Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

catena-Poly[[aquabis(1*H*-benzimidazole-κN^3)manganese(II)]-μ-adipato]

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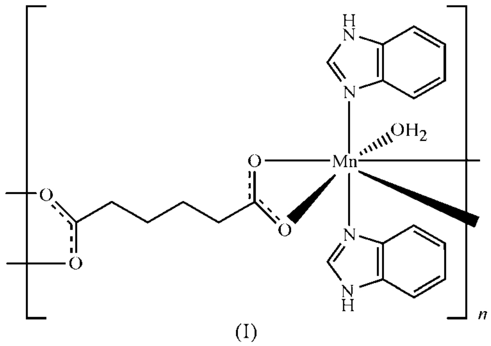
Received 28 June 2004
Accepted 27 January 2005
Online 11 March 2005

In the title polymeric complex, $[\mathrm{Mn}(\mathrm{C_6H_8O_4})(\mathrm{C_7H_6N_2})_2(\mathrm{H_2O})]_n$, the $\mathrm{Mn^{II}}$ atom is surrounded by two adipate dianions, two benzimidazole molecules and one coordinated water molecule. The Mn atoms and coordinated water molecule are located on a twofold axis, and the bridging adipate ligand is located on an inversion center. The adipate dianions bridge neighboring $\mathrm{Mn^{II}}$ atoms to form polymeric chains. Each $\mathrm{Mn^{II}}$ atom is seven-coordinate, the longest Mn—O bond length being 2.5356 (16) Å.

Comment

Water oxidation in the photosynthetic process of green plants (Bruckner *et al.*, 1993) is generally believed to occur at a manganese cluster located in the reaction center of photosystem II (Vincent & Christou, 1989). In order to mimic the manganese cluster, a series of manganese complexes bridged by carboxylate ligands have been synthesized in our laboratory, among which some crystal structures revealed the existence of significant electrostatic interaction between the Mn atom and the ligand (Nie *et al.*, 2001; Hu *et al.*, 2002; Liu & Xu, 2003). In the title $\mathrm{Mn^{II}}$ complex, (I), the seven-coordinate geometry clearly suggests electrostatic interaction between the $\mathrm{Mn^{II}}$ atom and the coordinated O atoms.



(I)

The $\mathrm{Mn^{II}}$ atom in (I) is surrounded by two adipate dianions, two benzimidazole (BZIM) molecules and one coordinated water molecule, as illustrated in Fig. 1. The Mn atom and the coordinated water molecule are located on a crystallographic twofold axis. The two benzimidazole molecules coordinate to the Mn atom in a *trans* mode. The Mn—N3 bond (Table 1) is longer than the Mn—N bonds in the imidazole complex of $\mathrm{Mn^{II}}$ [2.183 (3) and 2.190 (3) Å; Liu *et al.*, 2003]. The longer Mn—N3 bond is a result of the poor overlap of atomic orbitals between atoms Mn and N3, as verified by the large angle [19.53 (7)°] between the Mn—N3 bond and the mean plane of the BZIM group containing atom N1, and the appreciable deviation [0.762 (3) Å] of the Mn atom from the BZIM mean plane. Two carboxy O2 atoms and two BZIM N3 atoms form the equatorial coordination plane. The Mn atom lies almost in the equatorial plane, with a small displacement [0.0344 (12) Å] towards atom O1. This implies that the coordination geometry in the complex is not square pyramidal, and some bonding interaction occurs in the direction opposite to the Mn—O1 bond, as discussed below.

Two adipate dianions symmetrically coordinate to the Mn atom in a weak chelating mode (see Fig. 1). While the Mn—O2 distance and O2—Mn—O2$^{\mathrm{ii}}$ angle [symmetry code: (ii) $-x+1, y, -z+\frac{1}{2}$] imply a normal Mn—O2 coordinate bond, the longer distance of 2.5356 (16) Å suggests that the Mn—O3 bond is semi-coordinate, balancing the bonding interaction between atoms Mn and O1 and resulting in the Mn atom being located almost in the equatorial plane, as mentioned above.

Further evidence supporting the Mn—O3 bonding interaction is provided by the small Mn—O2—C11 bond angle. Several structures of manganese(II) complexes incorporating

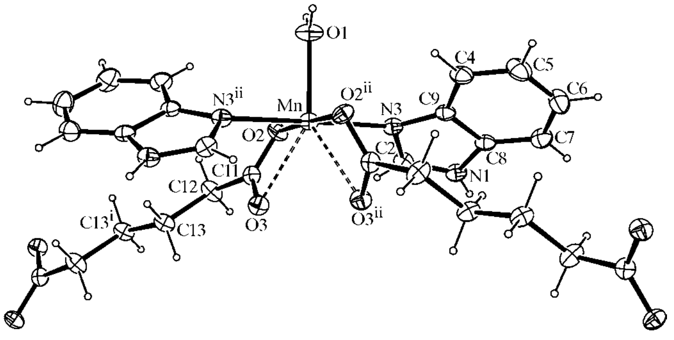


Figure 1
The structure of (I), showing 40% probability displacement ellipsoids. [Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $-x+1, y, -z+\frac{1}{2}$.]

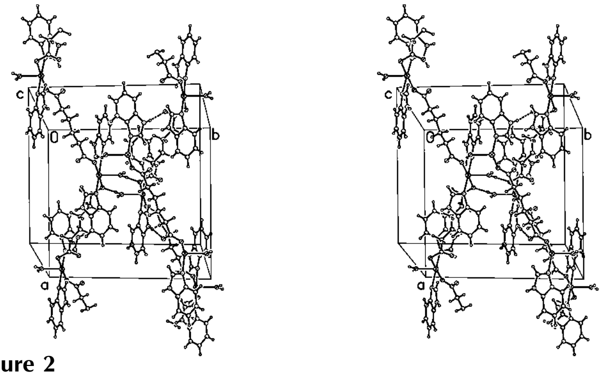


Figure 2
A stereoview of the molecular packing, showing polymeric chains. Dashed lines indicate hydrogen bonding between neighboring chains.

DOI: 10.1107/S0108270105003057

carboxylate groups have been reported, and the geometric parameters of their carboxyl groups are compared in Table 3. Two kinds of Mn—O2—C bond angles are observed in these structures, *viz.* either less than 100° or larger than 120°. Corresponding to these different Mn—O2—C angles, two kinds of Mn—O3 distances are observed in the structures. The smaller Mn—O2—C angle corresponds to a shorter Mn—O3 distance (shorter than 2.6 Å) and suggests a bonding interaction between atoms Mn and O3, *i.e.* the carboxyl group is chelating. The larger Mn—O2—C angle corresponds to a longer Mn—O3 distance (longer than 3.3 Å) and suggests a monodentate carboxyl group.

In the title Mn^{II} complex, both the Mn—O2—C11 bond angle and the Mn—O3 distance (Table 1) are close to those found in the chelate complexes but significantly different from those found in the monodentate complexes. These facts clearly indicate that the carboxyl group of adipate in the Mn^{II} complex acts as a chelating rather than a monodentate ligand. Thus, the Mn^{II} atom assumes a seven-coordinate geometry with a double-capped pyramidal configuration (Fig. 1).

The adipate dianion is located on an inversion center and has an extended, nearly coplanar, carbon skeleton, the C11—C12—C13—C13^{i} torsion angle being 173.5 (2)° [symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$]. This is different from the situation found in most adipate complexes. In the complexes reported previously, the flexible carbon skeleton of the adipate ion usually displays a curled conformation (Pajunen & Nasakkala, 1977; McCann *et al.*, 1997; Suresh *et al.*, 1997; Darensbourg *et al.*, 1996; Tosik *et al.*, 1995). For example, the adipate–Cu^{II} complex aquabis(benzimidazole)copper(II)-μ-adipate (Suresh & Bhadbhade, 1997) has the same chemical component (except for the central ion) and the same coordination mode for the adipate ion as the title Mn^{II} complex. However, in the Cu^{II} complex, the adipate ion displayed the curled conformation, resulting in cell dimensions that differ from those of the title Mn^{II} complex.

In (I), adipate dianions bridge neighboring Mn^{II} atoms through both terminal carboxyl groups to form polymeric complex chains, as shown in Fig. 2. Neighboring polymeric chains are linked to one another *via* O—H···O and N—H···O hydrogen bonds (Table 2) to form a three-dimensional network.

Aromatic π–π stacking has commonly been observed in crystal structures including BZIM. Although the centroid-to-centroid distance between the two imidazole rings is only 3.955 (17) Å in (I), the imidazole rings do not overlap one another and no π–π stacking occurs.

Experimental

An ethanol solution (5 ml) of BZIM (0.12 g, 1 mmol) was mixed with an aqueous solution (5 ml) of $Mn(CH_3COO)_2\cdot 4H_2O$ (0.25 g, 1 mmol) and the resulting mixture was refluxed for 30 min. An aqueous solution (5 ml) containing adipic acid (0.15 g, 1 mmol) and NaOH (0.08 g, 2 mmol) was added to the above mixture, and the resulting solution was refluxed for a further 1 h. After cooling to room temperature, the solution was filtered and single crystals of (I) were obtained from the filtrate after two weeks.

Crystal data

$[Mn(C_6H_8O_4)(C_7H_6N_2)_2(H_2O)]$
$M_r = 453.36$
Monoclinic, $C2/c$
$a = 15.159$ (4) Å
$b = 16.758$ (4) Å
$c = 8.954$ (2) Å
$\beta = 116.534$ (4)°
$V = 2035.0$ (9) Å^3
$Z = 4$
$D_x = 1.480$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5266 reflections
$\theta = 2.5$–24.0°
$\mu = 0.69$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.36 × 0.28 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
ω and φ scans
Absorption correction: empirical (*SADABS*; Bruker, 1999)
$T_{min} = 0.782$, $T_{max} = 0.881$
5725 measured reflections
2023 independent reflections
1536 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 26.1°$
$h = -18 \rightarrow 17$
$k = -17 \rightarrow 20$
$l = -11 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.086$
$S = 0.93$
2023 reflections
140 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.137 (2)	O3—C11	1.254 (2)
Mn—O2	2.2575 (15)	C11—C12	1.512 (3)
Mn—O3	2.5356 (16)	C12—C13	1.515 (3)
Mn—N3	2.2484 (18)	C13—C13^{i}	1.518 (4)
O2—C11	1.270 (3)		
O1—Mn—N3	90.60 (5)	O3—Mn—N3	104.48 (6)
O1—Mn—O2	91.14 (4)	N3^{ii}—Mn—N3	178.79 (9)
O1—Mn—O3	139.82 (4)	N3—Mn—O2	85.67 (6)
O2^{ii}—Mn—O2	177.71 (8)	N3—Mn—O2^{ii}	94.30 (6)
O3—Mn—O2^{ii}	123.70 (5)	C11—O2—Mn	97.65 (12)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O2^{iii}	0.85 (3)	1.88 (3)	2.729 (2)	178 (3)
N1—H1···O3^{iv}	0.86	1.96	2.792 (2)	163

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

Table 3
Comparative geometric parameters (Å, °) for selected carboxyl groups in Mn^{II} complexes with chelate and monodentate coordination modes.

Carboxylate	Mn—O2—C	Mn—O2	Mn—O3	Coordinate mode
Phthalate^{a}	92.6 (2)	2.260 (3)	2.284 (3)	Chelate
Benzoate^{b}	92.8 (2)	2.237 (2)	2.298 (2)	Chelate
Adipate^{c}	97.65 (12)	2.2575 (15)	2.5356 (16)	Chelate
Pyromelitate^{d}	125.4 (1)	2.146 (1)	3.324 (1)	Monodentate
Pyromelitate^{e}	123.0 (1)	2.241 (1)	3.329 (1)	Monodentate
Succinate^{f}	123.5	2.179	3.858	Monodentate
Succinate^{g}	130.5	2.163	3.448	Monodentate
Succinate^{h}	136.8 (3)	2.117 (3)	3.523 (3)	Monodentate

Notes: (*a*) Hu *et al.* (2002); (*b*) Liu & Xu (2003); (*c*) this work; (*d*) Hu *et al.* (2001); (*e*) Cheng *et al.* (2000); (*f*) Gupta *et al.* (1983); (*g*) Liu *et al.* (2001); (*h*) Liu *et al.* (2003).

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The water H atom was located in a difference Fourier map and refined with a fixed isotropic displacement parameter of 0.05 Å^2. Other H atoms were placed in calculated positions, with C—H distances of 0.93 (aromatic) and 0.97 Å (methylene), and N—H distances of 0.86 Å, and included in the final cycles of refinement in a riding model, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(carrier atom).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are grateful for support of this project by the National Natural Science Foundation of China (grant Nos. 29973036 and 20240430654).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1500). Services for accessing these data are described at the back of the journal.

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