Crystal structure of bis(2,2′-bipyrimidine-κ^2N,N')dichloro-manganese(II) — nitromethane (1:1), $MnCl_2(C_8H_6N_4)_2 \cdot CH_3NO_2$

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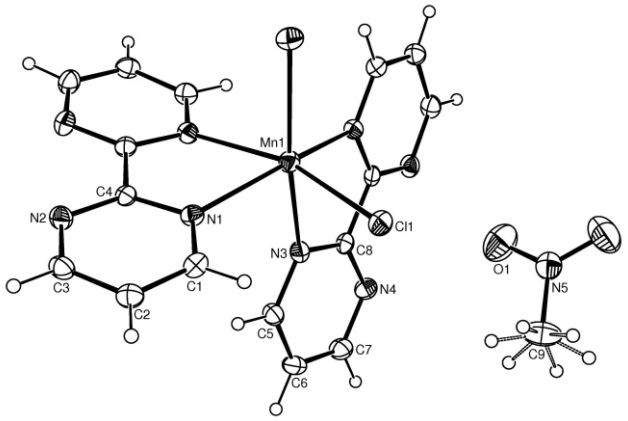

Abstract

$C_{17}H_{15}Cl_2MnN_9O_2$, orthorhombic, $C222_1$ (no. 20), a = 8.2605(4) Å, b = 11.9532(6) Å, c = 20.735(1) Å, V = 2047.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.091, 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 a CH_3NO_2 solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C_{methyl}). The methyl group of the nitromethane solvent molecule appears to be disordered. Its H atoms were modelled as disordered over two sites rotated by 60° from one another, with an occupancy ratio of 0.5 : 0.5. The highest peak (0.49 eÅ^{-3}) and the deepest hole (–0.43 eÅ^{-3}) in the difference Fourier map are located 1.26 Å and 0.82 Å from the atom Mn1, respectively. Because the Flack parameter is 0.01(3) in the final cycles of refinement, the absolute crystal structure can be regarded as correct.

Discussion

The title compound consists of a mononuclear Mn(II) complex and a nitromethane solvent molecule, and the asymmetric unit contains one half of the formula unit. In the previously reported crystal structure of the same reaction product, the single crystals were obtained from an *N,N*-dimethylformamide (DMF) solution at 70 °C and characterized as the dinuclear Mn(II) complex $[Mn_2Cl_4(bpym)_3]$, in which two Mn(II) ions are bridged by a 2,2′-bipyrimidine acting as a bis-chelating ligand [1]. It seems that the mononuclear complex $[MnCl_2(bpym)_2]$ decomposes in DMF solution at high temperature during crystallization to form the dinuclear complex.

In the title crystal structure, the Mn(II) ion is six-coordinated in a considerably distorted octahedral manner by four N atoms of the two bidentate 2,2′-bipyrimidine ligands and two Cl^- anions. The complex is located on a two-fold rotation axis running in the [010] direction passing through the Mn1 atom, whereas the nitromethane molecule is disposed about a two-fold rotation axis along [100] passing through the N5 and C9 atoms, and therefore, the methyl group appears to be disordered over two sites. The tight N–Mn–N chelating angle (∠N1–Mn1–N3^i = 70.37(9)°; symmetry code i: $-x,y,½-z$) and the Cl–Cl repelling (∠Cl1–Mn1–Cl1^i = 100.28(5)°) contribute the distortion of the ocataheron. The apical N3–Mn1–Cl1^i and N1–Mn1–N1^i bond angles are 162.76(7)° and 156.3(1)°, respectively. The Mn–N bond lengths are roughly equivalent (2.291(3) Å and 2.325(3) Å). The bpym ligands are nearly planar with a maximum deviation of 0.080(2) Å and the dihedral angle between the least-squares planes of the ligands is 72.16(4)°. In the crystal structure, the complexes are stacked in columns along [100]. When viewed down the [001], the successive complexes are stacked in the opposite direction. In the columns, several inter- and intramolecular π-π interactions between adjacent pyrimidine rings are present. The shortest distance between Cg1 (the centroid of ring N1–C4) and Cg2^{ii} (ring N3–C8, symmetry code ii: $½-x,½+y,½-z$) is 4.288(2) Å, and the dihedral angle between the ring planes is 5.9(2)°. Moreover, there are inter- and intramolecular C–H···Cl and C–H···N hydrogen bonds with d(C—Cl) = 3.450(3) - 3.700(4) Å and d(C—N) = 3.304(4) Å.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.20 × 0.23 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.42 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7507, 2527
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1883
$N(param)_{refined}$:	143
Program:	SHELXS-97, SHELXL-97 [2], ORTEP-3 [3], PLATON [4]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	8*c*		0.3774	0.4339	0.2864	0.039
H(2)	8*c*		0.5691	0.3959	0.3668	0.041
H(3)	8*c*		0.4874	0.2849	0.4539	0.041
H(5)	8*c*		0.2981	0.1987	0.2184	0.039
H(6)	8*c*		0.3920	0.0937	0.1309	0.041
H(7)	8*c*		0.2259	0.0758	0.0419	0.045
H(9A)	8*c*	0.50	0.2859	0.4625	0.0390	0.092
H(9B)	8*c*	0.50	0.2859	0.5773	–0.0008	0.092
H(9C)	8*c*	0.50	0.2859	0.4602	–0.0382	0.092

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)	4*b*	0	0.37936(5)	¼	0.0286(4)	0.0308(4)	0.0260(3)	0	–0.0001(3)	0
Cl(1)	8*c*	0.1696(1)	0.51079(7)	0.18943(4)	0.0347(5)	0.0389(5)	0.0369(5)	–0.0020(4)	0.0041(4)	0.0071(4)
N(1)	8*c*	0.2011(3)	0.3400(2)	0.3226(1)	0.025(2)	0.030(2)	0.028(2)	–0.001(1)	0.000(1)	–0.003(1)
N(2)	8*c*	0.2670(4)	0.2511(2)	0.4219(1)	0.031(2)	0.040(2)	0.028(2)	0.003(1)	–0.006(1)	–0.004(1)
N(3)	8*c*	0.0857(3)	0.2389(2)	0.1803(1)	0.029(2)	0.029(1)	0.027(2)	–0.001(1)	–0.002(1)	0.002(1)
N(4)	8*c*	0.0382(4)	0.1617(2)	0.0760(1)	0.040(2)	0.037(2)	0.029(1)	0.003(1)	0.003(1)	–0.006(1)
C(1)	8*c*	0.3496(4)	0.3859(3)	0.3212(2)	0.035(2)	0.033(2)	0.029(2)	–0.005(2)	0.004(2)	–0.002(2)
C(2)	8*c*	0.4630(4)	0.3654(3)	0.3688(2)	0.030(2)	0.036(2)	0.037(2)	–0.001(2)	0.001(2)	–0.004(2)
C(3)	8*c*	0.4139(4)	0.2982(3)	0.4195(2)	0.028(2)	0.042(2)	0.033(2)	0.006(2)	–0.006(2)	–0.006(2)
C(4)	8*c*	0.1680(4)	0.2738(2)	0.3731(1)	0.027(2)	0.027(2)	0.021(2)	0.002(1)	–0.001(1)	–0.006(1)
C(5)	8*c*	0.2316(4)	0.1901(3)	0.1813(2)	0.029(2)	0.034(2)	0.034(2)	0.002(2)	–0.003(2)	0.004(2)
C(6)	8*c*	0.2880(4)	0.1276(3)	0.1300(2)	0.027(2)	0.032(2)	0.045(2)	0.004(2)	0.005(2)	–0.001(2)
C(7)	8*c*	0.1883(5)	0.1168(3)	0.0782(2)	0.039(2)	0.039(2)	0.033(2)	0.004(2)	0.004(2)	–0.007(2)
C(8)	8*c*	–0.0045(5)	0.2209(2)	0.1273(1)	0.031(2)	0.024(2)	0.026(2)	–0.003(2)	0.002(2)	0.004(1)
O(1)	8*c*	–0.0034(6)	0.4257(2)	0.0273(2)	0.090(3)	0.075(2)	0.083(2)	–0.025(2)	0.016(3)	0.009(2)
N(5)	4*a*	0.0691(6)	½	0	0.053(3)	0.038(3)	0.038(2)	0	0	–0.004(2)
C(9)	4*a*	0.2463(7)	½	0	0.030(3)	0.070(4)	0.084(5)	0	0	–0.022(4)

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