Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 22 Sep 2006.

To cite this article: E. Coronado , F. Safina , D. Beltran , R. Burriel & R. L. Carlin (1989): Magnetic Characterization of the Ferrimagnetic Compounds $CoM(M'EDTA)_2.4H_2O$ (M,M′ = Co, Ni), Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 507-511

To link to this article: http://dx.doi.org/10.1080/00268948908037507

Mol. Cryst. Liq. Cryst., Vol. 176, pp. 507–512
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Printed in the United States of America

MAGNETIC CHARACTERIZATION OF THE FERRIMAGNETIC COMPOUNDS $CoM(M'EDTA)_2.4H_2O$ (M,M' = Co, Ni)

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Abstract Stimulated by the magnetic behaviors of the title compounds we have developed a general treatment for solving an exchange-coupled Ising chain made up of three magnetic sublattices which are ordered according to the sequence A-B-A--C--A-B-A--C. Exact expressions of the susceptibility and specific heat are derived for $S_a=S_b=1/2$ and $S_c=3/2$, including a local anisotropy on the later sublattice, D_c . The magnetic properties of the $CoCo(CoEDTA)_2.4H_2O$ compound are discussed on the basis of the developed model.

INTRODUCTION

An attractive approach to construct molecular systems ordering ferromagnetically consists of assembling ordered bimetallic chains so as to obtain 2-d or 3-d ordered bimetallic lattices. Based on that strategy we have obtained a new phase of bimetallic layered materials of formula $M^tM(M'EDTA)_2.4H_2O$ (in short $[M^tMM']$)[1,2]. The magnetic behaviors of [CoNiNi] and [CoCoCo] upon cooling down show: i) the typical features of low dimensional ferrimagnets (with a minimum of X_mT around 1 and 0.3K, respectively), and ii) a sharp peak of X_mT (at Tc=0.44 and 0.10K, respectively) suggesting a phase transition to a ferromagnetic state[3]. In this paper we discuss the low dimensional ferrimagnetic behavior of the cobalt compound in terms of a model that assumes three spin sublattices exchange-coupled by an Ising interaction.

PRELIMINARY REMARKS

The structure of the $[M^tMM']$ series[1] consists of ordered bimetallic layers of alternating octahedral sites M and M', with tetrahedral sites M^t connecting different MM' layers (see Figure 1). Note that there are two non equivalent connections between M and M´ within the layers, indicated in Figure 1 as continuous thick and thin lines.

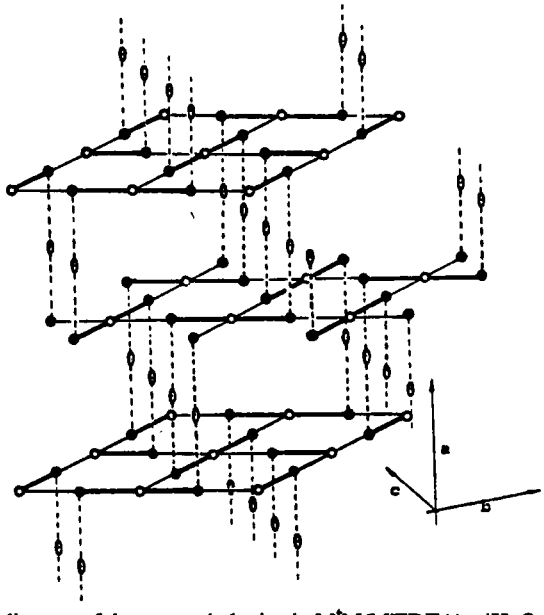

FIGURE 1. Schematic diagram of the magnetic lattice in $M^tM(M'EDTA)_2.4H_2O$.open circles: octahedral M, black circles: octahedral M', ellipses: tetrahedral M^t sites.

From the magnetic point of view, this implies that there should be an alternation within the layers not only in the size of the magnetic moment but also in the exchange coupling. Further, a third exchange coupling arises between M^t and M'. Clearly, the resulting (3-d) ferrimagnetic lattice is too complex to be modeled and a reduction of the problem is required. A way to do that results from assuming that one of the exchange couplings within the layers is much smaller than the other two, since the problem is then lowered to one dimension. This assumption can be justified in the case of the cobalt compound on the basis of the results obtained in the related bimetallic chain $CoCo(EDTA).6H_2O$; in that case, alternating metal distances along the chains, similar the observed ones within the layers, gave rise to a significant exchange alternation with one of the exchange couplings very close to zero $(J'/J < 0.01)$[4].

MODEL

Owing to the above remarks the magnetic lattice may be reduced to a chain formed by three sublattices which are ordered according to the sequence A-B-A--C--A-B-A--C, where A, B and C refer to the sites M', M and M^t, respectively, and dotted and full lines to the two different exchange couplings. Dealing with the cobalt compound, the sequence of magnetic moments along the chain may be schematized as

$$--S_a(g_a)\text{-}S_b(g_b)\text{-}S_a(g_a)--S_c(g_c)--S_a(g_a)\text{-}S_b(g_b)\text{-}S_a(g_a)--$$

with $S_a=S_b=1/2$ for octahedral sites, and $S_c=3/2$ for the tetrahedral one; g_a, g_b and g_c are the corresponding Landé factors at these sites. In view of the very anisotropic Kramers doublet ($g_{//} >> g_{\perp}$) showed by octahedral Co(II), an anisotropic exchange

model (Ising-type) is expected to describe conveniently the magnetic properties. The full Hamiltonian is written as:

$$H= \sum (- JS^z_{4i}S^z_{4i+1} - JS^z_{4i+1}S^z_{4i+2} - J'S^z_{4i+2}S^z_{4i+3} - J'S^z_{4i}S^z_{4i-1} - g_{4i}m_BHS^z_{4i} - g_{4i+1}m_BHS^z_{4i+1} - g_{4i+2}m_BHS^z_{4i+2} - g_{4i-1}m_BHS^z_{4i-1} - D_c(S^z_{4i-1})^2)$$

where S^z_j stands for the z-component of the spin operator located on site j, J and J' are the exchange couplings M'-M and M'-M^t, respectively. D_c is the zero field splitting on site C, and $g_{4i} = g_{4i+2} = g_a$, $g_{4i+1} = g_b$, $g_{4i+3} = g_c$ .This can be solved exactly by the transfer matrix method if the external magnetic field is assumed to be along the z-axis [5] .

A similar procedure to that reported for other ferrimagnetic chains [6,7] allows us to deduce the transfer matrix for the system under consideration :

$$T = \begin{pmatrix} T11 & T12 \\ T21 & T22 \end{pmatrix}$$

$T11 = A*E + B*G$ $\qquad$ $T12 = A*F + B*H$

$T21 = C*E + D*G$ $\qquad$ $T22 = C*F + D*H$

$A = 2\,r^{1/2}\cosh[(J+g_b\mu_BH)\beta/2]$ $\qquad$ $B = 2\,r^{1/2}\cosh[g_b\mu_BH\beta/2]$

$C = 2\,r^{-1/2}\cosh[g_b\mu_BH\beta/2]$ $\qquad$ $D = 2\,r^{-1/2}\cosh[(Jg_b\mu_BH)\beta/2]$

$E = 2\,r^{1/2}\sum_j k^{j^2}\cosh[(J'+g_c\mu_BH)\beta j]$ $\qquad$ $F = 2\,r^{1/2}\sum_j k^{j^2}\cosh[g_c\mu_BH\beta j]$

$G = 2r^{-1/2}\sum_j k^{j^2}\cosh[g_c\mu_BH\beta j]$ $\qquad$ $H = 2r^{-1/2}\sum_j k^{j^2}\cosh[(J'-g_c\mu_BH)\beta j]$

$k=\exp(D\beta)$, $r=\exp(g_a\mu_BH\beta)$, $\beta=1/k_BT$

The largest eigenvalue of the matrix (T) can be considered as the effective partition function per pair of sites Z, in the limit of very long chains. So, we obtain the following expression for the zero-field parallel susceptibility :

$$\chi_{II} = (N/\beta)[S_o'' + (S_oS_o'' - 2P_o'')/(S_o^2-4P_o)^{1/2}]/[S_o+(S_o^2-4P_o)^{1/2}]$$

where S_o and P_o are the values at zero field of the trace (S) and determinant (P) of T, respectively, and S_o'' and P_o'' are the second derivatives of (S) and (P) with respect to H, at zero field. For the specific heat, we obtain :

$$C_m/R = \beta^2[(Z_o''/Z_o)-(Z_o'/Z_o)^2]$$

where Z_O is the effective partition function per pair of sites af zero field, and Z_O' and Z_O'' are the first and second derivatives of Z_O with respect to b.

ANALYSIS OF THE MAGNETIC PROPERTIES OF [CoCoCo]

The above approach has allowed to obtain the exact solution for the parallel component of the magnetic susceptibility. In order to fit the experimental data it is reasonable to assume that these are accurately accounted by the parallel component, since the perpendicular contribution is weak (proportional to $g_{\perp}^2$) and decreases toward zero upon cooling down.

The low-temperature data are illustrated in Figure 2 along with the best fitted curves. The fitting procedure has not been straighforward in the present case, due to the large number of adjustable parameters. In order to reduce this number we have assumed a zero field splitting on the tetrahedral site larger than 10K in such a way that, in the range of temperature examined (T< 4K), only the doublet state is populated. On the other hand, it has been noticed that the position of the minimum of X_mT is only dependent of the smallest J-value. Conversely, a large interdependence among the three Landé parameters has been observed. In view of these remarks, several sets of parameters giving close agreement with experiment were found. Thus, the fitting curves reported in Figure 2 correspond to the following sets of parameters:

Fit I (solid line): $g_a=g_b=5.7$; $g_c=2.3$; J/k=-10K; J'/k= -0.8K; D_c/k=-15K

Fit II (dashed line): $g_a=3.2$;$g_b=5.8$;$g_c=3.5$; J/k=-1K; J'/k=-10K; D_c/k=-10K

Notice that due to the symmetrical distribution of B and C with respect to A, besides these two fits, there are two equivalent ones resulting from interchanging g_b by g_c and J by J'.

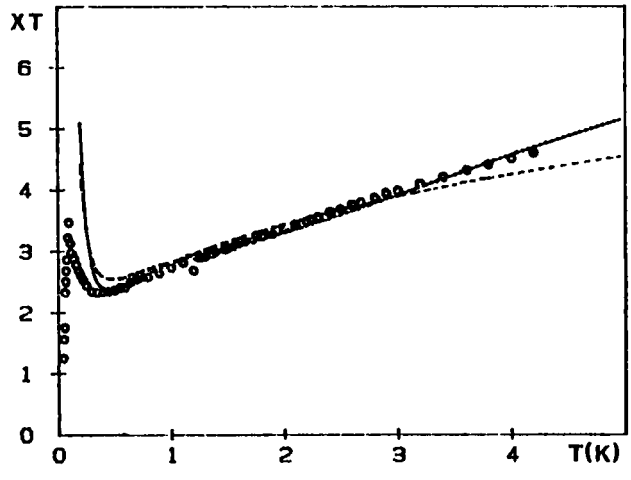

FIGURE 2. Magnetic behavior of [CoCoCo].

Despite this wide variety of sets of parameters, it is to be emphasized that in all cases the values of the exchange parameters stay relatively constant in the reported fits, with the largest J-value ranging between -10 and -15K and the smallest one close to -1K. In turn, the assignment of these values to the two exchange pathways is not unambigous. To rule out this ambigouity we have foccused on the values obtained for

the (g_a,g_b,g_c) sets. Thus, in view of the range of values commonly found for Co(II) in similar environments (ranging from 1 to 10 in octahedral sites, and around 2-2.5 in tetrahedral ones), we have noticed that only in the former set of parameters (Fit I) the tetrahedral g_c value is reasonable. Accordingly, we can assing unambigously the largest J-value to the M-M' interaction within the layer, and the smallest one to the M'-M^t interaction. The fact that the M-M' interaction within the layer results to be then similar to that previously found in the chain CoCo(EDTA).$6H_2O$ [4] supports this assignment.

Further experimental work, in particular specific heat measurements, are now required in order to complete the magnetic caracterization of these ferrimagnetic complexes and are in progress.

ACKNOWLEDGMENT

This work was supported in part by the Comisión Interministerial en Ciencia y Tecnología (Grant PB 85-0106-CO2-02) and the National Science Foundation (Grant DMR-8515224). F.S. thanks the Spanish Ministerio de Educación y Ciencia for a FPI fellowship.

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