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Crystal structure of di(μ_2-chloro)-dichloro-bis(2,3,5,6-tetra-2-pyridylpyrazine)dimanganese(II), $Mn_2Cl_4(C_{24}H_{16}N_6)_2$

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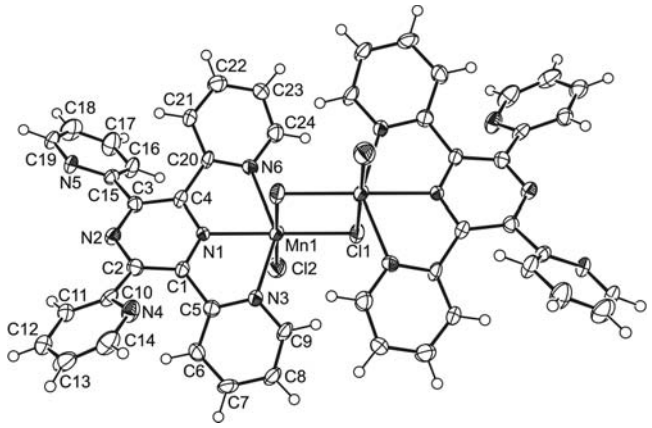

Abstract

$C_{48}H_{32}Cl_4Mn_2N_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 9.266(2) Å, b = 10.675(2) Å, c = 12.214(2) Å, α = 101.691(4)°, β = 107.474(4)°, γ = 101.157(4)°, V = 1085.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.141, T = 200 K.

Source of material

To a solution of $MnCl_2 \cdot 4H_2O$ (0.2021 g, 1.021 mmol) in EtOH (20 ml) was added 2,3,5,6-tetra-2-pyridylpyrazine (tppz, 0.1983 g, 0.511 mmol) and the mixture was stirred for 3 h at room temperature. The formed precipitate was separated by filtration, washed with EtOH and dried at 50 °C, to give a yellow powder (0.2649 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an *N*,*N*-dimethylformamide solution at 60 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The highest peak (0.67 e·Å^{-3}) and the deepest hole (–0.81 e·Å^{-3}) in the difference Fourier map are located 1.20 Å and 0.83 Å from the Mn1 atom, respectively.

Discussion

In the title complex, the two Mn(II) ions are bridged by the two Cl anionic ligands to form a dinuclear Mn(II) complex. The asymmetric unit contains one half of the title molecule; a center of inversion is located at the centroid of the complex. Each Mn atom is six-coordinated in a considerably distorted octahedral manner by three N atoms of the tridentate tppz ligand, two bridging Cl^- ligands and a Cl^- anion. The main contributions to the distortion are the tight N–Mn–N chelating angles (∠N1–Mn1–N3 = 70.9(1)° and ∠N1–Mn1–N6 = 71.3(1)°) and the Cl bridging, which results in non-linear *trans* arrangement of the N3–Mn1–N6 and N1–Mn1–Cl1 bonds (∠N3–Mn1–N6 = 141.7(1)° and ∠N1–Mn1–Cl1 = 167.4(1)°), whereas the Cl2–Mn1–Cl1^i (symmetry code i: 1–x,–y,–z) bond is almost linear (∠Cl2–Mn1–Cl1^i = 178.86(5)°). The three Mn—N bond lengths are roughly equivalent (d(Mn—$N_{pyrazine}$) = 2.244(3) Å; d(Mn—$N_{pyridyl}$) = 2.274(3) and 2.275(4) Å). On the contrary, the three Mn—Cl bond lengths are somewhat different. The Mn1—Cl1^i bridging bond (d(Mn1—Cl1^i) = 2.680(2) Å) is slightly longer than the other Mn—Cl bonds (d(Mn1—$Cl1_{bridging}$) = 2.454(1) Å and d(Mn1—Cl2) = 2.415(2) Å. The distance between the Mn atoms is relatively short with 3.823(1) Å.

In the crystal structure, the pyrazine ring is fairly distorted; the maximum deviation is 0.116(3) Å for C2 atom from the least-squares plane of the ring. The dihedral angles between the nearly planar pyridyl rings and the least-squares plane of their carrier pyrazine rings are 24.8(2)°, 34.7(2)°, 40.2(2)° and 27.1(2)°, respectively. The complex displays numerous inter- and intramolecular π-π interactions between the pyridyl rings. The shortest distance between Cg1 (the centroid of ring N4-C14) and Cg2^{ii} (ring N5-C19, symmetry code ii: 1–x,1–y,1–z) is 4.566(3) Å, and the dihedral angle between the ring planes is 47.3(3)°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.14 × 0.19 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.80 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6891, 4253
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2826
$N(param)_{refined}$:	298
Programs:	SHELXS-97, SHELXL-97 [1], PLATON [2], ORTEP-III [3]

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

Atom	Site	x	y	z	U_{iso}
H(6)	2*i*	0.2746	0.2630	0.4044	0.038
H(7)	2*i*	0.0216	0.1184	0.3059	0.042
H(8)	2*i*	–0.0314	–0.0427	0.1271	0.038
H(9)	2*i*	0.1606	–0.0378	0.0412	0.035
H(11)	2*i*	0.6286	0.5070	0.6611	0.034
H(12)	2*i*	0.5498	0.4365	0.8083	0.046
H(13)	2*i*	0.4482	0.2076	0.7782	0.054
H(14)	2*i*	0.4492	0.0594	0.6124	0.052

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(16)	2*i*	0.7866	0.6391	0.2425	0.041
H(17)	2*i*	0.9569	0.8485	0.2760	0.054
H(18)	2*i*	1.1588	0.9435	0.4625	0.056
H(19)	2*i*	1.1784	0.8354	0.6078	0.043
H(21)	2*i*	1.0313	0.4732	0.2972	0.036
H(22)	2*i*	1.1385	0.4337	0.1479	0.042
H(23)	2*i*	0.9728	0.3166	–0.0488	0.041
H(24)	2*i*	0.7104	0.2295	–0.0845	0.039

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*i*	0.47333(8)	0.17101(7)	0.05828(6)	0.0221(4)	0.0281(4)	0.0210(4)	–0.0018(3)	0.0056(3)	0.0016(3)
Cl(1)	2*i*	0.3551(1)	–0.0078(1)	–0.1298(1)	0.0312(6)	0.0297(6)	0.0221(6)	0.0016(5)	0.0028(5)	0.0007(5)
Cl(2)	2*i*	0.3141(2)	0.3150(1)	–0.0063(1)	0.0376(7)	0.0449(8)	0.0355(8)	0.0136(6)	0.0088(6)	0.0096(6)
N(1)	2*i*	0.5918(4)	0.2979(3)	0.2480(3)	0.019(2)	0.024(2)	0.016(2)	0.001(2)	0.007(2)	0.002(2)
N(2)	2*i*	0.7254(4)	0.4667(3)	0.4725(3)	0.024(2)	0.022(2)	0.024(2)	0.002(2)	0.006(2)	0.005(2)
N(3)	2*i*	0.3269(4)	0.1098(4)	0.1682(3)	0.025(2)	0.024(2)	0.022(2)	–0.001(2)	0.009(2)	0.001(2)
N(4)	2*i*	0.5236(5)	0.1901(4)	0.5337(4)	0.038(2)	0.025(2)	0.029(2)	–0.002(2)	0.005(2)	0.008(2)
N(5)	2*i*	0.9987(4)	0.6771(4)	0.5169(3)	0.025(2)	0.028(2)	0.024(2)	–0.001(2)	0.002(2)	–0.004(2)
N(6)	2*i*	0.7103(4)	0.3004(4)	0.0774(3)	0.026(2)	0.026(2)	0.024(2)	0.001(2)	0.013(2)	0.006(2)
C(1)	2*i*	0.5225(5)	0.2845(4)	0.3273(4)	0.023(2)	0.021(2)	0.021(2)	0.000(2)	0.005(2)	0.001(2)
C(2)	2*i*	0.6070(5)	0.3588(4)	0.4483(4)	0.027(2)	0.022(2)	0.028(3)	0.004(2)	0.011(2)	0.003(2)
C(3)	2*i*	0.7799(5)	0.4891(4)	0.3875(4)	0.023(2)	0.023(2)	0.021(2)	0.005(2)	0.007(2)	0.006(2)
C(4)	2*i*	0.7276(5)	0.3911(4)	0.2766(4)	0.021(2)	0.019(2)	0.019(2)	0.001(2)	0.002(2)	0.004(2)
C(5)	2*i*	0.3615(5)	0.1939(4)	0.2766(4)	0.028(3)	0.027(2)	0.024(3)	0.003(2)	0.011(2)	0.008(2)
C(6)	2*i*	0.2496(6)	0.2002(5)	0.3296(4)	0.036(3)	0.034(3)	0.022(3)	0.003(2)	0.014(2)	0.005(2)
C(7)	2*i*	0.1009(5)	0.1139(5)	0.2720(5)	0.023(3)	0.044(3)	0.037(3)	–0.001(2)	0.015(2)	0.014(3)
C(8)	2*i*	0.0680(5)	0.0213(5)	0.1655(4)	0.022(2)	0.031(3)	0.030(3)	–0.007(2)	0.003(2)	0.005(2)
C(9)	2*i*	0.1837(5)	0.0242(4)	0.1161(4)	0.025(3)	0.023(2)	0.028(3)	–0.008(2)	0.003(2)	0.003(2)
C(10)	2*i*	0.5720(5)	0.3213(4)	0.5483(4)	0.019(2)	0.023(2)	0.028(3)	–0.002(2)	0.002(2)	0.010(2)
C(11)	2*i*	0.5872(5)	0.4150(5)	0.6511(4)	0.027(3)	0.030(3)	0.023(3)	0.005(2)	0.007(2)	0.006(2)
C(12)	2*i*	0.5420(6)	0.3737(5)	0.7380(5)	0.028(3)	0.052(3)	0.025(3)	0.003(2)	0.004(2)	0.005(2)
C(13)	2*i*	0.4848(6)	0.2391(6)	0.7213(5)	0.025(3)	0.067(4)	0.037(3)	–0.002(3)	0.003(2)	0.024(3)
C(14)	2*i*	0.4822(6)	0.1520(5)	0.6209(5)	0.039(3)	0.039(3)	0.043(4)	–0.006(2)	0.004(3)	0.022(3)
C(15)	2*i*	0.8884(5)	0.6218(4)	0.4087(4)	0.021(2)	0.022(2)	0.024(3)	–0.001(2)	0.007(2)	0.004(2)
C(16)	2*i*	0.8683(6)	0.6815(5)	0.3176(5)	0.033(3)	0.029(3)	0.026(3)	–0.006(2)	0.000(2)	0.003(2)
C(17)	2*i*	0.9687(6)	0.8042(5)	0.3369(5)	0.050(3)	0.037(3)	0.035(3)	–0.005(3)	0.007(3)	0.013(3)
C(18)	2*i*	1.0860(7)	0.8602(5)	0.4466(6)	0.044(3)	0.027(3)	0.059(4)	–0.009(2)	0.017(3)	0.011(3)
C(19)	2*i*	1.0966(5)	0.7950(5)	0.5324(5)	0.024(3)	0.032(3)	0.033(3)	–0.005(2)	0.003(2)	–0.009(2)
C(20)	2*i*	0.8051(5)	0.3745(4)	0.1873(4)	0.023(2)	0.024(2)	0.014(2)	–0.002(2)	–0.001(2)	0.004(2)
C(21)	2*i*	0.9662(5)	0.4243(4)	0.2176(4)	0.026(3)	0.028(3)	0.024(3)	–0.003(2)	0.006(2)	–0.003(2)
C(22)	2*i*	1.0286(6)	0.4011(5)	0.1295(5)	0.028(3)	0.041(3)	0.036(3)	0.004(2)	0.013(2)	0.011(2)
C(23)	2*i*	0.9323(6)	0.3304(5)	0.0141(4)	0.029(3)	0.044(3)	0.025(3)	0.003(2)	0.013(2)	0.003(2)
C(24)	2*i*	0.7765(6)	0.2811(5)	–0.0059(4)	0.032(3)	0.035(3)	0.024(3)	0.003(2)	0.008(2)	0.006(2)

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