (I) were obtained after about 7 d. Analysis, calculated for $C_{16}H_{12}MnN_2O_6$: C 50.15, H 3.16, N 7.31%; found: C 50.08, H 3.12, N 7.29%.

Crystal data

$[Mn(C_4O_4)(C_{12}H_8N_2)(H_2O)_2]$	$Z = 4$
$M_r = 383.22$	$D_x = 1.584$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.764$ (3) Å	$\mu = 0.86$ mm^{-1}
$b = 8.2793$ (17) Å	$T = 295$ (2) K
$c = 14.218$ (3) Å	Block, yellow
$\beta = 97.24$ (3)°	$0.35 \times 0.32 \times 0.25$ mm
$V = 1607.3$ (6) Å^3	

Data collection

Rigaku R-AXIS RAPID area-detector diffractometer	15165 measured reflections
ω scans	3668 independent reflections
Absorption correction: multi-scan	3285 reflections with $I > 2\sigma(I)$
($ABSCOR$; Higashi, 1995)	$R_{int} = 0.025$
$T_{min} = 0.753$, $T_{max} = 0.814$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 0.3898P]$
$wR(F^2) = 0.075$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
3668 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
238 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Mn1—O1W	2.1485 (13)	Mn1—O2W	2.2013 (12)
Mn1—O3^i	2.1545 (12)	Mn1—N1	2.2571 (13)
Mn1—O1	2.1647 (12)	Mn1—N2	2.2792 (13)
O1W—Mn1—O3^i	86.15 (5)	O1—Mn1—N1	100.62 (5)
O1W—Mn1—O1	85.09 (5)	O2W—Mn1—N1	91.67 (4)
O3^i—Mn1—O1	170.00 (5)	O1W—Mn1—N2	104.97 (5)
O1W—Mn1—O2W	90.63 (5)	O3^i—Mn1—N2	91.72 (5)
O3^i—Mn1—O2W	97.08 (5)	O1—Mn1—N2	85.89 (5)
O1—Mn1—O2W	87.84 (4)	O2W—Mn1—N2	162.59 (4)
O1W—Mn1—N1	173.91 (5)	N1—Mn1—N2	73.60 (5)
O3^i—Mn1—N1	87.98 (4)		

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W1$\cdots$O4^i	0.839 (9)	2.011 (11)	2.7781 (18)	152 (2)
O1W—H1W2$\cdots$O2^{ii}	0.845 (9)	1.826 (10)	2.6701 (17)	177 (2)
O2W—H2W1$\cdots$O4^{iii}	0.853 (9)	1.940 (10)	2.7890 (16)	173.0 (17)
O2W—H2W2$\cdots$O2	0.851 (9)	2.011 (10)	2.8042 (17)	154.7 (17)

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

Water H atoms were located in a difference map and refined with O—H and H$\cdots$H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with U_{iso} (H) = $1.5U_{eq}$(O). All other H atoms were placed in calculated positions, with C—H = 0.93 Å (aromatic) and U_{iso} (H) = $1.2U_{eq}$(C), and were refined in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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