

# Synthesis and Magnetic Properties of Novel Fully Conjugated Polymeric Complexes Containing 1,10-Phenanthroline

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**ABSTRACT:** A novel fully conjugated polymer containing 1,10-phenanthroline (DAPcDOD) was first synthesized by the polycondensation of 2,7-dimethyl-2,4,6-octatriene-1,8-dial with 5,6-diamine-1,10-phenanthroline. Three polymeric complexes were first prepared by the reaction of DAPcDOD with NiSO<sub>4</sub>, CoCl<sub>2</sub>, and FeSO<sub>4</sub>, respectively. The structures of the polymer and the complexes were characterized by IR, <sup>1</sup>H-NMR, and elemental analysis. The magnetic behaviors of these complexes were measured as a function of magnetic

field strength (0–50 kOe) at 5 K and as a function of temperature (5–300 K) at a magnetic field strength of 30 kOe. The results show that DAPcDOD–Ni<sup>2+</sup> and DAPcDOD–Co<sup>2+</sup> were soft ferromagnets, whereas DAPcDOD–Fe<sup>2+</sup> exhibited the features of an antiferromagnet. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2498–2503, 2008

**Key words:** conjugated polymers; magnetic polymers; synthesis

## INTRODUCTION

Organic and polymeric magnetic materials have been studied extensively, and great progress has been achieved during the last 2 decades.<sup>1–4</sup> In particular, the soft ferromagnet tetrakis(dimethylamino)ethylene, first discovered by Wudl et al.<sup>5</sup> in 1991, sparked a series of investigations.

In recent years, Sun and coworkers<sup>6,7</sup> have carried out a series of studies on the preparation of poly(Schiff base)s containing bithiazole rings and their metal complexes, in which some of these complexes have shown soft ferromagnetic behaviors. It was found that aromatic heterocyclic polymers containing bithiazole rings are good ligands because the two nitrogen atoms in the bithiazole rings are able to chelate metal ions to form stable five-member rings.<sup>8,9</sup>

It is well known that the magnetic properties of polymeric complexes arise from the magnetic exchange interactions between the metal ions in the polymer matrix. Generally, these magnetic interactions are relatively strong through  $\pi$ -conjugated system compared with space interactions.<sup>10</sup> Therefore, the design and synthesis of polymeric complexes with conjugated structures might produce a new kind of interesting magnetic material. 1,10-Phenanthroline and its derivations play important roles in

supramolecular assemblies because they can also provide bidentate N-donor sites for chelating with metal ions to form bridge ligands,<sup>11–13</sup> except that 5,6-diamino-1,10-phenanthroline can be condensed with a variety of carbonyl-containing compounds to form additional derivatives. We first reported conjugated phenanthroline-containing poly(Schiff base)s (polymer synthesized by polycondensation of 5,6-diamine-1,10-phenanthroline (DAP) with terephthalaldehyde (TPA) (DAPcTPA) and the polymer synthesized by polycondensation of 5,6-diamine-1,10-phenanthroline (DAP) with isophthalaldehyde (IPA) (DAPcIPA)), which were prepared by the polycondensation of 5,6-diamine-1,10-phenanthroline (DAP) with terephthalaldehyde and isophthalaldehyde, respectively,<sup>14,15</sup> in which some of their metal complexes showed soft ferromagnetic behaviors. In this article, we discuss the synthesis and characterization of a novel fully conjugated poly(Schiff base) containing phenanthroline units and its metal complexes. The magnetic properties of these complexes were investigated for the first time.

## EXPERIMENTAL

### Materials

Dimethyl sulfoxide (DMSO) was refluxed with calcium hydride for 24 h, distilled under 533 Pa and at 64–65°C; a distillation cut was obtained and stored with a 0.4-nm molecular sieve. 2,7-Dimethyl-2,4,6-octatriene-1,8-dial (DOD) was synthesized in our

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laboratory. DAP was prepared according to the literature,<sup>16</sup> followed by several recrystallizations with ethanol.

### Synthesis of the poly(Schiff base) DAPcDOD

5,6-Diamino-1,10-phenanthroline (1.05 g, 5 mmol), DOD (0.82 g, 5 mmol), and DMSO (50 mL) were mixed in a round-bottom flask. The reactants were magnetically stirred at room temperature under a purified N<sub>2</sub> atmosphere. The color of the solution turned from yellow to brown after several minutes. Also, the increased viscosity was observed after 4 h. The solution was poured into a mixture of ethanol and water (1 : 1), and the precipitate was collected by filtration; washed successively with water, ethanol, and ether; and then dried *in vacuo* at 60°C for 24 h. The yield was 1.6 g (85.6%).

<sup>1</sup>H-NMR (CF<sub>3</sub>COOD, δ, ppm): 7.6, 8.8, 8.9 (H of 1,10-phenanthroline); 7.2 (CH=N proton resonances); 6.8 (CH=C proton resonances); 2.1 (methyl proton resonances). Fourier transform infrared (FTIR, cm<sup>-1</sup>): 1650 (C=N); 1604, 1564, 1535, 1490 (Ar ring); 1430, 1396, 1355, 1072, 963, 802, 738. Intrinsic viscosity: 0.20 dL/g (DMSO, 30°C).

ANAL. Calcd for (C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>)<sub>n</sub>: C, 78.11%; H, 5.32%; N, 16.57%. Found: C, 78.52%; H, 5.18%; N, 16.33%.

### Preparation of the polymeric complexes: DAPcDOD-Ni<sup>2+</sup>, DAPcDOD-Co<sup>2+</sup>, and DAPcDOD-Fe<sup>2+</sup>

NiSO<sub>4</sub> (or FeSO<sub>4</sub> or CoCl<sub>2</sub>) and the polymer DAPcDOD (molar ratio = 2 : 1) was added slowly to a stirred DMSO solution under a purified nitrogen atmosphere. The mixed solution was stirred at 80°C for 6–8 h, and then, the precipitate was formed. After it was filtered and washed successively with water and methanol, the remaining precipitate was soaked in methanol for 24 h and then isolated by filtration. After the filtrate was dried *in vacuo* at 60°C for 24 h, the polymeric complex was obtained.

#### DAPcDOD-Ni<sup>2+</sup>

IR (cm<sup>-1</sup>): 1653, 1608, 1586, 1565, 1539, 1491, 1447, 1404, 1362, 1109, 1081, 974, 815, 732.

ANAL. for 5.18% Ni: Calcd for the suggested formula [C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>(NiSO<sub>4</sub>)<sub>0.35</sub>]<sub>n</sub>: C, 67.35%; H, 4.59%; N, 14.28%. Found: C, 67.91%; H, 4.12%; N, 13.65%.

#### DAPcDOD-Co<sup>2+</sup>

IR (cm<sup>-1</sup>): 1652, 1610, 1587, 1567, 1539, 1489, 1430, 1404, 1361, 1199, 1078, 1008, 814, 735.

ANAL. for 5.92% Co: Calcd. for the suggested formula [C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>(CoCl<sub>2</sub>)<sub>0.39</sub>]<sub>n</sub>: C, 67.92%; H, 4.63%; N, 14.41%. Found: C, 67.13%; H, 4.01%; N, 13.18%.

#### DAPcDOD-Fe<sup>2+</sup>

IR (cm<sup>-1</sup>): 1653, 1616, 1569, 1539, 1489, 1455, 1403, 1375, 1356, 1120, 970, 808, 701.

ANAL. for 5.25% Fe: Calcd. for the suggested formula [C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>(FeSO<sub>4</sub>)<sub>0.37</sub>]<sub>n</sub>: C, 67.01%; H, 4.57%; N, 14.21%. Found: C, 66.71%; H, 4.03%; N, 13.37%.

### Measurements

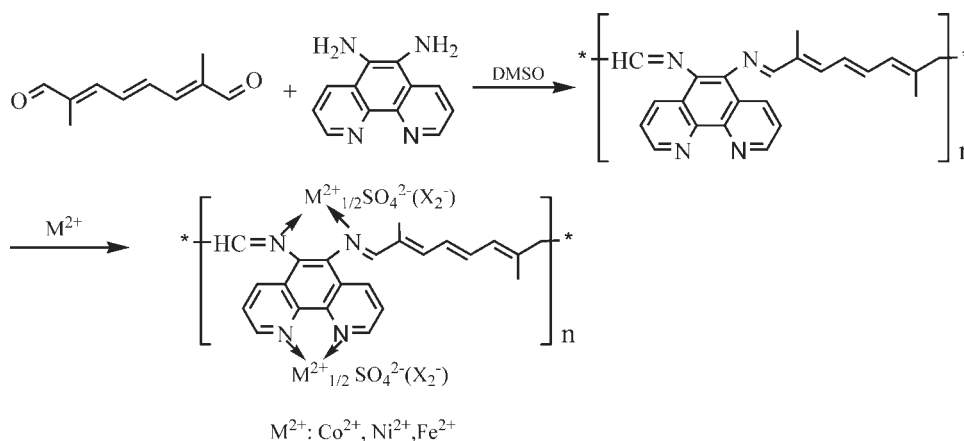
A Bruker Vector 22 FTIR spectrometer (Ettlingen, Germany) was used to record the IR spectra in KBr pellets. <sup>1</sup>H-NMR spectra were recorded on a Bruker Advance AMX-500NMR instrument in CF<sub>3</sub>COOD with tetramethylsilane as an internal standard. The intrinsic viscosity was measured in DMSO at 30°C. Elemental analyses for C, H, and N were performed using a ThermoFinnigan Flash EA112 elemental analyzer (Waltham, MA). The contents of metal (Fe, Co, and Ni) were obtained by complexometry. The magnetic properties of complexes were measured with a PPMS-9T magnetometer (Quantum Design, Sandiego, CA).

## RESULTS AND DISCUSSION

The polymer (DAPcDOD) and its metal complexes were prepared as shown in Scheme 1. A lower temperature was essential to obtain the polymers successfully, and the coordination reaction between the polymer and metal ions had to be carried out under purified nitrogen at about 80°C.

### Characterization of the polymer and its complexes

The structures of the poly(Schiff base) DAPcDOD were determined by IR and <sup>1</sup>H-NMR spectroscopy. Figure 1 shows the IR spectra of DAP, DOD, and DAPcDOD. The stretching vibration of the new bond C=N appeared at about 1650 cm<sup>-1</sup> for DAPcDOD. Compared with DAP and DAPcDOD, the very strong absorption at 1657 cm<sup>-1</sup> of the N–H bending vibration in the IR spectrum of DAP disappeared in that of DAPcDOD, and the C=O vibration of DOD at 1664 cm<sup>-1</sup> almost disappeared in that of DAPcDOD, too. In the IR spectrum of DAPcDOD, the conjugate C=C bond appeared at 1586 cm<sup>-1</sup>, and a sharp absorption peak appeared at 963 cm<sup>-1</sup>, which corresponded to the out-of-plane bending mode of C–H bond in the trans-CH=CH– groups, which showed that the generated double bonds were mainly in the trans configuration. As for the <sup>1</sup>H-NMR spectra, the resonance of the CH=N proton appeared as doublet at 7.2 ppm. The resonance at 6.8 ppm was that of CH=C protons; the resonance at δ = 2.1 ppm was of methyl protons. The peaks at 7.6, 8.8, and 8.9 ppm referred to the 1,10-phenanthroline proton resonances. Compared with the <sup>1</sup>H-NMR spectra of the



**Scheme 1** Synthetic routes of the poly(Schiff base) and its complexes.

monomer DAP, the peak of the  $-NH_2$  protons of DAPcDOD at 5.2 ppm disappeared.

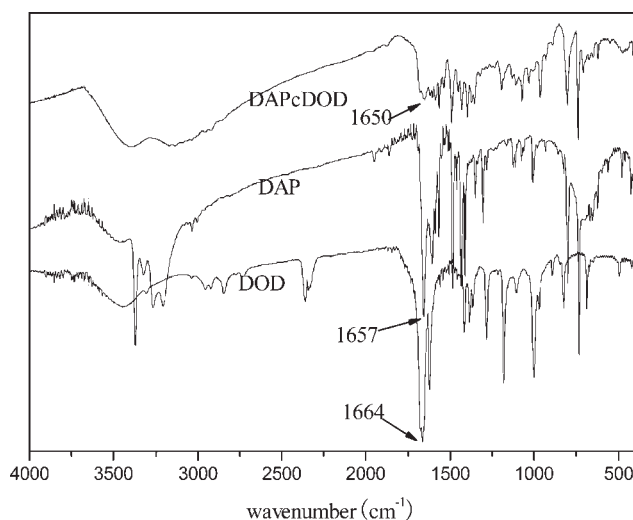
In comparison with DAPcDOD, significant changes were observed in the IR spectra of DAPcDOD- $Ni^{2+}$ , DAPcDOD- $Co^{2+}$ , and DAPcDOD- $Fe^{2+}$  (Fig. 2); for example, the IR absorption bands of DAPcDOD at 1651 (C=N), 1604, 1564, 1535, and 1490 (Ar ring)  $cm^{-1}$  blueshifted to 1653, 1608, 1586, 1565, 1539, and 1491  $cm^{-1}$  for DAPcDOD- $Ni^{2+}$ ; 1652, 1610, 1587, 1567, 1539, and 1489  $cm^{-1}$  for DAPcDOD- $Co^{2+}$ ; and 1653, 1616, 1569, 1539, and 1489  $cm^{-1}$  for DAPcDOD- $Fe^{2+}$ , respectively. This indicated that the coordination took place through the nitrogen atoms of the phenanthroline rings or the polymer skeleton because the skeletal vibrations of the phenanthroline rings needed higher energy after coordination with  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Fe^{2+}$ . Similar changes were observed within the region 1200–400  $cm^{-1}$  in the IR spectra of these complexes.

On the basis of the elemental analyses, the three complexes had the following formulas:  $[C_{22}H_{18}N_4$

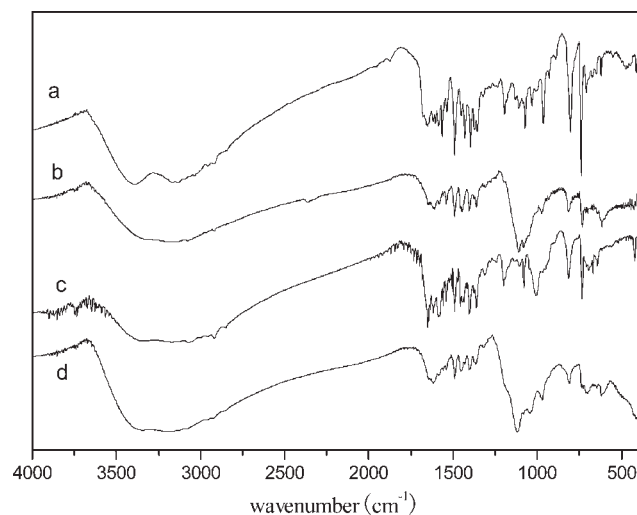
$(NiSO_4)_{0.35}]_n$  for DAPcDOD- $Ni^{2+}$ ,  $[C_{22}H_{18}N_4(CoCl_2)_{0.39}]_n$  for DAPcDOD- $Co^{2+}$ , and  $[C_{22}H_{18}N_4(FeSO_4)_{0.37}]_n$  for DAPcDOD- $Fe^{2+}$ , respectively. This means that about three or four repeating units incorporated one metal ion on average in the polymeric complexes. As proposed in Scheme 1, the metal ion and two phenanthroline units from adjacent polymer chains could form the coordination structure, in which nitrogen atoms acted as coordinating sites. This seems to be reasonable in view of the strong chelating tendency of bidentate dinitrogen ligands to metal ions.

### Magnetic properties of the complexes

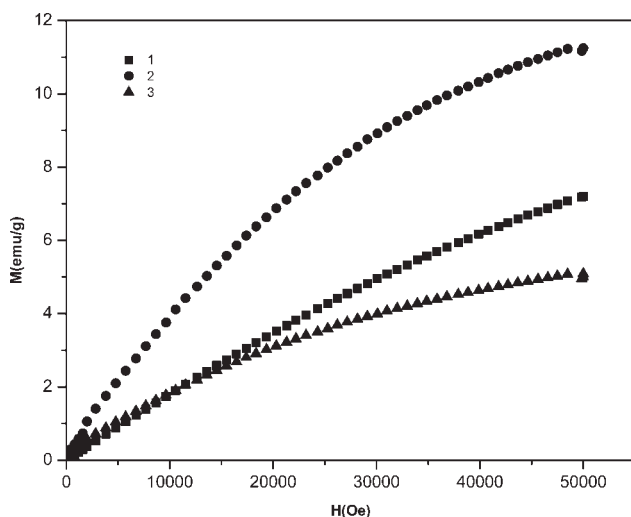
Figure 3 presents the typical ferromagnetic relationship between magnetization and applied field for the DAPcDOD- $Ni^{2+}$ , DAPcDOD- $Co^{2+}$ , and DAPcDOD- $Fe^{2+}$  complexes at 5 K. Their magnetization



**Figure 1** IR spectra of DAP, DOD, and DAPcDOD.



**Figure 2** IR spectra of the polymer and its complexes: (a) DAPcDOD, (b) DAPcDOD- $Ni^{2+}$ , (c) DAPcDOD- $Co^{2+}$ , and (d) DAPcDOD- $Fe^{2+}$ .

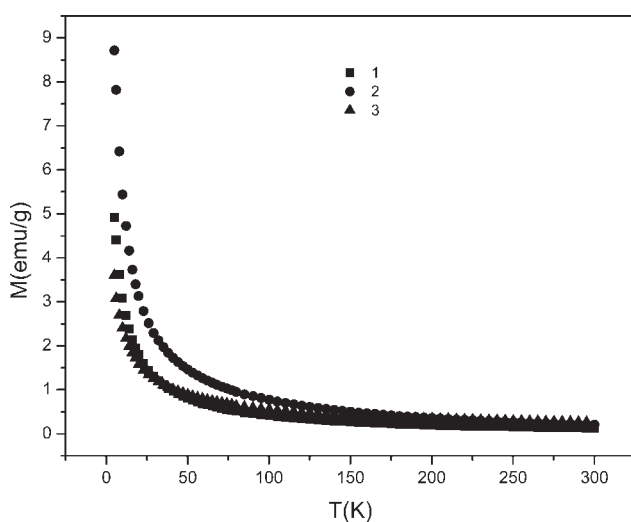


**Figure 3** Magnetization ( $M$ ) versus the magnetic field strength ( $H$ ) at 5 K for polymeric complexes: (1) DAPcDOD- $\text{Ni}^{2+}$ , (2) DAPcDOD- $\text{Co}^{2+}$ , and (3) DAPcDOD- $\text{Fe}^{2+}$ .

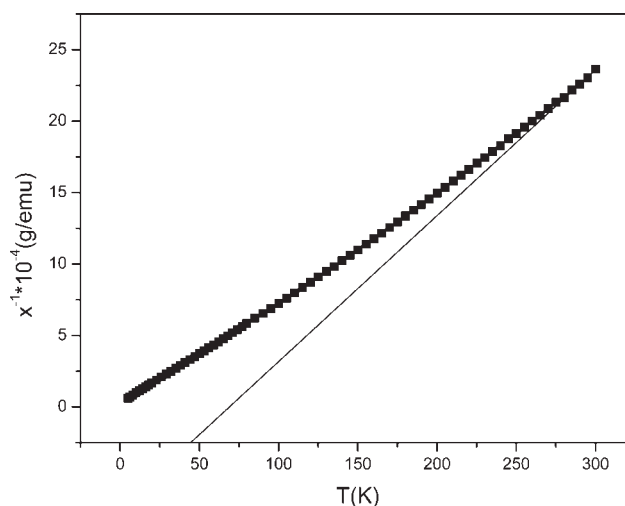
increased sharply below 30 kOe, which indicated spontaneous magnetization. The rising trend slowed down above 30 kOe, and then, the magnetization nearly approached saturation at about 50 kOe. The values of relative saturation magnetization were 6.8 emu/g for DAPcDOD- $\text{Ni}^{2+}$ , 10.5 emu/g for DAPcDOD- $\text{Co}^{2+}$ , and 5.0 emu/g for DAPcDOD- $\text{Fe}^{2+}$ , respectively.

Figure 4 shows the temperature dependence of the magnetization for the complexes DAPcDOD- $\text{Ni}^{2+}$ , DAPcDOD- $\text{Co}^{2+}$ , and DAPcDOD- $\text{Fe}^{2+}$  at an applied magnetic field of 30 kOe. The magnetization decreased with increasing temperature.

Figure 5 indicates that the reciprocal of the magnetic susceptibility ( $\chi^{-1}$ ) of DAPcDOD- $\text{Ni}^{2+}$  followed



**Figure 4** Magnetization ( $M$ ) versus the temperature ( $T$ ) at a magnetic field strength of 30 kOe for the polymeric complexes: (1) DAPcDOD- $\text{Ni}^{2+}$ , (2) DAPcDOD- $\text{Co}^{2+}$ , and (3) DAPcDOD- $\text{Fe}^{2+}$ .

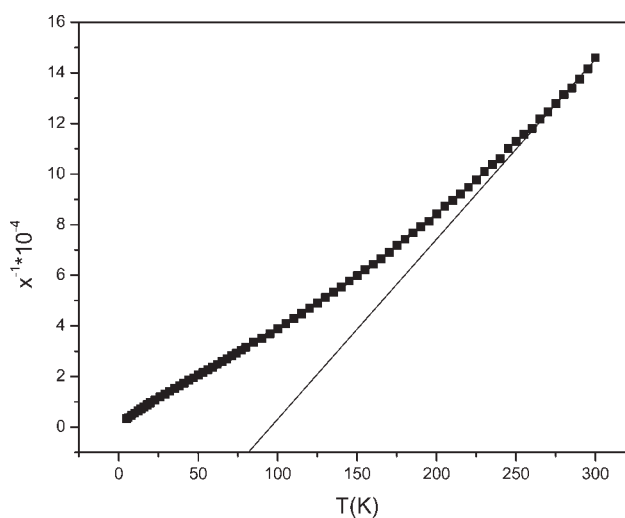


**Figure 5** Temperature ( $T$ ) dependence of  $\chi^{-1}$  for DAPcDOD- $\text{Ni}^{2+}$  under an applied field of 30 kOe. The straight line represents a fit to the Curie-Weiss law within 260–300 K.

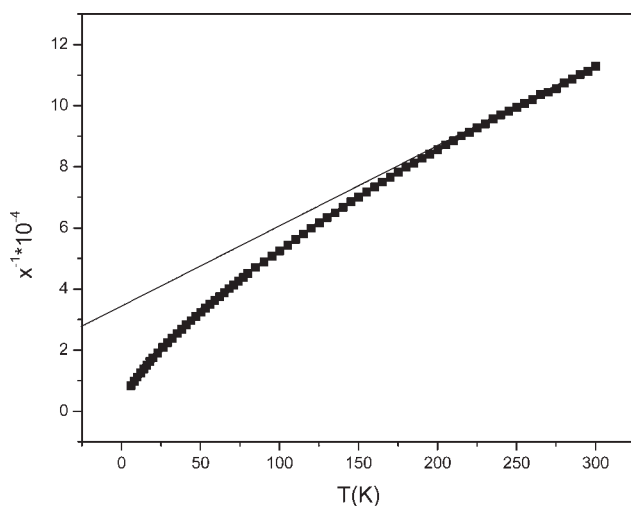
the Curie-Weiss relationship,  $\chi = C/(T - \theta)$  ( $C$  is the Curie constant and  $T$  is the temperature), in the range 260–300 K ( $\theta$  is the Curie-Weiss temperature). The positive  $\theta$  value (47 K) implied the existence of ferromagnetic coupling in the complex.<sup>17</sup> It was deduced that DAPcDOD- $\text{Ni}^{2+}$  exhibited ferromagnetism.

Figure 6 indicates that  $\chi^{-1}$  of DAPcDOD- $\text{Co}^{2+}$  followed the Curie-Weiss relationship,  $\chi = C/(T - \theta)$ , in the range 265–300 K. The positive  $\theta$  value (81 K) implied the existence of ferromagnetic coupling in the complex. We deduced that DAPcDOD- $\text{Co}^{2+}$  exhibited the characteristic phenomena of a ferromagnet.

Figure 7 indicates that  $\chi^{-1}$  of DAPcDOD- $\text{Fe}^{2+}$  followed the Curie-Weiss relationship,  $\chi = C/(T - \theta)$ ,



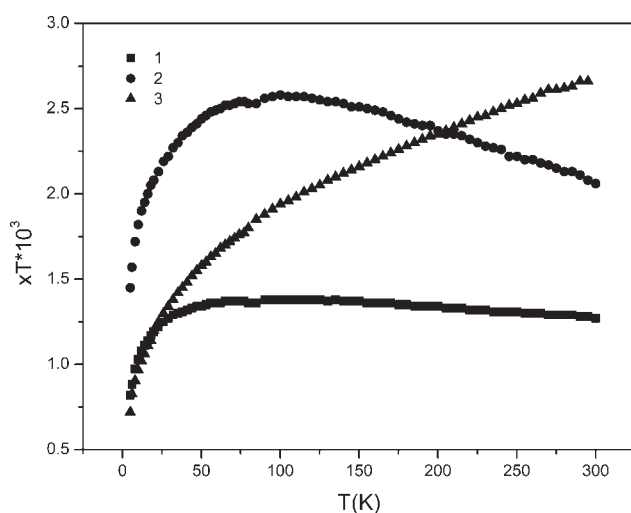
**Figure 6** Temperature ( $T$ ) dependence of  $\chi^{-1}$  for DAPcDOD- $\text{Co}^{2+}$  under an applied field of 30 kOe. The straight line represents a fit to the Curie-Weiss law within 265–300 K.



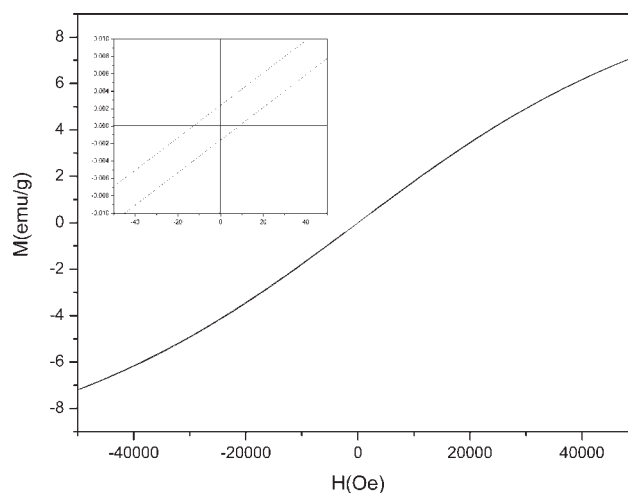
**Figure 7** Temperature ( $T$ ) dependence of  $\chi^{-1}$  for DAPcDOD-Fe $^{2+}$  under an applied field of 30 kOe. The straight line represents a fit to the Curie-Weiss law within 180–300 K.

in the range 180–300 K. The negative  $\theta$  value (–121 K) implied the existence of mainly antiferromagnetic interactions in this material.

The temperature dependences of  $\chi T$  for DAPcDOD-Ni $^{2+}$ , DAPcDOD-Co $^{2+}$ , and DAPcDOD-Fe $^{2+}$  are shown in Figure 8. The value of  $\chi T$  for DAPcDOD-Ni $^{2+}$  changed little with decreasing temperature above 50 K. However, when the temperature was below 50 K, the value of  $\chi T$  dramatically decreased, and the slope of  $\chi T$  sharply increased with decreasing temperature. This suggested that this system approached a magnetic phase transition when the temperature was near 50 K. The changes



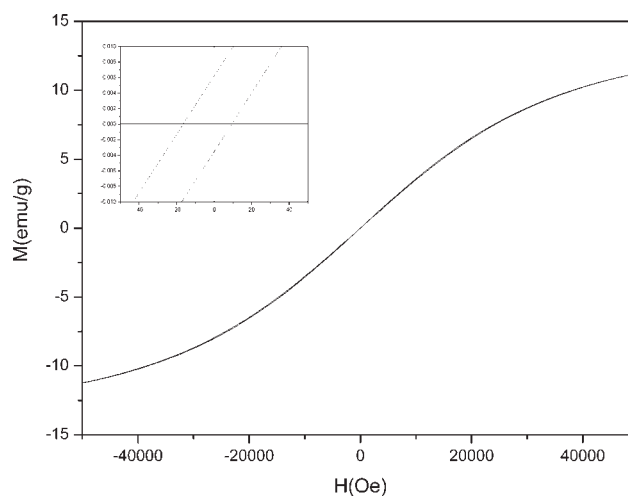
**Figure 8**  $\chi$  data at a magnetic field strength of 30 kOe for the polymeric complexes: (1) DAPcDOD-Ni $^{2+}$ , (2) DAPcDOD-Co $^{2+}$ , and (3) DAPcDOD-Fe $^{2+}$ .



**Figure 9** Magnetic hysteresis loop of DAPcDOD-Ni $^{2+}$  at 5 K. The inset shows an expanded view of the region from –50 to 50 Oe.  $M$  is the magnetization, and  $H$  is the magnetic field strength.

in the values of  $\chi T$  for DAPcDOD-Co $^{2+}$  and DAPcDOD-Fe $^{2+}$  were similar to those of DAPcDOD-Ni $^{2+}$ .

Field dependence hysteresis loops of DAPcDOD-Ni $^{2+}$  and DAPcDOD-Co $^{2+}$  were generated at 5 K (Figs. 9 and 10). Table I summarizes the magnetic properties of the DAPcDOD-Ni $^{2+}$ , DAPcDOD-Co $^{2+}$ , and DAPcDOD-Fe $^{2+}$  complexes. The results indicate that the three complexes showed the characteristic of a soft ferromagnet at low temperature because the observed remanence magnetization and coercive field had lower values. From the typical S shape and small area of the hysteresis loop, we deduced that DAPcDOD-Ni $^{2+}$  and DAPcDOD-Co $^{2+}$  were both soft ferromagnets.



**Figure 10** Magnetic hysteresis loop of DAPcDOD-Co $^{2+}$  at 5 K. The inset shows an expanded view of the region from –50 to 50 Oe.  $M$  is the magnetization, and  $H$  is the magnetic field strength.

**TABLE I**  
**Magnetic Properties of the DAPcDOD–Ni<sup>2+</sup>,  
 DAPcDOD–Co<sup>2+</sup>, and DAPcDOD–Fe<sup>2+</sup> Complexes**

Complex	Relative saturation magnetization (emu/g)	Remanence magnetization (emu/g)	Coercive field (Oe)	$\theta$ (K)
DAPcDOD–Ni <sup>2+</sup>	6.8	0.002	10	48
DAPcDOD–Co <sup>2+</sup>	10.5	0.006	9	81
DAPcDOD–Fe <sup>2+</sup>	5.0	0.007	180	–121

### CONCLUSIONS

Poly(Schiff base) DAPcDOD and the corresponding DAPcDOD–Ni<sup>2+</sup>, DAPcDOD–Co<sup>2+</sup>, and DAPcDOD–Fe<sup>2+</sup> complexes were first synthesized and then characterized. Also, the magnetic properties of the complexes were studied. On the basis of the field and temperature dependence of the magnetization and hysteresis loops, we concluded that DAPcDOD–Ni<sup>2+</sup> and DAPcDOD–Co<sup>2+</sup> were soft ferromagnets, whereas DAPcDOD–Fe<sup>2+</sup> was an antiferromagnet.

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