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SYNTHESIS AND CHARACTERIZATION OF MONOMERIC AND DIMERIC MANGANESE(II) AND ZINC(II) COMPLEXES OF PYRIDINE-2-CARBALDOXIME

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ABSTRACT. The syntheses and characterization of two complexes of manganese(II) and one complex of zinc(II) with the ligand pyridine-2-carbaldoxime, $C_6H_5N_2O$, are described. The monomeric manganese(II) complex *cis*-[Mn($C_6H_6N_2O)_2Cl_2$] (**1**) crystallizes in the orthorhombic space group *Pbcn* with 4 formula units in a cell of dimensions a = 12.479(3) Å, b = 10.348(2) Å, and c = 11. 974(2) Å. The structure has been refined to a final value of the conventional *R*-factor of 0.0330 based on 1513 observed independent reflections. The analogous zinc(II) complex, *cis*-[Zn($C_6H_6N_2O)_2Cl_2$] (**2**) also crystallizes in the orthorhombic space group *Pbcn* with 4 formula units in a cell of dimensions a = 12.215(2) Å, b = 10.383(2) Å, and c = 12. 016(2) Å. The structure has been refined to a final value of the conventional *R*-factor of 0.0377 based on 1117 observed independent reflections. The two complexes are isostructural, with the central metal atom lying on a crystallographic 2-fold axis. Both complexes are approximately octahedral, the coordination being provided by two *trans* pyridine nitrogen atoms and two *cis* amine nitrogen atoms from the oxime ligands, and by two *cis* chlorides. The dimeric manganese(II) complex [($C_6H_5N_2O$)(CH_3OH)ClMnCl_2MnCl(CH_3OH)($C_6H_6N_2O$)] (**3**) crystallizes in the monoclinic space group $P2_1/n$ with 2 formula units in a cell of dimensions a = 7.895(2) Å, b = 11.196(3) Å, and c = 12. 544(2) Å, and β = 98.39(2)°. The structure has been refined to a final value of the conventional *R*-factor of 0.0312 based on 1568 observed independent reflections. There is a crystallographic inversion center in the middle of the dimer relating one manganese center to the other. The geometry at each manganese(II) center is again roughly octahedral, coordination being provided by two nitrogen atoms from the oxime ligand, a terminal chloride ion *trans* to the amine nitrogen, the oxygen atom of the coordinated methanol molecule, and two bridging chlorides that link the two halves of the dimer. The Mn···Mn separation is 3.647(1) Å and the bridging Mn-Cl-Mn angle is 91.8(1)°. The temperature dependence of the magnetic susceptibility of **3** exhibits a maximum at approximately 8 K, indicative of a weak antiferromagnetic interaction between the two metal centers with J = 1.94(1) cm^{-1}. The EPR spectrum of **1** diluted into the corresponding Zn(II) host has been fitted to the parameters g = 2.00, A = 0.0084 cm^{-1}, D = 0.157 cm^{-1}, and E = 0.0005 cm^{-1}. The small value of E/D is consistent with the observed symmetry of the complex.

INTRODUCTION

We and others have long been interested in the relationships between molecular structure, on the one hand, and magnetic susceptibility, NMR and EPR spectroscopy on the other. The EPR spectra of crystalline complexes present the special consideration that the measurement generally requires the existence (and complete characterization) of a diamagnetic host with similar structure, size, and metallic sites as found in the paramagnetic complex. In the case of manganese(II) complexes, we have had some success in preparing and characterizing zinc(II) or cadmium(II) analogues for this purpose. We have, however, found that interpretation of the

spectra requires the complete structural characterization of both the paramagnetic
diamagnetic species because of the existence of several possible geometric isomers [1]. For s
of complexes, however, we have been able to demonstrate that in favorable circumstance
NMR spectra are of value in distinguishing between the various isomers in the diamag
species [1]. Similarly, it has long been known that the interpretation of the magnetic suscepti
data of magnetically coupled systems can only be accomplished in the light of their struct

Our previous work in these arenas has been confined to complexes with tridenta
tetradentate ligands. We here extend these concepts to complexes with asymmetric bide
ligands. A difficulty here is that there are very few known complexes of the type *cis*-[Mn(L)
or in general *cis*-$[Mn(L)_2X_2]$, for comparison. We here report the syntheses and characteriz
of three complexes of the bidentate ligand pyridine-2-carbaldoxime, $C_6H_6N_2O$, represent
manganese(II) monomer, its zinc(II) analogue, and a di-µ-chlorodimanganese(II) complex
complexes studied are *cis*-dichlorobis(pyridine-2-carbaldoximato)manganese[II],
$[Mn(C_6H_6N_2O)_2Cl_2]$ (**1**), its zinc(II) analogue (**2**), and di-µ-chloro-bis(chloromethanolato(pyri
2-carbaldoximato))dimanganese(II), $[(C_6H_6N_2O)(CH_3OH)ClMnCl_2MnCl(CH_3OH)(C_6H_6N_2O)$
The crystal structures of all three complexes have been determined, as have the EPR spect
1 doped into **2**, the ^{13}C NMR spectrum of **2**, and the temperature dependence of the mag
susceptibility of **3**.

EXPERIMENTAL

Syntheses. Pyridine-2-carbaldoxime was purchased from Fluka, AG and used without fu
purification.

Cis-dichlorobis(pyridine-2-carbaldoximato)manganese(II), $[Mn^{II}(C_6H_6N_2O)_2Cl_2]$ (1).
Manganese(II) chloride tetrahydrate (0.197 g, 1.00 mmol) and pyridine-2-carbaldoxime (0
g, 2.00 mmol) were dissolved in ethanol (99%, 5 mL). The solution was allowed to stand i
After several days, the compact yellow crystals that had separated were filtered off and wa
with ethanol (99%). Yield: 0.227 g (61%). Anal. calcd. for $[Mn(C_6H_6N_2O)_2Cl_2]$: Mn, 14.8
38.94; N, 15.14; H, 3.27; Cl, 19.16. Found: Mn, 14.62; C, 38.98; N, 15.22; H, 3.28; Cl, 1

Cis-dichlorobis(pyridine-2-carbaldoximato)zinc(II), $[Zn^{II}(C_6H_6N_2O)_2Cl_2]$ (2). This complex
synthesized in the manner described above for **1**, but with zinc(II) chloride (0.136 g, 1.00 m
in place of manganese chloride. After two days, the white crystals that had separated were fil
and washed as above, and recrystallized from hot ethanol to give large single crystals. Y
0.290 g (76%). Anal. calcd. for $[Zn(C_6H_6N_2O)_2Cl_2]$: C, 37.88; N, 14.72; H, 3.18; Cl, 1
Found: C, 37.69; N, 14.64; H, 3.18; Cl, 18.80.

Di-µ-chloro-bis(chloromethanolato(pyridine-2-carbaldoximato))dimanganese(II),
$[(C_6H_6N_2O)(CH_3OH)ClMnCl_2MnCl(CH_3OH)(C_6H_6N_2O)]$ (3). *Cis*-dichlorobis(pyridi
carbaldoximato)manganese(II) (0.240 g, 0.648 mmol) was refluxed for 6 h in methanol (75
The light yellow crystals that separated after partial evaporation were washed with metha
Yield: 0.110 g (39%). Anal. calcd. for $[Mn\,(C_6H_6N_2O)(CH_3OH)Cl_2]_2$: C, 30.03; N, 10.00; H,
Cl, 25.32. Found: C, 29.84; N, 10.05; H, 3.54; Cl, 25.43.

Solid solutions of **1** in **2** were made following the synthetic procedure described abov
2, but replacing small amounts of the zinc chloride with manganese(II) chloride tetrahydr

Analyses. The metal analysis was performed on a Perkin-Elmer 403 Atomic Absorption spectrophotometer. Carbon, hydrogen, nitrogen, and chlorine analyses were performed at the microanalytical laboratory of the H.C. Ørsted Institute using standard methods.

Physical measurements. ^{13}C NMR spectra were recorded on solid samples at room temperature on a Bruker MSL 300 spectrometer. EPR spectra were recorded on solid samples at several temperatures down to liquid nitrogen temperature on a Bruker ESP 300 spectrometer operating at X-band (9.38 GHz) with magnetic field modulation of 100 kHz, modulation amplitude of 5 G and microwave power of 20 mW. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 2-300 K at a field strength of 1.3 T. The susceptibility data were corrected for diamagnetism using Pascal's constants. The magnetic field was calibrated with $Hg[Co(NCS)_4]$.

X-ray structure determinations. The structures of the complexes **1**, **2**, and **3** were determined at room temperature on a Siemens P3 diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1)$ = 0.70926 Å; $\lambda(K\alpha_2)$ = 0.71354 Å] and a graphite monochromator. The data were corrected for absorption using semi-empirical techniques *via* psi scans. The structures were solved by direct methods and refined by full-matrix least-squares techniques using structure solution programs from the SHELXTL system [2]. Crystal data and experimental parameters are listed in Table 1.

Table 1. Crystallographic and data collection parameters.

Complex	1	2	3
Formula	$C_{12}H_{12}Cl_2MnN_4O_2$	$C_{12}H_{12}Cl_2ZnN_4O_2$	$C_{14}H_{20}Cl_4Mn_2N_4O_4$
System	Orthorhombic	Orthorhombic	Monoclinic
Space Group	*Pbcn*	*Pbcn*	$P2_1/n$
a (Å)	12.479 (3)	12.215 (2)	7.895 (2)
b (Å)	10.348 (2)	10.383 (2)	11.196 (3)
c (Å)	11.974 (2)	12.016 (2)	12.544 (2)
β (deg.)	90	90	98.39 (2)
V (Å^3)	1546.2 (6)	1524.0 (5)	1097.0 (4)
Z	4	4	2
μ (mm^{-1})	1.176	1.970	1.625
Index ranges	$-17 \leq h \leq 0$ $-14 \leq k \leq 0$ $0 \leq \ell \leq 16$	$0 \leq h \leq 15$ $0 \leq k \leq 13$ $0 \leq \ell \leq 15$	$-10 \leq h \leq 0$ $0 \leq k \leq 14$ $-16 \leq \ell \leq 16$
2θ range (deg.)	$4.0 \leq 2\theta \leq 60.0$	$4.0 \leq 2\theta \leq 55.0$	$4.0 \leq 2\theta \leq 55.0$
No. of reflections	2276	1750	2530
Observed reflections	1513	1117	1568
R (observed data)	0.0330	0.0377	0.0312
R_w (observed data)	0.0428	0.0470	0.0332
R (all data)	0.0540	0.0676	0.0644
R_w (all data)	0.0513	0.0641	0.0393
Goodness of fit	1.27	1.24	1.20

Cis-dichlorobis(pyridine-2-carbaldoximato)manganese(II), $[\mathrm{Mn^{II}(C_6H_6N_2O)_2Cl_2}]$ *(1).* The complex crystallizes in the centrosymmetric orthorhombic space group *Pbcn* with four molecules in the cell. A total of 2276 independent reflections was measured in the range $4^\circ \le 2\theta \le 60^\circ$, with the data gathered having $-17 \le h \le 0$, $-14 \le k \le 0$, $0 \le \ell \le 16$. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were included in calculated positions using a riding model and fixed isotropic displacement coefficients, while the hydrogen atom attached to oxygen was located in a difference Fourier map. The final values of the conventional and weighted *R* factors (on F) were $R1 = 0.0331$, and $wR2 = 0.0428$, based on 1513 observed independent intensities with $F \ge 6.0\ \sigma(F)$. The positional parameters are listed in Table 2.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for complex **1**.

Atom	x	y	z	U(eq)*
Mn(1)	5000	18(1)	7500	29(1)
Cl(1)	4284(1)	1502(1)	6068(1)	41(1)
N(1)	6626(1)	-208(2)	6689(2)	32(1)
N(2)	5895(1)	-1715(2)	8342(2)	34(1)
C(2)	7035(2)	614(3)	5941(2)	40(1)
C(3)	8108(2)	621(3)	5634(2)	49(1)
C(4)	8782(2)	-273(3)	6118(3)	54(1)
C(5)	8368(2)	-1143(3)	6879(2)	47(1)
C(6)	7291(2)	-1083(2)	7139(2)	33(1)
C(7)	6823(2)	-1970(2)	7963(2)	37(1)
O(1)	5542(1)	-2640(2)	9096(2)	48(1)

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

Cis-dichlorobis(pyridine-2-carbaldoximato)zinc(II), $[\mathrm{Zn^{II}(C_6H_6N_2O)_2Cl_2}]$ *(2).* The complex is isomorphous with the corresponding manganese crystals (**1**) above, crystallizing in the centrosymmetric orthorhombic space group *Pbcn* with four molecules in the cell. A total of 1750 independent reflections was measured in the range $4^\circ \le 2\theta \le 55^\circ$, with the data gathered having $0 \le h \le 15$, $0 \le k \le 13$, $0 \le \ell \le 15$. The refinement was performed as above for (**1**). The final values of the conventional and weighted *R* factors (on F) were $R1 = 0.0377$, and $wR2 = 0.0470$, based on 1117 observed independent intensities with $F \ge 6.0\ \sigma(F)$. The positional parameters are listed in Table 3.

Di-μ-chloro-bis(chloromethanolato(pyridine-2-carbaldoximato))dimanganese(II), $[\mathrm{(C_6H_6N_2O)(CH_3OH)ClMnCl_2MnCl(CH_3OH)(C_6H_6N_2O)}]$ *(3).* The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with two binuclear formula units in the cell. A total of 2530 independent reflections was measured in the range $4^\circ \le 2\theta \le 55^\circ$, with the data gathered having $-10 \le h \le 0$, $0 \le k \le 14$, $-16 \le \ell \le 16$. The refinement was performed as above for (**1**). The final values of the conventional and weighted *R* factors (on F) were $R1 = 0.0312$, and $wR2 = 0.0332$, based on 1568 observed independent intensities with $F \ge 6.0\ \sigma(F)$. The positional parameters are listed in Table 4.

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement coefficients (Å^2 x 10^3) for complex **2**.

Atom	x	Y	z	U(eq)*
Zn	5000	17 (1)	2500	29 (1)
Cl(1)	4247 (1)	1466 (1)	1139 (1)	38 (1)
N(1)	6555 (2)	-212 (3)	1710 (2)	29 (1)
N(2)	5835 (2)	-1691 (3)	3364 (2)	31 (1)
O(1)	5447 (2)	-2583 (3)	4126 (2)	44 (1)
C(2)	6965 (3)	600 (4)	953 (3)	37 (1)
C(3)	8046 (3)	580 (4)	629 (4)	46 (1)
C(4)	8734 (3)	-309 (4)	1088 (4)	50 (1)
C(5)	8327 (3)	-1176 (4)	1847 (3)	44 (1)
C(6)	7232 (3)	-11 03 (3)	2133 (3)	31 (1)
C(7)	6757 (3)	-1974 (4)	2973 (3)	35 (1)

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

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement coefficients (Å^2 x 10^3) for complex **3**.

Atom	x	Y	z	U(eq)*
Mn	1704 (1)	1113 (1)	5152 (1)	27 (1)
Cl(1)	1405 (1)	-988 (1)	5794 (1)	36 (1)
Cl(2)	2849 (1)	854 (1)	3462 (1)	39 (1)
O(1)	4293 (3)	1096 (2)	6162 (2)	42 (1)
N(1)	1931 (3)	3133 (2)	5189 (2)	30 (1)
N(2)	628 (3)	1811 (2)	6636 (2)	32 (1)
C(2)	1517 (4)	3675 (3)	6081 (3)	30 (1)
C(3)	1719 (5)	4890 (3)	6246 (3)	40 (1)
C(4)	2332 (5)	5569 (3)	5469 (3)	48 (1)
C(5)	2732 (5)	5023 (3)	4555 (3)	44 (1)
C(6)	2525 (5)	3800 (3)	4453 (3)	36 (1)
C(7)	811 (4)	2910 (3)	6854 (3)	35 (1)
O(6)	-89 (3)	1177 (2)	7408 (2)	44 (1)
C(1)	5438 (6)	2045 (4)	6442 (5)	80 (1)

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

RESULTS AND DISCUSSION

Description of the structures

Cis-dichlorobis(pyridine-2-carbaldoximato)manganese(II). $[Mn^{II}(C_6H_6N_2O)_2Cl_2]$ *(1).* The structure consists of monomeric $[Mn^{II}(C_6H_6N_2O)_2Cl_2]$ units that are well separated from each other. A view of the complex is provided in Figure 1. Principal bond lengths and angles are compared with those in complex (**2**) in Tables 5 and 6.

With four molecules *per* cell in this centrosymmetric orthorhombic space group, the complex is constrained to exhibit crystallographic symmetry. In the present case, the manganese atoms lie on a crystallographic two-fold axis. The geometry at manganese is approximately octahedr with ligation from the pyridine and amine nitrogen atoms of two ligands, and by two c chlorides. Using the notation developed for complexes with tetradentate ligands [3], the isom isolated here can be described as the *cis-α* isomer in which the pyridine nitrogen atoms are *tra* while the amine nitrogen atoms are mutually *cis* and are *trans* to the chlorides. The isomer sho in Figure 1 (and for the zinc analogue in Figure 2) exhibits the Λ configuration about the cent metal ion [4], and could be described as Λ-*cis*-α-[$\text{Mn}^{\text{II}}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2\text{Cl}_2$]. In this centrosymmet space group, however, there are an equal number of Δ isomers.

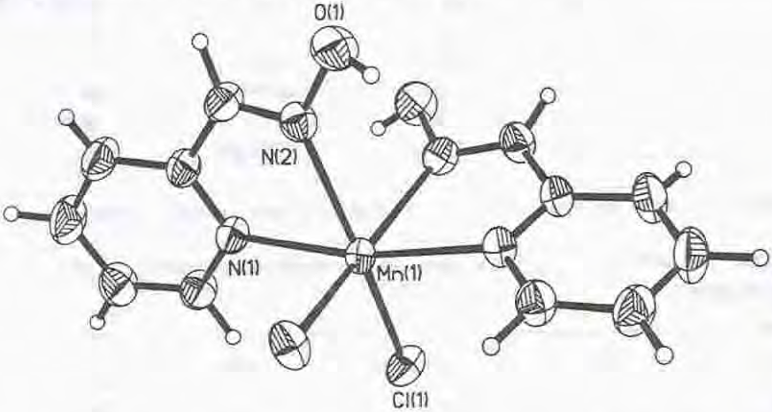

Figure 1. View of a single molecule of [$\text{Mn}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2\text{Cl}_2$], (**1**). Both here and in the follow figure, the molecule shown exhibits the Λ configuration about the central metal i but in this centrosymmetric space group there are an equal number of Δ isomers

Table 5. Selected bond lengths (Å) in complexes **1** and **2**.

Atoms	Distance (M = Mn)	Distance (M = Zn)	Atoms	Distance (M = Mn)	Distance (M = Zn)
M(l)-Cl(l)	2.469 (1)	2.406 (1)	M(l)-N(l)	2.262 (2)	2.137 (3)
M(l)-N(2)	2.341 (2)	2.294 (3)	N(l)-C(2)	1.337 (5)	1.337 (5)
N(l)-C(6)	1.341 (3)	1.340 (4)	N(2)-C(7)	1.271 (3)	1.256 (4)
N(2)-O(1)	1.388 (3)	1.385 (4)	C(2)-C(3)	1.390 (3)	1.377 (5)
C(3)-C(4)	1.378 (4)	1.364 (6)	C(4)-C(5)	1.382 (4)	1.374 (6)
C(5)-C(6)	1.380 (3)	1.383 (5)	C(6)-C(7)	1.469 (3)	1.475 (5)

Table 6. Selected bond angles (degrees) in complexes **1** and **2**.

Atoms	Angle (M = Mn)	Angle (M = Zn)	Atoms	Angle (M = Mn)	Angle (M = Zn)
Cl(l)-M-N(l)	95.2(1)	96.2(l)	Cl(l)-M-N(2)	161.5(1)	164.0(1)
N(l)-M-N(2)	71.2(1)	73.7(l)	Cl(l)-M-Cl(1A)	103.1(1)	102.6(1)
N(l)-M-Cl(lA)	92.2(1)	91.8(l)	N(2)-M-Cl(lA)	90.3 (1)	90.3(1)
N(l)-M-N(lA)	168.1(1)	167.2(2)	N(2)-M-N(1A)	99.4(1)	96.2(1)
N(2)-M-N(2A)	80.0(1)	78.7(l)	M-N(l)-C(2)	124.3(1)	124.4(2)
M-N(l)-C(6)	116.9(1)	117.2(2)	M-N(2)-O(1)	131.1(1)	131.6(2)
M N(2)-C(7)	116.1(2)	114.2(2)			

As was noted above, there are few examples of structurally characterized complexes of the type *cis*-$[Mn(L)_2Cl_2]$ (where L is a bidentate ligand) or *cis*-$[Mn(L)Cl_2]$ (where L is a tetradentate ligand); the notable exceptions to this statement include $[Mn(bpy)_2Cl_2]$ [5], (where bpy is 2,2'-bipyridine), $[Mn(C_{12}H_{22}N_6)Cl_2]$ (where the ligand is the cyclic hexamine 2,5,8,10,13,16-hexaazapentacyclo[8.6.1.1^{2,5}.0^{9,18}.0^{13,17}]octadecane [6] and $[Mn(C_{20}H_{22}N_4)Cl_2]$, where the ligand is the tetradentate N,N-bis((6-methylpyrid-2-yl)methyl)-N-2-pyridylmethylamine [7]. A number of other complexes have been synthesized, however [8]. The bond distances observed here for **1** are typical for manganese(II), with Mn-N (pyridine) distances of 2.262 (2) Å, Mn-N (amine) distances of 2.341 (2) Å, and Mn-Cl lengths of 2.469(1) Å. These values are all comparable to those reported for a number of related manganese(II) complexes, in which it is commonly observed that the Mn-N (pyridine) bonds are shorter than Mn-N (amine) bonds [1, 9-13]. The principal deviation from octahedral geometry is brought about by the constraint of the five-membered ring, the N(1)-Mn-N(2) bite angle being 71.2 (1)°.

Cis-dichlorobis(pyridine-2-carbaldoximato)zinc(II), $[Zn^{II}(C_6H_6N_2O)_2Cl_2]$ *(2).* As noted above, the crystals of the zinc complex are isomorphous with those of the manganese complex (**1**), and consequently the two structures are very similar. Like that of (**1**), the structure of (**2**) consists of monomeric $[Zn^{II}(C_6H_6N_2O)_2Cl_2]$ units that are well separated from each other. A view of the complex is provided in Figure 2. In order to demonstrate the structural similarity of the two complexes, the view chosen in Figure 2 is the same as that used in Figure 1 (above). Principal bond lengths and angles are compared with those in complex (**1**) in Tables 5 and 6. The bite angle of 73.7 (1)° in the zinc complex is slightly larger than that of 71.2 (1)° in (**1**).

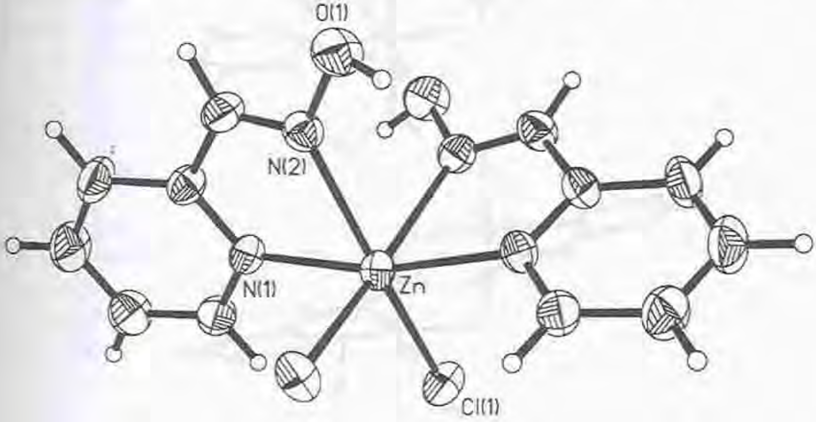

Figure 2. View of a single molecule of $[Zn(C_6H_6N_2O)_2Cl_2]$. (**2**).

Di-µ-chloro-bis(chloromethanolato(pyridine-2-carbaldoximato))dimanganese(II), $[(C_6H_6N_2O)(CH_3OH)ClMnCl_2MnCl(CH_3OH)(C_6H_6N_2O)]$ *(3).* The structure consists of binuclear $[(C_6H_6N_2O)(CH_3OH)ClMnCl_2MnCl(CH_3OH)(C_6H_6N_2O)]$ units that form relatively strong hydrogen bonds to neighboring dimers. A view of a single binuclear unit is presented as Figure 3, and the hydrogen bonding is depicted in Figure 4. Principal bond lengths and angles are listed in Table 7.

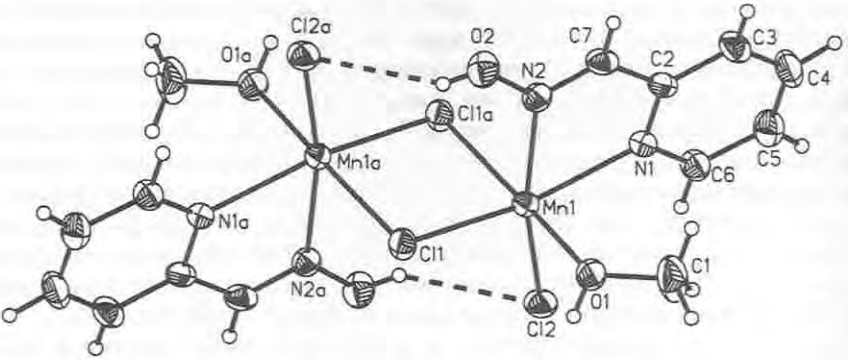

Figure 3. A single molecule of $[(C_6H_6N_2O)(CH_3OH)ClMnCl_2MnCl(CH_3OH)(C_6H_6N_2O)$
the crystals of complex (**3**), showing the intramolecular Cl(2)···H-O(2) hydro
bonding.

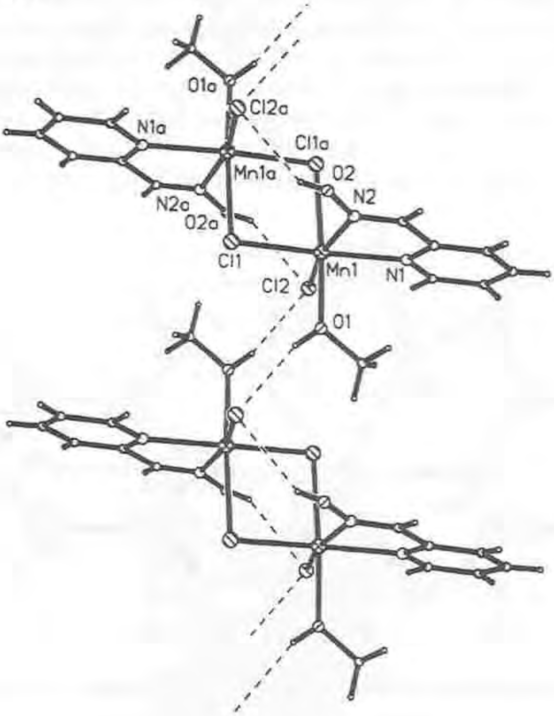

Figure 4. The hydrogen bonding scheme in complex **3**. The binuclear units are linke
chains along the crystallographic *a* axis by centrosymmetric pairs of Cl(2)···H-
hydrogen bonds involving the terminal chloride ligand of one unit and the met
oxygen atom of an adjacent molecule. In addition to the chloride bridge
binuclear units are also joined by centrosymmetric pairs of intramolecular Cl(2
O(2) hydrogen bonds involving the terminal chloride ligand of one half of the
and the oxime oxygen atom of the other half.

Table 7. Selected bond lengths (Å) and bond angles (degrees) in complex 3.

Bond lengths			
Atoms	Distance	Atoms	Distance
Mn(1)-Cl(1)	2.510 (1)	Mn(1)-Cl(2)	2.440 (1)
Mn(1)-O(1)	2.242 (2)	Mn(1)-N(1)	2.268 (3)
Mn(1)-N(2)	2.294 (3)	Mn(1)-Cl(1A)	2.569 (1)
Cl(1)-Mn(1A)	2.569 (1)	O(1)-C(1)	1.406 (5)
N(1)-C(2)	1.355 (4)	N(1)-C(6)	1.325 (5)
N(2)-C(7)	1.264 (4)	N(2)-O(2)	1.386 (4)
C(2)-C(3)	1.382 (5)	C(2)-C(7)	1.464 (5)
C(3)-C(4)	1.378 (6)	C(4)-C(5)	1.376 (6)
C(5)-C(6)	1.383 (5)		
Bond angles			
Atoms	Angles	Atoms	Angles
Cl(1)-Mn(1)-Cl(2)	103.4(1)	Cl(1)-Mn(1)-O(1)	86.0(1)
Cl(2)-Mn(1)-O(1)	93.9(1)	Cl(1)-Mn(1)-N(1)	159.9(1)
Cl(2)-Mn(1)-N(1)	95.6(1)	O(1)-Mn(1)-N(1)	86.2(1)
Cl(1)-Mn(1)-N(2)	89.7(1)	Cl(2)-Mn(1)-N(2)	166.9(1)
O(1)-Mn(1)-N(2)	87.7(1)	N(1)-Mn(1)-N(2)	71.4(1)
Cl(1)-Mn(1)-Cl(1A)	88.2(1)	Cl(2)-Mn(1)-Cl(1A)	92.4(1)
O(1)-Mn(1)-Cl(1A)	172.3(1)	N(1)-Mn(1)-Cl(1A)	97.5(1)
N(2)-Mn(1)-Cl(1A)	87.2(1)	Mn(1)-Cl(1)-Mn(1A)	91.8(1)
Mn(1)-O(1)-C(1)	129.4(2)	Mn(1)-N(1)-C(2)	115.8(2)
Mn(1)-N(1)-C(6)	125.6(2)	C(2)-N(1)-C(6)	118.4(3)
Mn(1)-N(2)-C(7)	117.6(2)	Mn(1)-N(2)-O(2)	129.0(2)
C(7)-N(2)-O(2)	113.2(3)	N(1)-C(2)-C(3)	121.9(3)
N(1)-C(2)-C(7)	116.5(3)	C(3)-C(2)-C(7)	121.6(3)
C(2)-C(3)-C(4)	118.8(4)	C(3)-C(4)-C(5)	119.4(4)
C(4)-C(5)-C(6)	118.6(4)	N(1)-C(6)-C(5)	122.8(3)
N(2)-C(7)-C(2)	118.0(3)		

With two formula units *per* cell in this centrosymmetric monoclinic space group, the complex is again constrained to exhibit crystallographic symmetry. In the present case, there is a crystallographic inversion center in the middle of the dimer, relating one half to the other. The geometry at manganese is again approximately octahedral, with ligation from the pyridine and amine nitrogen atoms of the ligand, by the terminal chloride ligand and methanol oxygen atom, and by two bridging chloride ligands. As can be seen in Figure 3, the isomer isolated here is the one in which the amine nitrogen atom is *trans* to the terminal chloride ligand. The terminal bond lengths are again unremarkable and comparable to those in (**1**), the Mn-N (pyridine) length of 2.268 (3) Å again being slightly shorter than the Mn-N (amine) distance of 2.294 (3) Å. The Mn-Cl(2) distance of 2.440 (1) Å involving the terminal chloride ligand is substantially similar to that of 2.469(1) Å in (**1**). The methanol molecule is tightly bound, with an associated Mn-O separation of 2.242 (2) Å [14, 15]. The chelate bite angle of 71.4 (1)° is again very similar to that of 71.2 (1)° observed in (**1**) above.

The Mn_2Cl_2 bridging framework is rigorously planar by symmetry. The bridging Mn-Cl(1) bond lengths of 2.510 (1) Å, Mn···Mn separation of 3.647 (1) Å and associated Mn-Cl-Mn = bridging angle of 91.8 (1)° are consistent with the range observed in previous examples of di-μ-chlorodimanganese(II) complexes [16-20].

As is shown in Figure 4, the binuclear units are linked into chains by centrosymmetric pairs of Cl(2)···H-O(1) hydrogen bonds involving the terminal chloride ligand of one unit and the methanol oxygen atom of an adjacent molecule. The Cl(2)···O(1) and Cl(2)···H(1) distances of 3.125 (1) Å and 2.371 Å and associated Cl(2)···H(1)-O(1) angle of 159° are all consistent with strong hydrogen bonding [21]. As is also shown in Figure 4, in addition to the chloride bridges the dimeric units are also linked by pairs of Cl(2)···H-O(2) hydrogen bonds involving the terminal chloride ligand of one half of the dimer and the oxime oxygen atom of the other half, with Cl(2)···O(2) and Cl(2)···H(2) distances of 3.227 (1) Å and 2.552 Å and an associated Cl(2)···H(2)-O(2) angle of 150°.

NMR spectroscopy

The ^{13}C NMR spectrum of the diamagnetic complex **2** is shown in Figure 5. As has been noted for other zinc(II) complexes with nitrogen donor ligands [1], NMR techniques are of value in distinguishing between the various isomers of these complexes. In the present case, the relatively high symmetry *(C_2)* of (**2**) leads to a very simple spectrum; a similar result was observed for the high symmetry isomers of Zn(bispicam)$_2$ (where bispicam is bis(2-pyridylmethyl)amine) [1]. Regrettably, at present we have been unable to isolate the other isomers of this complex for comparative purposes.

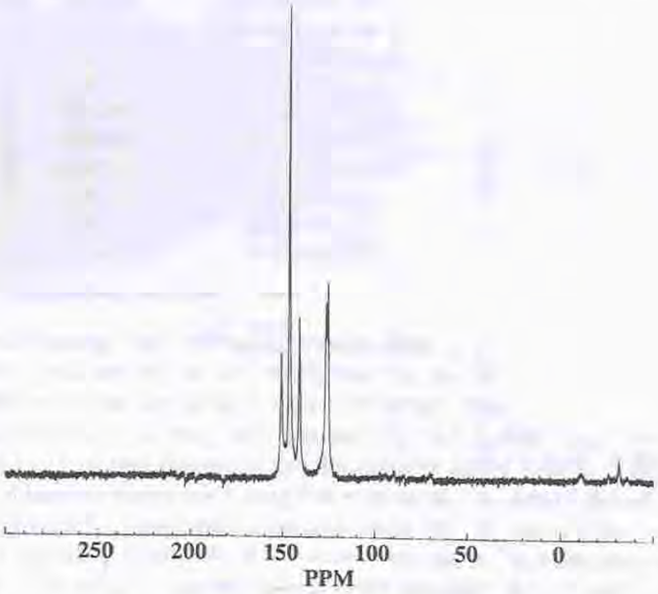

Figure 5. The ^{13}C NMR spectrum of the diamagnetic complex **2**.

Magnetic susceptibility

The temperature dependence of the magnetic susceptibility of (**3**) was measured in the temperature range 4-300 K. As is seen in Figure 6, the susceptibility exhibits a maximum at approximately 8 K, and the effective magnetic moment declines from 8.2 μ_B at room temperature to almost 0.1 μ_B at 4 K. This behavior is characteristic of a weakly antiferromagnetically coupled dimeric manganese(II) complex. The susceptibility data were analyzed by fitting to the expression

$$\chi'_{mol} = -\frac{N}{H}\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + C/T$$

where E_i are the energies of the 36 components of the groundstate manifold. The energies of the different components were obtained by means of the isotropic spin Hamiltonian operator

$$\mathcal{H} = g_a\mu_B S_a\cdot H + g_b\mu_B S_b\cdot H + JS_aS_b$$

where we have chosen $g_a = g_b$ since the crystal structure (above) demonstrates the equivalency of the two manganese centers.

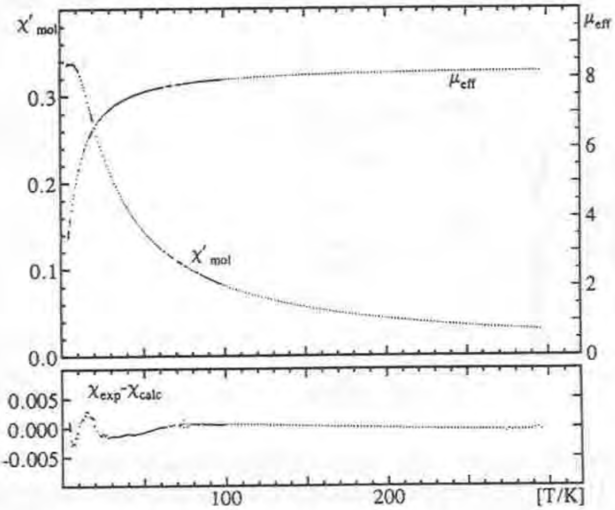

Figure 6. (Top) the temperature dependence of the magnetic susceptibility (cgs units) and the magnetic moment of $[(C_6H_6N_2O)(CH_3OH)ClMnCl_2MnCl(CH_3OH)(C_6H_6N_2O)]$ (**3**). (Bottom) the difference between the measured and calculated susceptibility.

The results of the fitting procedure were g = 1.98 (1) and J = 1.94 (1) cm^{-1} and 1.0% monomeric impurity. We have noted elsewhere [22] that for the simple Van Vleck Hamiltonian the relationship between the temperature at which the susceptibility maximizes and the value of J is given by the expression

$$J = 0.241(T_{max})$$

Application of this simple expression to the calculated value of J would lead to a calculated T_{max}

of 8.0 K, which is entirely consistent with the data shown in Figure 6. The lower curve in Figur 6 shows the difference between the measured and calculated susceptibilities. The small value c J found here is consistent with those observed in earlier studies of binuclear manganese(I complexes with single atom (O or Cl) bridges [18, 22], and also in some recently reporte oxalate-bridged binuclear manganese(II) complexes [12].

EPR spectra

The EPR spectrum of (**1**) diluted into the corresponding Zn(II) host (**2**) is shown in Figure 7. Th spectrum was interpreted using the spin Hamiltonian for $(S, I) = (5/2, 5/2)$

$$\mathcal{H} = g\mu_B B\cdot S + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2) + AS\cdot I$$

with μ_B and B the Bohr magneton and the magnetic field vector, respectively. The spi Hamiltonian parameters *g*, *D*, *E*, and *A* have their usual meanings [23].

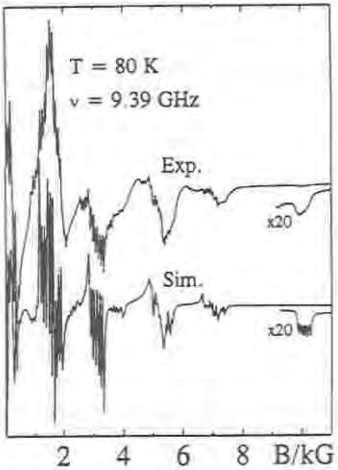

Figure 7. Experimental (upper trace) and simulated (lower trace) EPR spectra of *ci* $[Mn(C_6H_6N_2O)_2Cl_2]$ (**1**) doped into the corresponding zinc complex, (**2**).

The values of the spin Hamiltonian parameters were determined by performing comput simulations of the experimental spectrum [1, 24]. The value of *g* was set to 2.00 [23], and th value of *A* was determined by measuring the separation of the hyperfine lines in the experiment spectrum. The values of *D* and *E* were then found by trial and error. The simulated spectrum Figure 7 was calculated with the following parameters: $g = 2$, $A = 0.0084$ cm^{-1}, $D = 0.157$ cm and $E = 0.0005$ cm^{-1}. The value of *E* represents an upper limit.

The spectra exhibit a slight temperature dependence. At room temperature we find $D = 0.1$ cm^{-1}, the other parameters having the same values as above. Considering the low symmetry of t complex, the low *E/D* ratio seems, at first sight, surprising. The complex has crystallographic symmetry (*vide supra*), but the holohedric symmetry is close to S_4 with the N-Mn-N axis as t four-fold axis. This explains the observation of the low *E/D* ratio.

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Supplementary Material. Tables of anisotropic displacement parameters and hydrogen atom coordinates, and listings of observed and calculated structure amplitudes for each of the complexes **1**, **2**, and **3** are available from D.J.H.

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