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O. Piovesana [a], B. Chiari [a] & A. Cinti [a]
[a] Dipartimento di Chimica, Universitá di Perugia, 06100, Perugia, Italy

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NEXT-NEAREST NEIGHBOR EXCHANGE INTERACTIONS IN THE BIMETALLIC CHAIN COMPOUND $Cu(en)_2MnCl_4$.

O. PIOVESANA, B. CHIARI, A. CINTI
Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy.

Abstract The magnetic properties of the title compound reveal antiferromagnetic coupling between the next-nearest neighbor Mn(II) ions and no discernible MnCu coupling.

INTRODUCTION

One-dimensional chains with two different spins structurally ordered in an alternating manner, for example bimetallic chains of Mn(II) (S=5/2) and Cu(II) (S=1/2), are of intense current interest as potential starting blocks in the synthesis of molecular-based ferromagnets.[1]

This approach relies on a distinctive feature of such chains, i.e., exchange coupling of nearest-neighbor local spins, be it ferro- or antiferromagnetic in nature, stabilizes a ground state of high spin multiplicity.[1,2]

The important idea is that, owing to this property, control of local symmetries in the synthesis process should be of secondary importance to achieve a highly magnetic ground state for the individual chains, a prerequisite for going toward 3-D ordering.

In the present paper, we describe a new bimetallic chain compound of Mn(II) and Cu(II), $Cu_2(en)_2MnCl_4$, where en is H_2N-CH_2-CH_2-NH_2. The structural and magnetic properties of this compound show that, actually, symmetry can impose severe limitations to the use of bimetallic chains in the synthesis of molecular ferromagnets.

STRUCTURE OF THE COMPOUND

The structure of $Cu_2(en)_2MnCl_4$ (monoclinic space group $P2_1/a$, a=11.276(3), b=13.904(3), c=9.055(3) Å, β=91.26°, R=0.029) consists of 1-D 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.

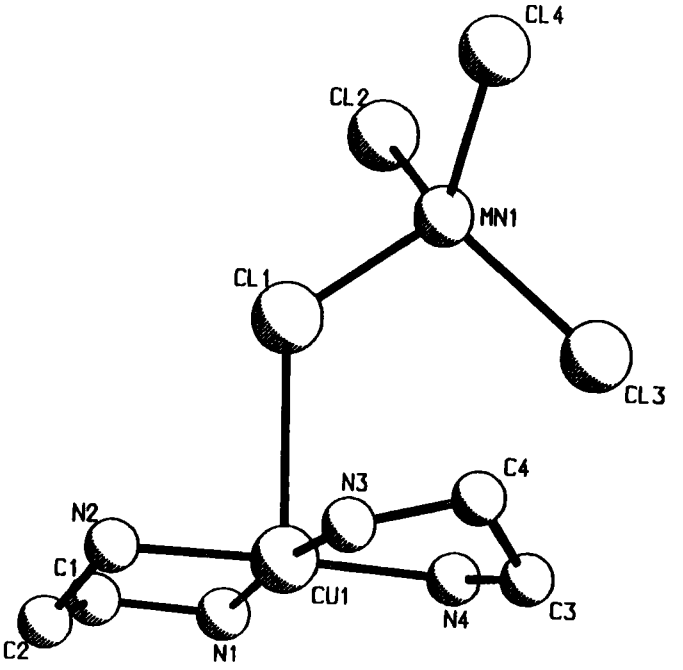


FIGURE 1. The asymmetric unit of $Cu(en)_2MnCl_4$.

The coordination environment around the Mn(II) ion closely approximates tetrahedral geometry, the average Cl-Mn-Cl angle being 109.3°. The Cu(II) ion has elongated octahedral surroundings; the equatorial positions are occupied by the nitrogen atoms from the organic ligands and

the axial positions by the bridging Cl(1) and Cl(4)' atoms (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. Owing to the slightly different bridging bond lengths and angles the Cu...Mn separation within the chain alternates between two values, 4.612(2) and 4.824(2) Å.

The shortest Mn...Mn, Cu...Cu, and Mn...Cu separations between metal atoms belonging to neighboring chains are those related to the a-glide translation: 8.747, 9.144, and 10,714 Å, respectively. The structural determination does not reveal any close contacts between chains that may be regarded as bonding interactions, suggesting that the individual chains in the structure are effectively isolated.

MAGNETIC PROPERTIES

The magnetic data for the compound are shown in Figure 2, in the $\chi_M T$ vs T fashion, χ_M being the molar magnetic susceptibility per MnCu unit. At room temperature the $\chi_M T$ 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, $\chi_M T$ remains quite constant until 20-10 K and then decreases to 1.48 emu·mol^{-1}·K at 1.6 K.

This behavior is stronly at variance with that expected for a regular nearest-neighbor magnetic chain, be it a uniform chain, characterized by a unique coupling constant, or an alternate system with alternation parameter $0<\alpha<1$. For ferromagnetic coupling all the spins are parallel to each other at 0 K and $\chi_M T$ diverges. When the coupling is antiferromagnetic $\chi_M T$ is also expected to diverge in the limit of T approaching zero, owing to the parallel alignment in the ground state of the $(S_{Mn}-S_{Cu})=2$ local spins.[1,2] For a system with uncoupled spins $\chi_M T$ should obviously remain

constant throughout the whole temperature range at 4.80 emu·mol^{-1}·K.

The low-temperature magnetic response of $Cu(en)_2MnCl_4$ is not even explicable in terms of antiferromagnetic exchange between chains. This interchain hypothesis was tested by fitting the experimental data to models obtained by adding a molecular field correction[3,4] to the reported formulas for

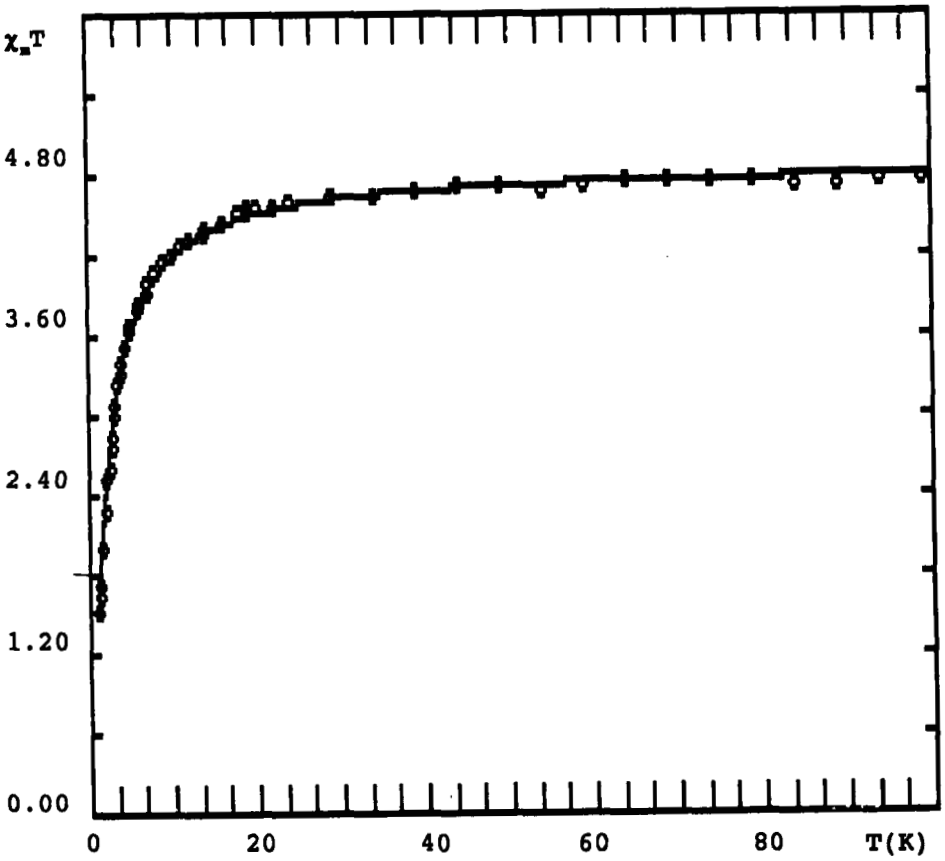


FIGURE 2. Temperature dependence of the $\chi_M T$ product of $Cu(en)_2MnCl_4$ between 1.5 and 100 K.

uniform alternating-spin chains[5,6] and regular alternating-spin-alternating-exchange chains[7] (where allowance can be

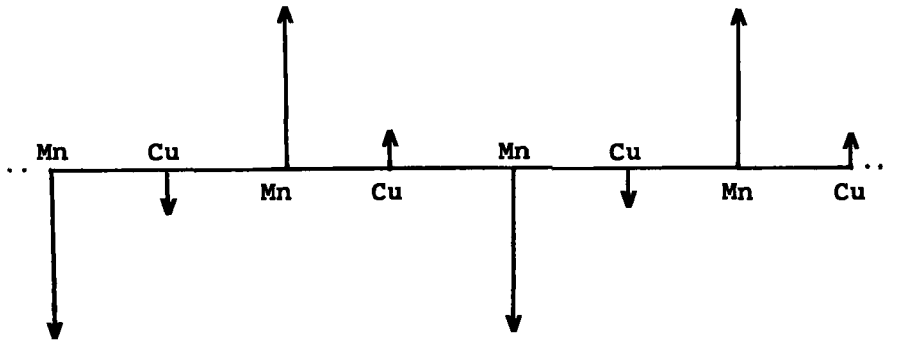
made for the slightly different Cu...Mn intrachain separations observed in the X-ray structure). The molecular field correction was taken in the form:

$$\chi = \chi_{chain}/[1-(nzJ'/Ng^2\mu_B^2)\chi_{chain}] \qquad (1)$$

The magnetic data could not be fit with this theory to any reasonable extent.

This feature, coupled with the structural determination which shows neither short contacts between chains nor any discernible interchain exchange pathway, leads to conclude that the origin of the observed decrease of $\chi_M T$ on lowering the temperature must be sought within the chains.

First, it is useful to consider again what may be expected from nearest neighbor interactions. For these to justify the low-temperature magnetic behavior of the compound, one must postulate the existence of exchange coupling of opposite sign within the chain, leading to the spin arrangement depicted below and, hence, to a nonmagnetic ground state.



Such an alternating ferromagnetic-antiferromagnetic exchange model[7] can approximately reproduce the experimental data (with J_1=6.57 cm^{-1}, J_2=-2.19 cm^{-1}, g_{Mn}=2.04, and g_{Cu}=1.97) but it is not thought to be realistic, since it cannot be

reconciled with the symmetry properties of the structural chain. The magnetic orbital of each copper atom has virtually the same orientation with respect to the d orbitals of its adjacent manganese atoms (vide infra).

In addition, graphical extrapolation to 0 K of the experimental $\chi_M T$ vs T plot gives a limiting nonzero value for $\chi_M T$.

It follows that nearest-neighbor interactions are insufficient to describe the magnetic structure of the compound. Next-nearest neighbor interactions must also be considered.

A relevant indication in this regard is given by the $\chi_M T$ value extrapolated at 0 K, ca. 0.4 emu·mol^{-1}·K, which agrees well with that expected for a Curie-behaved copper ion. This suggests that $\chi_M T$ be described as the sum of a temperature-independent contribution from Cu(II) and that of an antiferromagnetic S=5/2 chain.

A similar suggestion is given by calculational results obtained with use of a recently proposed Ising model in which next-nearest neighbor interactions are explicitly taken into account.[8] The results were in only a qualitative agreement with experiment (Ising models are intrinsically inadequate for Mn(II) and Cu(II)) but indicated a J_{Mn-Cu} close to zero.

In light of these considerations, the data were fitted by calculating the magnetic susceptibility according to eq 2,

$$\chi T = \chi_C (1 + \mu)/(1 - \mu) + N g_{Cu}^2 \mu_B^2 s(s + 1)/3kT \qquad (2)$$

where:

$$\chi_C = N g_{Mn}^2 \mu_B^2 S(S+1)/3kT \qquad \mu = \coth K - 1/K$$

$$K = 2JS(S+1)/kT \qquad S = 5/2; \quad s = 1/2.$$

The first term in this equation gives the magnetic susceptibility for an antiferromagnetic Mn(II) chain

according to the classical result of Fisher[9], scaled to a real spin of 5/2[10] and the second term pertains to the uncoupled s=1/2 spins. An excellent fit to the data was obtained with g_{Mn}=2.013, g_{Cu}=2.15, and J=-0.10 cm^{-1}. The agreement factor, defined as $F=\Sigma_i(\chi_i^{obs})^{-1}(\chi_i^{obs}-\chi_i^{calcd})^2$, was $F=3x10^{-3}$ for 75 observations. The theoretical curve between 1.6 and 100 K is given in Figure 2.

The apparent absence of CuMn exchange within the chain is surprising and tentatively attributed to a compensation of weak ferro- and antiferromagnetic contributions. Consider the following.

The site symmetry of copper is very close to C_{2v}. In such a symmetry the metal unpaired electron is described by a d_{xy}-like orbital directed toward the nitrogen ligands and transforming as b_1. Since the magnetic orbital does not mix with the d_{z2} orbital pointing toward the Cl(1) and Cl(4)' apical sites and transforming as a_1, the Cu...Mn exchange can be predicted to be weak.

In the $MnCl_4$ tetrahedron the p orbitals on each chlorine atom are combined in an antibonding fashion with the d orbitals of the Mn atom. Overlap of the p orbitals of the bridging chlorine atoms with the copper magnetic orbital will lead to an antiferromagnetic contribution, orthogonality will give a ferromagnetic contribution.

Using the conventional tetrahedral coordinate system, the lower lobe of the p_z and p_x orbitals of the bridging Cl(1) and Cl(4)' atoms will point toward the CuN_4 plane while the p_y orbitals will be virtually parallel to that plane.

The N(2)-Cu-Cl(1)-Mn torsional angle is -170.04°, so that the lower lobes of the p_z and p_x orbitals of Cl(1) are almost coplanar with the d_{xy} orbital lobe of Cu directed along the N(2)-N(4) axis and p_y is virtually parallel to the other lobe of d_{xy}. The overlap of d_{xy} with p_z and p_x leads to an antiferromagnetic contribution and the near orthogonality of d_{xy} and p_y to a ferromagnetic contribution.

The corresponding N(2)-Cu-Cl(4)'-Mn' torsional angle for

the Cl(4)' bridge is 88.48°, so that the interactions are virtually the same as before, with p_y giving zero overlap with the d_{xy} lobe directed along the N(2)-N(4) direction, and p_z and p_x interacting antiferromagnetically with the other lobe of d_{xy}.

The longer length of the Cu-Cl(4)' distance, as compared to the Cu-Cl(1) distance, is unlikely to introduce any difference between the Cu...Mn and Cu...Mn' interactions because a lengthening of the Cu-Cl distance has a similar effect on the d-p interactions that lead to the compensating ferro- and antiferromagnetic contributions in each bridge.

In light of these considerations, the Mn...Mn coupling is most lkely determined by second order interactions involving the copper d_{z2}-like filled orbital.

To sum up, the $Cu(en)_2MnCl_4$ chain, owing to symmetry, lacks Mn...Cu coupling and hence a highly magnetic ground state. Bimetallic compounds of Mn(II) and Cu(II) with structures similar to that observed here are, therefore, not suitable starting blocks for obtaining molecular ferromagnets.

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