Monomeric complexes of manganese(II) with tetradentate ligands: isolation of *cis*-diaquamanganese(II) and *cis*-dichloromanganese(II) species

Patricia A. Goodson, Aderemi R. Oki and Derek J. Hodgson[*]
Department of Chemistry, University of Wyoming, Laramie, WY 82071 (U.S.A.)

(Received May 28, 1990)

Abstract

The synthesis and characterization of the monomeric complexes *cis*-diaqua(*N,N'*-bis(2-methylpyrazyl)ethane-1,2-diamine)manganese(II) perchlorate monohydrate (**1**), or *cis*-[Mn(bispyzen)-$(H_2O)_2](ClO_4)_2 \cdot H_2O$, and *cis*-dichloro(*N,N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine) manganese(II) (**2**) are reported. The diaqua complex crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a cell of dimensions $a = 13.394(4)$, $b = 9.778(3)$, $c = 17.434(7)$ Å, $\beta = 103.15(3)°$. The structure has been refined to an R factor of 0.0485 based on 3857 independent intensities. The O–Mn–O bond angle in the complex is 93.9(1)°, and the Mn–O bond lengths are 2.137(3) and 2.158(3) Å. There is extensive hydrogen bonding in the crystals. The dichloro complex crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a cell of dimensions $a = 8.993(2)$, $b = 28.717(7)$, $c = 9.053(2)$ Å. $\beta = 118.84(1)°$. The structure has been refined to an R factor of 0.0370 based on 3276 independent intensities. The Cl–Mn–Cl bond angle in the complex is 99.4(1)°, and the Mn–Cl bond lengths are 2.402(1) and 2.467(1) Å. The axial Mn–N bond lengths of 2.423(2) and 2.456(3) Å are much longer than the equatorial Mn–N distances of 2.285(3) and 2.329(3) Å; this observed elongation of the axial bonds is presumably due to the steric crowding caused by the presence of the 6-methyl groups on the axial pyridine rings. The dichloro complex shows a quasi-reversible redox wave at 0.80 V *versus* Ag/AgCl corresponding to the Mn(II) ↔ Mn(III) couple.

Introduction

During the past few years we [1–3] and others [4] have been interested in the development of polynuclear transition metal ions formed from the interaction of two or more moles of *cis*-$[Cr(A)(OH)_2]^+$ (where A is a tetradentate ligand), or its cobalt(III) analogue, with metal halides. The resultant heteronuclear or homonuclear complex ion can be viewed as stemming from the interaction of the bidentate ligand $[Cr(A)(OH)_2]^+$ with the central metal ion, and complexes with two, three and four such ligands coordinated to a single metal have been isolated and characterized [1–4]. We have been anxious to expand this chemistry to the more redox active metal manganese, but are hampered by the scarcity in the literature of the necessary complexes *cis*-$[Mn(A)(OH)_2]$ or its presumed diaqua or dichloro precursors.

In the course of our related investigations on binuclear species of manganese with tetradentate ligands [5], we have discovered a convenient synthetic methodology for the isolation of these *cis*-diaqua- and *cis*-dichloromanganese(II) precursors. We here report the syntheses and characterization of one example of each type, *cis*-diaqua(*N,N'*-bis(2-methylpyrazyl)ethane-1,2-diamine)manganese(II) perchlorate monohydrate (**1**), or *cis*-[Mn(bispyzen)$(H_2O)_2](ClO_2)_2 \cdot H_2O$, and *cis*-dichloro(*N,N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine)manganese(II) (**2**).

Experimental

Synthesis of the complexes

cis-Diaqua(N,N'-bis(2-methylpyrazyl)ethane-1,2-diamine)manganese(II) perchlorate monohydrate (1)

To a solution of 0.200 g (0.82 mmol) *N,N'*-bis(2-methylpyrazyl)ethane-1,2-diamine [5] in 2 ml H_2O

---

[*] Author to whom correspondence should be addressed.

0020-1693/90/$3.50

TABLE 1. Crystallographic and data collection parameters

Complex	1	2
Formula	$MnC_{12}H_{22}Cl_2N_6O_{11}$	$MnC_{20}H_{22}N_4Cl_2$
Color	yellow	red–brown
System	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Cell dimensions		
a (Å)	13.394(4)	8.993(2)
b (Å)	9.778(3)	28.717(7)
c (Å)	17.434(7)	9.053(2)
β (°)	103.15(3)	118.84(1)
Volume (Å^3)	2223.2(14)	2048.0(8)
Z	4	4
$F(000)$	1132	916
Absorption coefficient (mm^{-1})	0.88	0.89
Index ranges	$0 \leqslant h \leqslant 17$	$0 \leqslant h \leqslant 11$
	$0 \leqslant k \leqslant 12$	$0 \leqslant k \leqslant 37$
	$-22 \leqslant l \leqslant 22$	$-11 \leqslant l \leqslant 11$
No. reflections	5014	5080
Observed reflections ($I > 3\sigma(I)$)	3857	3276
R	0.0485	0.0370
R_w	0.0701	0.0372

was added 0.296 g (0.82 mmol) manganese perchlorate hexahydrate. The solution was stirred for 15 min at ambient temperature, and then cooled at 0 °C for two days to give 0.327 g (73%) of yellow crystals. *Anal.* Calc. for $MnC_{12}H_{22}Cl_2N_6O_{11}$ (includes one mole of H_2O hydrate): C, 26.10; H, 4.02; Cl, 12.84; N, 15.22. Found*: C, 26.23; H, 3.96; Cl, 12.93; N, 15.15%.

cis-Dichloro(N,N-bis((6-methylpyrid-2-yl)methyl)-N-2-pyridylmethylamine)manganese(II) (2)

To a solution of 1.582 g (4.97 mmol) *N,N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine [5] in 10 ml acetonitrile was added 0.98 g (4.97 mmol) manganese(II) chloride tetrahydrate in 10 ml water. The solution was stirred for 10 min, followed by addition of a few drops of 30% hydrogen peroxide. The final solution was left at room temperature for 2 days, to yield 1.2 g of red–brown crystals (54.3%). *Anal.* Calc. for $MnC_{20}H_{22}Cl_2N_4$: C, 54.06; H, 4.99; Cl, 15.96; N, 12.61. Found*: C, 53.44; H, 4.96; Cl, 15.81; N, 12.52%.

Electrochemistry

Cyclic voltammograms were recorded in acetonitrile on a BAS 100A electrochemical analyzer using a glassy carbon or platinum working electrode, a platinum wire auxiliary electrode and a silver/silver chloride reference electrode. Solutions were approximately 1–2 mM, with 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

X-ray structure determinations

The structures of the complexes were determined at room temperature on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($\lambda K\alpha_1 = 0.70926$ Å; $\lambda K\alpha_2 = 0.71354$ Å) and a graphite monochromator. Crystal data and experimental parameters are tabulated in Table 1. The data were corrected for Lorentz–polarization effects and for absorption. The structures were solved by direct methods and refined by least-squares techniques; the programs used were from the SHELXTL system.

cis-Diaqua(N,N′-bis(2-methylpyrazyl)ethane-1,2-diamine)manganese(II) perchlorate monohydrate (1)

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with four formula units

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for **1**

	x	y	z	U_{eq}[a]
Mn(1)	2641(1)	2446(1)	922(1)	37(1)
O(1)	2793(2)	288(2)	715(2)	64(1)
O(2)	2431(2)	2154(3)	2090(1)	62(1)
N(1A)	4359(2)	2777(2)	1294(1)	39(1)
N(4A)	6409(2)	3393(3)	1870(2)	59(1)
N(8A)	2876(2)	4727(2)	1088(2)	42(1)
N(1B)	897(2)	2236(2)	446(1)	40(1)
N(4B)	−1073(2)	1443(3)	−282(2)	55(1)
N(8B)	2263(2)	3189(3)	−338(1)	44(1)
C(2A)	4642(2)	3978(3)	1617(2)	38(1)
C(3A)	5669(2)	4280(3)	1907(2)	52(1)
C(5A)	6123(2)	2204(4)	1535(2)	57(1)
C(6A)	5110(2)	1881(3)	1251(2)	48(1)
C(7A)	3821(2)	4987(3)	1691(2)	45(1)
C(9A)	2901(2)	5318(3)	311(2)	49(1)
C(2B)	613(2)	2127(3)	−336(2)	40(1)
C(3B)	−380(2)	1728(3)	−697(2)	51(1)
C(5B)	−792(2)	1595(3)	485(2)	55(1)
C(6B)	188(2)	1993(3)	860(2)	48(1)
C(7B)	1399(2)	2425(3)	−807(2)	50(1)
C(9B)	2071(2)	4668(3)	−313(2)	53(1)
Cl(1)	5359(1)	−1996(1)	939(1)	49(1)
O(3)	4393(2)	−1508(4)	553(3)	108(2)
O(4)	5487(2)	−3336(3)	658(2)	73(1)
O(5)	6095(3)	−1115(3)	737(3)	106(2)
O(6)	5405(5)	−2046(5)	1743(2)	143(3)
Cl(2)	−964(1)	4606(1)	−2335(1)	56(1)
O(7)	−1969(2)	5104(4)	−2689(2)	96(1)
O(8)	−795(3)	4693(4)	−1500(2)	92(1)
O(9)	−767(5)	3276(4)	−2550(3)	149(3)
O(10)	−299(3)	5496(6)	−2616(3)	147(2)
O(1W)	1786(2)	5187(3)	−2494(2)	89(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

---

*Analyses were performed by Atlantic Microlabs, Inc., Norcross, GA, U.S.A.

in the cell. Hydrogen atoms on the water molecules were located in a difference Fourier synthesis, but their positions were not refined. Other hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å), while non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0485$, $R_w = 0.0701$, based on 3857 independent data with $I > 3\sigma(I)$. The final values of the atomic positional parameters, along with their estimated standard deviations, are presented in Table 2. See also 'Supplementary material'.

cis-Dichloro(N,N-bis((6-methylpyrid-2-yl)methyl)-N-2-pyridylmethylamine)manganese(II) (2)

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with four formula units in the cell. Hydrogen atoms were refined isotropically, while non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0370$, $R_w = 0.0372$, based on 3276 independent data with $I > 3\sigma(I)$. The final values of the atomic positional parameters, along with their estimated standard deviations, are presented in Table 3. See also 'Supplementary material'.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq}[a]
Mn	5417(1)	1279(1)	7365(1)	34(1)
Cl(1)	3508(1)	1881(1)	7456(1)	50(1)
Cl(2)	3529(1)	622(1)	6525(1)	52(1)
N(1A)	7182(3)	1249(1)	10408(3)	37(1)
N(1B)	7607(3)	854(1)	7450(3)	40(1)
C(1A)	7297(4)	912(1)	11496(3)	44(1)
N(1C)	5248(3)	1607(1)	4787(3)	41(1)
N(1D)	7635(3)	1806(1)	8123(3)	36(1)
C(6B)	9156(4)	1593(1)	8168(5)	49(1)
C(5B)	9050(3)	1080(1)	7836(3)	36(1)
C(7A)	8007(4)	1994(1)	9777(3)	45(1)
C(4B)	10442(4)	853(1)	7902(4)	49(1)
C(5C)	6172(3)	1994(1)	5099(3)	43(1)
C(1C)	4451(4)	1441(1)	3183(4)	50(1)
C(5A)	8267(3)	1606(1)	11010(3)	41(1)
C(2C)	4585(5)	1672(1)	1905(4)	57(2)
C(3C)	5530(5)	2062(2)	2231(4)	61(2)
C(2A)	8535(5)	932(1)	13187(4)	58(2)
C(7C)	6936(4)	2182(1)	6861(3)	43(1)
C(1B)	7529(4)	394(1)	7132(4)	55(2)
C(4C)	6370(4)	2229(1)	3862(4)	53(2)
C(4A)	9509(4)	1638(1)	12669(4)	59(1)
C(6A)	6090(6)	519(1)	10832(5)	64(2)
C(3B)	10341(4)	384(1)	7569(5)	66(2)
C(2B)	8861(5)	150(1)	7191(6)	68(2)
C(3A)	9648(5)	1291(2)	13780(4)	63(2)
C(6C)	3470(7)	1003(2)	2859(6)	78(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Description of the structures

cis-Diaqua(N,N'-bis(2-methylpyrazyl)ethane-1,2-diamine)manganese(II) perchlorate monohydrate (1)

The structure consists of *cis*-$[Mn(A)(OH_2)_2]^{2+}$ cations, perchlorate anions and water molecules. A view of the cation is given in Fig. 1. Principal distances and angles in the cation are listed in Tables 4 and 5, respectively.

The geometry about the manganese center is roughly octahedral, the ligating atoms being two water molecules and four nitrogen atoms from the tetradentate ligand. As can be seen in Fig. 1, the isomer isolated here is the *cis*-diaqua species, as indicated by the O(1)–Mn–O(2) bond angle of 93.9(1)°. The Mn–O bond lengths of 2.158(3) and 2.137(3) Å fall within the range of values observed for Mn–OH_2 bonds in other Mn(II) complexes [6–9]. The other possible formulation, as a dihydroxo species of manganese(IV) of the type Mn(IV)–$(OH)_2$, would

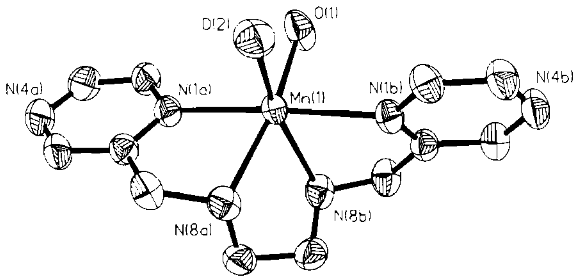

Fig. 1. View of the *cis*-$[Mn(bispyzen)(OH_2)_2]^{2+}$ cation in the crystals of $[Mn(bispyzen)(OH_2)_2](ClO_4)_2 \cdot H_2O$ (**1**). Hydrogen atoms are omitted for clarity.

TABLE 4. Bond lengths (Å) for **1**

Mn(1)–O(1)	2.158(3)	Mn(1)–O(2)	2.137(3)
Mn(1)–N(1A)	2.267(2)	Mn(1)–N(8A)	2.262(3)
Mn(1)–N(1B)	2.303(2)	Mn(1)–N(8B)	2.260(3)
N(1A)–C(2A)	1.320(4)	N(1A)–C(6A)	1.348(4)
N(4A)–C(3A)	1.330(4)	N(4A)–C(5A)	1.319(5)
N(8A)–C(7A)	1.472(3)	N(8A)–C(9A)	1.480(4)
N(1B)–C(2B)	1.335(4)	N(1B)–C(6B)	1.339(4)
N(4B)–C(3B)	1.331(5)	N(4B)–C(5B)	1.313(5)
N(8B)–C(7B)	1.461(4)	N(8B)–C(9B)	1.472(4)
C(2A)–C(3A)	1.385(4)	C(2A)–C(7A)	1.505(4)
C(5A)–C(6A)	1.371(4)	C(9A)–C(9B)	1.507(4)
C(2B)–C(3B)	1.391(4)	C(2B)–C(7B)	1.503(5)
C(5B)–C(6B)	1.382(4)	Cl(1)–O(3)	1.400(3)
Cl(1)–O(4)	1.424(3)	Cl(1)–O(5)	1.412(4)
Cl(1)–O(6)	1.389(4)	Cl(2)–O(7)	1.433(3)
Cl(2)–O(8)	1.424(3)	Cl(2)–O(9)	1.395(4)
Cl(2)–O(10)	1.410(5)		

TABLE 5. Bond angles (°) for **1**

O(1)–Mn(1)–O(2)	93.9(1)	O(1)–Mn(1)–N(1A)	93.4(1)
O(2)–Mn(1)–N(1A)	95.3(1)	O(1)–Mn(1)–N(8A)	165.9(1)
O(2)–Mn(1)–N(8A)	93.1(1)	N(1A)–Mn(1)–N(8A)	73.7(1)
O(1)–Mn(1)–N(1B)	88.8(1)	O(2)–Mn(1)–N(1B)	89.3(1)
N(1A)–Mn(1)–N(1B)	174.8(1)	N(8A)–Mn(1)–N(1B)	103.5(1)
O(1)–Mn(1)–N(8B)	99.2(1)	O(2)–Mn(1)–N(8B)	157.0(1)
N(1A)–Mn(1)–N(8B)	102.8(1)	N(8A)–Mn(1)–N(8B)	78.5(1)
N(1B)–Mn(1)–N(8B)	72.2(1)	Mn(1)–N(1A)–C(2A)	115.0(2)
Mn(1)–N(1A)–C(6A)	127.7(2)	C(2A)–N(1A)–C(6A)	117.2(2)
C(3A)–N(4A)–C(5A)	116.8(3)	Mn(1)–N(8A)–C(7A)	109.5(2)
Mn(1)–N(8A)–C(9A)	107.5(2)	C(7A)–N(8A)–C(9A)	113.1(2)
Mn(1)–N(1B)–C(2B)	113.9(2)	Mn(1)–N(1B)–C(6B)	127.4(2)
C(2B)–N(1B)–C(6B)	117.7(2)	C(3B)–N(4B)–C(5B)	117.2(3)
Mn(1)–N(8B)–C(7B)	110.7(2)	Mn(1)–N(8B)–C(9B)	106.8(2)
C(7B)–N(8B)–C(9B)	113.4(2)	N(1A)–C(2A)–C(3A)	120.7(3)
N(1A)–C(2A)–C(7A)	118.4(2)	C(3A)–C(2A)–C(7A)	120.9(3)
N(4A)–C(3A)–C(2A)	122.2(3)	N(4A)–C(5A)–C(6A)	121.8(3)
N(1A)–C(6A)–C(5A)	121.3(3)	N(8A)–C(7A)–C(2A)	110.5(2)
N(8A)–C(9A)–C(9B)	109.2(3)	N(1B)–C(2B)–C(3B)	120.4(3)
N(1B)–C(2B)–C(7B)	118.1(2)	C(3B)–C(2B)–C(7B)	121.5(3)
N(4B)–C(3B)–C(2B)	121.7(3)	N(4B)–C(5B)–C(6B)	122.4(3)
N(1B)–C(6B)–C(5B)	120.6(3)	N(8B)–C(7B)–C(2B)	110.9(2)
N(8B)–C(9B)–C(9A)	109.3(2)	O(3)–Cl(1)–O(4)	108.6(2)
O(3)–Cl(1)–O(5)	107.1(2)	O(4)–Cl(1)–O(5)	109.3(2)
O(3)–Cl(1)–O(6)	108.7(3)	O(4)–Cl(1)–O(6)	109.5(2)
O(5)–Cl(1)–O(6)	113.6(3)	O(7)–Cl(2)–O(8)	109.6(2)
O(7)–Cl(2)–O(9)	114.7(3)	O(8)–Cl(2)–O(9)	109.5(2)
O(7)–Cl(2)–O(10)	104.3(2)	O(8)–Cl(2)–O(10)	110.6(3)
O(9)–Cl(2)–O(10)	108.0(3)		

TABLE 6. Bond lengths (Å) for **2**

Mn–Cl(1)	2.467(1)	Mn–Cl(2)	2.402(1)
Mn–N(1A)	2.429(2)	Mn–N(1B)	2.285(3)
Mn–N(1C)	2.453(3)	Mn–N(1D)	2.329(2)
N(1A)–C(1A)	1.349(4)	N(1A)–C(5A)	1.336(4)
N(1B)–C(5B)	1.338(4)	N(1B)–C(1B)	1.346(4)
C(1A)–C(2A)	1.394(4)	C(1A)–C(6A)	1.479(5)
N(1C)–C(5C)	1.333(4)	N(1C)–C(1C)	1.359(4)
N(1D)–C(6B)	1.480(5)	N(1D)–C(7A)	1.470(4)
N(1D)–C(7C)	1.474(4)	C(6B)–C(5B)	1.498(4)
C(5B)–C(4B)	1.387(5)	C(7A)–C(5A)	1.513(4)
C(4B)–C(3B)	1.374(5)	C(5C)–C(7C)	1.501(4)
C(5C)–C(4C)	1.391(5)	C(1C)–C(2C)	1.389(6)
C(1C)–C(6C)	1.481(7)	C(5A)–C(4A)	1.376(4)
C(2C)–C(3C)	1.349(6)	C(3C)–C(4C)	1.381(5)
C(2A)–C(3A)	1.356(5)	C(1B)–C(2B)	1.366(6)
C(4A)–C(3A)	1.378(6)	C(3B)–C(2B)	1.378(6)

be predicted to exhibit significantly shorter Mn–O bond lengths; this is seen in the binuclear Mn(IV) cation $[L_2Mn_2(OH)_2(\mu\text{-}O)_2]^{2+}$, where the Mn(IV)–OH distance was 1.881(5) Å [10]. Also supportive of the formulation as a Mn(II) aqua complex is the location of two H atoms on each bonded oxygen at sensible distances and angles for coordinated water molecules.

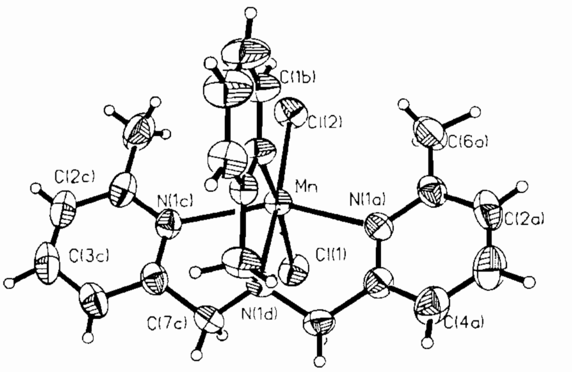

Fig. 2. View of *cis*-$[Mn(C_{20}H_{22}N_4)Cl_2]$ (**2**). Hydrogen atoms are omitted for clarity.

The *cis* N–Mn–N bond angles defined by the ligand chelate rings deviate significantly from 90°, the largest deviation being the N(1B)–Mn–N(8B) angle of 72.2(1)°. This same behavior was seen in the oxidized di-μ-oxodimanganese(III,III) complex containing this ligand [5]. The *trans* N–Mn–N angle is 174.8(1)°. As would be expected for a d^5 manganese(II) ion, there are no distortions among the Mn–N bond lengths (average = 2.273(20) Å).

There is extensive hydrogen bonding in the crystals, with all potential donor atoms participating except

TABLE 7. Bond angles (°) for 2

Cl(1)–Mn–Cl(2)	99.4(1)	Cl(1)–Mn–N(1A)	94.1(1)
Cl(2)–Mn–N(1A)	107.9(1)	Cl(1)–Mn–N(1B)	167.2(1)
Cl(2)–Mn–N(1B)	93.3(1)	N(1A)–Mn–N(1B)	82.1(1)
Cl(1)–Mn–N(1C)	92.1(1)	Cl(2)–Mn–N(1C)	106.9(1)
N(1A)–Mn–N(1C)	143.1(1)	N(1B)–Mn–N(1C)	83.9(1)
Cl(1)–Mn–N(1D)	92.6(1)	Cl(2)–Mn–N(1D)	168.0(1)
N(1A)–Mn–N(1D)	71.9(1)	N(1B)–Mn–N(1D)	74.7(1)
N(1C)–Mn–N(1D)	71.4(1)	Mn–N(1A)–C(1A)	129.1(2)
Mn–N(1A)–C(5A)	112.7(2)	C(1A)–N(1A)–C(5A)	118.0(2)
Mn–N(1B)–C(5B)	117.5(2)	Mn–N(1B)–C(1B)	124.2(2)
C(5B)–N(1B)–C(1B)	118.4(3)	N(1A)–C(1A)–C(2A)	120.8(3)
N(1A)–C(1A)–C(6A)	118.0(2)	C(2A)–C(1A)–C(6A)	121.2(3)
Mn–N(1C)–C(5C)	111.9(2)	Mn–N(1C)–C(1C)	129.8(2)
C(5C)–N(1C)–C(1C)	118.2(3)	Mn–N(1D)–C(6B)	112.8(2)
Mn–N(1D)–C(7A)	106.3(2)	C(6B)–N(1D)–C(7A)	111.7(2)
Mn–N(1D)–C(7C)	105.3(2)	C(6B)–N(1D)–C(7C)	111.5(3)
C(7A)–N(1D)–C(7C)	108.9(2)	N(1D)–C(6B)–C(5B)	115.7(3)
N(1B)–C(5B)–C(6B)	119.3(3)	N(1B)–C(5B)–C(4B)	121.7(3)
C(6B)–C(5B)–C(4B)	119.0(3)	N(1D)–C(7A)–C(5A)	111.1(2)
C(5B)–C(4B)–C(3B)	119.2(3)	N(1C)–C(5C)–C(7C)	116.4(3)
N(1C)–C(5C)–C(4C)	122.9(3)	C(7C)–C(5C)–C(4C)	120.6(3)
N(1C)–C(1C)–C(2C)	120.6(3)	N(1C)–C(1C)–C(6C)	117.9(3)
C(2C)–C(1C)–C(6C)	121.6(3)	N(1A)–C(5A)–C(7A)	116.1(2)
N(1A)–C(5A)–C(4A)	123.1(3)	C(7A)–C(5A)–C(4A)	120.7(3)
C(1C)–C(2C)–C(3C)	120.9(3)	C(2C)–C(3C)–C(4C)	119.0(4)
C(1A)–C(2A)–C(3A)	120.7(4)	N(1D)–C(7C)–C(5C)	111.4(2)
N(1B)–C(1B)–C(2B)	122.7(3)	C(5C)–C(4C)–C(3C)	118.3(3)
C(5A)–C(4A)–C(3A)	119.2(3)	C(4B)–C(3B)–C(2B)	119.1(4)
C(1B)–C(2B)–C(3B)	118.9(4)	C(2A)–C(3A)–C(4A)	118.2(3)

hydrogen atom H(11) on coordinated water molecule O(1). It is noteworthy that the pyrazine N(4) nitrogen atoms act as hydrogen bond acceptors; atom N(4A) forms a hydrogen bond to the uncoordinated water molecule with OW(1)···N(4A) and H(1W1)···N(4A) distances of 2.785(4) and 2.01 Å and associated OW(1)–H(1W1)···N(4A) angle of 152°, while N(4B) forms a hydrogen bond to the coordinated water molecule O(1) with O(1)···N(4B) and H(12)···N(4B) distances of 2.820(4) and 2.17 Å and associated O(1)–H(12)···N(4B) angle of 162°. In addition, as expected, several perchlorate oxygen atoms and the uncoordinated water molecule participate in hydrogen bonding. See also'Supplementary material'.

cis-Dichloro(N,N-bis((6-methylpyrid-2-yl)methyl)-N-2-pyridylmethylamine)manganese(II) (2)

The structure consists of *cis*-[Mn(A)Cl_2] molecules. A view of the molecule is given in Fig. 2. Principal distances and angles in the cation are listed in Tables 6 and 7, respectively.

The geometry about the manganese center is roughly octahedral, the ligating atoms being two chloride ligands and four nitrogen atoms from the tetradentate ligand. As can be seen in Fig. 2, the isomer isolated here is the *cis*-dichloro species, as indicated by the Cl(1)–Mn–Cl(2) bond angle of 99.4(1)°. The structure can be compared to those of *cis*-[Mn(bpy)$_2$Cl$_2$] [11] and *cis*-[Mn($C_{12}H_{22}N_6$)Cl_2] [12], in which the Cl–Mn–Cl bond angles are 100.7(5) and 105.6(1)°, respectively. The Mn–Cl bond lengths of 2.467(1) and 2.402(1) Å are again comparable to those of 2.392(1) to 2.449(1) Å in these related structures [11, 12].

The Mn–N bond lengths fall into two distinct groups. The axial Mn–N bond lengths are 2.423(2) and 2.456(3) Å while the equatorial values are 2.285(3) and 2.329(3) Å. These equatorial values are consistent with the values of 2.286(8) to 2.353(3) Å reported for similar complexes [11, 13, 14]. The observed elongation of the axial bond lengths is presumably due to the steric crowding at manganese caused by the presence of the 6-methyl groups on the axial pyridine ligands; a similar result was observed in the related di-μ-oxodimanganese(III,III) complex with this ligand, in which the axial Mn–N bond lengths were 2.353(8) and 2.386(8) Å [5]. In the unsubstituted [Mn(bpy)$_2$Cl$_2$], the axial bond lengths of 2.276(3) and 2.264(3) were slightly shorter than the equatorial values [11].

Electrochemistry

Complex **1** shows no reversible electrochemistry in the range 0 to +2.0 V versus Ag/AgCl. This observation is consistent with the behavior of the di-μ-oxodimanganese(III,III) complex of this ligand, which also shows no reversible redox couples in the cyclic voltammogram over this range [5]. Complex **2** shows a quasi-reversible redox couple at 0.80 V versus Ag/AgCl corresponding to the Mn(II)$\leftrightarrow$Mn(III) couple. This potential is much higher than the values of 0.150 and 0.186 V which we recently reported for some monomeric manganese Schiff base complexes [15], and presumably explains the stability of the present manganese(II) complex towards oxidation in aqueous solution by hydrogen peroxide.

Supplementary material

Hydrogen atom parameters, observed and calculated structure amplitudes and anisotropic thermal motion parameters for **1** and **2**, and a complete tabulation of the probable hydrogen bonding interactions in **1**, are available from the authors on request.

Acknowledgements

This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, through grant No. 19457-AC3, and by the National Science Foundation through grant No. CHE-8912675.

References

1 D. J. Hodgson, K. Michelsen, E. Pedersen and D. K. Towle, *J. Chem. Soc., Chem. Commun.*, (1988) 428.

2 D. J. Hodgson, K. Michelsen and E. Pedersen, *J. Chem. Soc., Chem. Commun.*, (1988) 1558.

3 K. M. Corbin, D. J. Hodgson, M. H. Lynn, K. Michelsen, K. M. Nielsen and E. Pedersen, *Inorg. Chim. Acta, 159* (1989) 129.

4 S. Müller and U. Thewalt, *Z. Naturforsch., Teil B, 44* (1989) 257.

5 P. A. Goodson, A. R. Oki, J. Glerup and D. J. Hodgson, *J. Am. Chem., Soc., 112* (1990) 6248, and refs. therein.

6 N. Nakasuka, S. Azuma, C. Katayama, M. Honda, J. Tanaka and M. Tanaka, *Acta Crystallogr., Sect. C, 41* (1985) 1176.

7 H. Tamura, K. Ogawa, T. Sakurai and A. Nakahara, *Inorg. Chim. Acta, 92* (1984) 107.

8 K. Wieghardt, U. Bossek, B. Nuber and J. Weiss, *Inorg. Chim. Acta, 126* (1987) 39.

9 L. C. Nathan, C. A. Doyle, A. M. Mooring, D. C. Zapien, S. K. Larsen and C. G. Pierpont, *Inorg. Chem., 24* (1985) 2763.

10 K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols and J. J. Girerd, *J. Am. Chem. Soc., 110* (1988) 7398.

11 P. O. Lumme and E. Lindell, *Acta Crystallogr., Sect. C, 44* (1988) 463.

12 P. Stolz, W. Saak, H. Strasdeit and S. Pohl, *Z. Naturforsch., Teil B, 44* (1989) 632.

13 M. V. Veidis, B. Dockum, F. F. Charron, W. M. Reif and T. F. Brennan, *Inorg. Chim. Acta, 53* (1981) L197.

14 T. J. R. Weakley, *Acta Crystallogr., Sect. B, 34* (1978) 281.

15 A. R. Oki and D. J. Hodgson, *Inorg. Chim. Acta, 170* (1990) 65.