Crystal structure of (μ_2-2,2′-bipyrimidine)-bis((2,2′-bipyrimidine)-tetrachlorodimanganese(II)), $Mn_2Cl_4(C_8H_6N_4)_3$

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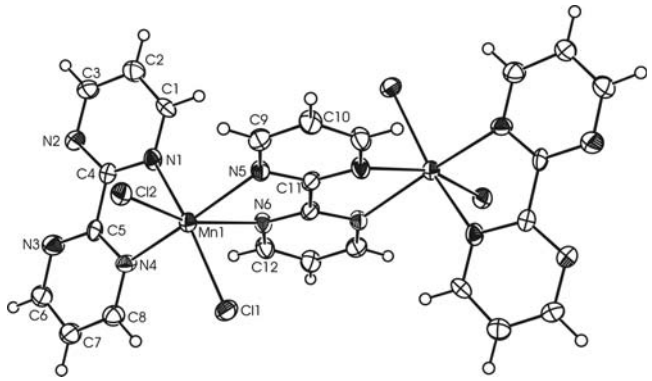

Abstract

$C_{24}H_{18}Cl_4Mn_2N_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 7.0731(9) Å, b = 7.383(1) Å, c = 15.180(2) Å, α = 100.363(3)°, β = 90.355(3)°, γ = 112.528(2)°, V = 717.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.057, $wR_{ref}(F^2)$ = 0.167, T = 200 K.

Source of material

To a solution of $MnCl_2 \cdot 4H_2O$ (0.0981 g, 0.496 mmol) in EtOH (30 ml) was added 2,2′-bipyrimidine (bpym; 0.1589 g, 1.005 mmol) and 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 (0.1571 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an *N*,*N*-dimethylformamide solution at 70 °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 (1.09 e·Å^{-3}) and the deepest hole (–1.41 e·Å^{-3}) in the difference Fourier map are located 1.27 Å and 0.87 Å from the atom Mn1, respectively.

Discussion

In the title complex, the two Mn(II) ions are bridged by a 2,2′-bipyrimidine ligand acting as a bis-chelating ligand to form a dinuclear Mn(II) complex, which is isomorphous with the analogous Fe(II) complex $[Fe_2Cl_4(bpym)_3]$ [1]. 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 four N atoms of the two distinct bpym ligands and two Cl^- anions. The tight N–Mn–N chelating angles (∠N1–Mn1–N4 = 72.0(2)° and ∠N5–Mn1–N6 = 70.0(2)°) and the Cl-Cl repelling (∠Cl1–Mn1–Cl2 = 104.77(6)°) contribute the distortion of the ocataheron. The apical bond angles ∠N1–Mn1–Cl1, ∠N6–Mn1–Cl2 and ∠N4–Mn1–N5 are 160.0(1)°, 161.2(1)° and 167.1(2)°, respectively. The Mn—Cl bond lengths are roughly equivalent (2.412(2) Å and 2.438(2) Å), but the Mn—N bond lengths are somewhat different. The Mn—$N_{lateral\text{-}bpym}$ bonds (d(Mn1—N1/N4) = 2.268(5) Å and 2.289(5) Å) are slightly shorter than the Mn—$N_{bridging\text{-}bpym}$ bonds (d(Mn1—N5) = 2.305(5) Å and d(Mn1—N6) = 2.375(5) Å). The lateral and bridging bpym ligands are nearly planar and the dihedral angle between the least-squares planes of the two ligands is 71.55(9)°. In the crystal structure, the complexes are stacked in columns along [100]. In the columns, numerous inter- and intramolecular π-π interactions between adjacent pyrimidine rings are present. The centroid-centroid distance between Cg1 (the centroid of ring N3-C6) and Cg1^i (symmetry code i: 2–x,2–y,z) is 4.018(4) Å, the ring planes are parallel and shifted by 2.208 Å.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.15 × 0.16 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.92 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5364, 3511
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2509
$N(param)_{refined}$:	190
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-III [3], PLATON [4]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.7628	0.5541	0.3106	0.045
H(2)	2*i*	0.5397	0.2775	0.2081	0.050
H(3)	2*i*	0.4707	0.3205	0.0648	0.046
H(6)	2*i*	0.8169	1.1948	–0.0253	0.051
H(7)	2*i*	1.0618	1.4604	0.0739	0.048
H(8)	2*i*	1.1567	1.4008	0.2103	0.042
H(9)	2*i*	1.2976	0.7204	0.3808	0.043
H(10)	2*i*	1.4037	0.6863	0.5205	0.043
H(12)	2*i*	0.7001	1.1639	0.3517	0.042

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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*	1.0939(1)	1.0088(1)	0.30348(6)	0.0349(5)	0.0279(4)	0.0221(4)	0.0127(4)	0.0006(3)	0.0042(3)
Cl(1)	2*i*	1.3195(2)	1.3452(2)	0.3727(1)	0.0475(9)	0.0287(7)	0.0347(8)	0.0151(6)	–0.0051(6)	0.0015(6)
Cl(2)	2*i*	1.3144(2)	0.8704(2)	0.2176(1)	0.0435(8)	0.0357(8)	0.0315(7)	0.0185(6)	0.0063(6)	0.0060(6)
N(1)	2*i*	0.8111(7)	0.7501(7)	0.2312(3)	0.028(2)	0.037(3)	0.022(2)	0.008(2)	–0.004(2)	0.005(2)
N(2)	2*i*	0.6305(8)	0.6139(7)	0.0864(3)	0.044(3)	0.030(3)	0.030(3)	0.009(2)	–0.002(2)	0.002(2)
N(3)	2*i*	0.7742(9)	0.9899(8)	0.0484(4)	0.046(3)	0.034(3)	0.038(3)	0.015(2)	–0.003(2)	0.008(2)
N(4)	2*i*	0.9783(7)	1.1123(7)	0.1885(3)	0.035(3)	0.023(2)	0.035(3)	0.013(2)	0.002(2)	0.006(2)
N(5)	2*i*	1.1338(7)	0.8791(7)	0.4263(3)	0.038(3)	0.032(2)	0.024(2)	0.021(2)	0.005(2)	0.007(2)
N(6)	2*i*	0.8743(8)	1.0619(7)	0.4139(3)	0.039(3)	0.035(3)	0.024(2)	0.021(2)	0.002(2)	0.008(2)
C(1)	2*i*	0.730(1)	0.5696(9)	0.2524(4)	0.050(4)	0.032(3)	0.031(3)	0.012(3)	0.006(3)	0.017(3)
C(2)	2*i*	0.598(1)	0.405(1)	0.1923(4)	0.040(4)	0.036(3)	0.040(4)	0.004(3)	0.004(3)	0.010(3)
C(3)	2*i*	0.556(1)	0.4329(9)	0.1084(4)	0.041(4)	0.027(3)	0.037(3)	0.004(3)	–0.003(3)	0.004(2)
C(4)	2*i*	0.7543(9)	0.7649(8)	0.1492(4)	0.031(3)	0.032(3)	0.022(3)	0.012(2)	0.001(2)	0.001(2)
C(5)	2*i*	0.8391(8)	0.9674(8)	0.1276(3)	0.030(3)	0.034(3)	0.017(2)	0.014(2)	–0.006(2)	0.000(2)
C(6)	2*i*	0.858(1)	1.173(1)	0.0301(4)	0.064(5)	0.038(3)	0.034(3)	0.026(3)	0.004(3)	0.011(3)
C(7)	2*i*	1.003(1)	1.331(1)	0.0882(4)	0.052(4)	0.034(3)	0.034(3)	0.018(3)	–0.004(3)	0.009(3)
C(8)	2*i*	1.059(1)	1.2941(9)	0.1684(4)	0.038(3)	0.032(3)	0.037(3)	0.016(3)	0.001(3)	0.007(3)
C(9)	2*i*	1.255(1)	0.7786(9)	0.4338(4)	0.040(3)	0.033(3)	0.036(3)	0.018(3)	0.005(3)	0.005(3)
C(10)	2*i*	1.318(1)	0.7575(9)	0.5160(4)	0.044(4)	0.042(3)	0.034(3)	0.027(3)	–0.002(3)	0.010(3)
C(11)	2*i*	1.0716(9)	0.9485(8)	0.5044(4)	0.035(3)	0.025(3)	0.025(3)	0.014(2)	–0.001(2)	0.001(2)
C(12)	2*i*	0.747(1)	1.1564(9)	0.4092(4)	0.041(3)	0.041(3)	0.029(3)	0.020(3)	0.003(2)	0.011(3)

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References

1. Sun, J.-S.; Zhao, H.; Ouyang, X.; Clérac, R.; Smith, J. A.; Clemente-Juan, J. M.; Gómex-Garcia, C.; Coronado, E.; Dunbar, K. R.: Structures, Magnetic Properties, and Reactivity Studies of Salts Containing the Dinuclear Anion $[M_2Cl_6]^{2-}$ (M = Mn, Fe, Co). Inorg. Chem. **38** (1999) 5841-5855.
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
3. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
4. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.