metal-organic papers

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cis-Aquachlorobis(1,10-phenanthroline-κ^2N,N')-manganese(II) 4-formylbenzoate trihydrate

The title compound, $[MnCl(C_{12}H_8N_2)_2(H_2O)](C_8H_5O_3)\cdot 3H_2O$, consists of cis-$[Mn(phen)_2(H_2O)Cl]^+$ cations (phen = 1,10-phenanthroline), 4-formylbenzoate anions and solvent water molecules. The Mn^{II} atom is coordinated by four N atoms of two phen ligands, one Cl atom and one aqua ligand, forming a distorted octahedral geometry. A three-dimensional network is formed by O—H···O/Cl hydrogen bonds and π–π stacking interactions.

Comment

4-Formylbenzoic acid (abbreviated as Hfmbz), which crystallizes in two forms (Haisa *et al.*, 1976), has been used in the synthesis of metal carboxylates. Recently, we have reported the structures of some transition metal complexes (Deng *et al.*, 2006*b,c,d*). In the molecule of $[Mn(fmbz)_2(imidazole)_2(H_2O)_2]$, the 4-formylbenzoate ligand coordinates to the Mn^{II} atom in a monodentate mode (Deng *et al.*, 2006*a*). For the present study, we used 1,10-phenanthroline (phen) instead of imidazole, yielding $[Mn(phen)_2(H_2O)Cl]fmbz\cdot 3H_2O$, (I), in which 4-formylbenzoate acts as a counter-anion.

(I)
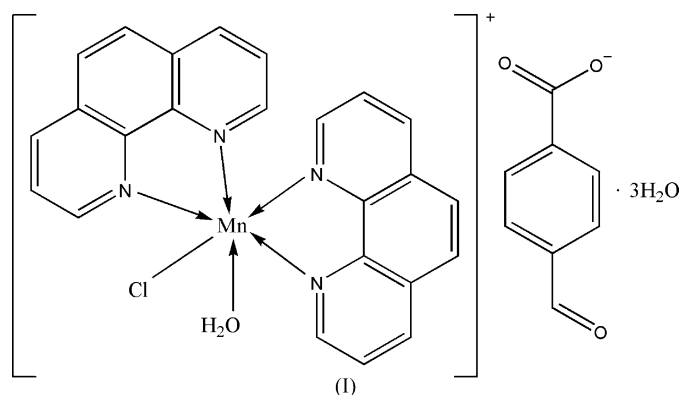
The Mn^{II} atom is six-coordinated in a distorted octahedral environment (Fig. 1). The cation, anion and water molecules form extensive intermolecular hydrogen bonds (Table 2), connecting the components into a layer structure. There are π–π stacking interactions between adjacent phen rings along the *a* axis, with a centroid–centroid separation of 3.593 (3) Å; the π–π stacking leads to a three-dimensional supramolecular network.

Experimental

Manganese diacetate tetrahydrate (0.122 g, 0.5 mmol) was added to an aqueous ethanol solution (20 ml, 1:1 *v/v*) of 4-formylbenzoic acid (0.15 g, 1 mmol) and 1,10-phenanthroline (0.2 g 1 mmol). The pH

value of the mixture was about 5. The filtered solution was allowed to evaporate at room temperature, and colorless prismatic crystals of (I) were obtained after several days (yield 69%). Analysis calculated for $C_{32}H_{29}ClN_4O_7Mn$: C 57.20, H 4.35, N 8.34%; found: C 57.24, H 4.34, N 8.36%.

Crystal data

[MnCl(C₁₂H₈N₂)₂(H₂O)]-
  (C₈H₅O₃)·3H₂O
$M_r = 671.98$
Triclinic, $P\overline{1}$
$a = 10.719\ (2)$ Å
$b = 11.849\ (2)$ Å
$c = 12.971\ (3)$ Å
$\alpha = 103.33\ (3)°$
$\beta = 94.42\ (3)°$

$\gamma = 104.23\ (3)°$
$V = 1538.2\ (6)$ Å³
$Z = 2$
$D_x = 1.451$ Mg m⁻³
Mo $K\alpha$ radiation
$\mu = 0.57$ mm⁻¹
$T = 295\ (2)$ K
Prism, colorless
$0.38 \times 0.28 \times 0.19$ mm

Data collection

Rigaku R-AXIS RAPID
  diffractometer
ω scans
Absorption correction: multi-scan
  (ABSCOR; Higashi, 1995)
  $T_{min} = 0.812$, $T_{max} = 0.899$

15102 measured reflections
6947 independent reflections
4816 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.109$
$S = 1.09$
6947 reflections
430 parameters
H atoms treated by a mixture of
  independent and constrained
  refinement

$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.6199P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å⁻³
$\Delta\rho_{min} = -0.45$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Mn1—O1W	2.1272 (18)	Mn1—N1	2.300 (2)
Mn1—N2	2.2602 (19)	Mn1—N3	2.319 (2)
Mn1—N4	2.2717 (19)	Mn1—Cl1	2.4491 (10)
O1W—Mn1—N2	102.95 (7)	N4—Mn1—N3	72.66 (7)
O1W—Mn1—N4	94.20 (8)	N1—Mn1—N3	88.76 (8)
N2—Mn1—N4	155.69 (7)	O1W—Mn1—Cl1	91.04 (6)
O1W—Mn1—N1	85.04 (8)	N2—Mn1—Cl1	96.37 (6)
N2—Mn1—N1	73.46 (7)	N4—Mn1—Cl1	100.46 (6)
N4—Mn1—N1	91.26 (7)	N1—Mn1—Cl1	167.89 (5)
O1W—Mn1—N3	165.37 (7)	N3—Mn1—Cl1	97.57 (6)
N2—Mn1—N3	87.89 (7)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O3W	0.85 (2)	1.93 (3)	2.765 (3)	170 (3)
O1W—H1W2···O2	0.86 (2)	1.80 (2)	2.652 (2)	174 (3)
O2W—H2W1···O1ⁱ	0.85 (3)	1.87 (3)	2.711 (3)	169 (4)
O2W—H2W2···Cl1	0.85 (3)	2.40 (3)	3.228 (3)	164 (4)
O3W—H3W1···O2W	0.86 (3)	2.04 (3)	2.878 (4)	164 (3)
O3W—H3W2···O4Wⁱ	0.86 (3)	1.96 (3)	2.807 (4)	167 (4)
O4W—H4W1···O1ⁱ	0.86 (3)	1.94 (3)	2.779 (3)	164 (4)
O4W—H4W2···Cl1	0.85 (3)	2.48 (3)	3.306 (3)	162 (4)

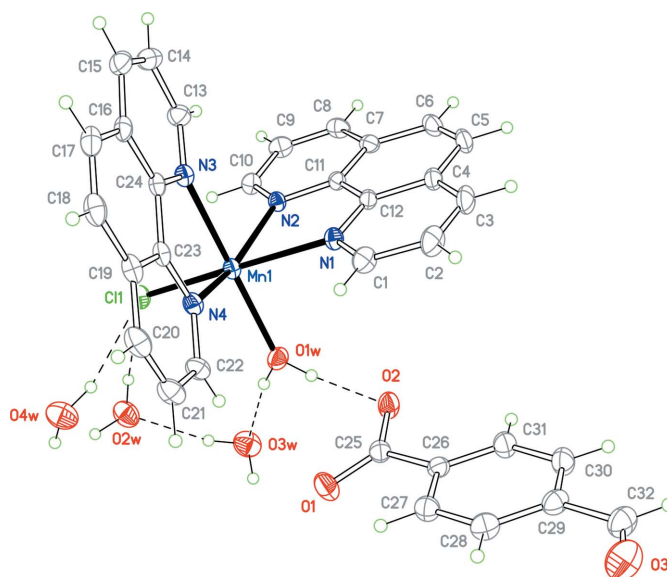Symmetry code: (i) $-x + 2, -y + 2, -z + 2$.

Figure 1
The asymmetric unit of the title complex, with displacement ellipsoids drawn at the 30% probability level. The hydrogen bonds are denoted by dashed lines.

Carbon-bound H atoms were placed in calculated positions, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and were refined in the riding-model approximation. The H atoms of the water molecules were located in difference Fourier maps and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: RAPID-AUTO (Rigaku, 1998); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MSC, 2002); 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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