Magnetic ordering in M(ox)(bpy) system (M=Fe, Co, Ni; ox=C$_2$O$_4^{2-}$; bpy=4,4'-bipyridine)

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The temperature and field dependence of the magnetization have been measured to investigate the magnetic properties of the first oxalate–bpy mixed-ligand framework with a general formula M(ox)(bpy) (M = Fe(II), Co(II), Ni(II); ox = C$_2$O$_4^{2-}$; bpy = 4,4'-bipyridine). All compounds in the M(ox)(bpy) system crystallize in an orthorhombic structure with space group Immm (No. 71), in which the magnetic M ions form one-dimensional chains along the a axis. Spontaneous magnetic orderings with transition temperatures of 12, 13, and 26 K have been found for Fe(ox)(bpy), Co(ox)(bpy), and Ni(ox)(bpy), respectively. The nature of the ordering in Ni(ox)(bpy) is antiferromagnetic, however it may exhibit a metamagnetic transition at high magnetic fields. The type of ordering in Fe(ox)(bpy) and Co(ox)(bpy) is also antiferromagnetic but with canting, or so-called weak ferromagnetism. The residual moment resulting from the canting is larger in Fe(ox)(bpy) than in Co(ox)(bpy). The values of $\mu_{\text{eff}}$ obtained by fitting $\chi(T)$ indicate a high spin state for M ions in all three compounds. The origin of the magnetic ordering in these compounds is attributed to antiferromagnetic exchange interactions between the M ions through the bridging oxalate molecules along the magnetic chain and interchain M–M couplings along the [111] direction. © 2000 American Institute of Physics. [S0021-8979(00)91708-0]

INTRODUCTION

Advances in material design and synthesis have provided new materials for the study of low dimensional magnetism. A number of recently synthesized materials with the structure of metalorganic coordination networks exhibited rich magnetic phenomena.1–3 Among these interesting materials are quasi-one-dimensional antiferromagnets. In this article, we report the results of magnetic measurements on a series of newly synthesized polymer networks containing transition metal-oxalate chains, M(ox)(bpy), where M represents a divalent transition metal, Fe(II), Co(II), or Ni(II), and ox is an oxalate (C$_2$O$_4^{2-}$); and bpy is 4,4'-bipyridine (C$_{10}$H$_8$N$_2$). The interesting magnetic properties observed for the M(ox)(bpy) system provide us with a unique opportunity to examine how the strength of the M–M exchange interaction depends on the M–M distance, total local spin numbers, and interchain distance, since all compounds in the M(ox)(bpy) system have the same crystalline structure.

RESULTS AND DISCUSSION

All M(ox)(bpy) (M=Fe, Co, and Ni) compounds crystallize in the orthorhombic crystal system, space group Immm (No. 71). The unit cell parameters are $a=5.476$, $b= 10.946$, $c=11.471$ Å for Fe(ox)(bpy); $a=5.385$, $b=10.945$, $c=11.374$ Å for Co(ox)(bpy); and $a=5.378$, $b=10.967$, $c=11.443$ Å for Ni(ox)(bpy), respectively. All metal atoms are divalent with an octahedral coordination formed by bonding with four oxygen atoms from oxalate ions (C$_2$O$_4^{2-}$) and two nitrogen atoms from bipyridine molecules. The M–M distances within the two-dimensional net

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in the a and c directions are given by a (5.38–5.48 Å) and c (11.37–11.47 Å), respectively. Although the M–M separations in the c direction are probably too large for any significant magnetic interactions, it is anticipated that significant magnetic exchange interactions in the a direction are likely.

In Fig. 1 we show the low temperature magnetic susceptibility of Fe(ox)(bpy), Co(ox)(bpy), and Ni(ox)(bpy). A magnetic field of 1 kG was applied for all of these measurements. The anomalies seen in each \( \chi(T) \) data set indicate spontaneous magnetic orderings in all three compounds. The transition temperatures are 12 K for Fe(ox)(bpy), 13 K for Co(ox)(bpy), and 26 K for Ni(ox)(bpy). In a temperature range well above the ordering temperature, the \( \chi(T) \) data for each compound were fit to a modified Curie–Weiss law, \( \chi(T) = \chi_0 + C/(T + \theta) \). The resulting effective magnetic moment given by the expression \( \mu_{\text{eff}} = 2.83 (C)^{1/2} \), are 4.71, 5.45, and 4.33 \( \mu_B \) for Fe(ox)(bpy), Co(ox)(bpy), and Ni(ox)(bpy), respectively. These values of \( \mu_{\text{eff}} \) indicate a high spin state for each M(II) ion. The Curie–Weiss temperatures, \( \theta \), obtained from the fits are \(-33, -98, \) and \(-89 \) K for the Fe, Co, and Ni compounds, respectively. Although the \( \chi(T) \) curves near the transition temperature for both Fe(ox)(bpy) and Co(ox)(bpy) are similar to \( \chi(T) \) curves near a ferromagnetic transition, the negative \( \theta \) values suggest an antiferromagnetic ordering in these compounds.

The \( \chi(T) \) data measured at \( H = 50 \) kG for the three compounds are shown in Fig. 2. The shape of the \( \chi(T) \) curve for Ni(ox)(bpy) at 50 kG is similar to the shape of \( \chi(T) \) at 1 kG shown in Fig. 1, but \( T_N \) is shifted down from 26 K for \( H=1 \) kG to 21 K for \( H=50 \) kG. However, the Fe and Co \( \chi(T) \) curves at 50 kG are substantially different from the 1 kG curves shown in Fig. 1. In particular, the \( \chi(T) \) at 50 kG shows typical antiferromagnetic behavior.

In Fig. 3 we show the field-dependent magnetization, \( M(H) \), for Fe(ox)(bpy) measured at different temperatures. No sizable hysteresis was observed. \( M(H) \) measured at 16 K showed paramagnetic behavior, as one would expect for temperatures above the magnetic ordering temperature. \( M(H) \) at 2 K exhibited linear behavior for \( H>15 \) kG. This strongly suggests an antiferromagnetic state. However, \( M(H) \) in the \( H<15 \) kG region exhibited curvature indicating ferromagneticlike behavior. In fact, \( M(H) \) over the entire range is of the form that one would expect for a canted antiferromagnet. The resulting nonzero magnetic moment for this type of ordering explains why the anomaly seen in the low field, \( (H = 1 \) kG), \( \chi(T) \) data looks like that expected for a ferromagnet. In Fig. 3 consider the \( M(H, 16 \) K) curve and the \( M(H, 2 \) K) curve. Above a critical field \( H_c \approx 27 \) kG, the magnitude of \( M(H) \) is smaller at 2 K than at 16 K, indicating an antiparallel alignment of the moments in the direction of the field. This ‘crossover’ is consistent with the behavior of \( \chi(T) \) measured for fields less than 50 kG. The \( M(H) \) data for Co(ox)(bpy) yielded similar behavior. We therefore conclude that the nature of the magnetic ordering in both the Fe and...
the Co compounds is the same. However, the critical field at which the crossover of the two $M(H)$ curves (above and below the ordering temperature) occurs for the Co compound is $H_c \approx 11$ kG, much lower than the $H_c \approx 27$ kG observed for Fe(ox)(bpy). A larger amount of energy is required to reorient the Fe moments. In addition, a small hysteresis was observed in the $M(H)$ measured at 2 K for Co(ox)(bpy).

Finally the results of $M(H)$ measurements on Ni(ox)(bpy) are presented in Fig. 4. In contrast to $M(H)$ data for the Fe and Co compounds, the $M(H)$ curves for the Ni compound are almost linear in the lower field range ($H < 30$ kG). In this range and below $T_N$ (26 K), the magnitude of $M(H)$ decreases as the temperature is lowered, as expected for a typical antiferromagnet. However, some interesting features were observed with higher applied fields, i.e., $H > 30$ kG. First, a crossover of the $M(H)$ curves for 30 and 20 K is seen around $H = 43$ kG, with $M(H)$ at 20 K larger than $M(H)$ at 30 K for fields greater than 43 kG. It should be noticed that this crossover is opposite to that observed in Figure 3 for the Fe compound. In the Fe compound case the $M$ values were larger (at high fields) for higher temperatures, not lower temperatures. Second, an upturn in $M(H)$ at 2 K is seen near $H = 48$ kG. It is anticipated that the $M(H)$ curve at 2 K will intersect the $M(H)$ at 30 K at a field $H > 55$ kG. These types of slope changes in $M(H)$ below $T_N$ suggest some kind of metamagnetic behavior where the ground state magnetic structure changes with the application of a field.

Under an applied field larger than a critical field $H_c$, the Ni magnetic moments of the compound are reoriented to different directions, resulting in a larger contribution to $M(H)$. Similar metamagnetic transitions have been observed in MCl$_2$(bpy) (M=Fe, Co, and Ni), another quasi-one-dimensional magnetic system, and some other related chain systems.

In conclusion, we have found several interesting magnetic properties for the M(ox)(bpy) system, including rather high magnetic ordering temperatures, remarkably 26 K for Ni(ox)(bpy), weak ferromagnetism in Fe(ox)(bpy) and Co(ox)(bpy), and metamagnetism in Ni(ox)(bpy). The origin of these phenomena is the strong M–M antiferromagnetic exchange interaction through extended oxalate bridges. As described in Ref. 4, the magnetic M ions at the octahedral sites form chains with intrachain separation of 5.303–5.476 Å. Although the M–M separation is quite large, the bonding between the oxalates and the M ion makes the transmission of the M–M magnetic coupling very effective. Strong M–M coupling through the oxalate bridges have been found in other organic systems. We believe that the magnetic ordering in these compounds is dominated by an intrachain M–M antiferromagnetic interaction. However, differences in the magnetic behavior of the three compounds were observed. It is possible that an interchain M–M coupling along the [111] direction, in which the M–M interchain separation ranges from 8.290 to 8.387 Å, are also involved. Furthermore, the total spin and the local crystalline symmetry at the M site may play important roles as well.

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