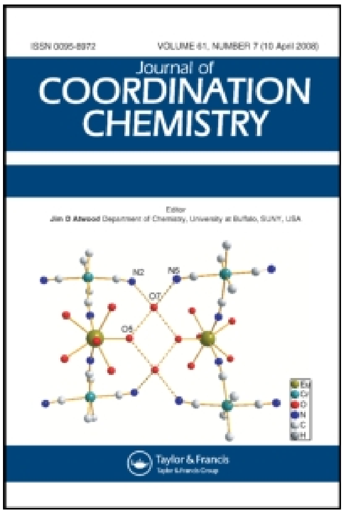

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Onaka, Satoru , Hong, Li , Ito, Mitsuhiro , Sunahara, Tetsuya , Imai, Hiroyuki and Inoue, Katsuya(2005) 'Rational synthesis and X-ray structural study of manganese-pyridine-alcohol derivatives', Journal of Coordination Chemistry, 58: 17, 1523 — 1530

To link to this Article: DOI: 10.1080/00958970500078619

URL: http://dx.doi.org/10.1080/00958970500078619

Journal of Coordination Chemistry
Vol. 58, No. 17, November 2005, 1523–1530

Rational synthesis and X-ray structural study of manganese–pyridine–alcohol derivatives

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(*Received 23 March 2004; revised 15 September 2004; in final form 10 February 2005*)

Systematic syntheses of manganese derivatives with 2-pyridineethanol, 2-pyridinemethanol and 2,6-pyridinedimethanol as chelating ligands have been undertaken to produce [*trans*-$Mn(C_5H_4N\text{-}2\text{-}CH_2CH_2OH)_2Cl_2$] (**1**), [*cis*-$Mn_2(\mu\text{-}Cl)_2(Cl)_2(C_5H_4N\text{-}2\text{-}CH_2CH_2OH)_2(OH_2)_2$] (**2**), [*cis*-$Mn_2(\mu\text{-}Cl)_2(C_5H_4N\text{-}2\text{-}CH_2OH)_4$]$Cl_2$ (**3**) and [$MnCl\{\eta^3\text{-}C_5H_3N\text{-}2,6\text{-}(CH_2OH)_2\}\{\eta^2\text{-}(C_5H_3N\text{-}2,6\text{-}(CH_2OH)_2)\}$]Cl (**4**). The complexes were characterized by single-crystal X-ray diffraction. The oxidation state of the manganese ions in these complexes is 2+. Magnetic data are measured down to 2 K; in dimer complexes (**2** and **3**) a significant antiferromagnetic interaction is observed between two manganese ions.

Keywords: 2-Pyridineethanol; 2,6-Pyridinedimethanol; X-ray analysis; Antiferromagnetic interaction

1. Introduction

In a previous study we demonstrated that 2-pyridinemethanol (L1) is a ubiquitous and yet very versatile chelating ligand towards manganese; L1 coordinates to Mn^{2+} and/or Mn^{3+} through N and O atoms in these new derivatives [1]. The resulting structure (monomer or polymer) depends on coexisting ligands such as $C_6F_5(CO_2)^-$ and $C_6F_4(CO_2)_2^{2-}$. To test the hypothesis that the coordination chemistry of the pyridine–alcohol ligand is controlled by the carbon chain length of the alcohol moiety and/or the number of $–CH_2OH$ units, 2-pyridineethanol (L2) and 2,6-pyridinedimethanol (L3) were examined. The only structurally characterized example of a Mn–L2 complex has been reported recently by Christou and coworkers for the $[Mn_{18}]^{2+}$ cluster, in which 2-pyridineethanol functions in two different modes, $C_5\mathit{N}H_4\text{-}2\text{-Et-}\mathit{O}^-$ and $C_5\mathit{N}H_4$-2-EtOH [2]. However, simple examples with a single manganese ion are rare and a systematic study of the synthesis of such complexes is desirable. Syntheses of several

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis
DOI: 10.1080/00958970500078619

metal complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with L2 and/or L3 have been reported recently [3]. The present study originated for a rational synthesis of a monomer and a dimer. Tailored synthesis of a monomer and a dimer is possible by simply changing the molar ratio between the manganese ion and L2. A dimer with L1 can also be synthesized similarly; the new complexes have been characterized by single-crystal X-ray analysis. This article outlines new vistas for pyridine–alcohol as a ligand towards manganese.

2. Experimental

2.1. *Materials and general procedures*

Syntheses and manipulations were generally performed under ambient conditions. 2-Pyridineethanol was purchased from Tokyo Kasei Kogyo Co., Ltd. Other chemicals and solvents were purchased from Wako Pure Chemical Ind., Ltd. or Aldrich. IR spectra were measured on a Jasco FTIR 460+ spectrometer.

2.2. *Synthesis of [trans-Mn(C_5H_4N-2-CH_2CH_2OH)$_2$$Cl_2$] (1)*

Some 0.310 g (2.5 mmol) of 2-pyridineethanol (L2) was dissolved in 6 mL of absolute ethanol. To this was added solid $MnCl_2 \cdot 4H_2O$ (0.400 g, 2.0 mmol) in small portions and the mixture was stirred at room temperature for 24 h. The resulting pale pink solution was left at room temperature for 1 week to afford colorless single crystals. Yield 51%. Anal. Calcd for $C_{14}H_{18}Cl_2MnN_2O_2$(%): C, 45.18; H, 4.86; N, 7.53. Found: C, 44.99; H, 4.87; N, 7.49. IR (KBr disk): 3228 (vs; ν(OH)), 1602 (vs), 1567 (s), 1489 (s), 1442 (vs), 1333 (m), 1310 (s), 1065 (s), 1024 (vs), 788 (m), 774 (s), 761 (s), 742 (vs) (only strong absorptions are registered hereafter).

2.3. *Synthesis of [cis-Mn_2(μ-Cl)$_2$(Cl)$_2$(C_5H_4N-2-CH_2CH_2OH)$_2$(OH_2)$_2$] (2)*

Some 0.25 g (2.0 mmol) of 2-pyridineethanol (L2) was dissolved in 6 mL of absolute ethanol. To this was added solid $MnCl_2 \cdot 4H_2O$ (0.59 g, 3.0 mmol) in small portions and the mixture was stirred at room temperature for 24 h. The resulting pale pink solution was left at room temperature for 1 week to afford pale pink single crystals. Yield 32% based on the manganese salt. Anal. Calcd for $C_{14}H_{18}Cl_2Mn_2N_2O_2$(%): C, 31.49; H, 4.15; N, 5.25. Found: C, 31.27; H, 4.04; N, 5.24. IR (KBr disk): 3558 (vs; ν(OH)), 3348 (vs; ν(OH)), 1602 (vs), 1567 (s), 1487 (s), 1444 (vs), 1320 (m), 1302 (s), 1079 (s), 1030 (vs), 783 (m), 760 (s), 753 (vs).

2.4. *Synthesis of [cis-Mn_2(μ-Cl)$_2$(C_5H_4N-2-CH_2OH)$_4$]$Cl_2 \cdot xH_2O$ (3)*

Some 0.22 g (2.0 mmol) of 2-pyridinemethanol (L1) was dissolved in 6 mL of absolute ethanol. To this was added solid $MnCl_2 \cdot 4H_2O$ (0.59 g, 3.0 mmol) in small portions and the mixture was stirred at room temperature for 24 h. The resulting pale pink solution was left at room temperature for 1 week to afford pale pink single crystals. Yield 30% based on the manganese salt. Satisfactory analysis was not obtained because the content of H_2O varied for every cycle of synthesis and analysis. The main IR peaks are almost coincident with that of **2**, especially additional very strong ν(OH) at 3390 cm^{-1} indicates the existence of free H_2O molecules. IR (KBr disk): 3390 (vs; ν(OH)), 3064 (vs; ν(OH)), 1608 (vs), 1568 (s), 1488 (s), 1456 (vs), 1431 (s), 1410 (s), 1364 (s), 1332 (m), 1062 (s), 1042 (vs), 1018 (s), 780 (m), 773 (s), 730 (s). A single-crystal X-ray diffraction study revealed two free H_2O.

2.5. *Synthesis of [MnCl{η^3-C_5H_3N-2,6-(CH_2-OH)$_2$}{η^2-(C_5H_3N-2,6-(CH_2OH)$_2$)}]Cl (4)*

Some 0.42 g (3.0 mmol) of 2,6-pyridinedimethanol (L3) was dissolved in 10 mL of mixed ethanol/H_2O (1 : 1). To this was added solid $MnCl_2 \cdot 4H_2O$ (0.40 g, 2.0 mmol) in small portions and the mixture was stirred at room temperature for 24 h. The resulting pale yellow solution was left at room temperature for 1 week to afford pale pink single crystals. Yield 46% based on the manganese salt. Anal. Calcd for $C_{14}H_{18}Cl_2MnN_2O_4$(%): C, 41.61; H, 4.49; N, 6.93. Found: C, 41.66; H, 4.44; N, 7.01. IR (KBr disk): 3284 (s, sh), 3074 (vs; ν(OH)), 1604 (vs), 1579 (s), 1448 (s), 1431 (vs), 1419 (s), 1332 (m), 1051 (vs), 1032 (vs), 765 (m), 732 (s).

2.6. *Single-crystal X-ray analysis*

Suitable crystals of these four compounds were obtained from the recrystallization processes described above. The selected crystals were glued to the top of a fine glass rod. Accurate cell dimensions were determined by least-square refinements of 20–25 reflections on a MAC MXC3 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The reflection data were collected at room temperature. Complete crystal data are collated in table 1. The structures were solved by direct methods, using SIR97 for these four crystals, and refined by full-matrix least-squares with anisotropic thermal parameters for all nonhydrogen atoms using SHELXS97 on F^2 [4]. The positions of H atoms were assigned with common isotropic displacement factors and were refined by use of geometrical restraints in the final refinement cycle. The final R and wR_2 values are also listed in table 1. Tables of atomic coordinates, thermal parameters and bond lengths and angles are available as supplementary material, CCDC Nos 232546 (**1**), 232547 (**2**), 232548 (**3**) and 232549 (**4**). Selected bond lengths and angles are given in table 2.

2.7. *Magnetic measurements*

Magnetic data were measured with a SQUID magnetometer (Quantum Design MPMS-XL) between 2 and 300 K under a 5000 G magnetic field. The fit and the analysis of the data were made by use of the computer software Kaleida-Graph 3.52.

3. Results and discussion

The versatility of 2-pyridinemethanol as a ubiquitous ligand was demonstrated in our previous article [1]. In addition, our recent study has demonstrated that L1 is a very important ligand for constructing a new single molecule magnet (SMM), in which four manganese ions are tethered by L1 to afford an Mn_4 cluster [5]. These findings

Table 1. Crystal data and structure refinement.

Compound	**1**	**2**	**3**	**4**
Chemical formula	$MnC_{14}H_{18}N_2O_2Cl_2$	$Mn_2C_{14}H_{18}N_2O_2Cl_2$	$Mn_2C_{24}H_{28}N_4O_4Cl_4$	$MnC_{14}H_{18}N_2O_4Cl_2$
Formula weight	372.15	678.15	688.20	404.15
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P21/n$	$P21/n$	$P\bar{1}$	$P\bar{1}$
a/Å	13.107(2)	13.523(3)	7.882(4)	7.888(2)
b/Å	10.692(2)	7.140(1)	9.752(4)	8.417(2)
c/Å	12.338(4)	10.718(2)	11.427(3)	14.380(3)
α/°	90.00	90.00	73.50(3)	77.56(2)
β/°	108.5(2)	91.39(2)	71.02(3)	81.97(2)
γ/°	90.00	90.00	77.12(4)	66.19(2)
V/Å^3	1639.6(7)	1034.6(3)	788.1(7)	851.4(3)
Z	4	4	1	2
D_{calc}/g cm^{-3}	1.51	1.71	1.45	1.58
Crystal dimensions/mm^3	$0.5 \times 0.4 \times 0.2$	$0.55 \times 0.45 \times 0.35$	$0.7 \times 0.6 \times 0.4$	$0.5 \times 0.4 \times 0.2$
μ(Mo Kα)/mm	1.15	1.18	1.18	1.17
Scan type	2θ–ω	2θ–ω	2θ–ω	2θ–ω
Scan range	$1.15 + 0.35 \tan\theta$	$1.15 + 0.35 \tan\theta$	$1.15 + 0.35 \tan\theta$	$1.15 + 0.35 \tan\theta$
Scan speed/° min^{-1}	6	6	6	6
2θ max/°	50	55	50	55
Temperature/K	298	298	298	298
Unique reflections	2813	2377	2782	3916
Data reduction cutoff	2406	2088	2510	3140
No. of parameters refined	262	162	176	280
R	0.05	0.04	0.12	0.05
Rw	0.14	0.11	0.11	0.11

$R = \Sigma\|F_o - |F_c\|/\Sigma|F_o|$; $Rw = \{\Sigma w[(|F_o - F_c|)^2]/\Sigma w(F_o^2)^2\}^{1/2}$ where $w = 1/[\sigma^2((F_o^2) + (ap)^2 + bp)]$.

led us to explore the coordination chemistry of the ethyl analog, 2-pyridineethanol (L2), as a potential ligand for constructing a new SMM with a smaller number of core manganese ions. As described earlier, tailored synthesis of mononuclear and dinuclear manganese complexes, **1** and **2**, respectively, can be easily attained by controlling the molar ratio of the ligand L2 to the manganese. Similarly, a dinuclear manganese complex with L1 (**3**) is obtained when a large excess of manganese(II) chloride is used. Unfortunately, single crystals of the mononuclear manganese complex were not obtained with a large excess of L1, although a previous study demonstrated that the mononuclear manganese complex with three L1 ligands was obtained upon mixing manganese perchlorate with L1 and azopyridine [1]. For 2,6-pyridinedimethanol (L3), one L3 functions as a tridentate ligand while the other L3 functions as a bidentate ligand through N and one alcoholic O atom in **4**, even though an excess of L3 is used. In these four complexes, each alcoholic proton persists upon coordination to the manganese ion, as exemplified by the strong ν(OH) IR peak (figure 1). The positions of these alcoholic protons can be determined by the Fourier maps of X-ray diffraction analysis. Therefore, L1, L2 and L3 are neutral ligands and the oxidation state of the manganese ions in these four new complexes is 2+. Magnetic data described below support this assignment.

The molecular structures of these new complexes are shown in figures 2–5; the basic structures of these four new complexes are octahedral. Two Cl^- occupy the *cis* positions in **1**, whereas two Cl^- bridge two Mn(II) ions in **2** and **3**. Each Mn(II) ion in **2** has one chelating L2, terminal H_2O and Cl^- in addition to a bridging Cl^- ion. Two L1 ligands chelate to respective Mn(II) ions in **3**. Perhaps the longer alkyl chain in L2 demands

Table 2. Selected bond lengths (Å) and angles (°).

	1	**2**	**3**	**4**
Mn(1)–N(1)	2.31(8)	2.26(5)	2.23(0)	2.22(6)
Mn(1)–N(2)	2.26(9)		2.22(7)	2.32(8)
Mn(1)–Cl(1)	2.51(0)	2.54(5)	2.50(2)	
Mn(1)–Cl(2)	2.47(9)	2.52(5)		2.40(3)
Mn(1)–O(1)	2.20(7)	2.17(3)	2.20(6)	2.15(6)
Mn(1)–O(2)	2.23(9)	2.19(4)	2.19(8)	2.31(6)
Mn(1)–O(3)				2.21(7)
Cl(1)–Mn(1)–Cl(2)	96.7(3)	94.7(4)		
Cl(1)–Mn(1)–N(1)	98.8(1)	88.4(4)	96.5(4)	
Cl(1)–Mn(1)–N(2)	88.7(0)		98.5(0)	
Cl(1)–Mn(1)–O(1)	170.0(3)	91.9(0)	168.5(0)	
Cl(1)–Mn(1)–O(2)	87.0(6)	93.3(9)	94.2(5)	
Cl(2)–Mn(1)–N(1)	88.8(6)	169.8(2)		95.1(5)
Cl(2)–Mn(1)–N(2)	88.7(0)			96.1(2)
Cl(2)–Mn(1)–O(1)	92.7(1)	85.7(2)		145.9(6)
Cl(2)–Mn(1)–O(2)	175.6(7)	91.5(1)		90.4(6)
N(1)–Mn(1)–N(2)	169.9(3)		158.3(2)	158.4(7)
N(1)–Mn(1)–O(1)	84.5(2)	84.5(1)	73.7(3)	107.9(8)
N(1)–Mn(1)–O(2)	88.4(8)	97.9(7)	90.1(6)	68.8(2)
N(2)–Mn(1)–O(1)	86.9(9)		92.5(7)	71.1(1)
N(2)–Mn(1)–O(2)	85.2(1)		73.2(6)	129.2(6)
O(1)–Mn(1)–O(2)	83.6(3)	174.2(2)	91.9(2)	75.7(3)
Cl(2)–Mn(1)–O(3)				110.7(7)
N(1)–Mn(1)–O(3)				70.8(4)
N(2)–Mn(1)–O(3)				88.0(0)
O(1)–Mn(1)–O(3)				100.4(3)
O(2)–Mn(1)–O(3)				135.7(0)

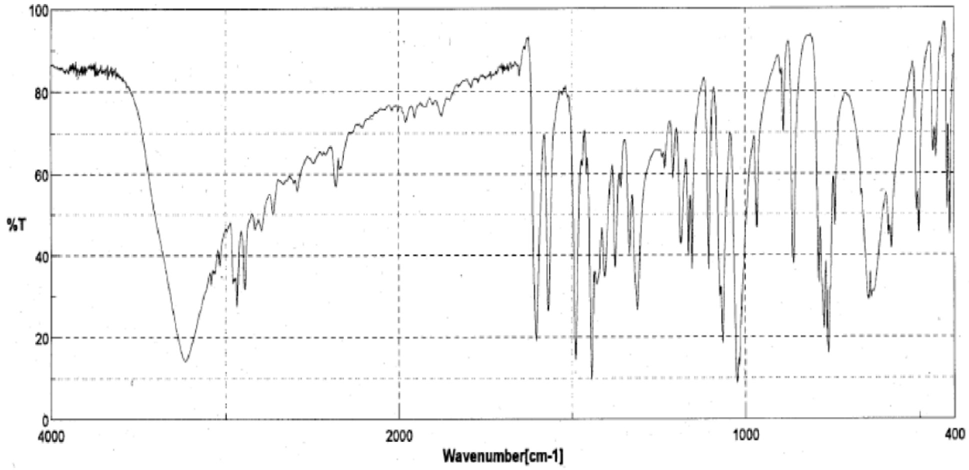

Figure 1. IR spectrum of **1** indicating the existence of the OH group.

more space around the Mn(II), thus vitiating another coordination of L2 for **2**. The Mn–Mn distances are 3.72 and 3.63 Å for **2** and **3**, respectively. Two different coordination modes of L3 are demonstrated in **4**. One of the L3 ligands functions as a tridentate chelating ligand, while the other L3 is a bidentate ligand leaving one

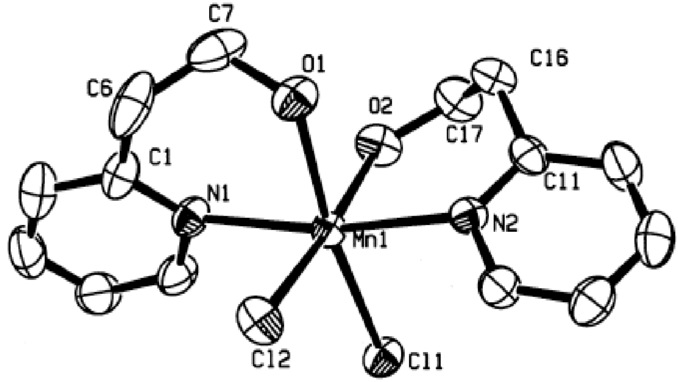

Figure 2. ORTEP drawing of **1** with atom-numbering scheme. Thermal ellipsoids are at the 50% probability level. H atoms are omitted for clarity.

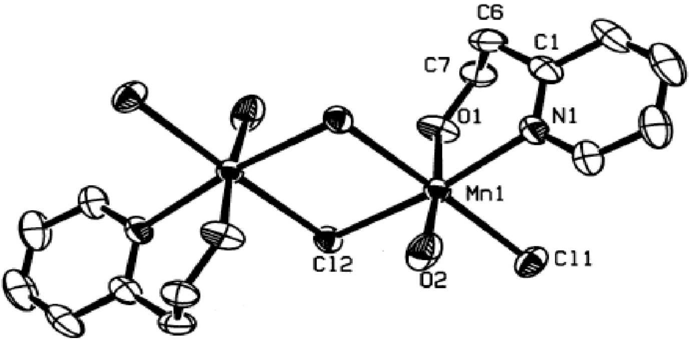

Figure 3. ORTEP drawing of **2** with atom-numbering scheme. Thermal ellipsoids are at the 50% probability level. H atoms are omitted for clarity.

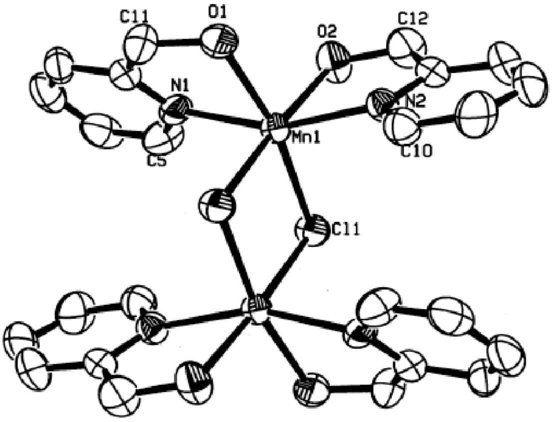

Figure 4. ORTEP drawing of **3** with atom-numbering scheme. Thermal ellipsoids are at the 50% probability level. H atoms are omitted for clarity.

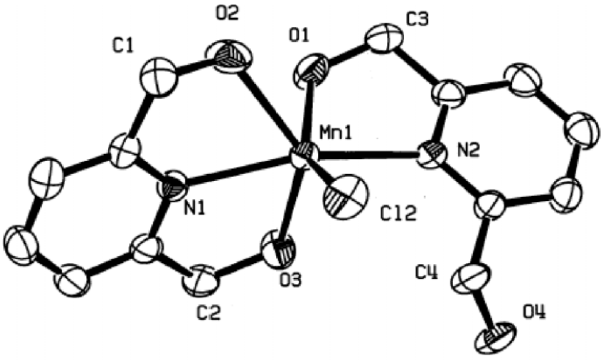

Figure 5. ORTEP drawing of **4** with atom-numbering scheme. Thermal ellipsoids are at the 50% probability level. H atoms are omitted for clarity.

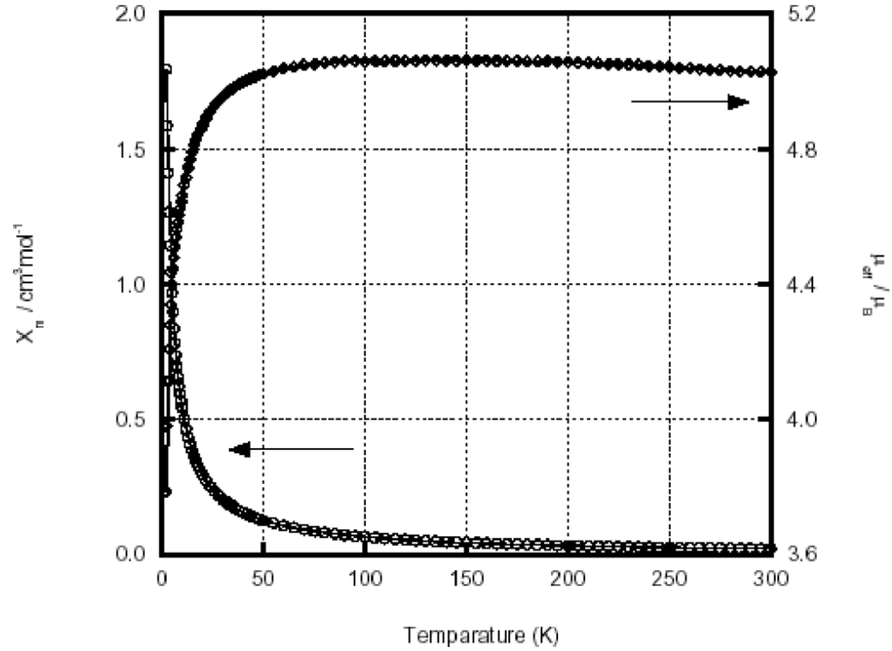

Figure 6. χ_m (○) and μ_{eff} (△) plots *vs* temperature. Solid lines represent a least-squares fit of the data to the theoretical equation [6].

alcohol group free; a shoulder at 3284 cm^{-1} in the IR spectrum should be assigned to this free OH group. A Cl^- ligand occupies the sixth coordination site.

Selected bond lengths and angles for these complexes are collected in table 2. The Mn–N and Mn–O bond lengths are in the normal range for these pyridine–alcohol derivatives [1]. Bond angle data around the Mn(II) ion in **4** indicate severe distortion from an ideal octahedron. Presumably this is the reason why one L3 functions as a bidentate ligand.

The oxidation states of each manganese ion were determined by measuring magnetic data. Effective magnetic moments (μ_{eff}) for these complexes are 5.92, 5.2, 5.03 and 5.91 BM, respectively, for **1**–**4**. Effective magnetic moments of mononuclear complexes **1** and **4** are quite close to that of the spin-only value. However, μ_{eff} values for **2** and **3** are reduced significantly due to interaction between two Mn(II) ions. The exchange interaction constant, *J*, was calculated by use of the Van Vleck equation for the high-spin Mn(II) ion with the $3d^5$ configuration and they are -0.14 and $-0.36\,\text{cm}^{-1}$, respectively, for **2** and **3** [6]. A typical example of the fitting is shown in figure 6. *J* gains its negative value with the decrease in the Mn–Mn distance, suggesting that **2** and **3** are antiferromagnetic and the antiferromagnetic interaction increases with the decrease in the Mn–Mn distance [7].

Acknowledgements

This research was funded by Grants-in-Aid for Scientific Research on Priority Area (No. 12023221 "Metal-assembled Complexes") and by Grants-in-Aid for Scientific Research (No. 14540514) from the Ministry of Education, Science, Sports and Culture, Japan.

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