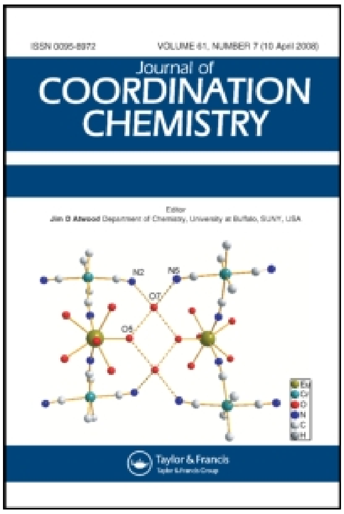

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Synthesis and crystal structure of aquabis(imidazole)bis[4-methylbenzoato(1-)]manganese(II)

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Synthesis and crystal structure of aquabis(imidazole)bis[4-methylbenzoato(1-)]manganese(II)

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The complex $Mn(im)_2(4\text{-mbo})_2 \cdot H_2O$ (im = imidazole, 4-mbo = 4-methylbenzoate) has been prepared and its structure determined by X-ray diffraction methods. Mn(II) assumes a distorted octahedral coordination geometry formed by imidazole, water molecules and 4-mbo anions. Two 4-mbo ligands bind to Mn(II) with different coordination modes, one as a monodentate and the other as a chelate. Comparison of measured Mn–O bond distances and corresponding bond angles with those of other Mn(II) complexes incorporating monodentate carboxylate ligands suggests more electrostatic interaction between the Mn and carboxyl O atoms of the title complex. The interplanar distance between parallel imidazole rings [3.470 (13) Å] is indicative of aromatic π–π stacking, whereas the distance between the parallel benzene rings of neighboring 4-mbo anions [3.761(13) Å] is a normal van der Waals contact. Extensive hydrogen bonding occurs between the complex molecules.

Keywords: Manganese(II); Methylbenzoate; Imidazole; Crystal structure; Electrostatic interactions; Aromatic stacking

1. Introduction

Over the past decade, many efforts have concentrated on elucidating the nature of the biological unit responsible for water oxidation in the photosynthesis of green plants. The process of water splitting is generally believed to occur at a manganese cluster [1]. In a systematic investigation of the molecular structures of manganese complexes that might be useful as models for the active site, we have accumulated structural evidence for a more electrostatic interaction in Mn–O(carboxyl) bonds in multinuclear Mn(II) complexes [2–4]. In the title mononuclear Mn(II) complex, structural data clearly suggest electrostatic bonding.

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2. Experimental

2.1. *Synthesis*

$MnCl_2 \cdot 2H_2O$ (0.33 g, 2 mmol) and imidazole (0.14 g, 2 mmol) were dissolved in an acetonitrile/water solution (15 cm^3) containing 4-methylbenzoic acid (0.27 g, 2 mmol) and NaOH (0.08 g, 2 mmol). The solution was refluxed for 3 h. After cooling to room temperature, the solution was filtered. Colorless, single crystals of the title complex were obtained from the filtrate after 1 week. Elemental analyses were performed on a Carlo-Erba 1160 instrument. Anal. Calc. for $C_{22}H_{24}MnN_4O_5$(%): C, 55.07; N, 11.68; H, 5.05; Found: C, 55.11; N, 11.32; H, 5.52. IR spectra were measured (KBr pellets) in the 4000–400 cm^{-1} range using a Nicolet 5DX FT-IR spectrophotometer.

2.2. *Crystal structure determination*

X-ray diffraction intensities of a single crystal (approximate dimensions $0.37 \times 0.35 \times 0.30$ mm) of the complex were collected on a Rigaku RAXIS-RAPID diffractometer at room temperature with Mo Kα radiation up to $2\theta = 50.2°$. A total of 13 281 reflections were collected, of which 3923 were independent ($R_{int} = 0.019$) and 3448 observed with $I > 2\sigma(I)$. The usual Lp and empirical absorption corrections [5] were applied. The crystal structure was solved by direct methods followed by Fourier syntheses. Structure refinement was performed by full-matrix least-squares procedures on F^2 using SHELX-97 [6]. H atoms on the water molecule were located in a difference Fourier map and refined with fixed isotropic displacement parameters of 0.05 Å^2. Methyl group protons were refined from electron densities with $U_{iso}(H) = 1.5U_{eq}$ of carbon atoms. H atoms on aromatic rings were placed in calculated positions with C–H = 0.93 Å and N–H = 0.86 Å, and were included in the final cycles of refinement in a riding model, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms; final $R = 0.033$ and $wR = 0.040$ for observed reflections, $R = 0.080$ and $wR = 0.088$ for independent reflections, with $w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 1.5877P]$, where $P = (F_o^2 + 2F_c^2)/3$.

2.2.1. Crystal data. $C_{19}H_{20}N_4O_5Mn$, $M = 479.39$, monoclinic, space group $P2_1/n$, $a = 14.1696(13)$, $b = 5.9807(8)$, $c = 26.5375(15)$ Å, $\beta = 93.217(3)°$, $V = 2245.4(4)$ Å^3, $Z = 4$, $F(000) = 996$, $D_c = 1.418$ g cm^{-3}, μ(Mo Kα) = 0.629 mm^{-1}, $S = 1.123$, $(\Delta\rho)_{max} = 0.25$, $(\Delta\rho)_{min} = -0.31$ e Å^{-3}.

3. Results and discussion

3.1. *Crystal structure*

Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in table 1 and selected bond distances and angles are listed in table 2. Full lists of crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 248305.

The molecular structure of the complex is illustrated in figure 1. Mn(II) assumes a distorted octahedral coordination geometry. Two imidazole molecules coordinate *trans* to Mn with normal Mn–N bond distances. Two methylbenzoate anions bind to Mn with different coordination modes, one as a monodentate and the other

Table 1. Final coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms of the complex.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Mn	0.38343(2)	0.21042(5)	0.63575(1)	0.0320(1)
O1	0.4707(1)	0.1916(2)	0.71201(6)	0.0406(5)
O2	0.4644(1)	0.5052(2)	0.66912(6)	0.0400(5)
O3	0.3061(1)	0.3030(3)	0.57013(7)	0.0587(7)
O4	0.3046(1)	0.6615(3)	0.54887(6)	0.0566(6)
O5	0.3458(1)	−0.1425(3)	0.63880(7)	0.0405(5)
N1	0.5044(1)	0.1141(3)	0.58992(7)	0.0402(6)
N2	0.6034(2)	0.1282(4)	0.52965(8)	0.0571(8)
N3	0.2547(1)	0.2937(3)	0.67822(7)	0.0403(6)
N4	0.1447(2)	0.4484(4)	0.72055(8)	0.0521(7)
C1	0.5382(2)	0.2370(5)	0.55424(9)	0.0497(8)
C2	0.6120(2)	−0.0780(5)	0.5505(1)	0.058(1)
C3	0.5507(2)	−0.0865(4)	0.58722(9)	0.0495(8)
C4	0.2354(2)	0.4514(4)	0.71015(9)	0.0486(8)
C5	0.1027(2)	0.2808(5)	0.6938(1)	0.0573(9)
C6	0.1716(2)	0.1860(5)	0.6682(1)	0.0550(9)
C11	0.4967(1)	0.3907(4)	0.70655(8)	0.0328(7)
C12	0.5667(2)	0.4937(4)	0.74349(8)	0.0343(6)
C13	0.5946(2)	0.3815(4)	0.78741(9)	0.0419(8)
C14	0.6575(2)	0.4791(5)	0.82231(9)	0.0499(8)
C15	0.6960(2)	0.6890(4)	0.81417(9)	0.0458(8)
C16	0.6681(2)	0.7983(4)	0.76979(9)	0.0433(8)
C17	0.6039(2)	0.7041(4)	0.73512(8)	0.0380(7)
C18	0.7672(2)	0.7938(6)	0.8514(1)	0.071(1)
C21	0.2744(2)	0.4650(4)	0.54470(8)	0.0389(7)
C22	0.1952(2)	0.4165(4)	0.50670(8)	0.0354(7)
C23	0.1579(2)	0.5808(4)	0.47516(9)	0.0504(8)
C24	0.0826(2)	0.5349(5)	0.4414(1)	0.0581(9)
C25	0.0425(2)	0.3262(5)	0.43746(9)	0.0498(8)
C26	0.0824(2)	0.1617(5)	0.4683(1)	0.0565(9)
C27	0.1562(2)	0.2044(4)	0.5025(1)	0.0492(8)
C28	−0.0418(2)	0.2760(6)	0.4022(1)	0.074(1)

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Mn–O1	2.314(2)	Mn–O2	2.257(1)
Mn–O3	2.080(2)	Mn–O5	2.180(2)
Mn–N1	2.232(2)	Mn–N3	2.253(2)
O1–C11	1.257(3)	O2–C11	1.270(3)
O3–C21	1.250(3)	O4–C21	1.254(3)
N1–C1	1.311(3)	N1–C3	1.372(3)
N2–C2	1.354(4)	N2–C1	1.330(3)
N3–C6	1.356(3)	N3–C4	1.307(3)
N4–C5	1.347(4)	N4–C4	1.329(3)
C2–C3	1.343(4)	C5–C6	1.345(4)
C11–C12	1.489(3)	C15–C18	1.508(4)
C21–C22	1.494(3)	C25–C28	1.507(4)
O1–Mn–O2	57.33(5)	O1–Mn–O3	167.32(6)
O1–Mn–O5	92.31(6)	O1–Mn–N1	94.31(6)
O1–Mn–N3	88.91(6)	O2–Mn–O3	110.66(6)
O2–Mn–O5	149.53(6)	O2–Mn–N1	91.53(6)
O2–Mn–N3	92.22(6)	O3–Mn–O5	99.81(7)
O3–Mn–N1	89.83(7)	O3–Mn–N3	87.52(7)
O5–Mn–N1	88.12(7)	O5–Mn–N3	89.36(7)
N1–Mn–N3	175.99(7)	Mn–O1–C11	89.92(12)
Mn–O2–C11	92.21(12)	Mn–O3–C21	144.60(16)

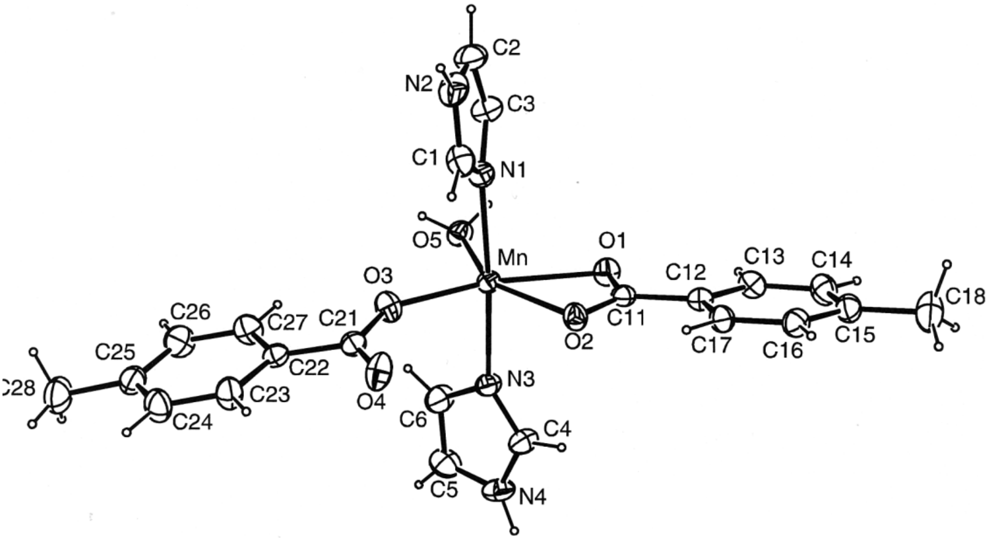

Figure 1. The molecular structure of the title compound drawn with 30% probability displacement ellipsoids, showing the atom numbering scheme.

Table 3. A comparison of Mn–O–C bond angles (°) and Mn–O bond distances (Å) in some Mn(II) complexes incorporating monodentate carboxylate ligands.

Carboxylate	Mn–O–C	Mn–O	Ref.
Pyromelitate	123.0(1)	2.241(1)	[7]
Succinate	123.5(2)	2.179(2)	[8]
Succinate	130.5(2)	2.163(2)	[9]
Pyromelitate	125.4(1)	2.146(1)	[10]
Adipate	131.1(2)	2.140(2)	[11]
Methylbenzoate	144.6(2)	2.080(2)	This work

as a chelate. As expected, Mn–O1 [2.314(2) Å] and Mn–O2 [2.257(1) Å] bonds in the chelating mode are much longer than the monodentate Mn–O3 bond [2.080(2) Å]. A water molecule also coordinates to Mn with an Mn–O distance of 2.180(2) Å.

Several Mn(II) complexes have been reported in which a carboxylate group acts as a monodentate. A comparison of Mn–O bond distances and corresponding bond angles in these complexes is presented in table 3. The Mn–O3 bond distance of 2.080(2) Å in the title complex is appreciably shorter than that found for other species, ranging from 2.140(2) to 2.241(1) Å [7–11]. In addition, the Mn–O3–C21 bond angle of 144.58(18)° in the title complex is the largest of those listed and suggests poor overlap of atomic orbitals of Mn and O3. This strongly suggests a more electrostatic interaction for the Mn–O3 bond. Moreover, the small O2–Mn–O5 bond angle of 149.53(6)° indicates poor overlap of atomic orbitals of Mn and O2, whereas the O1–Mn–O3 bond angle of 167.32(6)° suggests good overlap for Mn and O1. However, the Mn–O2 bond is significantly shorter than the Mn–O1 bond in the same carboxyl group. This is also clearly related to the more electrostatic nature of the Mn–O2 bond.

Parallel imidazole rings of neighboring Mn(II) complex molecules overlap each other as shown in figure 2(a). The interplanar distance of 3.470(13) Å indicates the existence

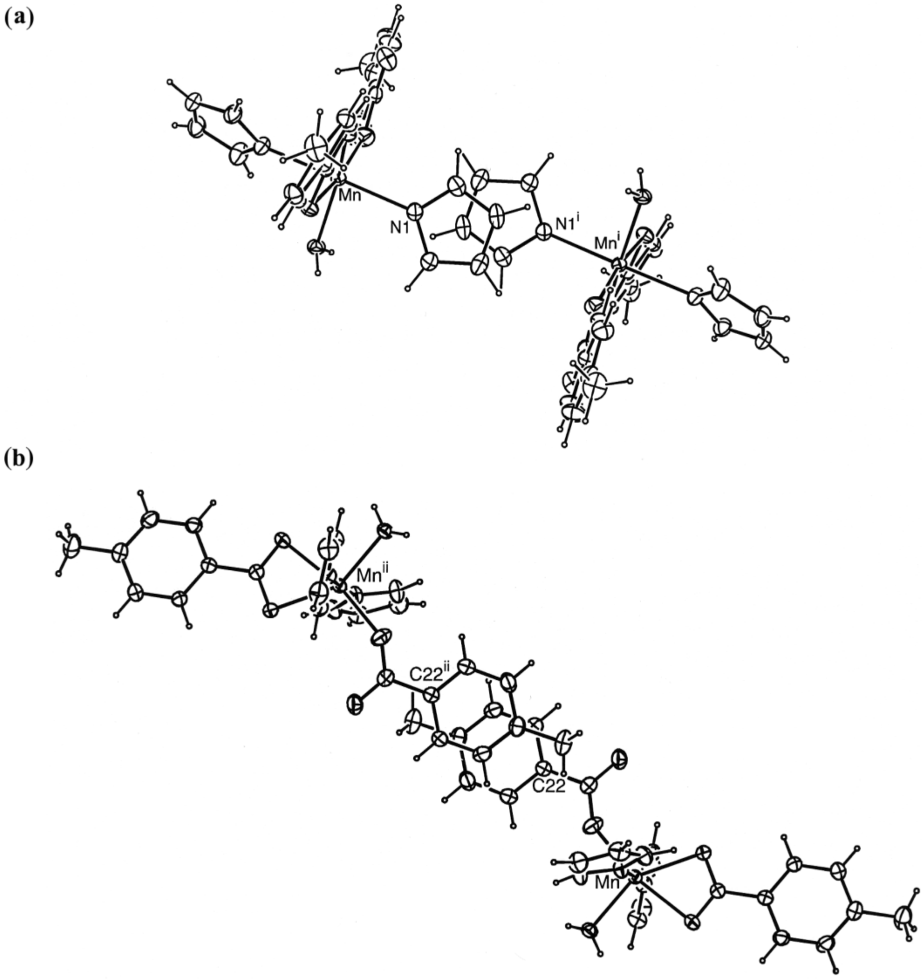

Figure 2. (a) Intermolecular π–π stacking between the imidazole rings; symmetry code (iv): $1-x$, $-y$, $1-z$. (b) van der Waals contacts between benzene rings; symmetry code (v): $-x$, $1-y$, $1-z$.

Table 4. Hydrogen-bond parameters (Å,°) for the complex.

Donor	H	Acceptor	D–H	H···A	D···A	D–H–A
N2	H2	$O4^{i}$	0.86	1.96	2.816(3)	171
N4	H4	$O1^{ii}$	0.86	2.04	2.885(3)	166
O5	H5A	$O2^{iii}$	0.84(3)	1.99(3)	2.785(2)	159(3)
O5	H5B	$O4^{iii}$	0.81(3)	1.88(3)	2.693(2)	177(3)

Symmetry codes used are: (i) $1-x$, $1-y$, $1-z$; (ii) $1/2-x$, $1/2+y$, $3/2-z$; (iii) x, $-1+y$, z.

of π–π stacking interactions. Although partial overlap is also observed for the parallel benzene rings of the methylbenzoate ligands of adjacent molecules (figure 2(b)), the interplanar distance of 3.761(13) Å is characteristic of a normal van der Waals contact. An intermolecular hydrogen-bonding network is evident in the crystal (table 4).

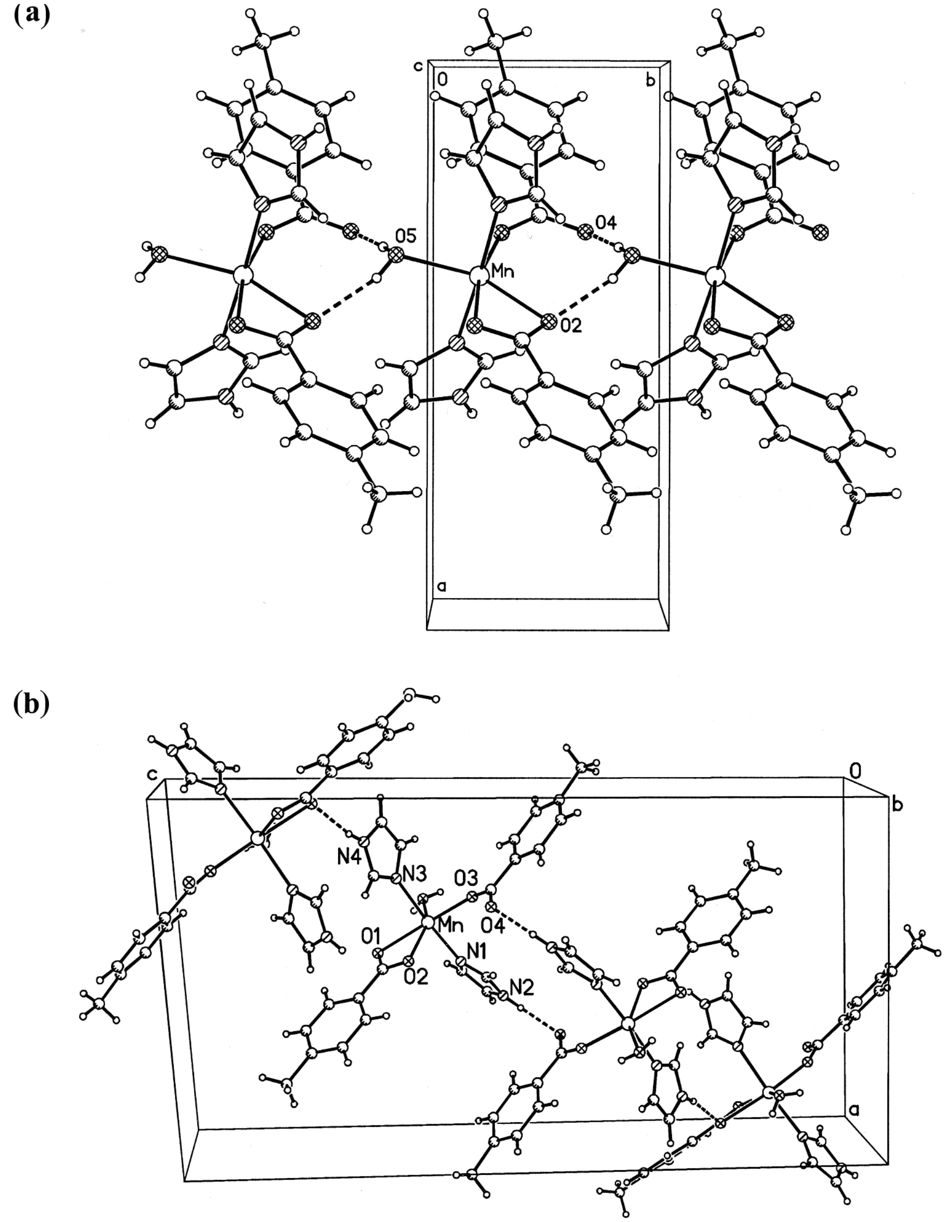

Figure 3. (a) Packing in the unit cell. Dashed lines indicate intermolecular O–H···O hydrogen bonding. (b) Unit cell packing diagram with dashed lines indicating intermolecular N–H···O hydrogen bonding.

While coordinated water molecules link adjacent Mn(II) complex molecules via O–H···O hydrogen bonds, as shown in figure 3(a), imidazole molecules link with neighboring complexes via N–H···O hydrogen bonds (figure 3(b)) to form a three-dimensional supramolecular structure.

3.2. *IR spectra*

In the IR spectrum of the complex, four strong peaks are assigned to stretching vibrations of carboxyl groups. Peaks at 1594 and 1403 cm^{-1} are assigned to $\nu_{\mathrm{as}}(\mathrm{coo})$ and $\nu_{\mathrm{s}}(\mathrm{coo})$, respectively, of the monodentate carboxyl group, and peaks at 1540 and 1515 cm^{-1} are assigned to $\nu_{\mathrm{as}}(\mathrm{coo})$ and $\nu_{\mathrm{s}}(\mathrm{coo})$, respectively, of the chelating carboxyl group. The $\Delta\nu$ values of 191 and 25 cm^{-1} are in agreement with other values found for monodentate and chelating carboxyl groups, respectively [12]. The stretching vibration of coordinated water appears at 3414 cm^{-1}. The lower frequency corresponds to its contribution to the hydrogen-bonding network in the crystal.

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