1D ferrimagnetism in homometallic chains

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The magnetic properties of the cobalt zigzag chain $Co(bpy)(NCS)_2$ (bpy = 2,2′-bipyridine) are discussed on the basis of an Ising-chain model that takes into account alternating Landé factors. It is emphasized, for the first time, that a homometallic chain containing only one type of site can give rise to a 1D ferrimagneticlike behavior.

I. INTRODUCTION

One-dimensional ferrimagnetism is generally associated with ordered bimetallic chains made up of two different metal ions with unequal spins located on two alternating sites.[1] Actually, such behavior is not exclusive for this type of system. 1D ferrimagnetism can also occur in homometallic chains, provided alternating (different) sites within the chains,[2] or when considering a particular stacking of the metal ions, like intertwining double chains,[3] or when there is an odd number of interacting ions per unit cell.[4]

We discuss the magnetic properties of the homometallic cobalt chain $Co(bpy)(NCS)_2$ on the basis of the Ising-chain model. For the first time, the ferrimagnetic character is reported in a homometallic chain containing only one type of site.

II. RESULTS AND DISCUSSION

The cobalt compound belongs to a series of the empirical formula $M(bpy)(NCS)_2$ (bpy = 2,2′-bipyridine) previously reported.[5] The structure consists of polymeric zigzag chains with stepwise cobalt-thiocyanate bridging groups and octahedral metal centers (Fig. 1). The magnetic properties of this compound in the temperature range 1.5–40 K are shown through a plot of χT vs T in Fig. 2. The main features to be emphasized are (i) a round minimum of χT located around 10 K that is the typical characteristic of one-dimensional ferrimagnets, and (ii) a maximum at 4 K, followed by a sharp decrease at lower temperatures that suggests a transition to long-range magnetic ordering.

In discussing the magnetic properties of this compound we have to bear in mind that due to the combined effect of spin-orbit coupling and local distortion of the octahedral site, the high-spin Co^{+} ion behaves as a very anisotropic spin $S = \frac{1}{2}$ at low enough temperatures ($<$ 20–30 K). Then, an anisotropic Ising model should be closely approximated. However, alternating g components along the chain have to be assumed in order to account for the experimental minimum of χT. Accordingly, the experimental values are fitted to a $S = \frac{1}{2}$ two-sublattice Ising-chain model, for which exact solutions of the zero-field components of the susceptibility have been derived.[2] The best-fit values to the parallel component to χ are $J/k = -17$ K, $g_{a\parallel} = 2.1$ and $g_{b\parallel}$ 4.85. As can be seen from Fig. 2, this set of parameters provides a very good description of the magnetic data over the entire temperature region of interest. In particular, the rounded minimum of χT is well reproduced by the model. Notice that in this fit, the perpendicular component of χ has been neglected. This assumption is reasonable since its contribution is weak and nearly constant in the region of interest, and hence the 1D ferrimagnetism is fully accounted for by the parallel component.[2]

III. CONCLUDING REMARKS

The only previous example of a homometallic chain exhibiting 1D ferrimagnetism is the compound $Co_2(EDTA)\cdot 6H_2O$. This compound belongs to an isostructural series of bimetallic compounds formulated as $MM'(EDTA)\cdot 6H_2O$ ($M,M' = $ Mn, Co, Ni, Cu, Zn^{2+}). Their structure consists of infinite zigzag chains built up from two alternating octahedral sites according to the scheme

$$--M(H_2O)_4O_2—M'(EDTA)--$$
$$M(H_2O)_4O_2—M'(EDTA)--,$$

where dashed and full lines refer to alternating metallic distances. In that case ferrimagnetism has been attributed to the presence of two different (alternating) metallic sites which give rise to alternating Landé factors, and thus to noncompensated magnetic moments.[2]

In the present case, since only one type of site is present, the magnetic moments are compensated, and thus another

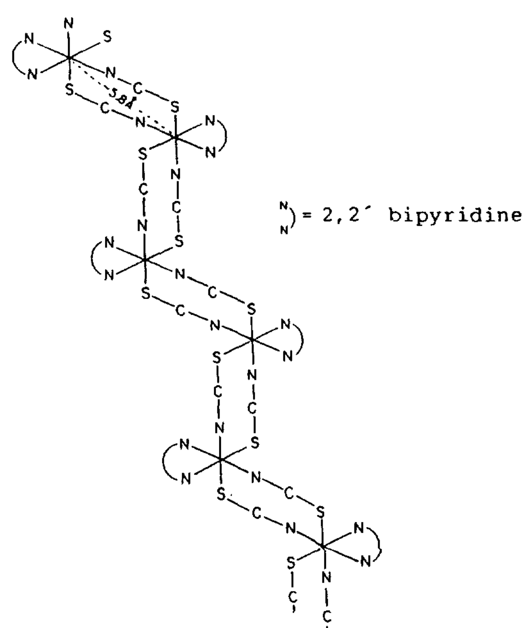

FIG. 1. Proposed polymer structure for $Co(bpy)(NCS)_2$.

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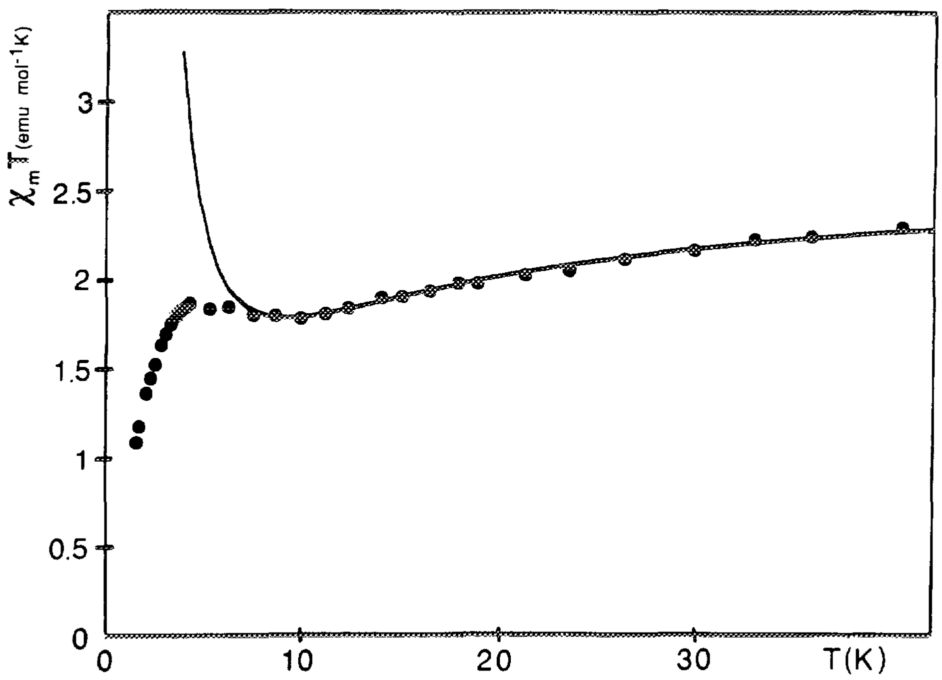

FIG. 2. Magnetic behavior of the compound Co(bpy)(NCS)$_2$. The solid line corresponds to the best fit from an $S = \frac{1}{2}$ Ising-chain model with alternating Landé factors.

origin needs to be invoked. We believe that the observed 1D ferrimagnetism comes from the combined effect of the spin anisotropy of the site and the zigzag arrangement of the chains. In this way, the anisotropic g tensors on two consecutive sites may have different orientations with respect to the principal magnetic axes, which give rise to alternating (and different) g components along this direction. In other words, 1D ferrimagnetism arises from a noncompensation between the components of the anisotropic magnetic moments due to the zigzag geometry of the chains.

Finally, we have assumed in this work that the low-dimensional regime is limited by the occurrence of long-range magnetic order at about 4 K. Further measurements, like specific-heat measurements, are now required in order to prove the point.

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