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Diaquabis(2,4′-bipyridyl-*N*′)dichloromanganese(II)

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.007 Å
R factor = 0.062
wR factor = 0.163
Data-to-parameter ratio = 11.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The Mn atom in the title compound, $[MnCl_2(C_{10}H_8N_2)_2(H_2O)_2]$, occupies a centre of symmetry. The pyridine rings are planar and all bond distances are normal. Bond-valence calculations show that the Mn—O bond is weaker than both the Mn—N and Mn—Cl bonds. The molecules are held together in the crystal by hydrogen bonds.

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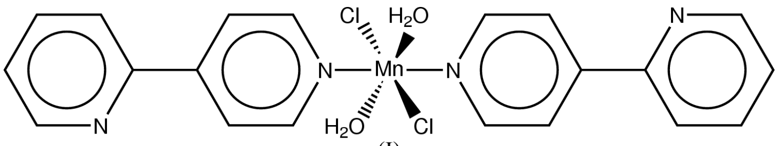
Comment

This work forms part of a continuing study of 2,4′-bipyridyl complexes with copper(II) and manganese(II) salts (Bartczak *et al.*, 1998; Kruszynski *et al.*, 2001). Although coordination compounds of these salts with 2,2′-bipyridyl and 4,4′-bipyridyl have been extensively investigated, there are only a small number of reports describing structures of 2,4′-bipyridyl complexes. The structure determination of the title compound, (I), was thus undertaken.



(I)

All interatomic distances in (I) are normal. The molecular geometry of (I) (Fig. 1) is similar to diaquadi(acetato-*O*)-bis(2,4′-bipyridyl)manganese(II) (Bartczak *et al.*, 1998). The Mn atom occupies a centre of symmetry and adopts almost ideal square-bipyramidal (4+2) coordination. It has been stated that the bond length to bond valence correlation represents a measure of the strength of a bond that is independent of the atomic size (Brown, 1994). The application of this correlation allows us to compare the relative importance of Mn—N, Mn—O and Mn—Cl bonds for different molecules and to check the valence-sum rule for coordinated atoms (Sieroń & Bukowska–Strzyżewska, 1999). The valence sum rule states that the sum of the valences of the bonds formed by an atom is equal to the valence (formal oxidation state) of the atom. The bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ (Brown, 1992, 1997), where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single-bond length between i and j atoms) (Sieroń & Bukowska–Strzyżewska, 1999). The $R_{\text{Mn-O}}$, $R_{\text{Mn-N}}$ and $R_{\text{Mn-Cl}}$ were taken as 1.790, 1.87 and 2.13 (O'Keeffe & Brese, 1991), respectively. The computed bond valences of the manganese are $\nu_{\text{Mn-O}} = 0.30$, $\nu_{\text{Mn-N}} = 0.35$ and $\nu_{\text{Mn-Cl}} = 0.35$ v.u. (valence units), thus the computed valence of the Mn1 atom is 2.00 v.u., which is consistent with the formal oxidation state of manganese. According to bond valences it can be stated that the Mn—O

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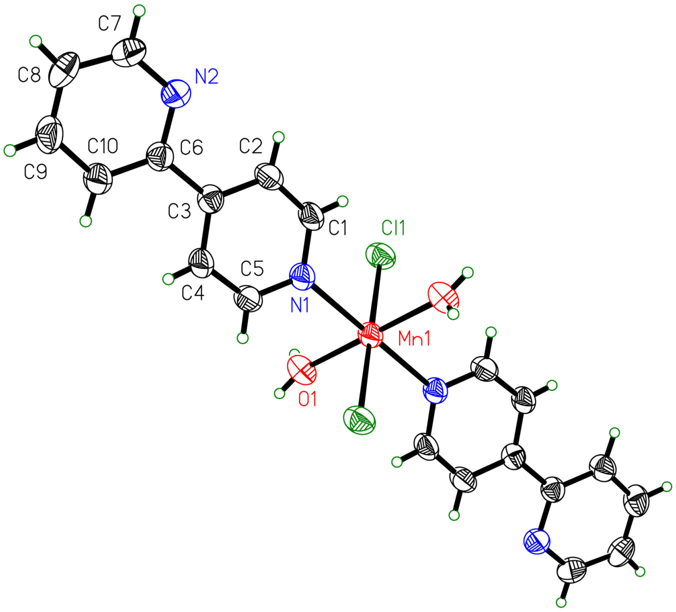

Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

bond is distinctly weaker than other manganese bonds, which can be explained by weak O1—H1O···Cl1 and C10—H10···Cl1 hydrogen bonds (for details see Table 2). All least-squares planes of the manganese polyhedra are exactly planar by symmetry. The dihedral angle between least-squares planes calculated through Mn1/O1/Cl1 and Mn1/O1/N1 is 88.84 (11)°, between Mn1/O1/N1 and Mn1/Cl1/N1 is 85.59 (9)° and between Mn1/O1/Cl11 and Mn1/Cl1/N1 is 87.76 (9)°. The pyridine rings are planar within 3 s.u.'s and are inclined at 4.97 (5)° to each other within each 2,4′-bipyridyl group. The pyridyl ring attached to manganese forms dihedral angles of 89.52 (14), 48.69 (14) and 45.80 (12)° with the least-squares planes calculated through Mn1/O1/Cl1, Mn1/O1/N1 and Mn1/Cl1/N1, recpectively. The decrease in the H—O—H angle, which has a value of 92 (7)°, and the diffusion of the electron density of the H atoms in the water molecule seen in the difference Fourier map is imposed by the O—H···Cl^{i} and O—H···N^{ii} hydrogen bonds [the Cl^{i}···O···N^{ii} angle is 89.83 (13)°] [symmetry codes: (i) $-x+1$, $-y$, $-z$; (ii) x, y, $z+1$]. The crystals of the title compound are held together by strong O—H···N, and weak O—H···Cl and C—H···Cl hydrogen bonds (Desiraju & Steiner, 1999), resulting in a three-dimensional infinite framework (Fig. 2 and Table 2).

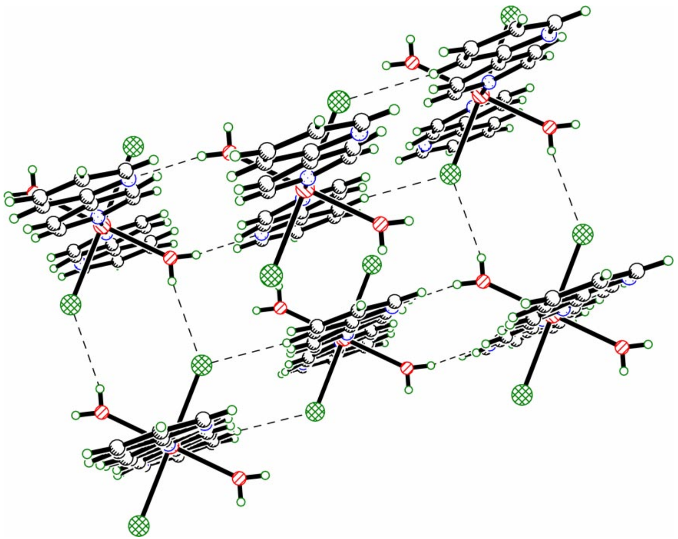

Figure 2
Part of the molecular packing of the title compound showing intermolecular hydrogen bonds creating a three-dimensional net structure. Hydrogen bonds are indicated by dashed lines.

Experimental

A solution of 4.3 mmol of manganese(II) chloride in 20 ml water was added to a solution of 12.8 mmol of 2,4′-bipyridyl in 10 ml water containing a few drops of 95% EtOH. The mixture was heated at 353 K for 15 min and allowed to cool (Czakis–Sulikowska & Kałużna, 1999). After several days, a fine crystalline compound was obtained. The product was dissolved in the equivolume mixture of water and 95% EtOH, and the solution was kept at 277 K. After one month, plate-shaped crystals had grown.

Crystal data

$[MnCl_2(C_{10}H_8N_2)_2(H_2O)_2]$
$M_r = 474.24$
Triclinic, $P\bar{1}$
$a = 6.8000$ (7) Å
$b = 8.6443$ (8) Å
$c = 8.9244$ (9) Å
$\alpha = 84.512$ (10)°
$\beta = 79.866$ (9)°
$\gamma = 77.834$ (9)°
$V = 503.87$ (9) Å^3

$Z = 1$
$D_x = 1.563$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3348 reflections
$\theta = 5$–22°
$\mu = 0.95$ mm^{-1}
$T = 291$ (1) K
Plate, light yellow
0.36 × 0.28 × 0.16 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)
$T_{min} = 0.727$, $T_{max} = 0.864$
4700 measured reflections
1790 independent reflections
1755 reflections with $I > 2\sigma(I)$

$R_{int} = 0.069$
$\theta_{max} = 25.1°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -9 \rightarrow 10$
2 standard reflections every 50 reflections intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.163$
$S = 1.19$
1790 reflections
163 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 1.3653P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—O1	2.237 (4)	Mn1—Cl1	2.5173 (12)
Mn1—N1	2.263 (4)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···Cl1^{i}	0.69 (6)	2.64 (6)	3.307 (4)	163 (7)
O1—H1*P*···N2^{ii}	0.77 (6)	2.12 (6)	2.851 (5)	159 (6)
C10—H10···Cl1^{iii}	0.92 (6)	2.76 (6)	3.668 (5)	173 (5)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $x, y, 1+z$; (iii) $x, y-1, z$.

Data collection: *CrysAlis CCD* (UNIL IC & Kuma, 2000); cell refinement: *CrysAlis RED* (UNIL IC & Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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