catena-Poly[[tris(1*H*-benzimidazole-*κN*³)-manganese(II)]-*μ*-maleato-*κ*²*O*,*O*′:*κO*″]

Zi-Qiang Hu, Yong Ni and Guo-Qiao Lai*

Key Laboratory of Organosilicon Chemistry and Materials Technology of the Education Ministry, Hangzhou Teachers College, People's Republic of China

Correspondence e-mail: guoqiaol@163.com

In the title compound, $[Mn(C_4H_2O_4)(C_7H_6N_2)_3]_n$, maleate dianions bridge neighbouring Mn^{II} ions to form helical polymeric chains. The Mn ion assumes a distorted octahedral coordination geometry, formed by two maleate and three benzimidazole ligands. One maleate carboxyl group chelates to the Mn atom with longer Mn—O bond distances while the other carboxyl group coordinates in a monodentate manner to the Mn atom.

Comment

The chemical behaviour of manganese complexes has attracted much attention in terms of their catalytic activity in some industrial and biochemical processes (Kono & Fridovich, 1983; Wu *et al.*, 2001). As part of our ongoing investigation on polymerization reactions catalysed by variable valence manganese complexes, we present here the X-ray structure of the title Mn^{II} complex, (I).

(I)
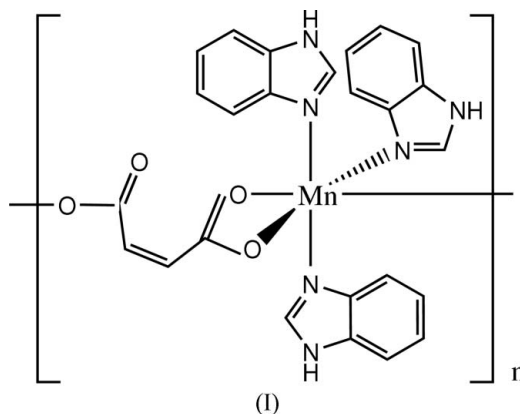
The structure of (I) consists of polymeric complex chains (Fig. 1). The maleate dianions bridge neighbouring Mn^{II} ions through both carboxyl groups, one in a chelating mode and the other in a monodentate mode. The Mn—O bond distances involving the chelating carboxyl group [O1—Mn—O2 = 55.76 (7)°] are much longer than that involving the monodentate carboxyl group (Table 1). Three benzimidazole N atoms coordinate to the Mn atom to complete the distorted octahedral coordination geometry. The large N23—Mn—O3^i angle of 117.82 (10)° [symmetry code: (i) $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$] indicates a significant degree of distortion.

The C1-carboxyl group of the maleate dianion is twisted with respect to the carbon backbone mean plane by 28.1 (3)°; the Mn ion bonded to the C1-carboxyl group is thus displaced from the backbone mean plane by a relatively small amount [0.145 (8) Å]. The maleate C3-carboxyl group is nearly
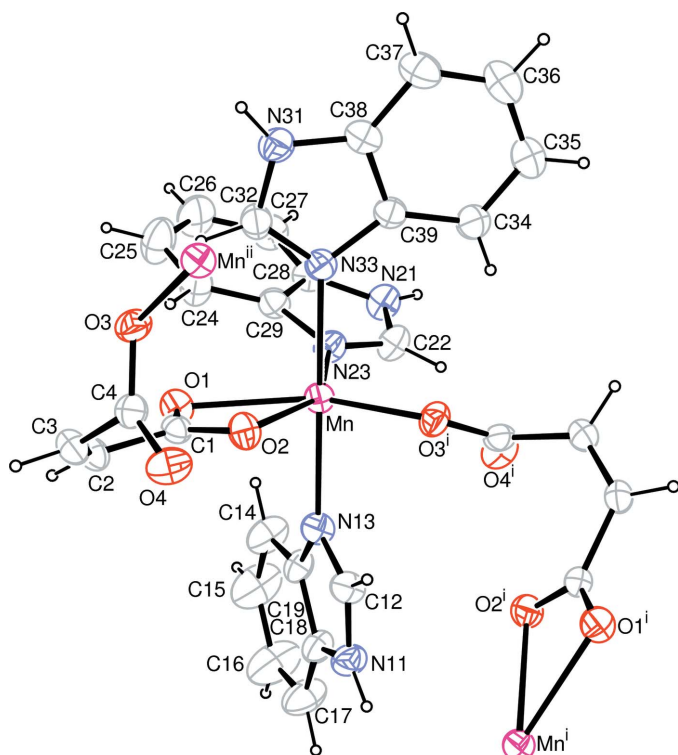
Figure 1
A segment of the polymeric structure of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). [Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.]
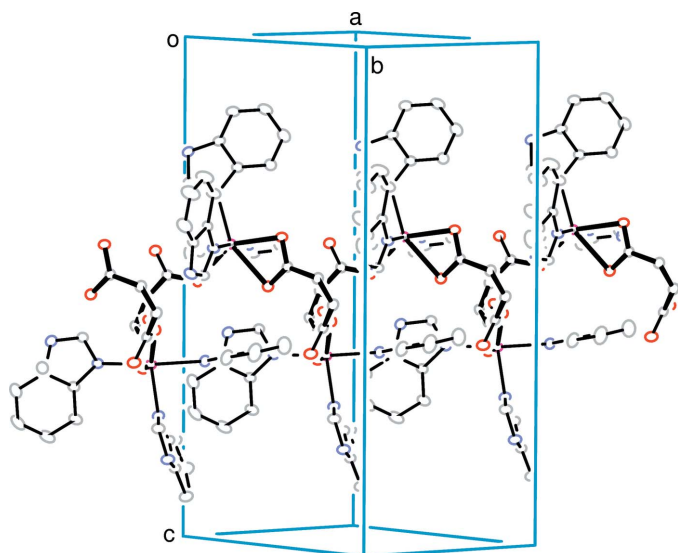

Figure 2
The packing of (I), showing a fragment of the helical complex chain. H atoms have been omitted for clarity.

perpendicular to the carbon backbone [dihedral angle = $80.6 (2)°$], resulting in the O3-bridged Mn^{ii} atom being out of the backbone mean plane by $-1.318 (8)$ Å [symmetry code: (ii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$]. Overall, the maleate dianions bridge neighbouring Mn atoms to form a helical polymeric chain (Fig. 2), in agreement with the situation found in the isostructural Co^{II} analogue (Xue *et al.*, 2003).

The crystal packing is stabilized by N—H···O hydrogen bonds between benzimidazole ligands and neighbouring carboxyl groups (Table 2).

Experimental

A hot aqueous solution (5 ml) of maleic acid (2 mmol) and Na$_2$CO$_3$ (2 mmol) was mixed with an aqueous solution (5 ml) of MnCl$_2$·2H$_2$O (2 mmol). The mixture was refluxed for 1 h, after which time an ethanol solution (5 ml) of benzimidazole (4 mmol) was added dropwise and the resulting mixture refluxed for another 3 h and filtered. Single crystals of (I) were obtained from the solution after 10 d.

Crystal data

[Mn(C$_4$H$_2$O$_4$)(C$_7$H$_6$N$_2$)$_3$]	Mo $K\alpha$ radiation
$M_r = 523.41$	Cell parameters from 17602
Orthorhombic, $P2_12_12_1$	reflections
$a = 9.3455 (13)$ Å	$\theta = 2.4$–$25.0°$
$b = 12.2596 (13)$ Å	$\mu = 0.58$ mm^{-1}
$c = 21.3592 (19)$ Å	$T = 295 (2)$ K
$V = 2447.2 (5)$ Å^3	Block, colourless
$Z = 4$	$0.29 \times 0.13 \times 0.10$ mm
$D_x = 1.421$ Mg m^{-3}	

Data collection

Rigaku R-AXIS RAPID diffractometer	4528 independent reflections
ω scans	3945 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.048$
	$\theta_{max} = 25.5°$
$T_{min} = 0.838$, $T_{max} = 0.935$	$h = -10 \rightarrow 11$
19932 measured reflections	$k = -14 \rightarrow 14$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.18$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
4528 reflections	$\Delta\rho_{min} = -0.54$ e Å^{-3}
325 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1935 Friedel Pairs
	Flack parameter: 0.01 (2)

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.310 (2)	Mn—N13	2.221 (3)
Mn—O2	2.378 (2)	Mn—N23	2.217 (2)
Mn—O3^i	2.169 (2)	Mn—N33	2.261 (3)
C1—O1—Mn	92.84 (19)	C4—O3—Mn^{ii}	119.5 (2)
C1—O2—Mn	90.02 (18)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···O3^{iii}	0.86	2.04	2.855 (3)	158
N21—H21···O1^{iv}	0.86	1.98	2.811 (4)	162
N31—H31···O4^{ii}	0.86	2.06	2.850 (4)	152

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

H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and were refined as riding, with $U_{iso}(H) = 1.2U_{eq}(carrier)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Kono, Y. & Fridovich, I. (1983). *J. Biol. Chem.* **258**, 6015–6020.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Version 3.00. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Wu, Z.-Y., Xu, D.-J. & Feng, Z.-X. (2001). *Polyhedron*, **20**, 281–284.
Xue, Y.-H., Xu, D.-J. & Gu, J.-M. (2003). *Acta Cryst.* C**59**, m387–m389.