Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Maria Cristina Burla , Brunetto Chiari , Antonio Cinti & Olivo Piovesana (1995): Structure and Magnetism of a New 2-D Bimetallic Compound of Mn(II) and Cu(II), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 273:1, 211-217

To link to this article: http://dx.doi.org/10.1080/10587259508031857

Mol. Cryst. Liq. Cryst., 1995, Vol. 273, pp. 211–217
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STRUCTURE AND MAGNETISM OF A NEW 2-D BIMETALLIC COMPOUND OF Mn(II) AND Cu(II).

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ABSTRACT We present the X-ray structure and the magnetic properties of the new compound $\{[Cu(en)_2]_3[Mn(NCS)_6]\}(NCS)_2$ (en = $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$).

INTRODUCTION

In recent years there has been an intensive search for molecular-based ferromagnets with high T_c.[1]

Most of the strategies so far developed on this purpose have made use of ferromagnetic or ferrimagnetic 1-D chains as structural building blocks.[1,2] Ferromagnetic ordering below a critical temperature (that is most generally a 3-D phenomenon, it may exceptionally occur in two dimensions but never in one dimension) can be achieved if the 1-D chains are assembled in a ferromagnetic fashion within the crystal. In that case, for a Heisenberg model, $T_c = S^2(|J_{intrachain} J_{interchain}|)^{1/2}/k$. Thus, the success of the 1-D approach crucially depends on our ability to govern both the sign and magnitude of interchain exchange within the crystal lattice.

From a chemical viewpoint, the not easy task of controlling factors such as the relative positions of the chains in the structure or interchain distances between magnetic centers has to be accomplished through the synthesis process, lattice changes induced by thermal treatments etc.

Although, in principle, systems in which the spin carriers are chemically linked in a 2-D or 3-D network should offer prominent advantages over the 1-D ones, attempts at

constructing such networks of higher dimensionality have been relatively few.[3,4] With an aim toward increasing the number of 2-D bimetallic systems and contributing to understand their potential, we here describe a novel compound of Mn(II) and Cu(II), this being $\{[Cu(en)_2]_3[Mn(NCS)_6]\}(NCS)_2$, where en = $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$.

STRUCTURAL INFORMATION

The compound crystallizes in the triclinic space group $P\bar{1}$. Cell constants are: a = 11.175(2), b = 11.832(2), c = 9.197(2) Å, α = 111.47(2), β = 103.35(2), γ = 98.45(2) °. Z = 1. The structure was refined to an R value of 0.034, for 2377 reflections and 189 parameters.

A schematic view of the structure, along the [0 0 1] direction, is presented in Figure 1. Each Mn(II) ion is octahedrally coordinated to six N-bound NCS^- groups, each of which is S-bound to the apical position of a nearly planar $Cu(en)_2$ fragment. All the Mn^(NCS) angles are ~ 172° but the bridging (NCS)^Cu angles are of two types: ~90° in the case of the four bridgind ligands occupyng the equatorial positions on the Mn atom and ~145° for the remaining two. Owing to this feature, cross-linked chains directed along the [1 0 0] and [0 1 1] directions, respectively, generate infinite pseudo 2-D networks parallel to (0 1 $\bar{1}$). In each plane, the chain along [1 0 0] consists of alternating and uniformly spaced Mn and Cu atoms (Mn...Cu = 5.599 Å, (NCS)^Cu ~ 90°), while two Cu atoms intervene between successive Mn atoms along [0 1 1]. The Mn...Cu separation along this latter direction alternates between 5.587 Å and 6.862 Å; the corresponding (NCS)^Cu bridging angles are ~90° and ~145°, respectively.

The shortest M...M interplanar contact occurs between Mn and Cu, 6.435 Å.

MAGNETIC PROPERTIES

The magnetic behavior of the compound is presented in Figure 2, in the χT vs T fashion, χ being the corrected molar

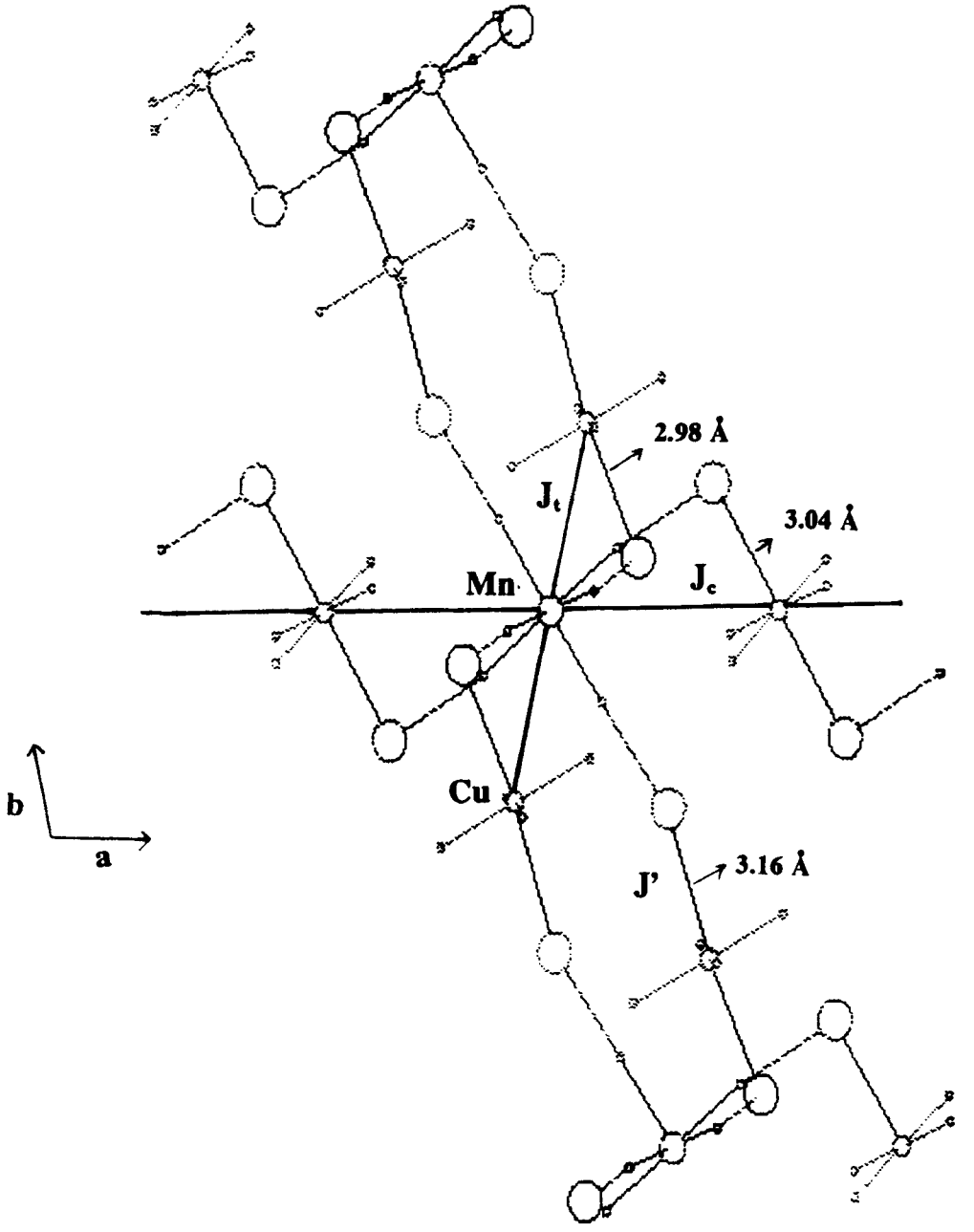

Figure 1. A schematic view of the structure of the compound along the c axis. The carbon atoms of the ligands, as well as the non-coordinate NCS^- anions have been omitted for clarity.

magnetic susceptibility per $MnCu_3$ unit. At room temperature, the χT product has a value of 5.80 $emu.mol^{-1}.K$, appropriate for three S=1/2 and one S=5/2 virtually independent spins.

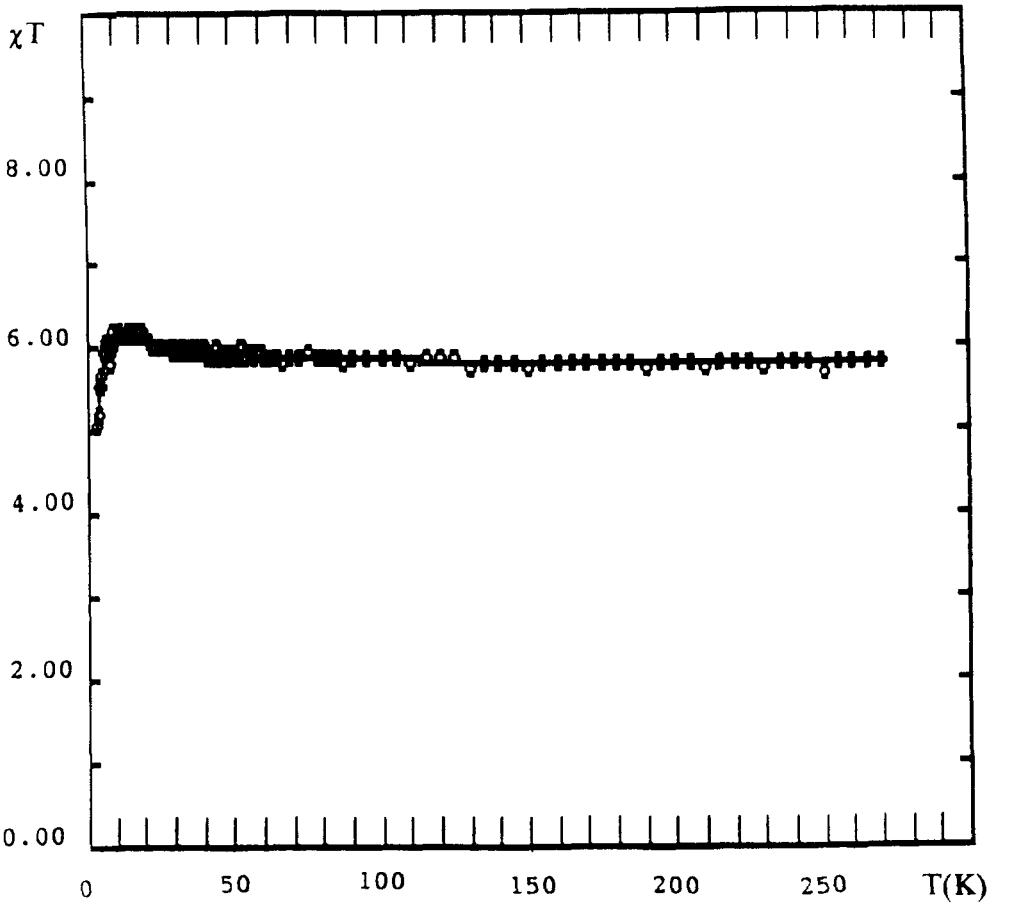

Figure 2. Plot of χT (per MCu_3 unit) vs T between 3 and 270 K. The full line through the data represents the fit discussed in the text.

Upon cooling, χT weakly increases, reaches a maximum (6.21 $emu.mol^{-1}.K$) around 20 K, and finally decreases steeply when T approaches zero.

Neglecting interactions between bimetallic planes, the exchange problem for the present compound involves a 2-D spin Hamiltonian with at least three coupling constants,

corresponding to the three different separations observed between nearest neighboring Mn(II) and Cu(II) ions along the [1 0 0] and [0 1 1] crossing chains. Since such a complex Hamiltonian cannot presently be used for data analysis, the following approximate model, suggested by the structural data, was tentatively selected for estimating exchange.

As indicated in Figure 1, the 90° exchange pathways involve apical Cu-S distances (3.041(1) Å and 2.984(1) Å) that are considerably shorter than the corresponding distance of 3.156(1) Å for the 145° exchange pathway. Figure 1 also shows that if the increase in the Cu-S distance is accompanied by a significant decrease in the magnitude of the exchange coupling constant, as expected from orbital overlap considerations alone, the 2-D network can be treated as a system of weakly interacting 1-D chains.

The chains, formed by the alternation of (Cu-Mn-Cu) trinuclear units and Cu atoms along the [1 0 0] direction, can be schematized as hereunder, where S_t symbolizes the effective spin of the trinuclear unit.

$$\ldots S_t \ldots . S_{Cu} \ldots . S_t \ldots . S_{Cu} \ldots$$

On the assumption of purely isotropic interactions, the magnetic susceptibility of the S_tS_{Cu} chain, χ_{chain}, can be generated considering S_t as a classical spin (whatever the temperature may be, $7/2 \leq S_t \geq 3/2$) and S_{Cu} as a quantum spin.[5] The equation for χ_{chain} (per $MnCu_3$ unit, and writing the exchange constant as -2J) is:

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

where P, Q and R are functions of $2J_c/kT$, J_c being the exchange integral between the S_t and S_{Cu} spins.

At each temperature, the S_t effective spin is given by eq

2, where χ_t is the susceptibility of the trinuclear unit.

$$S_t = \{-1 + [(1 + 4\chi_t T/(g_t^2 0.1251)]^{1/2}\}/2 \quad (2)$$

χ_t is calculated from eq 3, where J_t describes the Mn(II)...Cu(II) interaction within the trimer.

$$\chi_t = (N\mu_\beta^2 g_t^2/4kT)\,[10 + 35\exp(5J_t/kT) + 35\exp(7J_t/kT) + 84\exp(12J_t/kT)] / [2 + 3\exp(5J_t/kT) + 3\exp(7J_t/kT) + 4\exp(12J_t/kT)] \quad (3)$$

Residual 2-D interactions were accounted for by the addition of a mean field correction term to eq 1. The equation for the susceptibility (per $MnCu_3$ unit) then has the form of eq 4. J' is the interchain exchange-coupling energy, and z is the number of nearest neighbors, two in this case.

$$\chi = \chi_{chain}/[1 - \chi_{chain}(2zJ'/Ng^2\mu_\beta^2)] \quad (4)$$

The best fit from eq 4 to the data was found for J_t = +1.28 cm^{-1}, J_c = +0.32 cm^{-1}, and J' = -0.09 cm^{-1} (with g_t = 2.04 and g_{Cu} = 2.13). $F = \Sigma_i (\chi_i^{obs})^{-1}(\chi_i^{obs} - \chi_i^{calcd})^2 = 4\times10^{-3}$, for 118 observations. As it also appears from Figure 2, the fit may be considered as fairly good.

The exchange constants are all weak, as reasonably expected from the rather large distances between magnetic ions, and the $|J_t| > |J_c| > |J'|$ sequence parallels the relative lengths of the proposed superexchange paths. In addition the equal sign found for J_t and J_c is consistent with the similar bridging geometry ((N-C-S)^Cu ~ 90°) within the trinuclear units and the chains along [1 0 0].

The unusual ferromagnetic coupling between Mn(II) and Cu(II) suggested by the model for the 90° bridging geometry may be traced back to the nature of the ligand orbital that interacts more strongly with the copper xy-like magnetic orbital directed toward the nitrogen ligands. This is[6] the

HOMO π_x^{nb} α [$3p_x(S)$-$2p_x(N)$] orbital whose lobes point toward the CuN_4 plane. For an (N-C-S)^Cu angle of ~90° there is zero overlap between this orbital and the xy magnetic orbital of copper, which favors ferromagnetic Mn(II)...Cu(II) exchange.

To conclude, the present compound, despite a seemingly favorable[1c,2] structure in which Mn(II) and Cu(II) are the nearest neighboring magnetic ions throughout the whole lattice, is far from being a suitable candidate for molecular ferromagnetism. Actually, it exhibits a ground state of low spin multiplicity. Model calculations indicate that such a feature arises from exchange of opposite sign between the Mn(II) and Cu(II) ions. The ferromagnetic exchange between Mn(II) and Cu(II), although unusual, may be explained by local symmetry considerations.

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