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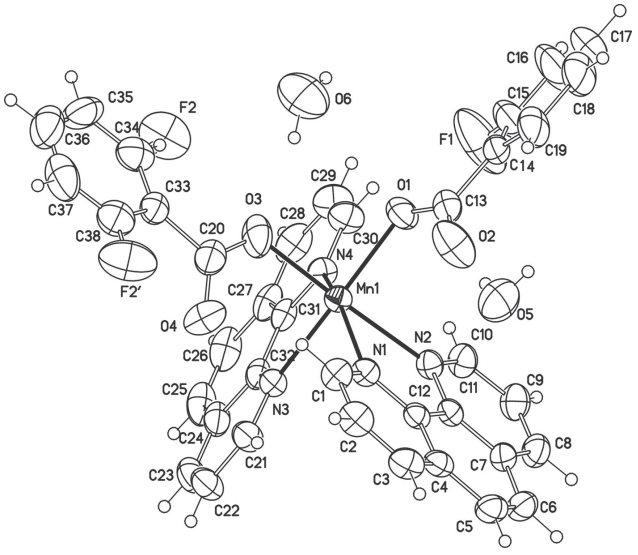
Crystal Structure of bis(2-fluorbenzoato-κ*O*)-bis (1,10-phenanthroline-κ^2*N*,*N*′)manganese(II) dihydrate, $C_{38}H_{28}F_2MnN_4O_6$



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Abstract

$C_{38}H_{28}F_2MnN_4O_6$, monoclinic, $P2_1/c$ (no. 14), $a =$ 11.0710(3) Å, $b = 25.4046(7)$ Å, $c = 11.7681(3)$ Å, $\beta =$ 93.496(1)°, $V = 3303.67(15)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0540$, $wR_{ref}(F^2) = 0.1504$, $T = 293$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

$MnCl_2{\cdot}2H_2O$ (0.24 g,1.48 mmol) was dissolved in water and then 1M Na_2CO_3 solution was added. $MnCO_3$ was obtained by filtration. The product was washed with distilled water five times. The freshly prepared $MnCO_3$, 1,10-phenanthroline monohydrate (phen · H_2O; 0.06 g, 0.30 mmol), 2-fluorbenzoic acid (0.05 g, 0.36 mmol), 15 mL CH_3OH / H_2O (v/v, 1:2) were mixed and stirred for ca. 2.5 h. Subsequently, the resulting suspension was heated in a 25 mL Teflon-lined stainless steel autoclave at 423 K for 7 days. After cooling to room temperature, the solid was filtered off. The resulting yellowish filtrate was allowed to stand at room temperature for 6 month, afforded yellow block crystals. Anal. Calcd. for $C_{38}H_{28}F_2MnN_4O_6$(%), C: 62.56, H: 3.87, N: 7.68; Found: C: 62.36, H: 3.87, N: 7.62.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.22 × 0.22 × 0.12 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.47 mm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24530, 5803, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3971
$N(param)_{refined}$:	470
Programs:	CrysAlis^{PRO} [1], SHELX [2], DIAMOND [3]

Experimental details

One F atom was found to be disordered in the occupancy factor of 0.4 for the F2 and 0.6 for F2′ occupancy were estimated from the refinement with isotropic displacement parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

The crystal structure of the title compound is similar to the structure of related 1,10-phenantroline complexes [4–6].

The asymmetric unit of the title crystal structure consists of a $[Mn(L)_2(phen)_2]$(HL = 2-fluorbenzoic acid, phen = 1,10-phenanthroline) complex and two water molecules (*cf*. the figure). Within the complex, each Mn atom is coordinated by four N atoms from two bidentate chelating phenanthroline

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Mn1	0.73842(4)	0.86967(2)	0.80216(4)	0.04891(19)
N1	0.6920(2)	0.78547(10)	0.7484(2)	0.0523(7)
N2	0.6658(3)	0.87086(10)	0.6102(2)	0.0522(7)
N3	0.5384(3)	0.88302(11)	0.8417(2)	0.0555(7)
N4	0.7011(3)	0.95904(10)	0.8027(2)	0.0554(7)
F1	1.0197(5)	0.96524(13)	0.6380(5)	0.204(2)
F2[a]	0.8908(8)	0.9323(3)	1.1610(9)	0.142(3)
F2′[b]	0.7908(5)	0.7617(2)	1.2162(6)	0.148(2)
O1	0.9128(2)	0.88887(11)	0.7497(2)	0.0782(8)
O2	0.9513(3)	0.81094(13)	0.6835(3)	0.1188(13)
O3	0.8107(3)	0.86900(15)	0.9749(2)	0.1038(11)
O4	0.6854(4)	0.80966(17)	1.0309(3)	0.1287(14)
O5	0.9664(4)	0.70278(15)	0.6254(3)	0.1333(14)
H5A	0.9616	0.7352	0.6425	0.160*
H5B	1.0364	0.7007	0.5997	0.160*
O6	1.0279(4)	0.9432(2)	0.9619(5)	0.190(2)
H6A	1.0492	0.9703	0.9256	0.228*
H6B	0.9600	0.9275	0.9552	0.228*
C1	0.7093(3)	0.74325(13)	0.8132(3)	0.0628(9)
H1	0.7415	0.7478	0.8874	0.075*
C2	0.6821(4)	0.69254(14)	0.7763(4)	0.0712(11)
H2	0.6968	0.6640	0.8247	0.085*
C3	0.6339(4)	0.68514(14)	0.6691(4)	0.0691(10)
H3	0.6146	0.6514	0.6435	0.083*
C4	0.6133(3)	0.72824(13)	0.5969(3)	0.0560(9)
C5	0.5625(3)	0.72351(15)	0.4837(3)	0.0676(10)
H5	0.5394	0.6905	0.4559	0.081*
C6	0.5473(3)	0.76558(16)	0.4162(3)	0.0700(10)
H6	0.5132	0.7614	0.3426	0.084*
C7	0.5827(3)	0.81691(14)	0.4555(3)	0.0567(9)
C8	0.5725(4)	0.86159(16)	0.3862(3)	0.0702(11)
H8	0.5410	0.8590	0.3113	0.084*
C9	0.6092(4)	0.90889(16)	0.4300(3)	0.0728(11)
H9	0.6036	0.9390	0.3850	0.087*
C10	0.6546(4)	0.91202(14)	0.5406(3)	0.0649(10)
H10	0.6790	0.9448	0.5687	0.078*
C11	0.6304(3)	0.82346(12)	0.5672(3)	0.0487(8)
C12	0.6459(3)	0.77808(12)	0.6405(3)	0.0480(8)
C13	0.9761(3)	0.85760(17)	0.6975(3)	0.0638(10)
C14	1.0883(3)	0.87883(19)	0.6479(3)	0.0690(11)
C15	1.1064(5)	0.9301(2)	0.6219(5)	0.1114(19)
C16	1.2086(8)	0.9483(3)	0.5774(7)	0.181(4)
H16	1.2173	0.9841	0.5631	0.217*
C17	1.2962(8)	0.9150(5)	0.5544(8)	0.185(5)
H17	1.3661	0.9274	0.5234	0.222*
C18	1.2839(6)	0.8631(4)	0.5760(6)	0.160(4)
H18	1.3460	0.8400	0.5602	0.192*
C19	1.1796(4)	0.8435(3)	0.6215(4)	0.1105(18)
H19	1.1707	0.8076	0.6340	0.133*
C20	0.7696(4)	0.8430(2)	1.0472(4)	0.0796(10)
C21	0.4588(4)	0.84607(17)	0.8636(3)	0.0718(10)
H21	0.4831	0.8111	0.8608	0.086*
C22	0.3410(4)	0.8568(2)	0.8902(4)	0.0875(13)
H22	0.2877	0.8295	0.9037	0.105*
C23	0.3047(4)	0.9075(2)	0.8964(3)	0.0876(14)
H23	0.2262	0.9152	0.9148	0.105*
C24	0.3853(4)	0.94820(18)	0.8751(3)	0.0706(11)
C25	0.3566(5)	1.0033(2)	0.8835(3)	0.0895(15)
H25	0.2795	1.0131	0.9026	0.107*
C26	0.4377(5)	1.04064(19)	0.8647(3)	0.0849(14)
H26	0.4158	1.0758	0.8707	0.102*
C27	0.5567(4)	1.02779(15)	0.8356(3)	0.0667(10)
C28	0.6460(5)	1.06504(16)	0.8170(3)	0.0839(13)
H28	0.6291	1.1008	0.8228	0.101*
C29	0.7574(5)	1.04896(15)	0.7904(4)	0.0845(13)
H29	0.8168	1.0735	0.7760	0.101*
C30	0.7821(4)	0.99588(14)	0.7847(3)	0.0727(11)
H30	0.8594	0.9855	0.7674	0.087*
C31	0.5890(3)	0.97439(13)	0.8273(3)	0.0542(8)
C32	0.5019(3)	0.93408(15)	0.8477(3)	0.0563(9)
C33	0.8250(3)	0.84887(16)	1.1677(3)	0.0646(9)
C34	0.8746(4)	0.8937(2)	1.2140(5)	0.0881(14)
H34[b]	0.8791	0.9230	1.1670	0.106*
C35	0.9179(5)	0.8986(3)	1.3236(7)	0.137(3)
H35	0.9509	0.9300	1.3515	0.164*
C36	0.9109(7)	0.8553(5)	1.3912(6)	0.158(4)
H36	0.9391	0.8578	1.4671	0.190*
C37	0.8660(6)	0.8101(3)	1.3540(5)	0.127(2)
H37	0.8637	0.7811	1.4022	0.152*
C38	0.8228(4)	0.8066(2)	1.2426(5)	0.0909(13)
H38[a]	0.7908	0.7747	1.2161	0.109*

Occupancies: [a] = 0.4, [b] = 0.6.

ligands and two O atoms from two 2-fluorbenzoato ligands to complete a significantly distorted MnN_4O_2 environment with d(Mn–N) = 2.280(2)–2.350(3) Å, d(Mn–O) = 2.120(2) and 2.144(3) Å. The dihedral angle between the two phen ligands is 83.82(5)°. The interplanar phen-to-phen distances of the π–π stacking interactions between adjacent phen ligands are 3.38(9) Å. Moreover, the solvated water molecules and carboxyl O atoms show hydrogen bonding interactions with d(O—H···O) = 2.74(7)–3.08 Å, <(O—H···O) = 162–180°. Through the π-π stacking and hydrogen bonds complexes and water molecules are interlinked to form the 3D supramolecular network.

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