Crystal structure of [bis[(2-(2-chloro-6-fluorophenyl)-1*H*-imidazo-[4,5-*f*][1,10]phenanthroline-κ^2N,N')]manganese(II) benzene-1,4-dicarboxylato-2,5-dicarboxylic acid], $[Mn(C_{19}H_{10}N_4FCl)_2(C_{10}H_4O_4)]$

Zhi-Guo Kong[*, I, II], Xiao-Yuan Ma[I, II] and Shuai Ma[I, II]

[I] Jilin Normal University, College of Chemistry, Siping 136000, P. R. China
[II] Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Jilin Normal University, Siping 136000, P. R. China

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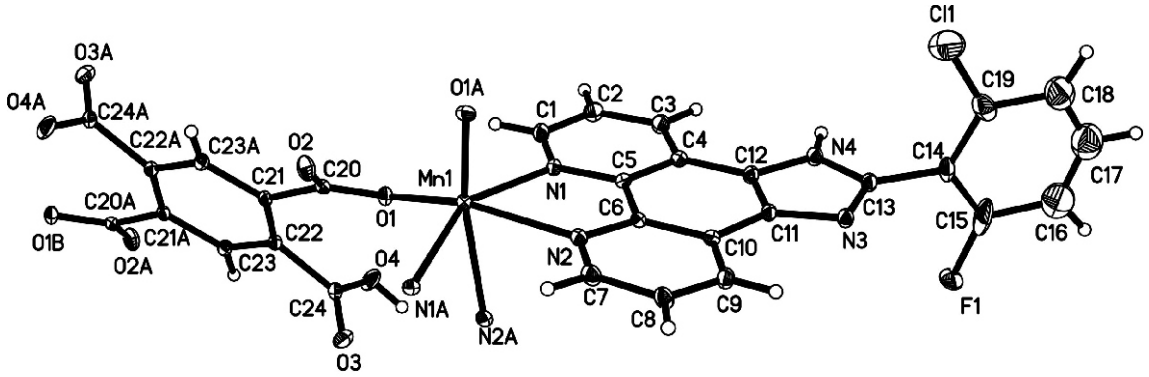

Abstract

$C_{48}H_{24}Cl_2F_2MnN_8O_8$, monoclinic, *C*12/*c*1 (no. 15), a = 18.878(5) Å, b = 13.481(5) Å, c = 19.633(5) Å, β = 121.659(5)°, V = 4253.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.065, $wR_{ref}(F^2)$ = 0.183, T = 293 K.

Source of material

The pH value of a mixture of $MnCl_2 \cdot 4H_2O$ (0.5 mmol), benzene-1,2,4,5-tetracarboxylic acid (H_4btc, 0.5 mmol) and 2-(2-chloro-6-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (L, 0.5 mmol) in 12 mL distilled water was adjusted to between 5 and 6 by addition of triethylamine. The resultant solution was heated at 460 K in a Teflon-lined stainless steel autoclave for five days. The reaction system was then slowly cooled to room temperature. Pale yellow crystals suitable for single crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 46 % based on Mn(II)).

Experimental details

All H atoms were positioned geometrically with d(C—H) = 0.93 Å and refined as riding, with U_{iso}(H) = 1.2 U_{eq}(carrier).

Discussion

2-(2-Chloro-6-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (L) as an important 1,10-phenanthroline derivative possesses aromatic systems and is a good candidate for the construction of metal-organic supramolecular architectures [1]. Here, we selected H_4btc as an organic linker and L as a N-chelating ligand, generating a new Mn(II) coordination polymer.

Each Mn(II) atom shows a distorted octahedral coordination sphere, formed by four nitrogen atoms from different ligands L, and two carboxylate oxygen atoms from different H_2btc dianions. The dianions link two neighboring Mn(II) atoms to a chain structure. The large conjugated ligands L are attached on opposite sides of the chains. The π-π stacking interactions as well as the N–H···O and O–H···N hydrogen bonds further stabilize the crystal structure.

* Correspondence author (e-mail: kongzhiguo1977@yahoo.com.cn)

Table 1. Data collection and handling.

Crystal:	pale yellow block size 0.20 × 0.22 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.14 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	61.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9548, 4945
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2568
$N(param)_{refined}$:	285
Programs:	SHELXS-97, SHELXL-97, SHELXTL [2]

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

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.3202	0.3223	0.1907	0.039
H(2)	8*f*	0.1871	0.2791	0.0967	0.045
H(3)	8*f*	0.1651	0.1514	0.0105	0.043
H(7)	8*f*	0.6207	0.1023	0.2178	0.042
H(8)	8*f*	0.6163	–0.0323	0.1445	0.043
H(9)	8*f*	0.4911	–0.0921	0.0463	0.040
H(16)	8*f*	0.0784	–0.3316	–0.2358	0.132
H(17)	8*f*	0.0596	–0.2677	–0.3469	0.130
H(18)	8*f*	0.1139	–0.1327	–0.3609	0.109
H(23)	8*f*	0.4395	0.4155	0.5617	0.031
H(4A)	8*f*	0.3699	0.2156	0.4320	0.071
H(4)	8*f*	0.1658	0.0110	–0.0837	0.038

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}
C(1)	8*f*	0.3102(2)	0.2697(3)	0.1561(2)	0.035(2)	0.029(2)	0.029(2)	0.004(2)	0.013(2)	–0.006(2)
C(2)	8*f*	0.2319(3)	0.2451(3)	0.1006(3)	0.033(2)	0.035(2)	0.041(2)	0.011(2)	0.017(2)	–0.002(2)
C(3)	8*f*	0.2195(3)	0.1684(3)	0.0494(3)	0.028(2)	0.033(2)	0.036(2)	0.003(2)	0.009(2)	–0.003(2)
C(4)	8*f*	0.2848(1)	0.1145(2)	0.0531(1)	0.027(2)	0.025(2)	0.025(2)	0.001(2)	0.011(2)	–0.000(2)
C(5)	8*f*	0.3619(1)	0.1427(2)	0.1112(1)	0.028(2)	0.020(2)	0.023(2)	0.001(2)	0.011(2)	0.001(2)
C(6)	8*f*	0.4321(1)	0.0899(2)	0.1182(1)	0.023(2)	0.022(2)	0.020(2)	–0.001(2)	0.005(2)	0.000(2)
C(10)	8*f*	0.4250(1)	0.0092(2)	0.0687(1)	0.027(2)	0.024(2)	0.023(2)	0.002(2)	0.008(2)	0.002(2)
C(11)	8*f*	0.3469(1)	–0.0176(2)	0.0089(1)	0.024(2)	0.023(2)	0.024(2)	0.002(2)	0.007(2)	–0.003(2)
C(12)	8*f*	0.2809(1)	0.0338(2)	0.0019(1)	0.025(2)	0.026(2)	0.027(2)	0.000(2)	0.008(2)	–0.004(2)
C(7)	8*f*	0.5685(2)	0.0783(3)	0.1794(2)	0.024(2)	0.041(2)	0.031(2)	0.002(2)	0.007(2)	–0.002(2)
C(8)	8*f*	0.5669(3)	–0.0035(3)	0.1344(2)	0.027(2)	0.043(2)	0.029(2)	0.007(2)	0.009(2)	–0.005(2)
C(9)	8*f*	0.4952(2)	–0.0386(3)	0.0780(2)	0.029(2)	0.030(2)	0.033(2)	0.002(2)	0.011(2)	–0.008(2)
C(13)	8*f*	0.2462(2)	–0.0782(3)	–0.0919(2)	0.027(2)	0.027(2)	0.027(2)	0.004(2)	0.006(2)	–0.006(2)
C(14)	8*f*	0.1944(2)	–0.1346(2)	–0.1649(2)	0.027(2)	0.043(2)	0.036(2)	0.005(2)	0.005(2)	–0.019(2)
C(15)	8*f*	0.1575(2)	–0.2211(3)	–0.1598(2)	0.044(3)	0.066(4)	0.104(5)	–0.018(3)	0.017(3)	–0.055(4)
C(16)	8*f*	0.1046(3)	–0.2725(3)	–0.2342(3)	0.104(3)	0.103(3)	0.116(3)	–0.001(2)	0.053(2)	–0.010(2)
C(17)	8*f*	0.0947(2)	–0.2324(3)	–0.3004(2)	0.103(3)	0.107(3)	0.107(3)	0.009(2)	0.050(2)	–0.015(2)
C(18)	8*f*	0.1252(3)	–0.1534(4)	–0.3110(2)	0.089(3)	0.097(3)	0.084(3)	0.018(2)	0.044(2)	–0.007(2)
C(19)	8*f*	0.1777(2)	–0.1007(2)	–0.2398(2)	0.042(3)	0.079(4)	0.040(3)	0.022(3)	0.007(2)	–0.004(3)
C(20)	8*f*	0.5163(2)	0.4083(3)	0.3679(2)	0.024(2)	0.024(2)	0.020(2)	0.002(2)	0.006(2)	0.002(2)
C(21)	8*f*	0.5089(2)	0.4535(2)	0.4373(2)	0.021(2)	0.023(2)	0.020(2)	–0.000(2)	0.005(2)	–0.003(2)
C(22)	8*f*	0.4724(2)	0.4037(2)	0.4771(2)	0.023(2)	0.021(2)	0.023(2)	–0.001(2)	0.008(2)	–0.002(2)
C(23)	8*f*	0.4638(2)	0.4504(2)	0.5383(2)	0.027(2)	0.024(2)	0.025(2)	–0.007(2)	0.012(2)	–0.001(2)
C(24)	8*f*	0.4530(3)	0.2946(3)	0.4642(2)	0.032(2)	0.026(2)	0.023(2)	–0.005(2)	0.011(2)	–0.005(2)
O(1)	8*f*	0.4655(2)	0.3433(2)	0.3274(2)	0.032(2)	0.028(1)	0.026(1)	–0.008(1)	0.011(1)	–0.006(1)
O(2)	8*f*	0.5719(2)	0.4349(2)	0.3539(2)	0.027(2)	0.053(2)	0.034(2)	–0.011(1)	0.015(1)	–0.012(1)
O(3)	8*f*	0.5052(2)	0.2335(2)	0.4833(2)	0.045(2)	0.026(2)	0.048(2)	–0.002(1)	0.021(2)	0.002(1)
O(4)	8*f*	0.3776(2)	0.2757(2)	0.4381(2)	0.036(2)	0.027(2)	0.069(2)	–0.012(1)	0.021(2)	–0.005(1)
Mn(1)	4*e*	½	0.26099(6)	¼	0.0250(4)	0.0229(4)	0.0193(4)	0	0.0083(3)	0
N(1)	8*f*	0.3732(2)	0.2194(2)	0.1620(2)	0.029(2)	0.023(2)	0.024(2)	0.001(1)	0.010(1)	–0.004(1)
N(2)	8*f*	0.5035(2)	0.1246(2)	0.1730(2)	0.026(2)	0.028(2)	0.024(2)	0.003(1)	0.007(1)	–0.001(1)
N(3)	8*f*	0.3245(2)	–0.0891(2)	–0.0503(2)	0.025(2)	0.028(2)	0.028(2)	0.004(1)	0.006(1)	–0.006(1)
N(4)	8*f*	0.2171(2)	–0.0057(2)	–0.0629(2)	0.022(2)	0.029(2)	0.030(2)	0.001(1)	0.004(1)	–0.006(1)
Cl(1)	8*f*	0.2160(1)	–0.0021(1)	–0.2524(1)	0.097(1)	0.086(1)	0.102(2)	0.007(1)	0.046(1)	0.018(1)
F(1)	8*f*	0.1672(2)	–0.2635(2)	–0.0862(2)	0.089(2)	0.050(2)	0.036(2)	–0.025(2)	0.028(2)	0.008(1)

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