Crystal structure of diaquabis(benzoato-κ*O*)(1,10-phenanthroline-κ^2*N*,*N*′)- manganese(II) 1.5 hydrate, $C_{26}H_{25}MnN_2O_{7.5}$

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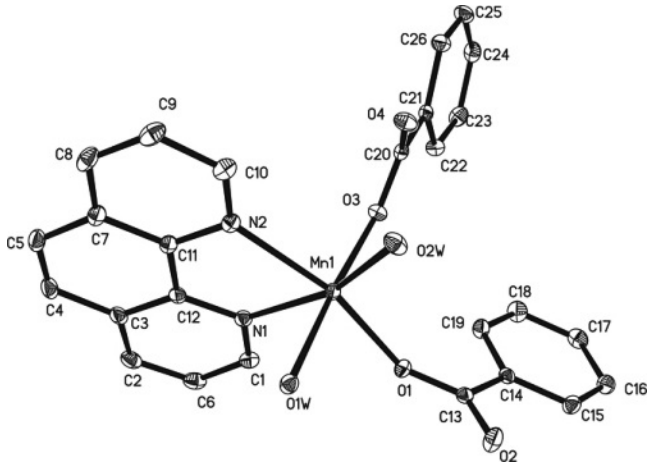

Abstract

$C_{26}H_{25}MnN_2O_{7.5}$, tetragonal, $I4_1/a$ (no. 88), a = 29.373(3) Å, c = 11.469(2) Å, V = 9894.7 Å^3, Z = 16, $R_{gt}(F)$ = 0.0330, $wR_{ref}(F^2)$ = 0.0791, T = 293 K.

Table 1. Data collection and handling.

Crystal:	yellow prisms, size 0.12×0.15×0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.85 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	38290, 5643
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5524
$N(param)_{refined}$:	330
Programs:	SHELX [11]

Source of material

The mixture of $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.12 g, 0.5 mmol) and (benzoic acid, 0.12 g, 0.1 mmol) in 10 mL aqueous solution was stirred for about 10 minutes to give a red solution at 70 °C. The pH value of the reaction mixture was adjusted to about 6 by the slow addition of a NaOH solution (1 mol/L). After 3 hours stirring at 70 °C, 5 mL of a methanol solution of 1,10-phenanthroline (0.5 mmol, 0.09 g) was added and the solution was stirred and heated for 4 h at 70 °C, followed by filtration. The pale yellow crystals were separated from the mother liquor by slow evaporation at room temperature after one week.

Experimental details

H atoms bonded to N and O atoms were located in a difference electron density map and refined with distance restraints of O–H = 0.84(2) and N–H = 0.87(2) Å, and with U_{iso}(H) = 1.2U_{eq}(N, O). Other H atoms were positioned geometrically and refined using a riding model, with C–H = 0.95-0.99 Å and with U_{iso}(H) = 1.2 times U_{eq}(C).

Discussion

The study of coordination polymers has gained great recognition as an important interface between synthetic chemistry and materials science and provides a solid foundation for understanding how molecules can be organized and how functions can be achieved. In the recent years, the supramolecular chemistry of transition metal-organic polymers based on coordination bonds and/or weaker intermolecular forces (such as hydrogen bonding and π–π stacking interaction) has been widely investigated due to their variety of intriguing architectures and topologies [1-4] and their potential applications in magnetism, electric conductivity, molecular adsorption, heterogeneous catalysis, and fluorescent materials [5-9]. A great research effort was made to obtain designed and predictable frameworks and properties by using an versatile organic ligand and functional metal ions in *situ* solvothermal synthesis. Aromatic carboxlic acids attract our interest because of their importance in crystal engineering, especially as they tend to form strong and directional hydrogen bonds [10]. In this paper, we report the synthesis and the crystal structure of a new manganese(II) complex with 1,10-phenanthroline and benzoic acid. The structure of the title complex $Mn(phen)(Bz)_2(H_2O)_2{\cdot}1.5H_2O$ crystallizes in the tetragonal system space group $I4_1/a$ with an asymmetric unit of one Mn(II) ion, two Bz^- ligands, one *phen* ligand, two coordinated water molecules, and 1.5 lattice water molecules. The Mn^{2+} ion in the title structure is six-coordinated by two O atoms (O1W, O2W) from two distinct coordinated water molecules, two O atoms (O1, O3) from two distinct Bz^- units, and two N atoms (N1, N2) from *phen* (Mn1–O, 2.1192(10)-2.1998(10) Å, Mn1–N, 2.2733(12)-2.2923(12) Å), giving rise to a distorted octahedral geometry with L–Mn–L (L = O, N) bond angles ranging from 72.88(4)° to 176.51(4)°. The adjacent neutral mononuclear motifs are bound together by intermolecular hydrogen bonds through carboxylic oxygen atoms, coordinated water molecules and uncoordinated water molecules to create 1D chain architecture. Furthermore, the extended 3D supramolecular network is formed through π–π stacking interactions.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	16*f*	0.7594	0.7129	0.1592	0.027
H(2A)	16*f*	0.6663	0.7961	0.0206	0.033
H(4A)	16*f*	0.6854	0.8357	–0.1704	0.033
H(5A)	16*f*	0.7352	0.8484	–0.3172	0.032
H(6A)	16*f*	0.6877	0.7462	0.1664	0.033
H(8A)	16*f*	0.8125	0.8332	–0.4093	0.033
H(9A)	16*f*	0.8814	0.7956	–0.4019	0.033
H(10A)	16*f*	0.8973	0.7486	–0.2448	0.028
H(15A)	16*f*	0.9090	0.6239	0.4357	0.028
H(16A)	16*f*	0.8931	0.5485	0.4774	0.032
H(17A)	16*f*	0.8406	0.5090	0.3667	0.032
H(18A)	16*f*	0.8032	0.5451	0.2145	0.034
H(19A)	16*f*	0.8189	0.6206	0.1728	0.027
H(22A)	16*f*	0.8082	0.5782	–0.0129	0.027
H(23A)	16*f*	0.7865	0.5036	–0.0440	0.032
H(24A)	16*f*	0.8133	0.4644	–0.2054	0.031
H(25A)	16*f*	0.8619	0.5002	–0.3350	0.031
H(26A)	16*f*	0.8858	0.5741	–0.3007	0.026
H(1WA)	16*f*	0.8897	0.7888	0.1398	0.024
H(1WB)	16*f*	0.8782	0.8090	0.0346	0.024
H(2WA)	16*f*	0.9516	0.7202	–0.0104	0.032
H(2WB)	16*f*	0.9289	0.6927	–0.0857	0.032
H(3WA)	16*f*	0.9294	0.7534	0.2796	0.027
H(3WB)	16*f*	0.9406	0.7985	0.3038	0.027
H(4WA)	16*f*	1.0128	0.7696	–0.3864	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)	16*f*	0.854991(7)	0.720830(7)	0.01324(2)	0.0156(1)	0.0149(1)	0.0153(1)	0.00065(7)	–0.00109(7)	0.00087(7)
C(1)	16*f*	0.75088(5)	0.73291(5)	0.1002(1)	0.0226(7)	0.0243(7)	0.0197(7)	–0.0021(6)	0.0001(5)	–0.0031(6)
C(2)	16*f*	0.69479(5)	0.78232(6)	0.0184(1)	0.0198(7)	0.0309(8)	0.0311(8)	0.0059(6)	–0.0028(6)	–0.0121(6)
C(3)	16*f*	0.72477(5)	0.79179(5)	–0.0739(1)	0.0209(7)	0.0192(7)	0.0264(7)	0.0030(5)	–0.0074(6)	–0.0079(6)
C(4)	16*f*	0.71366(5)	0.82145(5)	–0.1690(1)	0.0271(8)	0.0223(7)	0.0334(8)	0.0081(6)	–0.0132(7)	–0.0051(6)
C(5)	16*f*	0.74330(6)	0.82902(5)	–0.2565(1)	0.0351(9)	0.0185(7)	0.0276(8)	0.0018(6)	–0.0148(7)	–0.0001(6)
C(6)	16*f*	0.70744(5)	0.75286(6)	0.1053(1)	0.0225(7)	0.0345(9)	0.0254(8)	–0.0011(6)	0.0037(6)	–0.0092(6)
C(7)	16*f*	0.78720(5)	0.80768(5)	–0.2572(1)	0.0283(8)	0.0149(6)	0.0222(7)	–0.0048(6)	–0.0097(6)	–0.0004(5)
C(8)	16*f*	0.81918(6)	0.81400(5)	–0.3471(1)	0.0383(9)	0.0217(7)	0.0216(7)	–0.0101(6)	–0.0089(6)	0.0062(6)
C(9)	16*f*	0.86008(6)	0.79190(5)	–0.3426(1)	0.0309(8)	0.0311(8)	0.0202(7)	–0.0124(7)	–0.0005(6)	0.0046(6)
C(10)	16*f*	0.86939(5)	0.76361(5)	–0.2471(1)	0.0214(7)	0.0263(8)	0.0212(7)	–0.0065(6)	–0.0009(6)	0.0009(6)
C(11)	16*f*	0.79956(5)	0.77855(5)	–0.1647(1)	0.0207(7)	0.0140(6)	0.0195(6)	–0.0033(5)	–0.0056(5)	–0.0018(5)
C(12)	16*f*	0.76764(5)	0.77021(5)	–0.0713(1)	0.0194(7)	0.0145(6)	0.0198(6)	–0.0010(5)	–0.0049(5)	–0.0043(5)
C(13)	16*f*	0.87718(5)	0.67871(5)	0.2679(1)	0.0198(7)	0.0182(7)	0.0147(6)	0.0028(5)	0.0028(5)	0.0003(5)
C(14)	16*f*	0.86566(5)	0.63003(5)	0.2996(1)	0.0180(6)	0.0169(6)	0.0164(6)	0.0027(5)	0.0032(5)	0.0006(5)
C(15)	16*f*	0.88779(5)	0.60815(5)	0.3912(1)	0.0284(8)	0.0218(7)	0.0191(7)	0.0000(6)	–0.0020(6)	0.0024(5)
C(16)	16*f*	0.87828(6)	0.56295(5)	0.4161(1)	0.0356(9)	0.0224(7)	0.0210(7)	0.0050(6)	0.0009(6)	0.0056(6)
C(17)	16*f*	0.84679(6)	0.53937(5)	0.3500(1)	0.0330(8)	0.0180(7)	0.0302(8)	–0.0015(6)	0.0068(7)	0.0037(6)
C(18)	16*f*	0.82448(6)	0.56095(5)	0.2588(2)	0.0278(8)	0.0228(8)	0.0350(9)	–0.0050(6)	–0.0024(7)	0.0001(6)
C(19)	16*f*	0.83392(5)	0.60621(5)	0.2339(1)	0.0228(7)	0.0214(7)	0.0244(7)	0.0008(6)	–0.0024(6)	0.0022(6)
C(20)	16*f*	0.86570(4)	0.63153(5)	–0.1257(1)	0.0158(6)	0.0192(7)	0.0153(6)	0.0022(5)	–0.0027(5)	0.0010(5)
C(21)	16*f*	0.84968(4)	0.58394(5)	–0.1524(1)	0.0152(6)	0.0182(6)	0.0177(6)	0.0021(5)	–0.0027(5)	–0.0001(5)
C(22)	16*f*	0.81954(5)	0.56242(5)	–0.0769(1)	0.0240(7)	0.0242(7)	0.0204(7)	–0.0009(6)	0.0013(6)	–0.0013(6)
C(23)	16*f*	0.80617(6)	0.51778(5)	–0.0959(1)	0.0298(8)	0.0246(8)	0.0253(7)	–0.0062(6)	–0.0021(6)	0.0056(6)
C(24)	16*f*	0.82223(5)	0.49434(5)	–0.1925(1)	0.0296(8)	0.0172(7)	0.0316(8)	–0.0012(6)	–0.0091(6)	–0.0006(6)
C(25)	16*f*	0.85155(5)	0.51567(5)	–0.2695(1)	0.0277(8)	0.0234(8)	0.0274(8)	0.0028(6)	–0.0021(6)	–0.0088(6)
C(26)	16*f*	0.86562(5)	0.56014(5)	–0.2494(1)	0.0205(7)	0.0234(7)	0.0219(7)	–0.0001(6)	0.0007(5)	–0.0040(6)
O(1)	16*f*	0.85423(4)	0.69683(3)	0.18749(9)	0.0279(5)	0.0198(5)	0.0160(5)	0.0034(4)	–0.0023(4)	0.0026(4)
O(1W)	16*f*	0.86914(3)	0.78880(3)	0.08514(9)	0.0241(5)	0.0166(5)	0.0193(5)	–0.0018(4)	–0.0030(4)	0.0023(4)
O(2)	16*f*	0.90822(4)	0.69818(4)	0.3237(1)	0.0294(6)	0.0220(5)	0.0304(6)	–0.0053(4)	–0.0114(5)	0.0062(4)
O(2W)	16*f*	0.92629(3)	0.71687(4)	–0.0412(1)	0.0161(5)	0.0273(6)	0.0358(6)	0.0011(4)	–0.0011(4)	–0.0098(5)
O(3)	16*f*	0.84389(3)	0.65313(3)	–0.04854(9)	0.0206(5)	0.0181(5)	0.0203(5)	0.0007(4)	0.0029(4)	–0.0033(4)
O(3W)	16*f*	0.93630(4)	0.78043(3)	0.24762(9)	0.0276(6)	0.0184(5)	0.0204(5)	–0.0017(4)	–0.0031(4)	–0.0010(4)
O(4)	16*f*	0.89959(3)	0.64713(4)	–0.17953(9)	0.0204(5)	0.0237(5)	0.0256(5)	–0.0034(4)	0.0060(4)	–0.0050(4)
O(4W)	8*e*	1	$\frac{3}{4}$	–0.3384(1)	0.0383(9)	0.0198(7)	0.0236(7)	0.0002(6)	0	0
N(1)	16*f*	0.78035(4)	0.74129(4)	0.0152(1)	0.0182(6)	0.0173(6)	0.0182(6)	–0.0010(4)	–0.0013(4)	–0.0022(4)
N(2)	16*f*	0.84042(4)	0.75706(4)	–0.1598(1)	0.0189(6)	0.0173(6)	0.0185(6)	–0.0035(4)	–0.0026(4)	0.0002(4)

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