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Bis(pyridinecarboxylato-*O*,*N*)(pyridinecarboxylato-*O*,*N*)manganese(III) hydroxide

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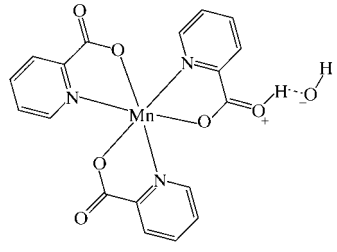
The title complex, $[Mn(C_5H_4NCO_2)_2(C_5H_4NCOOH)]OH$, consists of a cation and a hydroxide ion. The Mn atom is coordinated by three N atoms and three O atoms from three pyridinecarboxylate ligands, and has a distorted octahedral geometry, with Mn—N distances ranging from 2.157 (1) to 2.233 (1) Å and Mn—O distances from 1.910 (1) to 1.927 (4) Å. One ligand is protonated as the acid form. This forms one of two independent hydrogen bonds, to the anion.

Comment

The chemistry of manganese in various oxidation states with primarily carboxylate ligation is currently receiving much attention (Christou, 1989). These studies have been stimulated partly because manganese plays an essential and specific role in many redox-active metalloenzymes, including the photosynthetic Oxygen Evolving Complex superoxide dismutase, pseudocatalase and ribonucleotide reductase (Dexheimer *et al.*, 1989; Wieghardt, 1989). We report here a new type of



(I)

crystal structure, a new synthetic route and a different oxidation state for manganese from what has been observed before in this area (Figgis *et al.*, 1978).

The title complex, (I), consists of a cation and a hydroxide ion. The Mn atom is coordinated by three N atoms and three O atoms from three pyridinecarboxylate ligands, and has a distorted octahedral geometry, with Mn—N distances ranging from 2.157 (1) to 2.233 (1) Å and Mn—O distances from 1.910 (1) to 1.927 (4) Å. One ligand is protonated as the acid form. This forms one of two independent hydrogen bonds (Table 2), to the anion.

Experimental

$Mn(OAc)_2(H_2O)_4$ and pyridinecarboxylic acid were dissolved in pyridine and absolute EtOH, and solid (^{n}Bu$_4$N)[MnO_4] was added in small portions with stirring, affording a bronze precipitate that was filtered, washed with a mixture solvent comprising pyridine and absolute EtOH, and dried in a desiccator containing silica gel. Well shaped single crystals were obtained by a diffusion method.

Crystal data

$[Mn(C_6H_4NO_2)_2(C_6H_5NO_2)]OH$
M_r = 439.26
Monoclinic, $C2/c$
a = 30.523 (6) Å
b = 8.4111 (17) Å
c = 13.914 (3) Å
β = 94.40 (3)°
V = 3561.6 (12) Å^3
Z = 8
D_x = 1.638 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4099 reflections
θ = 1–27°
μ = 0.791 mm^{-1}
T = 293 (2) K
Plate, brown
0.16 × 0.10 × 0.08 mm

Data collection

KappaCCD diffractometer
φ and ω scans with κ offsets
6842 measured reflections
4099 independent reflections
3882 reflections with $I > 2\sigma(I)$
R_{int} = 0.0762
θ_{max} = 27.53°
$h = -39 \rightarrow 39$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 17$
Intensity decay: <0.005%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.067
S = 0.860
4099 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0600P)^2 + 0.5500P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0139 (4)

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.9094 (8)	O4—C12	1.2009 (12)
Mn1—O5	1.9174 (7)	O5—C18	1.3066 (11)
Mn1—O3	1.9274 (9)	O6—C18	1.2303 (13)
Mn1—N1	2.1566 (10)	N1—C5	1.2849 (12)
Mn1—N3	2.2215 (8)	N1—C1	1.3412 (12)
Mn1—N2	2.2328 (9)	N2—C7	1.3429 (12)
O1—C6	1.3223 (13)	N2—C11	1.3700 (13)
O2—C6	1.2183 (12)	N3—C17	1.3334 (12)
O3—C12	1.3237 (12)	N3—C13	1.3427 (11)
O1—Mn1—O5	174.91 (3)	N3—Mn1—N2	162.14 (3)
O1—Mn1—O3	89.64 (4)	C6—O1—Mn1	117.54 (6)
O5—Mn1—O3	95.28 (4)	C12—O3—Mn1	119.83 (7)
O1—Mn1—N1	80.79 (4)	C18—O5—Mn1	119.68 (6)
O5—Mn1—N1	94.27 (3)	C5—N1—C1	126.54 (9)
O3—Mn1—N1	170.41 (3)	C5—N1—Mn1	125.50 (7)
O1—Mn1—N3	103.39 (3)	C1—N1—Mn1	107.74 (6)
O5—Mn1—N3	78.04 (3)	C7—N2—C11	119.37 (8)
O3—Mn1—N3	88.97 (4)	C7—N2—Mn1	108.02 (6)
N1—Mn1—N3	93.77 (4)	C11—N2—Mn1	132.18 (7)
O1—Mn1—N2	88.81 (4)	C17—N3—C13	119.84 (8)
O5—Mn1—N2	90.96 (3)	C17—N3—Mn1	131.30 (6)
O3—Mn1—N2	77.96 (4)	C13—N3—Mn1	108.52 (6)
N1—Mn1—N2	101.12 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O7	0.85	2.09	2.7672 (19)	136
O7—H7A···O5^{i}	0.96	2.24	2.9473 (17)	130

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

The positions of all H atoms were fixed geometrically.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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