Crystal structure of diaqua-*bis*(5-nitrobenzene-3-carboxy-1,2-dicarboxylato)-*bis*(1-(3-(1*H*-benzimidazol-1-yl)propyl)-benzimidazole)manganese(II), $[Mn(H_2O)_2(O_2NC_9H_3O_6)_2(C_{17}H_{17}N_4)_2]$, $C_{52}H_{44}MnN_{10}O_{18}$

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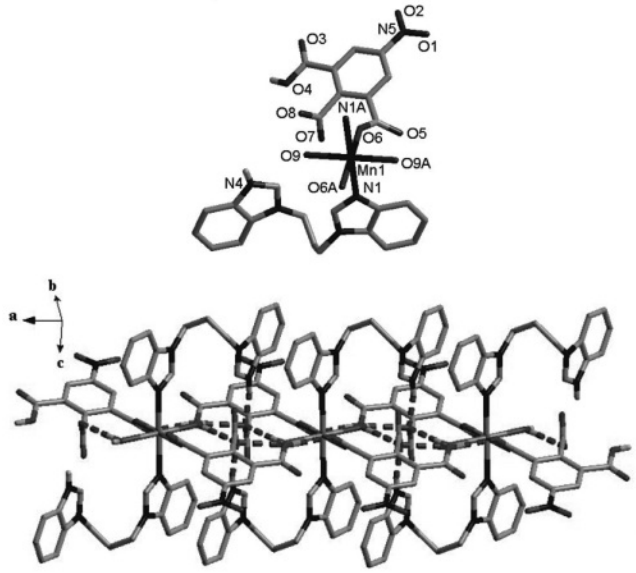

Abstract

$C_{52}H_{44}MnN_{10}O_{18}$, monoclinic, $P2_1/c$ (no. 14), a = 8.6941(8) Å, b = 12.970(1) Å, c = 21.384(2) Å, β = 95.145(1)°, V = 2401.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.0376, $wR_{ref}(F^2)$ = 0.0900, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.38×0.42×0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.69 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17528, 4463
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3873
$N(param)_{refined}$:	368
Programs:	SHELX [11]

Source of material

A mixture of H_3nbtc (5-nitro-1,2,3-benzenecarboxylic acid, 0.1 mmol, 23.1 mg), bbp (0.1 mmol, 27.6 mg), $Mn(OAc)_2{\cdot}4H_2O$ (0.1 mmol, 24.2 mg), KOH (0.1 mmol, 5.6 mg) and H_2O 12 mL was placed in a Teflon-lined stainless steel vessel, heated to 413 K for 3 days, and then cooled to room temperature within 24 h. Colourless block-shaped crystals of the title complex were obtained.

Discussion

Recently, the design and construction of metal-organic frameworks (MOFs) of paramagnetic metal ions became interesting in the field of molecular magnetism and materials chemistry due to their fascinating structural diversities and potential application as functional materials [1-6]. Organic bridging ligands, such as aromatic multicarboxylate ligands, which not only bind several metal centers of specific coordination geometry but also can transmit the magnetic interactions, are widely employed to construct such extended architectures. Among organic bridging ligands, 5-nitro-1,2,3-benzenecarboxylic acid (H_3nbtc) possesses several interesting characteristics: (a) it has three carboxyl groups which may be completely or partially deprotonated, inducing various coordination modes and allowing interesting structures with higher dimensions; (b) it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the numbers of deprotonated carboxyl groups [7-10]. There are one Mn(II) ions, two Hnbtc, two Hbbp, and two coordinated water molecules in the asymmetric unit of the title complex (Figure top). Mn1 is six-coordinated with a distorted octahedral geometry by two O atoms from two Hnbtc, two N atoms from two Hbbp molecules and two water molecules. The apical positions are occupied by two N atoms from two Hbbp ligands with the N1–Mn1–N1$^{\#1}$ angle of 180.00(12) °. The bond lengths of Mn1–N1/Mn1–N1$^{\#1}$ (Symmetry code: $^{\#1}$: -x, -y, -z) are all 2.2858(17) Å and the ones of Mn–O are 2.1392(14) Å (Mn1–O6/Mn1–O6$^{\#1}$) and 2.2314(14) Å (Mn1–O9/Mn1–O9$^{\#1}$). The title complex units are further connected by hydrogen bonding, N(4)–H(4D)···O(8)$^{\#2}$ (Symmetry code: $^{\#2}$: -x+1, -y, -z, d(N···O) = 2.622(2) Å, the N–H···O angle of 162.6 °) and O(4)–H(4)···O(5)$^{\#3}$ (Symmetry code: $^{\#3}$: x+1, y, z, d(O···O) = 2.507(2) Å, the O–H···O angle of 177.9 °), to form an one-dimensional supramolecular chain. In addition, there are hydrogen bonds interactions between the coordinated water molecule and the uncoordinated carboxylate oxygen atoms O(9)–H(1W)···O(8) (d(O···O) = 2.734(2)Å, the O–H···O angle of 176.6 °), O(9)–H(2W)···O(8)$^{\#2}$ (Symmetry code: $^{\#2}$: -x+1, -y, -z, d(O···O) = 2.944(2) Å, the O–H···O angle of 132.6 °) and O(9)–H(2W)···O(4)$^{\#2}$ (d(O···O) = 3.101(2) Å, the O–H···O angle of 149.3 °) (Figure bottom). These hydrogen bonding interactions bring further stability of the title complex.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(4D)	4*e*	0.5855	–0.1625	0.0518	0.040
H(4)	4*e*	0.7924	0.2382	0.0872	0.056
H(1W)	4*e*	0.3104	–0.0012	0.0107	0.049
H(2W)	4*e*	0.2975	–0.0952	–0.0147	0.049

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Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(2A)	4*e*	0.1628	–0.1712	0.0914	0.042
H(4A)	4*e*	–0.0290	–0.1389	0.2950	0.045
H(5)	4*e*	–0.2311	–0.0257	0.3068	0.049
H(6)	4*e*	–0.3386	0.0703	0.2236	0.047
H(7)	4*e*	–0.2416	0.0633	0.1261	0.042
H(8A)	4*e*	0.2470	–0.2804	0.1853	0.047
H(8B)	4*e*	0.1261	–0.2863	0.2353	0.047
H(9A)	4*e*	0.2528	–0.1552	0.2937	0.049
H(9B)	4*e*	0.3680	–0.2457	0.2848	0.049

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(10A)	4*e*	0.3638	–0.0548	0.2218	0.048
H(10B)	4*e*	0.4963	–0.0946	0.2703	0.048
H(11)	4*e*	0.4273	–0.0656	0.1133	0.040
H(13)	4*e*	0.7944	–0.3279	0.0730	0.052
H(14)	4*e*	0.8969	–0.4316	0.1544	0.060
H(15)	4*e*	0.8230	–0.4140	0.2542	0.056
H(16)	4*e*	0.6382	–0.2942	0.2774	0.046
H(20)	4*e*	0.0631	0.4179	0.0668	0.031
H(22)	4*e*	0.5053	0.5076	0.0683	0.033

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	2*a*	0	0	0	0.0260(2)	0.0212(2)	0.0236(2)	–0.0013(2)	0.0005(2)	–0.0015(2)
N(1)	4*e*	–0.0014(2)	–0.0664(1)	0.09897(8)	0.039(1)	0.030(1)	0.0264(9)	0.0008(8)	0.0030(8)	0.0026(7)
N(2)	4*e*	0.0967(2)	–0.1640(1)	0.17910(8)	0.036(1)	0.034(1)	0.032(1)	0.0038(8)	0.0017(8)	0.0071(8)
N(3)	4*e*	0.5019(2)	–0.1582(1)	0.18503(8)	0.037(1)	0.030(1)	0.029(1)	0.0040(8)	0.0044(8)	0.0017(8)
N(4)	4*e*	0.5777(2)	–0.1731(1)	0.09107(8)	0.040(1)	0.036(1)	0.0245(9)	–0.0016(8)	0.0022(8)	0.0036(8)
N(5)	4*e*	0.2291(2)	0.5857(1)	0.06554(9)	0.039(1)	0.024(1)	0.041(1)	0.0058(9)	0.0090(8)	–0.0015(8)
O(1)	4*e*	0.0916(2)	0.6046(1)	0.0589(1)	0.040(1)	0.0325(9)	0.094(2)	0.0114(8)	0.017(1)	0.0023(9)
O(2)	4*e*	0.3294(2)	0.6521(1)	0.07218(9)	0.052(1)	0.0217(8)	0.082(1)	–0.0065(8)	0.0037(9)	–0.0070(8)
O(3)	4*e*	0.7408(2)	0.4088(1)	0.07195(9)	0.0300(9)	0.0321(9)	0.077(1)	–0.0069(7)	0.0084(8)	0.0017(8)
O(4)	4*e*	0.6983(2)	0.2403(1)	0.07961(8)	0.0207(7)	0.0285(8)	0.063(1)	0.0002(6)	0.0026(7)	–0.0010(7)
O(5)	4*e*	–0.0148(2)	0.2343(1)	0.10566(8)	0.0238(8)	0.0429(9)	0.051(1)	–0.0040(7)	0.0084(7)	–0.0068(8)
O(6)	4*e*	0.0969(2)	0.1438(1)	0.03298(7)	0.0366(9)	0.0282(8)	0.048(1)	–0.0076(7)	0.0023(7)	–0.0126(7)
O(7)	4*e*	0.4126(2)	0.1190(1)	0.12861(7)	0.056(1)	0.0320(8)	0.0265(8)	0.0089(7)	0.0093(7)	0.0052(7)
O(8)	4*e*	0.4431(2)	0.1127(1)	0.02637(6)	0.0318(8)	0.0263(7)	0.0267(8)	0.0027(6)	0.0067(6)	–0.0054(6)
O(9)	4*e*	0.2462(2)	–0.0500(1)	0.00327(7)	0.0299(8)	0.0298(8)	0.0394(9)	0.0016(6)	0.0039(6)	–0.0067(7)
C(1)	4*e*	–0.0772(2)	–0.0428(2)	0.1518(1)	0.034(1)	0.026(1)	0.028(1)	–0.0057(9)	0.0014(9)	0.0001(9)
C(2)	4*e*	0.0980(3)	–0.1396(2)	0.1179(1)	0.039(1)	0.035(1)	0.031(1)	0.001(1)	0.006(1)	0.001(1)
C(3)	4*e*	–0.0169(2)	–0.1033(2)	0.2029(1)	0.031(1)	0.029(1)	0.029(1)	–0.0033(9)	0.0016(9)	0.0007(9)
C(4)	4*e*	–0.0713(3)	–0.0989(2)	0.2617(1)	0.041(1)	0.043(1)	0.028(1)	–0.005(1)	0.000(1)	0.003(1)
C(5)	4*e*	–0.1916(3)	–0.0318(2)	0.2680(1)	0.044(1)	0.049(1)	0.030(1)	–0.007(1)	0.009(1)	–0.006(1)
C(6)	4*e*	–0.2557(3)	0.0271(2)	0.2177(1)	0.042(1)	0.034(1)	0.043(1)	–0.001(1)	0.007(1)	–0.006(1)
C(7)	4*e*	–0.1990(3)	0.0231(2)	0.1593(1)	0.040(1)	0.028(1)	0.036(1)	–0.001(1)	–0.001(1)	0.0020(9)
C(8)	4*e*	0.1921(3)	–0.2399(2)	0.2143(1)	0.039(1)	0.034(1)	0.046(1)	0.005(1)	0.001(1)	0.010(1)
C(9)	4*e*	0.3088(3)	–0.1911(2)	0.2630(1)	0.041(1)	0.050(2)	0.032(1)	0.009(1)	0.003(1)	0.005(1)
C(10)	4*e*	0.4205(3)	–0.1158(2)	0.2367(1)	0.045(1)	0.041(1)	0.035(1)	0.004(1)	0.008(1)	–0.006(1)
C(11)	4*e*	0.4896(3)	–0.1210(2)	0.1268(1)	0.036(1)	0.031(1)	0.033(1)	0.001(1)	–0.0014(9)	0.0044(9)
C(12)	4*e*	0.6558(2)	–0.2481(2)	0.1276(1)	0.031(1)	0.030(1)	0.033(1)	–0.0047(9)	0.0008(9)	0.0013(9)
C(13)	4*e*	0.7639(3)	–0.3208(2)	0.1134(1)	0.041(1)	0.045(1)	0.044(1)	0.004(1)	0.009(1)	–0.004(1)
C(14)	4*e*	0.8238(3)	–0.3819(2)	0.1621(1)	0.045(2)	0.043(2)	0.062(2)	0.013(1)	0.009(1)	0.004(1)
C(15)	4*e*	0.7783(3)	–0.3715(2)	0.2226(1)	0.041(1)	0.041(1)	0.058(2)	0.006(1)	–0.002(1)	0.019(1)
C(16)	4*e*	0.6691(3)	–0.3006(2)	0.2371(1)	0.041(1)	0.040(1)	0.034(1)	–0.002(1)	0.003(1)	0.010(1)
C(17)	4*e*	0.6081(2)	–0.2390(2)	0.1879(1)	0.030(1)	0.028(1)	0.032(1)	–0.0018(9)	0.0014(9)	0.0026(9)
C(18)	4*e*	0.0880(2)	0.2175(2)	0.06988(9)	0.023(1)	0.024(1)	0.032(1)	0.0010(8)	–0.0019(8)	0.0010(9)
C(19)	4*e*	0.2139(2)	0.2987(2)	0.06979(9)	0.023(1)	0.023(1)	0.023(1)	–0.0006(8)	0.0014(8)	–0.0039(8)
C(20)	4*e*	0.1671(2)	0.4009(2)	0.06741(9)	0.022(1)	0.027(1)	0.028(1)	0.0041(8)	0.0022(8)	–0.0040(8)
C(21)	4*e*	0.2778(2)	0.4767(2)	0.06601(9)	0.034(1)	0.019(1)	0.027(1)	0.0016(8)	0.0055(9)	–0.0017(8)
C(22)	4*e*	0.4331(2)	0.4547(2)	0.06820(9)	0.029(1)	0.024(1)	0.031(1)	–0.0040(9)	0.0060(9)	–0.0009(9)
C(23)	4*e*	0.4808(2)	0.3521(2)	0.07029(9)	0.025(1)	0.025(1)	0.024(1)	–0.0003(8)	0.0040(8)	0.0002(8)
C(24)	4*e*	0.3718(2)	0.2726(1)	0.07099(8)	0.024(1)	0.023(1)	0.0182(9)	0.0013(8)	0.0033(7)	–0.0021(8)
C(25)	4*e*	0.6533(2)	0.3368(2)	0.0738(1)	0.026(1)	0.029(1)	0.031(1)	–0.0019(9)	0.0045(9)	–0.0018(9)
C(26)	4*e*	0.4141(2)	0.1586(2)	0.07660(9)	0.020(1)	0.024(1)	0.026(1)	0.0002(8)	0.0032(8)	–0.0017(8)

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