Exchange Interactions in the Bimetallic Chain Compound Cu(ethylenediamine)$_2$MnCl$_4$[1]

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The synthesis, crystal structure, and magnetic properties are reported for the new bimetallic compound $Cu(en)_2MnCl_4$, where en = $H_2NCH_2CH_2NH_2$. The compound, $C_4H_{16}N_4Cl_4CuMn$, crystallizes in the monoclinic space group $P2_1/a$. Cell dimensions are as follows: $a = 11.276(3)$ Å, $b = 13.904(3)$ Å, $c = 9.055(3)$ Å, $\beta = 91.26(2)°$; $Z = 4$; R(unweighted) = 0.029. The structure consists of chains in which alternating Mn(II) and Cu(II) ions are bridged by chloride ligands. The coordination environment is tetrahedral for Mn(II) and elongagted octahedral for Cu(II), the apical positions being occupied by the bridging ligands and the basal ones by the nitrogen atoms from the organic ligand. In the crystal, the chains lie in magnetically equivalent layers separated by about 7 Å. The magnetic susceptibility of the compound has been measured over the range 2−300 K. At room temperature the χT product (per MnCu unit) has a value of 4.80 emu·mol^{-1}·K, as expected for uncoupled $S = {}^5/_2$ and $S = {}^1/_2$ spins. When the temperature is lowered, χT remains quite constant until 20−10 K and then decreases to 1.54 emu·mol^{-1}·K at 1.6 K. Comparison between theory and experiment has been made with use of 1-D and 2-D models. The decrease of χT observed at low temperature for the compound is attributed to either a dominant Mn(II)···Mn(II) antiferromagnetic interaction within the chain or, alternatively, cooperative intrachain and interchain Mn(II)···Cu(II) interactions of opposite signs.

Introduction

Chains of Mn(II) ($S = {}^5/_2$) and Cu(II) ($S = {}^1/_2$) structurally ordered in an alternating manner are of intense current interest as potential starting blocks in the synthesis of molecular-based ferromagnets.[1−4]

Such an approach follows from the basic concept that as strict orthogonality of the magnetic orbitals cannot be achieved for a M(high-spin d^5)−M′(d^1) pair irrespective of local symmetries, an exchange interaction between Mn(II) and Cu(II) is most likely antiferromagnetic in nature.[4] So far reported Mn(II)···Cu(II) couplings conform to such a view.

In a pseudo-1-D chain, AF coupling of alternating $S = {}^5/_2$ and $S = {}^1/_2$ spins produces a ground state with all the $S = {}^5/_2$ spins aligned in the same direction. Interchain exchange in the crystal, provided that the shortest M···M contacts between adjacent chains occur between Mn(II) and Cu(II) ions, may extend the parallel alignment of the larger spins to the scale of the whole lattice, giving rise to spontaneous magnetization below a critical temperature, T_c.[3,4] Thus, three-dimensional ferromagnetic order is the end product of dominant Mn(II)···Cu(II) antiferromagnetic interactions along the chains and between the chains.

From a chemical point of view, therefore, a main task is to achieve systems in which Mn(II) and Cu(II) are the nearest-neighboring magnetic ions at the scale of the whole lattice. The distinct advantage over the synthesis of, e.g., a homopolymetallic system with all nn interactions ferromagnetic is that local symmetry requirements for strict or accidental orthogonality of the magnetic orbitals are avoided.

In this paper, we describe a new bimetallic compound of Mn(II) and Cu(II), $Cu(en)_2MnCl_4$, where en is $H_2NCH_2CH_2NH_2$. The compound has a structure composed of ordered bimetallic chains with shortest interchain M···M contacts, albeit loose, of the Mn(II)···Cu(II) type, but it shows magnetic properties that are quite different from those expected.

Experimental Section

Syntheses. (A) A 3.52-g (58.6 mmol) quantity of the en ligand was dissolved in absolute ethanol (40 mL). This solution was added to a solution of $CuCl_2·2H_2O$ (5.00 g, 29.3 mmol) in the same solvent (40 mL). The addition was made over a period of 10 min, at room temperature and with constant stirring. After the resulting blue solution was allowed to stand at room temperature for 2 h, a blue-violet crystalline precipitate of $Cu(en)_2Cl_2$ was collected by filtration, washed with absolute ethanol, and dried in a thermostated oven at 105 °C: yield 6.16 g (82%). Anal. Calcd for $C_4H_{16}N_4Cl_2Cu$: C, 18.86; H, 6.33; N, 22.00. Found: C, 19.04; H, 6.25; N, 21.95.

(B) A 5.09-g (20 mmol) quantity of $Cu(en)_2Cl_2$ was dissolved in absolute ethanol, at 60−70 °C. To the resulting solution was added 3.96 g (20 mmol) of $MnCl_2·4H_2O$ dissolved in 50 mL of ethanol. The addition was made over a period of 15 min, at 60 °C and with constant stirring. The reaction mixture was refluxed for an additional 30 min. After cooling of the solution to room temperature, crystallization was allowed to continue for about 3 h before violet, crystalline $Cu(en)_2MnCl_4$ was collected by filtration, washed with absolute ethanol, and dried under vacuum at 60 °C: yield 6.4 g (84%); mp 274−278 °C. Anal. Calcd for $C_4H_{16}N_4Cl_4CuMn$: C, 12.62; H, 4.24; N, 14.78. Found: C, 12.50; H, 4.25; N, 14.50.

Crystals of larger size, more suitable for X-ray analysis, were obtained in the following way. A 1.00-g quantity of the compound was dissolved in 70 mL of methanol, at room temperature. The solution was filtered. Absolute ethanol (80 mL) was added to the filtrate. After 36 h of standing at room temperature, well-formed violet crystals (0.4 g) were collected by filtration and dried under vacuum: mp 278−280 °C.

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Table 1. Crystallographic Data for $Cu(en)_2MnCl_4$

$C_4H_{16}N_4Cl_4CuMn$	fw = 380.5
cryst class: monoclinic	$T = 20$ °C
space group $P2_1/a$	$\lambda = 0.7107$ Å
$a = 11.276(3)$ Å	$\varrho = 1.752$ g·cm^{-3}
$b = 13.904(3)$ Å	$\mu = 31$ cm^{-1}
$c = 9.055(3)$ Å	transm coeff = 0.75−0.99
$\beta = 91.26(2)°$	$R = 0.029$
$V = 1419.3$ A^3	$R_w{}^a = 0.033$
$Z = 4$	

^{a} $R_w = (\Sigma(w|F_o| - |F_c|)^2)^{1/2}/(\Sigma wF_o^2)^{1/2}$; $w = (\sigma^2|F_o| + 0.0005F_o^2)^{-1}$.

Magnetic Susceptibility Measurements. Variable-temperature magnetic susceptibility measurements were performed in the range 2−290 K, with use of a Faraday type magnetometer equipped with a helium continuous-flow cryostat built by Oxford Instruments. Susceptibilies were corrected[5] for the diamagnetism of the ligand system (-161×10^{-6} emu·mol^{-1}) and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} emu/Cu atom). Our analyses did not include any zero-field splitting.

Crystallographic Data Collection and Structure Determination. A violet prismatic crystal with dimensions 0.25 × 0.20 × 0.15 mm^3 was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with a graphite-monochromatized Mo Kα radiation. Cell parameters were determined by a least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging between 15 and 24°. Cell dimensions and additional crystal data are listed in Table 1. The space group resulted from systematic extinctions. The intensities of the $\pm hkl$ reflections were collected up to $2\theta = 50°$; the $\omega-2\theta$ scan technique was employed, the scan range between 1.8° and the speed 0.06° s^{-1}. A total of 2798 independent reflections were measured; of these, 1460, having $I \leq 3\sigma(I)$, were considered as "unobserved" and excluded from the refinement. Three standard reflections that were measured periodically showed no apparent variation in intensity during the data collection. The data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections, according to the method of North et al.[6]

The structure was solved by direct methods with the SIR88 program[7] and refined by the full-matrix least-squares method with use of the SHELX-76 package of programs.[8] Anisotropic thermal parameters were refined for non-hydrogen atoms. The hydrogen atoms were included at the calculated positions (C−H = 1.08 Å) and refined with an overall temperature factor, $U = 0.06$ Å^2. The refinement was carried out with use of 129 parameters and 1338 independent reflections. The atomic scattering factors were taken from ref 8 for the Cl, C, N, and H atoms and from ref 9 for the Cu and Mn atoms; a correction for anomalous dispersion was included. Final positional parameters are given in Table 2.

Results

Description of the Structure. The structure of $Cu(en)_2MnCl_4$ consists of chains in which alternating Mn(II) and Cu(II) ions are bridged by chloride ligands. The chains are generated by unit cell translations of the $Cu(en)_2MnCl_4$ asymmetric unit, shown in Figure 1, along the c axis.

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Cu(en)_2MnCl_4$

	x/a	y/b	z/c	$U_{eq}{}^a$
Cu	−1954(1)	5089(0)	7544(1)	32(0)
Mn	−3109(1)	4905(1)	2634(1)	34(1)
Cl(1)	−1964(2)	5645(1)	4567(2)	42(1)
Cl(2)	−4436(1)	5981(1)	1475(2)	43(1)
Cl(3)	−4079(2)	3580(1)	3707(2)	44(1)
Cl(4)	−1732(1)	4463(1)	782(2)	40(1)
N(1)	−3364(4)	5885(3)	8049(6)	37(3)
N(2)	−1016(4)	6298(3)	8059(6)	38(3)
C(1)	−3005(6)	6899(4)	8296(8)	43(4)
C(2)	−1785(6)	6899(5)	9006(8)	48(4)
N(3)	−546(5)	4224(4)	7288(7)	46(4)
N(4)	−2914(5)	3905(4)	7106(6)	39(3)
C(3)	−2138(7)	3064(5)	7108(11)	65(6)
C(4)	−992(8)	3327(5)	6512(11)	69(6)

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized thermal tensor.

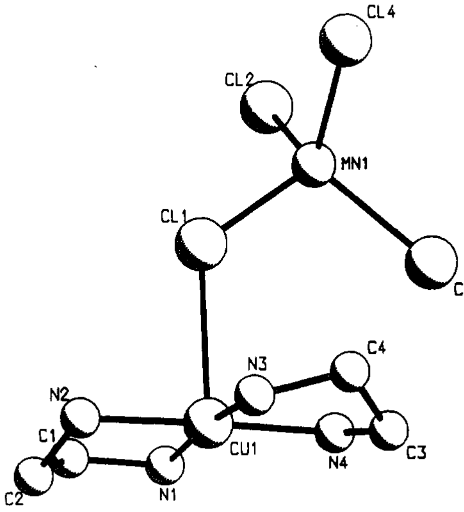

Figure 1. View of the $Cu(en)_2MnCl_4$ asymmetric unit. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg)

Cu−N(1)	1.999(5)	Cu−Cl(4)	3.063(2)
Cu−N(2)	2.034(5)	Mn−Cl(1)	2.385(2)
Cu−N(3)	2.009(5)	Mn−Cl(2)	2.347(2)
Cu−N(4)	2.005(5)	Mn−Cl(3)	2.362(2)
Cu−Cl(1)	2.804(2)	Mn−Cl(4)	2.391(2)
N(1)−Cu−N(2)	84.4(2)	N(4)−Cu−Cl(1)	92.6(1)
N(2)−Cu−N(3)	96.5(2)	N(4)−Cu−Cl(4)	89.3(1)
N(3)−Cu−N(4)	84.8(2)	Cl(1)−Cu−Cl(4)	175.5(1)
N(4)−Cu−N(1)	94.1(2)	Cl(1)−Mn−Cl(3)	106.4(1)
N(4)−Cu−N(2)	177.8(2)	Cl(2)−Mn−Cl(3)	112.6(1)
N(3)−Cu−N(1)	173.0(2)	Cl(3)−Mn−Cl(4)	113.7(1)
N(2)−Cu−Cl(1)	89.1(1)	Cl(1)−Mn−Cl(2)	112.5(1)
N(2)−Cu−Cl(4)	89.1(1)	Cl(1)−Mn−Cl(4)	106.0(1)
N(3)−Cu−Cl(1)	92.4(1)	Cl(2)−Mn−Cl(4)	105.5(1)
N(3)−Cu−Cl(4)	83.8(1)	Cu−Cl(1)−Mn	125.3(1)
N(1)−Cu−Cl(1)	94.6(1)	Cu−Cl(4)′−Mn′	123.9(1)
N(1)−Cu−Cl(4)	89.3(1)		

The Mn(II) coordination environment closely approximates tetrahedral symmetry, the average Cl−Mn−Cl bond angle being 109.3°. The Cu(II) ion has elongated octahedral surroundings; the equatorial positions are occupied by the nitrogen atoms from the organic ligand and the axial positions by the bridging Cl(1) and Cl(4)′ ions (Cu−Cl(1) = 2.804(2) Å, Cu−Cl(4)′ = 3.063(2) Å, Cl(1)−Cu−Cl(4)′ = 175.5(1)°). The CuN_4 fragment is largely planar. The Cu−Cl(1)−Mn and Cu−Cl(4)′−Mn′ bridging angles are 125.3(1) and 123.9(1)°, respectively (′ = x, y, z + 1). The alternating Cu···Mn and Cu···Mn′ intrachain separations are 4.612(2) and 4.824(2) Å, respectively.

As shown in Figure 2, the symmetry of the chain is close to C_2, successive CuN_4 fragments being related by the 2-fold rotation axis of the intervening $MnCl_4$ tetrahedron bisecting the

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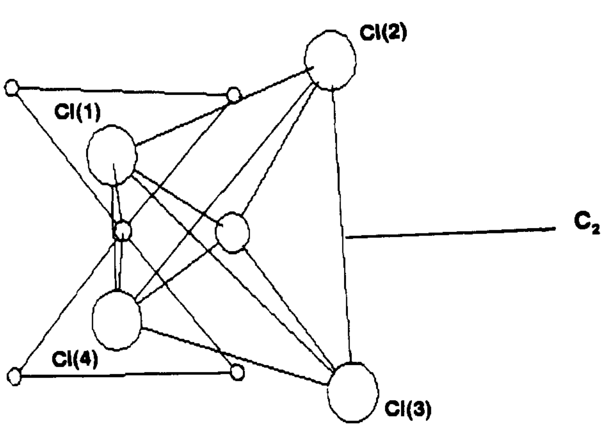


Figure 2. Schematic view of $Cu(en)_2MnCl_4$ along the *c* axis, showing the C_2 symmetry of the chain. The edges of the Cl_4 tetrahedron are also shown.

Cl(2)−Cl(3) and Cl(1)−Cl(4) edges. The main deviation from ideal symmetry is represented by the nonequivalent Cu•••Mn separations.

In the crystal, the Cl-bridged chains assemble in layers orthogonal to [010]. The shortest M•••M contacts between layers occur between Cu and the Mn atoms at $-^1/_2 - x$, $^1/_2 + y$, $1 - z$, 6.699 Å, and at $-^1/_2 - x$, $-^1/_2 + y$, $1 - z$, 7.210 Å.

The chain arrangement within a layer is schematically shown in Figure 3. The shortest interchain M•••M[10] and N•••Cl separations occur along the *a* direction. These are Cu•••Mn″ = 5.566 Å (″ = $-1 - x$, $1 - y$, $1 - z$), Cu•••Mn‴ = 5.715 Å (‴ = $-x$, $1 - y$, $1 - z$), N(1)•••Cl(3)″ = 3.346 Å, N(4)•••Cl(2)″ = 3.282 Å, N(2)•••Cl(4)‴ = 3.418 Å, and N(3)•••Cl(1)‴ = 3.328 Å. The alternate arrangement of $MnCl_4$ tetrahedra and CuN_4Cl_2 pseudooctahedra in the *a* direction approximates 2-fold rotational symmetry around either the C_2 axis of $MnCl_4$ bisecting the Cl(2)−Cl(4) and Cl(1)−Cl(3) edges or the Cl(1)−Cu−Cl(4)′ axis of CuN_4Cl_2.

The above interchain N•••Cl distances are not significantly different from the sum of van der Waals radii of N and Cl, 3.30 ± 0.10 Å.[11] So, in the absence of accurately located hydrogen atoms, there is no clear evidence for the presence (or absence) of attractive hydrogen-bonding interactions. However, the NH stretching and bending modes in the vibrational spectrum of the compound appear as sharp bands of medium intensity, at frequencies ($\nu_{as} = 3303$ cm^{-1}, $\nu_s = 3240$ cm^{-1}, $\nu_b = 1573$ cm^{-1}) that closely correspond to those found for several related $M(en)_2^{2+}$ complexes,[12−14] e.g. $Pt(en)_2PtCl_4$ ($\nu_{as} = 3291$ cm^{-1}, $\nu_s = 3216$ cm^{-1}, $\nu_b = 1575$ cm^{-1}),[12] in which H-bonding interactions have been estimated as either absent or very weak. On this basis, the individual chains appear to be basically held together by van der Waals forces.

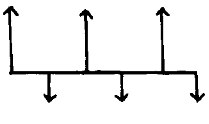
Magnetic Properties. The magnetic behavior of the compound is represented in Figure 4, in the χT vs T fashion, χ being the corrected molar magnetic susceptibility per MnCu unit. At room temperature, the χT value is 4.80 emu•mol^{-1}•K, close to that expected for uncoupled $S = {}^5/_2$ and $S = {}^1/_2$ spins (4.75 emu•mol^{-1}•K for $g_{Mn} = g_{Cu} = 2$). When the temperature is lowered, χT remains quite constant until 20−10 K and then decreases to 1.54 emu•mol^{-1}•K at 1.6 K.

The $1/\chi$ vs T plot above ca. 20 K gives a Curie constant, *C*, of 2.804 cgsu•K. For $g_{Mn} = 2$,[15,16] the calculated *g* value for Cu is 2.13. These *g* values were held constant during all the fitting calculations described below.

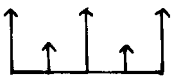
Discussion

We first note that the decrease of χT observed at low temperature for $Cu(en)_2MnCl_4$ cannot be reconciled with the presence of a 1-D system with dominant exchange between nearest-neighbor spins.

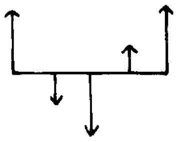
In an antiferromagnetic nn chain ($J < 0$) the uncompensated ($S_{Mn} - S_{Cu}$) = 2 local spins are parallel to each other in the ground state (**1a**) and χT diverges in the limit of T approaching zero. Yet to be reported dominant ferromagnetic nn coupling ($J > 0$) should produce a similar result at low temperature since all the spins would have the same alignment at 0 K (**1b**).



1a



1b



1c

In principle, the decrease of χT on lowering T might be ascribed to the presence of a nonmagnetic ground state determined by alternating ferromagnetic−antiferromagnetic exchange (**1c**), similar to that recently observed for some other linear chain systems having asymmetrically bridged spin centers.[17−19] Such a spin arrangement, however, is not tenable for $Cu(en)_2MnCl_4$. Owing to the above-mentioned C_2 symmetry of the chain, the interacting orbitals along the Mn•••Cu pathway have the same relative orientation as those along the adjacent Mn•••Cu′ pathway. This ensures equal sign for the corresponding exchange interactions.

From what precedes, it emerges that interactions other than 1-D exchange between nn spins must play a significant role in the magnetic structure of the compound.

As these additional interactions can be either intrachain or interchain in origin and there are no precedents to guide a choice, both the possibilities of quasi 1-D and 2-D exchange are examined.

In the intrachain hypothesis, the observed decrease of χT with T may be related to antiferromagnetic coupling of next-nearest-neighboring $S = {}^5/_2$ spins. A rationale for this comes from the geometry of the CuN_4Cl_2 fragments. The site symmetry at copper is very close to C_{2v} (and not far from C_{4v}; the average deviation of the N−Cu−N angles from 90° is 5.3°). In C_{2v} symmetry the Cu(II) unpaired electron is mostly described by an *xy*-like orbital directed toward the nitrogen ligands and transforming as a_2. Since in C_{2v} there is no admixture of out-of-plane components into the in-plane a_2 orbital, significant delocalization of spin density from Cu(II) to the apical Cl bridges cannot occur and the overlap density between the magnetic orbitals around the bridging atoms is virtually zero. Therefore,[4] very weak Cu(II)−Cl−Mn(II) superexchange is expected.

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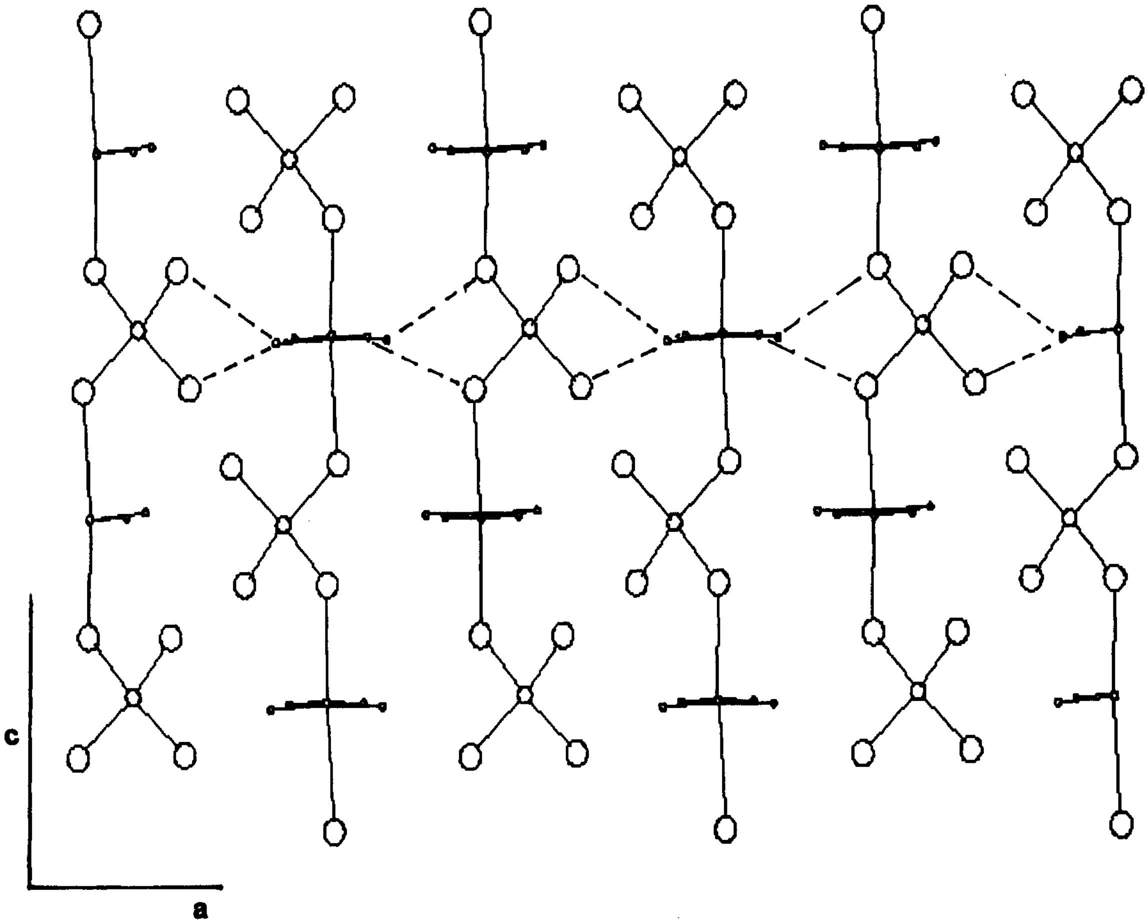

Figure 3. Schematic view, approximately along the *b* axis, of the chain arrangement in a layer. Dashed lines indicate the N$\cdots$Cl contacts discussed in the text.

Under the circumstances, Mn(II)$\cdots$Mn(II)′ superexchange mediated by the filled z^2-like orbital of the Cl−Cu(en)$_2$−Cl manifold might overcome the Mn(II)$\cdots$Cu(II) and, of course, Cu(II)$\cdots$Cu(II)′ interactions. We note that a rather similar situation has permitted the direct observation of significant coupling of fourth-neighboring spins in a linear tetramer of Cu(II).[20]

As no reliable theoretical model is available to treat next-nearest-neighbor interactions explicitly,[21] we tested the above concepts by calculating the magnetic susceptibility of the chain, χ_{chain}, in the limit of vanishingly small Mn(II)$\cdots$Cu(II) and Cu(II)$\cdots$Cu(II)′ interactions; i.e., a temperature-independent contribution from Cu(II) was added to the susceptibility expression for a linear chain of $S = {}^5/_2$ spins, as in eq 1, where the first term describes a Mn(II) chain according to the classical result of Fisher[22] scaled to a real spin of ${}^5/_2$.[23]

$$\chi_{\text{chain}} = C(1 + \mu)/(1 - \mu) + Ng_{\text{Cu}}^2\mu_{\text{B}}^2 s(s + 1)/3kT \quad (1)$$

$$C = Ng_{\text{Mn}}^2\mu_{\text{B}}^2 S(S + 1); \quad \mu = \coth(K) - 1/K$$

$$K = 2JS(S + 1)/kT; \quad S = {}^5/_2;\ s = {}^1/_2$$

Residual 2-D interactions were accounted for by the addition of a mean field correction term[24,25] to eq 1. The equation for the susceptibility (per Mn−Cu pair) then has the form (2), where

$$\chi = \chi_{\text{chain}}/[1 - \chi_{\text{chain}}(2zJ'/Ng^2\mu_{\text{B}}^2)] \quad (2)$$

J' is the interchain coupling constant and z is the number of interacting neighbors, 2 in this case. Other symbols have their usual meaning.

The best fit from eq 2 to the data was found with $J = 0.10(1)$ cm^{-1} and $J' = 0.003(1)$ cm^{-1}, and as it appears from Figure 4 (in the χT vs T form), it may be considered as fairly good. The agreement factor, defined as $F = \sum_i(\chi_i^{\text{obs}})^{-1}(\chi_i^{\text{obs}} - \chi_i^{\text{calcd}})^2$, was $F = 2.9 \times 10^{-3}$, for 75 observations. As in subsequent calculations, only data below 100 K were used.

In terms of total exchange energies ($E_{\text{ex}} = |4J_{\text{AB}}S_{\text{A}}S_{\text{B}}|$),[4,26,27] the magnitude of the intrachain Mn$\cdots$Mn interaction is 2.50 cm^{-1}, that of the interchain Mn$\cdots$Cu interaction is 0.015 cm^{-1}, and the 1-D character of the chain is given by $|5J'/25J| = 6 \times 10^{-3}$. According to these results, therefore, the material consists of virtually isolated next-nearest-neighbor chains.

In the 2-D hypothesis, we must assume a significant role of the most likely weak exchange propagated by the long Cu−N−H$\cdots$Cl−Mn interchain pathways, and thus, in light of the results from the preceding model, the notion of dominant Mn(II)$\cdots$Mn(II) intrachain exchange must be abandoned in favor

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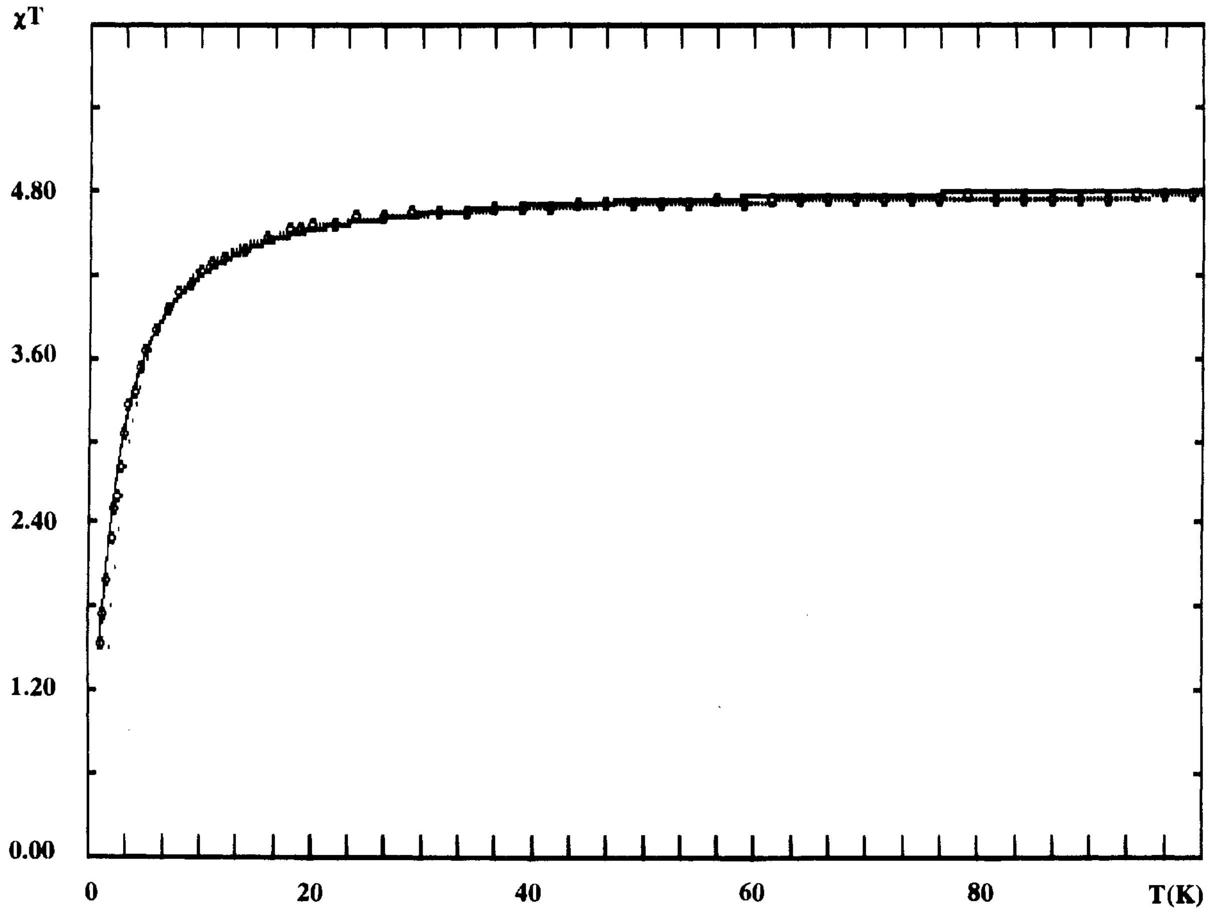
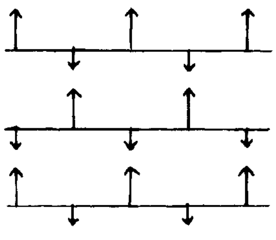


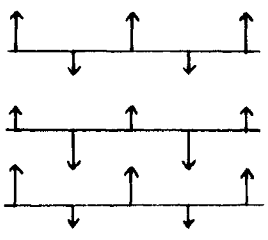
Figure 4. Experimental and theoretical temperature dependence of χT for $Cu(en)_2MnCl_4$ between ca. 2 and 100 K. The solid line through the data was generated by the 1-D model eq 2 and the dotted line by the 2-D model eq 3.

of cooperative intrachain and interchain, feeble Mn(II)···Cu(II) interactions. A model can be based on the following concept.

Each layer in the structure is formed by cross-linked chains directed along *a* and along *c*, respectively. An antiferromagnetic coupling of Mn(II) and Cu(II) along both the *a* and *c* directions will tend to align all the $S = {}^5/_2$ spins in the 2-D network parallel to each other (**2a**) while antiferromagnetic coupling along *a* and ferromagnetic coupling along *c* or vice versa will lead to a cancellation of the spins (**2b**). In the former case χT should increase at low temperature (as experimentally observed for, e.g., $(NBu_4)_2[Mn_2Cu(opba)]_3$[3] or $MnCu(pbaOH)(H_2O))$,[28] and in the latter it should decrease, which could be at the origin of the behavior of the present compound.



2a



2b

In the absence of rigorous models, an estimate of exchange was attempted by treating the magnetic susceptibility of the 2-D system as that of a *c* (or *a*) directed chain of classic spins, these being the effective spins, S_{eff}, per Mn–Cu pair along the chains in the other direction. The 2-D system is mimicked as a chain of chains.[29] The expression for the susceptibility (per Mn–Cu pair) has the form of eq 3,[22] where, at each temperature, S_{eff} is given by eq 4. The model of Pei et al,[30] which can make

$$\chi = [N\mu_B^2 g_{eff}^2 S_{eff}(S_{eff} + 1)/3kT](1 + \mu)/(1 - \mu) \qquad (3)$$

$$\mu = \coth(K) - 1/K; \quad K = 2J'S_{eff}(S_{eff} + 1)/kT$$

$$S_{eff} = \{-1 + [1 + 4\chi_{chain}T/(0.1251\ g_{eff}^2)]^{1/2}\}/2 \qquad (4)$$

allowance for alternating exchange, was used to generate χ_{chain}. In this model the spin Hamiltonian has the form of eq 5, where

$$H = -2J\sum_i S_1^i[(1 + \alpha)S_2^i + (1 - \alpha)S_2^{i+1}] \qquad (5)$$

the exchange constant is written as $-2J$ to conform to eq 3. The alternating exchange strengths are described by $J(1 + \alpha)$ and $J(1 - \alpha)$; $\alpha \neq 0$ corresponds to an alternating chain and $\alpha = 0$ to a uniform chain. On the assumption of purely isotropic interactions and considering S_{Mn} as a classical spin and S_{Cu} as a quantum spin, the following expression for the magnetic susceptibility (per MnCu unit) is deduced:

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$$\chi_{\text{chain}} = (N\mu_\beta^2/3kT)\{g_{\text{Cu}}^2[S_{\text{Cu}}(S_{\text{Cu}}+1)(1-P)+2RQ] + 4g_{\text{Cu}}g_{\text{Mn}}S_{\text{Cu}}S_{\text{Mn}}(R+Q) + g_{\text{Mn}}^2S_{\text{Mn}}^2[(S_{\text{Mn}}+1)(1-P)/S_{\text{Mn}}+2P]\}/(1-P) \quad (6)$$

Formulas for P, Q, and R that have been found convenient to use are given in the Appendix. An accurate best fit ($F = 4.2 \times 10^{-3}$) of eq 3 to the data was achieved with $J = 0.56(1)$ cm^{-1}, $\alpha = 0.00(1)$, $J' = -0.12(1)$ cm^{-1}, and $g_{\text{eff}} = 2.00(1)$. The calculated curve is shown in Figure 4.

The different signs of the exchange parameters found for the two chains are clearly in agreement with the proposed 2-D hypothesis. Such a feature, although unusual, might not be too surprising since the quite small absolute values calculated for both J and J' are consistent with nearly compensated opposing AF and F contributions ($J = J_{\text{AF}} + J_{\text{F}}$),[4,31] which, in light of the structural features discussed above, are presumably very weak. In other terms, the model results suggest a situation in which it takes little to turn the balance between J_{AF} and J_{F} on either side. Recently reported weak ferromagnetic interactions between[32] Gd(III) and nitronyl nitroxides or between[33,34] Gd(III) and Cu(II) are worthy of note in this regard.

Without additional experimental evidence, there does not seem to be much point in speculating on which of the two chains in the present structure might be the ferromagnetic one.

Conclusions

The ground state of low-spin multiplicity revealed by the magnetic data for $Cu(en)_2MnCl_4$ must be reconciled with a structure composed of ordered bimetallic chains with shortest M···M interchain contacts, albeit loose, of the Mn(II)···Cu(II) type. This cannot be done unless the usually accepted notion of dominant antiferromagnetic exchange between nearest-neighboring Mn(II) and Cu(II) is released.

The magnetic data are reproduced comparably well by two inconsonant models based on either a vanishingly small Mn(II)···Cu(II) interaction that leads to dominant intrachain AF coupling of second-neighbor Mn(II) ions or, alternatively, cooperative intrachain and interchain Mn(II)···Cu(II) interactions of opposite signs. The study of an isolated Cu(II)–Mn(II) dimer similar in structure to the $Cu(en)_2MnCl_4$ unit will assist in answering the question of which model is an artifact of the other. Efforts in this direction are under way. However, whatever the right model may be, $Cu(en)_2MnCl_4$, in spite of a seemingly favorable structure in which Mn(II) and Cu(II) are the nearest-neighboring magnetic ions at the scale of the whole lattice, is not a suitable candidate for molecular ferromagnetism, and this is most likely determined by local symmetries.

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Appendix

$$X = 2J/kT; \quad p = -2XS_{\text{Mn}}; \quad m = \alpha p; \quad z = (p^2 - m^2)/4$$

$$a = \cosh(p/2) - \cosh(m/2); \quad b = \cosh(p/2) + \cosh(m/2)$$

$$c = p\sinh(p/2) - m\sinh(m/2); \quad d = p\sinh(p/2) + m\sinh(m/2)$$

$$A_0 = (4/z)(-2a + c); \quad B_0 = 2a/z$$

$$A_1 = (8/z^2)[-a(12 - m^2) - z(3b + 2a - d/2) + 6c]$$

$$B_1 = (2/z^2)(4a + zb - 2c)$$

$$P = A_1/A_0; \quad P_1 = B_0/A_0; \quad P_2 = B_1/A_0$$

$$Q = XS_{\text{Mn}}[(1+\alpha)P_1 + (1-\alpha)P_2]$$

$$R = XS_{\text{Mn}}[(1-\alpha)P_1 + (1+\alpha)P_2]$$

These formulas are useful since the function of eq 6 becomes discontinuous when X is small (less than about 0.2). This can be avoided by approximating (when $X < 0.2$) $\sinh(X)$ and $\cosh(X)$ as $(X + X^3/3!)$ and $(1 + X^2/2! + X^4/4!)$, respectively. This gives the following expressions for P, P_1, and P_2:

$$P = z(1-\alpha^2)/[12(1-\alpha^2) + 3z(1+\alpha^2)]$$

$$P_1 = [12 + X^2(1+\alpha^2)]/[48 + 12X^2(1+\alpha^2)]$$

$$P_2 = X^2(1+\alpha^4)/[48(1-\alpha^2) + 12X^2(1-\alpha^4)]$$

Supplementary Material Available: Tables giving bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (2 pages). Ordering information is given on any current masthead page.

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