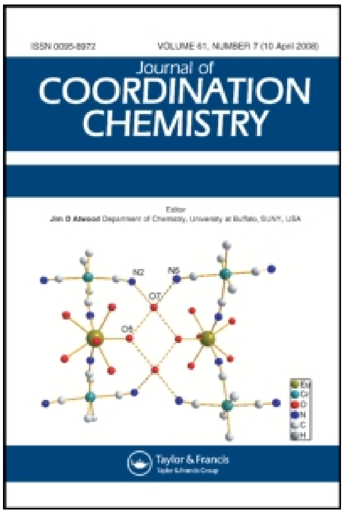

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A novel heterospin tetranuclear Mn^{II}-type complex incorporating a macrocyclic oxamide $[Mn(CuL)_3](ClO_4)_2$: synthesis, crystal structure and magnetic properties

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A NOVEL HETEROSPIN TETRANUCLEAR $Mn^{II}Cu^{II}_3$-TYPE COMPLEX INCORPORATING A MACROCYCLIC OXAMIDE $[Mn(CuL)_3](ClO_4)_2$: SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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A novel oxamidato-bridged $Mn^{II}Cu^{II}_3$ heterospin tetranuclear complex incorporating a macrocyclic oxamide, 2,3-dioxo-5,6:14,15-dibenzo-1,4,8,12-tetraazacyclopentadeca-7,12-diene, was prepared and characterized spectroscopically, structurally and magnetically. The structure consists of tetranuclear units in which the central manganese(II) atom is linked to each external copper(II) ion via the *exo-cis* oxygen atoms of the oxamidato macrocyclic ligand. The temperature dependence of the magnetic susceptibility for the complex was analyzed by means of the Hamiltonian $\hat{H} = -2J\hat{S}_{Mn}(\hat{S}_{Cu1} + \hat{S}_{Cu2} + \hat{S}_{Cu3})$ with $J = -14.01\,cm^{-1}$.

Keywords: Macrocyclic oxamide; Heterospin complex; Crystal structure; Spectroscopic characterization; Magnetic property

INTRODUCTION

During the past two decades, the field of molecular magnets has attracted the attention of scientists from many disciplines. The major research goals in the field of molecular magnetism are the chemical design of molecular assemblies that exhibit spontaneous magnetization and the rationalization of magnetostructural correlation [1]. Polynuclear macrocyclic complexes are an active field of research for designing and synthesizing new magnetic materials [2–6]. A successful strategy leading to polynuclear systems is to use metal cations to link relatively stable coordination compounds containing potential bridging units, that is 'complex ligands' [7–9]. A good example of a 'complex ligand' is Cu(oxpn) (oxpn = *N*,*N*-bis(3-aminopropyl)oxamide), one of the mononuclear copper(II) complexes of *N*,*N′*-bis(coordinating group)-substituted

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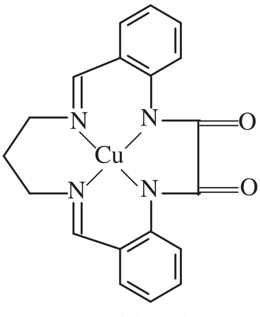

(CuL)

SCHEME 1 The chemical structure of the precursor CuL.

oxamides [2]. With these complexes as precursors, many oxamido-bridged polynuclear complexes have been prepared and studied magnetically. This approach has been extended recently by using macrocyclic analogues of the oxamides [5,6,10]. Noncyclic oxamides may adopt *cis* or *trans* conformations on coordination, and this flexibility allows less control over the type of complex formed [7]. The macrocyclic oxamides allow us to synthesize polynuclear systems in a more controlled fashion. Only a few examples of discrete μ-oxamidato $Mn^{II}Cu_3^{II}$-type tetranuclear complexes have been reported [4,5]. Although it is well known that molecular topology has an important influence on magnetic properties, few X-ray structural characterizations have been performed for $Mn^{II}Cu_3^{II}$-type complexes. In the present work, by using the macrocyclic oxamido–copper(II) complex as a complex ligand (Scheme 1), we assemble a polymetallic system containing different paramagnetic metal ions derived from the precursor CuL and Mn(II) (ligand L is 2,3-dioxo-5,6: 14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,12-diene) (see Scheme 1). Herein we describe the synthesis, crystal structure, spectroscopic characterization and magnetic properties of this tetranuclear $Mn^{II}Cu_3^{II}$-type complex.

EXPERIMENTAL

Synthesis of the CuL (Precursor)

The ligand L was prepared according to literature methods [11]. The CuL precursor was prepared by refluxing and stirring a mixture of the ligand L (0.294 g, 1 mmol), 1,3-propanediamine (0.16 mL, 2 mmol) and $Cu(Ac)_2 \cdot H_2O$ (0.2 g, 1 mmol) for 2 h in 20 mL of MeOH and 2 drops of 2 M NaOH. After cooling and filtering, the precipitate obtained was washed with water, methanol and diethyl ether successively, and dried under vacuum. Yield: 52%. Anal. Calcd. for $C_{19}H_{16}CuN_4O_2$(%): C, 57.6; H, 4.07; N, 14.15. Found: C, 57.32; H, 4.04; N, 14.21. IR (KBr disk, cm^{-1}) $\nu_{C=O}$ 1640; $\nu_{C=N}$ 1610, 1590.

Preparation of the Title Complex

A solution of 10 mL of MeOH containing $Mn(ClO_4)_2 \cdot 6H_2O$ (37.0 mg, 0.1 mmol) was added to the CuL (118.5.0 mg, 0.3 mmol) in 20 mL of MeOH with stirring and gentle heating. The mixture was stirred for a further 30 min and then filtered. Dark green crystals were obtained from the filtrate after several days. IR (KBr disk, cm^{-1}): 3426 (m), 2935 (w), 1630 (vs), 1553 (m), 1483 (s), 1092 (br), 914 (m), 768 (s). Anal. Calcd. for $C_{57}H_{48}Cl_2Cu_3MnN_{12}O_{14}$(%): C, 47.48; H, 3.33; N, 11.66. Found: C, 47.39; H, 3.33; N, 11.51.

X-ray Analysis

A dark green single crystal ($0.62 \times 0.53 \times 0.48\,mm^3$) of the title complex was selected and mounted on a Siemens SMART diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystallographic data are given in Table I. Atomic coordinates and equivalent isotropic displacement parameters as well as selected bond lengths and angles for the complex are given in Tables II and III. The structure was solved with direct methods using the SHELXS-97 program [12]. The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using the SHELXL-97 package [13]. Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 208947. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Physical Measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Carlo-Erba-1106 instrument. The infrared spectrum was recorded on a Perkin-Elmer

TABLE I Crystallographic data and data collection parameters for the complex

Formula	$C_{57}H_{48}Cl_2Cu_3MnN_{12}O_{14}$
Formula weight	1441.53
Crystal size	$0.62 \times 0.53 \times 0.48$ mm
Crystal system	Trigonal
Space group	P-3
a (Å)	22.6599(4)
b (Å)	22.6599(4)
c (Å)	19.0106(4)
α (°)	90
β (°)	120
γ (°)	90
V (Å^3)	8453.6(3)
Z	2
θ range (°)	1.04–24.98
Index ranges	$-26 \le h \le 13$, $-26 \le k \le 26$, $-22 \le l \le 20$
μ (mm^{-1})	1.511
F(000)	4392
T (K)	293(2)
Reflections measured	27 504
Unique reflections	9898
R(int)	0.0404
R_1, wR_2 [$I > 2\sigma(I)$]	0.0663, 0.1540
R_1, wR_2 (all data)	0.0990, 0.1760

$R_1 = \sum w(|F_0| - |F_c|)^2$; $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^c 2)^2]^{1/2}$. $w = 1/[\sigma^2(F_0^2) + (0.0525p)^2 + 36.0210p]$, where $p = (F_0^2 + 2F_c^2)/3$.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the complex

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Cu1	4675(1)	5210(1)	7474(1)	42(1)
Mn1	3333(1)	6667(1)	7813(1)	32(1)
O1	3457(2)	5980(2)	7100(2)	47(1)
O2	3923(2)	6302(2)	8386(2)	40(1)
N1	4212(3)	5582(3)	6876(3)	39(1)
N2	4601(2)	5804(2)	8224(3)	35(1)
N3	5151(3)	4893(3)	8140(4)	54(2)
N4	4560(3)	4553(3)	6691(4)	58(2)
C1	3908(3)	5842(3)	7278(3)	36(1)
C2	4155(3)	5993(3)	8028(3)	33(1)
C3	4924(3)	5997(3)	880(3)	37(1)
C4	4944(3)	6510(4)	310(4)	48(2)
C5	5288(4)	6685(4)	9936(4)	58(2)
C6	5632(4)	6369(5)	0184(4)	67(2)
C7	5626(4)	5875(4)	9776(4)	65(2)
C8	5292(3)	5675(4)	9119(4)	48(2)
C9	5358(4)	5150(4)	8748(5)	58(2)
C10	5306(5)	4344(5)	7960(5)	74(3)
C11	5393(5)	4277(5)	199(5)	80(3)
C12	4739(5)	4017(4)	6812(5)	78(3)
C13	4372(4)	4586(5)	6062(5)	70(3)
C14	4171(4)	5042(4)	5760(4)	62(2)
C15	4047(4)	4983(5)	5022(5)	78(3)
C16	3846(5)	5377(7)	4690(5)	92(4)
C17	3786(4)	5874(6)	5049(5)	79(3)
C18	3912(4)	5950(4)	5767(4)	60(2)
C19	4095(3)	5533(4)	6141(4)	48(2)
Cl1	6478(1)	6332(1)	6879(1)	76(1)
O11	6852(3)	7051(3)	6756(4)	96(2)
O12	5871(4)	6029(4)	6562(7)	167(5)
O13	6304(7)	6267(6)	7618(6)	196(5)
O14	6861(5)	6057(6)	6801(8)	193(5)
Cl2	3139(1)	3364(2)	8196(1)	90(1)
O21	3622(4)	3124(5)	8243(4)	132(4)
O22	2759(4)	3101(4)	7567(4)	107(3)
O23	2693(4)	3085(5)	8780(4)	137(3)
O24	3488(4)	4081(5)	8228(5)	148(4)

U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and bond angles (°) for the complex

Cu1–N1	1.998(5)	Cu1–N3	2.014(6)
Cu1–N2	2.023(5)	Cu1–N4	2.028(6)
Mn1–O2$^{\#1}$	2.181(4)	Mn1–O2$^{\#2}$	2.181(4)
Mn1–O2	2.181(4)	Mn1–O1$^{\#2}$	2.184(4)
Mn1–O1$^{\#1}$	2.184(4)	Mn1–O1	2.184(4)
N1–Cu1–N3	175.1(2)	N1–Cu1–N2	83.4(2)
N3–Cu1–N2	91.8(2)	N1–Cu1–N4	89.5(2)
N3–Cu1–N4	95.4(3)	N2–Cu1–N	169.2(2)
O2$^{\#1}$–Mn1–O2$^{\#2}$	97.23(15)	O2$^{\#1}$–Mn1–O2	97.23(15)
O2$^{\#2}$–Mn1–O2	97.23(15)	O2$^{\#1}$–Mn1–O1$^{\#2}$	108.31(17)
O2$^{\#2}$–Mn1–O1$^{\#2}$	73.72(16)	O2–Mn1–O1$^{\#2}$	153.66(17)
O2$^{\#1}$–Mn1–O1$^{\#1}$	73.72(16)	O2$^{\#2}$–Mn1–O1$^{\#1}$	153.66(17)
O2–Mn1–O1$^{\#1}$	108.31(17)	O1$^{\#2}$–Mn1–O1$^{\#1}$	85.52(19)
O2$^{\#1}$–Mn1–O1	153.66(17)	O2$^{\#2}$–Mn1–O1	108.31(17)
O2–Mn1–O1	73.72(16)	O1$^{\#2}$–Mn1–O1	85.52(19)
O1$^{\#1}$–Mn1–O1	85.52(19)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}\, -y+1,\ x-y+1,\ z$; $^{\#2}\, -x+y,\ -x+1,\ z$.

SYSTEM 2000 FT-IR spectrometer using KBr pellets. An electronic spectrum was recorded on a Hitachi U-3010 spectrophotometer and an X-band ESR spectrum was measured on a Brucker ESP-300 spectrometer. Variable-temperature magnetic susceptibilities (in the temperature range 5–300 K) were measured on a Quantum Design MPMS-7 SQUID magnetometer in a field of 1 T. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

RESULTS AND DISCUSSION

Crystal Structure

The asymmetric unit contains three symmetrically and crystallographically independent molecular fragments. Each molecular fragment is built from two ClO_4^- ions and one cation. An ORTEP drawing of the complex cation $[Mn(CuL)_3]^{2+}$ is shown in Fig. 1(a).

Within the cation the central manganese(II) ion links to each external copper(II) via the *exo-cis* oxygen atoms of the oxamidato macrocyclic ligand with an Mn–Cu separation of 5.53 Å, resulting in a tetranuclear unit. The Mn(II) ion is hexacoordinated by six oxygen atoms from three CuL units. Mn–O bonds range from 2.181(4) to 2.184(4) Å. The dihedral angles between the planes that share the Mn1 (Mn1–O1–O2–C1–C2, Mn1–O1A–O2A–C1A–C2A and Mn1–O1B–O2B–C1B–C2B) are 70.4° or 109.6°. Each terminal copper(II) ion is coordinated by four nitrogen atoms of the macrocyclic organic ligand with the CuN_4 chromophore exhibiting almost planarity, with average Cu–N bond distances of 1.998(5)–2.028(6) Å. Cu1 is displaced from the least-squares plane by 0.0667–0.0668 Å. Copper(II) and manganese(II) atoms are not coplanar with the bridging oxamido group that lies between them, with maximum root mean square deviation of 0.8806 Å. Furthermore, the planarity of the oxamido skeleton reveals that the amidate nitrogens are sp^2 hybridized and that the π-carbonyl electrons are delocalized to the conjugated oxamido skeleton. This is further supported by the average C–O and C–N bond lengths (1.260 and 1.380 Å, respectively), which are shorter than expected for single C–O or C–N bonds (*ca* 1.481 and 1.462 Å, respectively) [10]. The three macrocyclic oxamide moieties linked to the center manganese ion look like the 'vanes' of a 'windmill'. The packing of the molecules in *b* orientations is shown in Fig. 1(b). The *b*-axis orientation can be viewed as a one-dimensional chain. The form of the chain may be due to weak intermolecular interaction between the 'vanes' of adjacent 'windmills'. The neighboring vanes are separated by about 3.86 Å.

Spectroscopic Characterization

The IR spectrum of the complex shows two characteristic strong bands at *ca* 1600 and 1453 cm^{-1} (due to the N–C–O stretching) for the bridging oxamido group [2]. The typical absorption band at *ca* 1092 cm^{-1} for the perchorate ion is also observed [14].

The electronic absorption spectrum of the complex in MeOH below 350 nm is dominated by intense bands due to charge-transfer transitions in the CuL part. In the 500–1000 nm region, a relatively strong broad band centered at 619 nm is attributed to the spin-allowed d–d transitions of Cu(II) in an environment close to square-planar [15]. The coordination environment of manganese(II) in the complex can be viewed as a distorted octahedron. Thus, the ground state of manganese(II) is $^6A_{1g}$ according to

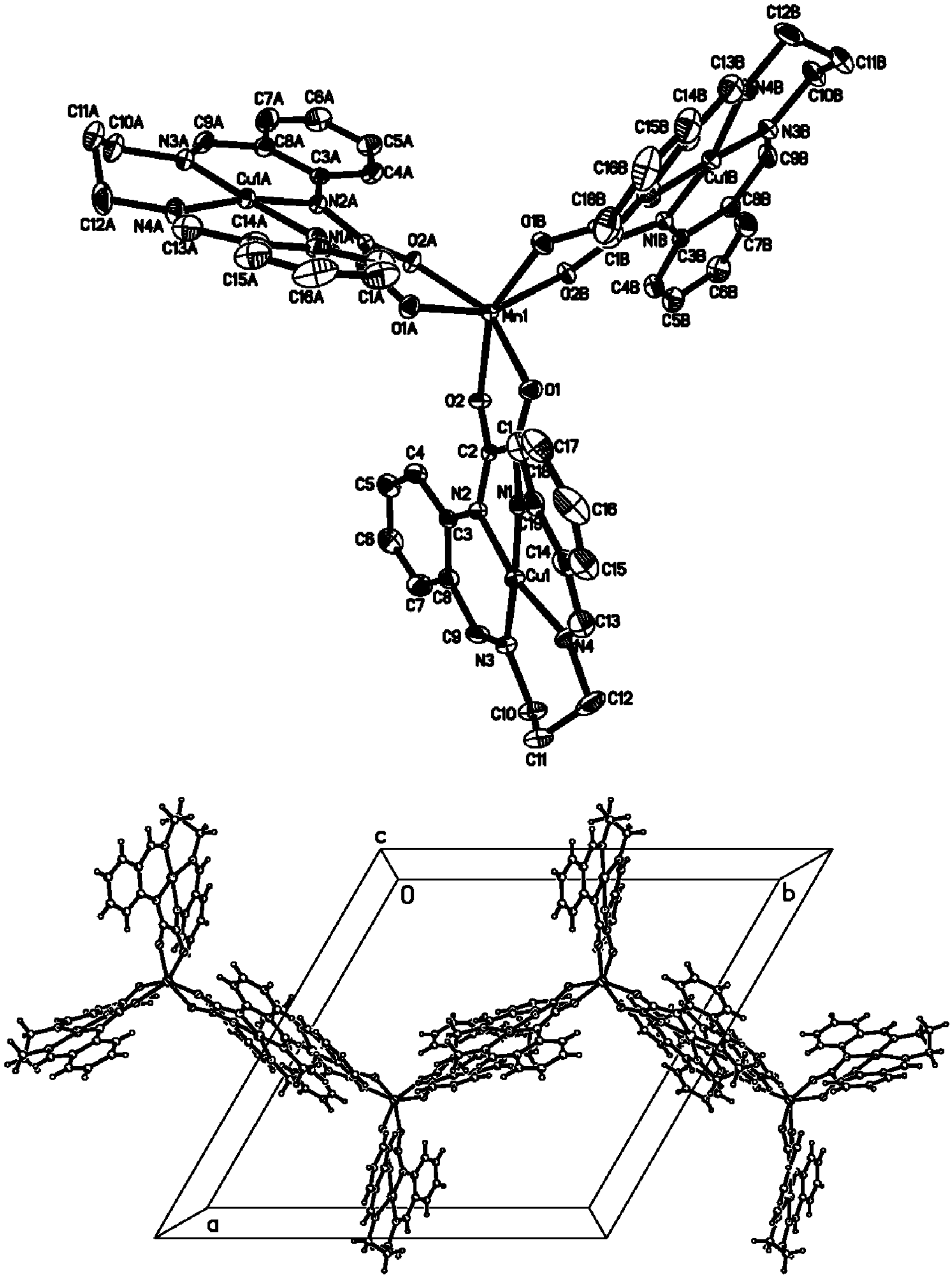

FIGURE 1 (a) An ORTEP view of the tetranuclear complex cation with the atom numbering. (b) Packing diagram of the complex in *b* orientation.

ligand field theory. Assuming Mn(II) has *Oh* symmetry, d–d transitions of manganese(II) ($^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^4T_{2g}(G)$, $^4A_{1g}, \ldots$) are spin forbidden, which is in agreement with the fact that there is no characteristic band of manganese(II) in the spectrum of the complex [16].

The polycrystalline X-band ESR spectrum was measured at room temperature. The spectrum exhibits a broad signal centered at $g = 2.06$, indicating a magnetic exchange interaction between the manganese(II) ion and copper(II) ions [17]. The linewidth ΔH_{pp} is about 396 G. According to Kambe's approach [18], the coupling between $S = 5/2$ spin ($\mathrm{Mn^{II}}$) and three $S = 1/2$ spins ($\mathrm{Cu^{II}}$) gives rise to eight spin states. On the basis of the Boltzmann distribution and the parameters obtained from magnetic studies, all the coupled spin states are significantly populated at room temperature, and all make their contributions to the ESR absorption, thus resulting in a broad signal.

Magnetic Properties

The temperature dependence of the magnetic susceptibility for the complex was investigated in the temperature range 5–300 K, with an applied field of 1 T. The plot of $\chi_{\mathrm{M}}T$ (and χ_{M}) *versus* T, where χ_{M} is the molar magnetic susceptibility corrected for the core diamagnetism and T is the absolute temperature, is shown in Fig. 2. The $\chi_{\mathrm{M}}T$ value is equal to $4.37\,\mathrm{cm^3\,K\,mol^{-1}}$ at 300 K, lower than the spin-only value expected for one $S = 5/2$ ($\mathrm{Mn^{II}}$) and three $S = 1/2$ ($\mathrm{Cu^{II}}$) uncorrelated spins ($5.50\,\mathrm{cm^3\,K\,mol^{-1}}$) indicating the presence of antiferromagnetic interactions between the spin carriers.

The magnetic data were fitted to the theoretical expression (for the temperature dependence of the magnetic susceptibility) deduced from the spin Hamiltonian $\dot{H} = -2J\dot{S}_{\mathrm{Mn}}(\dot{S}_{\mathrm{Cu1}} + \dot{S}_{\mathrm{Cu2}} + \dot{S}_{\mathrm{Cu3}})$. The theoretical expression is:

$$\chi_M = \frac{Ng^2\beta^2}{KT}\left(\frac{A}{B}\right) + N_\alpha,$$

where $A = 2 + 10\exp(4J/kT) + 20\exp(7J/kT) + 28\exp(10J/kT) + 56\exp(13J/kT) + 60 \times \exp(18J/kT)$, $B = 3 + 5\exp(4J/kT) + 10\exp(7J/kT) + 7\exp(10J/kT) + 14\exp(13J/kT) + 9\exp(18J/kT)$, J is the exchange integral between copper(II) and manganese(II) ions, N_α is the temperature-independent paramagnetism ($380 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$) [19], and

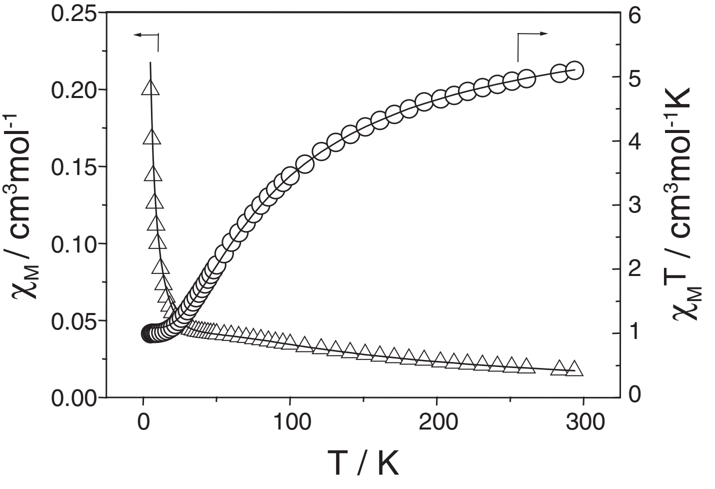

FIGURE 2 The χ_{M} and $\chi_{\mathrm{M}}T$ *vs.* T plots of the complex; the solid lines represent the best theoretical fitting.

the other symbols have their usual meanings. The best fitting gives $J = -14.0\,\mathrm{cm}^{-1}$, $g = 2.08$, The agreement factor $R = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2 / \sum \chi_{\mathrm{obsd}}$ is 7.6×10^{-4}.

According to Kahn [20], the antiferromagnetic interaction between copper(II) and manganese(II) arises from the nonzero overlap between the d_z^2 or $\mathrm{d}_{x^2-y^2}$ magnetic orbitals centered on the two metal ions and delocalized toward the ligands. The main factor influencing the magnitude of the interaction is the overlap between the molecular orbitals of the bridging groups and the singly-occupied d-metal orbitals. The larger the overlap, the stronger the antiferromagnetic interaction. One structural factor influencing the strength of antiferromagnetic interaction is the value of the dihedral angle (γ) between the mean equatorial plane of the metal ion (Mn1–O1–O2–C1–C2) and the oxiamido plane (N1–N2–N3–N4): the smaller the value of γ, the stronger the antiferromagnetic coupling [21,22]. The relatively large γ value (*ca* 10.8°) of this complex results in weak antiferromagnetic coupling between Cu(II) and Mn(II).

Acknowledgments

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