metal-organic papers

cis-Dibromobis(4,4′-dimethyl-2,2′-bipyridine)-manganese(II)

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The title compound, $[MnBr_2(C_{12}H_{12}N_2)_2]$, has a twofold axis, and the Mn^{II} atom is coordinated by four N atoms from two 4,4′-dimethyl-2,2′-bipyridine (dmbpy) ligands and two bromide anions, forming a distorted octahedral environment. The Mn—N and Mn—Br bond distances are 2.261 (2)–2.297 (3) and 2.6193 (5) Å, respectively. The dihedral angle between the pyridine rings of each dmbpy ligand is 16.09 (9)°.

Comment

One of the most important processes in nature occurs in the oxygen evolving complex of photosystem II in green plants. Manganese ions are the essential components in the active center of photosystem II. The coordination sphere of manganese is believed to be composed of O and N donors. In this paper, we report the synthesis and crystal structure of the title compound, cis-$[MnBr_2(dmbpy)_2]$ (dmbpy is 4,4′-dimethyl-2,2′-bipyridine), (I).

(I)
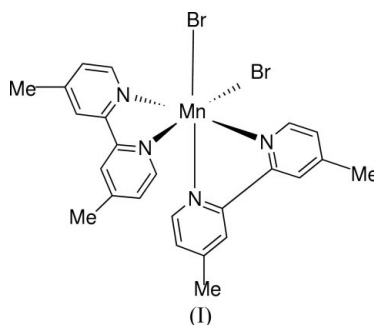
As illustrated in Fig. 1, the complex has a twofold axis, and the Mn^{II} atom is located in a distorted octahedral environment formed by two dmbpy ligands and two bromide anions in a cis arrangement. The trans angles around the Mn atom are in the range 161.8 (1)–167.51 (6)° (Table 1). In the dmbpy ligand, the dihedral angle between the pyridine rings is 16.09 (9)°. The average Mn—N bond length is 2.279 (3) Å and the N—Mn—N chelate angle is 71.66 (8)°. The corresponding values in cis-$[IrCl_2(dmbpy)_2]PF_6$ are 2.052 (5) Å and 78.9 (2)° (Yoshikawa et al., 2003).

Experimental

The title compound, (I), was prepared by the follwing method. A solution of 4,4′-dimethyl-2,2′-bipyridine (1.0 mmol) in methanol was added dropwise to a stirred aqueous solution (10 ml) of $MnBr_2$ (0.5 mmol). All the insoluble products were filtered off and the green solution was left to stand at room temperature. Several days later, X-ray quality single crystals of (I) were obtained (yield 35%).

Crystal data

[MnBr$_2$(C$_{12}$H$_{12}$N$_2$)$_2$]
$M_r = 583.23$
Orthorhombic, $Pbcn$
$a = 15.2773 (9)$ Å
$b = 10.2049 (5)$ Å
$c = 15.4099 (7)$ Å
$V = 2402.5 (2)$ Å^3
$Z = 4$
$D_x = 1.612$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 29 251
  reflections
$\theta = 2.4–30.4°$
$\mu = 3.90$ mm^{-1}
$T = 200.2$ K
Prism, yellow
$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID Imaging
  Plate diffractometer
ω scans
Absorption correction: multi-scan
  (*ABSCOR*; Higashi, 1995)
  $T_{min} = 0.293$, $T_{max} = 0.458$
26 269 measured reflections

3606 independent reflections
2542 reflections with $I > 2\sigma(I)$
$R_{int} = 0.095$
$\theta_{max} = 30.4°$
$h = -21 \rightarrow 21$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.116$
$S = 1.34$
3606 reflections
153 parameters

Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—Mn1	2.6193 (5)	N1—C5	1.334 (4)
Mn1—N1	2.261 (2)	N2—C7	1.331 (4)
Mn1—N2	2.297 (3)	N2—C11	1.334 (4)
N1—C1	1.334 (4)	C1—C2	1.367 (4)
Br1—Mn1—Br1^i	100.47 (3)	N1—Mn1—N1^i	161.8 (1)
Br1—Mn1—N1	98.86 (6)	N1—Mn1—N2	71.66 (8)
Br1—Mn1—N1^i	92.75 (6)	N1—Mn1—N2^i	94.64 (9)
Br1—Mn1—N2	167.51 (6)	N2—Mn1—N2^i	84.5 (1)
Br1—Mn1—N2^i	88.33 (6)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

All H atoms were placed at calculated positions and the methyl H atoms were allowed to rotate freely about the C—Me bond. Finally, the positional parameters of the H atoms were fixed, and their U_{iso} parameters were refined (C—H = 0.81–0.99 Å). The maximum and
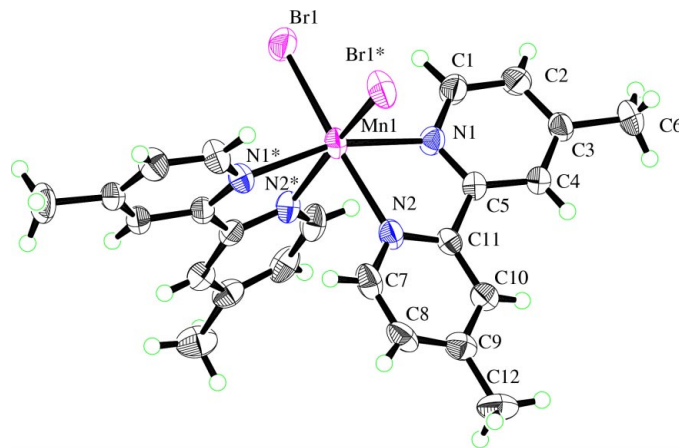

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. [Symmetry code: (*) $-x, y, \frac{1}{2} - z$.]

minimum difference-density peaks are 0.87 Å from Br1 and 1.20 Å from Mn1, respectively.

  Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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