

## PREPARATION AND MAGNETIC PROPERTIES OF POLYMERIC COMPLEXES CONTAINING 1,10-PHENANTHROLINE\*

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**Abstract** A series of polymeric complexes were prepared from  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  and poly(Schiff base) (DAPcIPA), which was obtained by polycondensation of 5,6-diamino-1,10-phenanthroline (DAP) with isophthalaldehyde (IPA). The structures of the polymer and the polymeric complexes were characterized by IR,  $^1\text{H}$ -NMR and elemental analysis. The magnetic behavior of these complexes was measured as a function of magnetic field strength ( $0\text{--}3.98 \times 10^6$  A/m) at 5 K and as a function of temperature (5–300 K) at a magnetic field strength of  $2.39 \times 10^6$  A/m. Experimental results show that DAPcIPA- $\text{Ni}^{2+}$ , DAPcIPA- $\text{Co}^{2+}$  are soft ferromagnets while DAPcIPA- $\text{Fe}^{2+}$  exhibits features of an antiferromagnet.

**Keywords:** Synthesis; Polymer containing phenanthroline; Polymeric complexes; Organic soft ferromagnets.

### INTRODUCTION

Design and synthesis of magnetic polymers are one of great challenges in today's magnetic material research, and some significant achievements have been made in this field. A report on the observation of first soft ferromagnet below 16 K, a complex of  $\text{C}_{60}$  with one of the strongest organic donors tetrakis(dimethylamino)ethylene (TDAE), attracted a great deal of attention<sup>[1]</sup>. A series of investigations were carried out to elucidate the nature of this unusual magnetic phenomenon of TDAE- $\text{C}_{60}$ <sup>[2–4]</sup>, but up to now, no other soft ferromagnets were reported.

In recent years, our group has worked on the synthesis of bithiazole-based polymers and their metal complexes for developing functional materials<sup>[5]</sup>. A variety of novel polymer-metal complexes containing bithiazole moieties were obtained and some of them displayed interesting magnetic properties<sup>[6–13]</sup>. It is well known that the magnetic property of polymeric complexes arises from the magnetic exchange interactions between metal ions in the polymer matrix. Generally, this magnetic interaction is relatively strong through  $\pi$ -conjugated system as compared to the space interaction<sup>[14]</sup>. Therefore, design and synthesis of polymeric complexes with a conjugated structure might get a new kind of magnetic materials. In this paper, we report the preparation of a novel poly(Schiff base) containing phenanthroline and its  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  metal complexes (Scheme 1). The magnetic of complexes behaviors were investigated for the first time.

### EXPERIMENTAL

Dimethylsulfoxide (DMSO) was refluxed with calcium hydride for 24 h and distilled under 533 Pa, 64–65°C distillation cut was obtained and stored up with 0.4 nm molecular sieve. 5,6-diamino-1,10-phenanthroline (DAP) were synthesized according to the literatures<sup>[15]</sup>, followed by several recrystallizations, using ethanol as solvent.

Polymers and their complexes were prepared by following the methods below.

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### Synthesis of Poly(Schiff base)s DAPcIPA

2.10 g (10 mmol) of 5,6-diamino-1,10-phenanthroline (DAP), 1.34 g (10 mmol) of isophthalaldehyde and DMSO (100 mL) as solvent were added to a round-bottom flask. The mixture was magnetically stirred at room temperature under purified  $N_2$  atmosphere. The colour of the solution turned from yellow to brown upon reaction after a few minutes. The reaction solution became homogeneous as the reaction proceeds. After 3–4 h, the viscosity of the solution increased. The solution was poured into ethanol:water (1:1), and then a red-brown precipitate was formed and filtered, washed successively with water, ethanol and ether, and dried under vacuum at 60°C for 24 h. The yield is 3.0 g (87.2 %).  $^1H$ -NMR (DMSO- $d_6$ ):  $\delta$  = 7.8, 8.05, 8.6, 8.7, 8.9, and 9.1 are 1,10-phenanthroline rings and benzene protons resonances,  $\delta$  = 9.2 is  $CH=N$  protons resonances,  $\delta$  = 10.2 is polymer chain end  $-CHO$  protons resonances; FT-IR: 1696 ( $C=N$ ), 1647, 1576, 1559, 1506 (Ar ring), 1489, 1430, 1399, 1340, 1271, 1236, 1072, 1029, 803, 738, 698, 668  $cm^{-1}$ . Intrinsic viscosity  $[\eta]$  = 0.27 dL/g (DMSO, 30°C). Elemental analysis: Calcd. for  $[C_{12}H_{12}N_4]_n$ : C, 67.92%; H, 5.66%; N, 26.42%. Found: C, 67.27%; H, 5.83%; N, 25.61%.

### Preparation of Polymeric Complexes: DAPcIPA- $Ni^{2+}$ , DAPcIPA- $Co^{2+}$ , DAPcIPA- $Fe^{2+}$

$NiSO_4$  ( $FeSO_4$  or  $CoCl_2$ ) solution was added slowly into a stirred DMSO solution of polymer (DAPcIPA) in purified nitrogen atmosphere, and stirring was continued for 6–8 h at 80°C. A precipitate was formed, filtered and washed successively with water and methanol, then the precipitated complex was soaked in methanol for 24 h. The complex was isolated by filtration and dried under vacuum at 60°C for 24 h.

DAPcIPA- $Ni^{2+}$ : IR: 1698, 1651, 1606, 1583, 1506, 1488, 1451, 1404, 1362, 1258, 1080, 980, 814, 732 and 668  $cm^{-1}$ . The content of Ni is 7.89%. The elemental analysis: Calcd. for the suggested formula  $[C_{12}H_{12}N_4(NiSO_4)_{0.36}]_n$ : C, 53.79%; H, 4.48%; N, 20.92%. Found: C, 53.17%; H, 4.29%; N, 19.53%.

DAPcIPA- $Co^{2+}$ : IR: 1699, 1652, 1605, 1575, 1447, 1404, 1357, 1198, 1076, 1046, 980, 813, 736, 693, and 641  $cm^{-1}$ . The content of Co is 8.74%. The elemental analysis: Calcd. for the suggested formula  $[C_{12}H_{12}N_4(CoCl_2)_{0.39}]_n$ : C, 54.82%; H, 4.57%; N, 21.32%. Found: C, 55.05%; H, 4.82%; N, 20.73%.

DAPcIPA- $Fe^{2+}$ : IR: 1700, 1652, 1607, 1580, 1452, 1405, 1120, 1045, 980, 813, 739 and 605  $cm^{-1}$ . The content of Fe is 7.03%. The elemental analysis: Calcd. for the suggested formula  $[C_{12}H_{12}N_4(FeSO_4)_{0.33}]_n$ : C, 54.94%; H, 4.58%; N, 21.36%. Found: C, 54.3%; H, 4.07%; N, 20.42%.

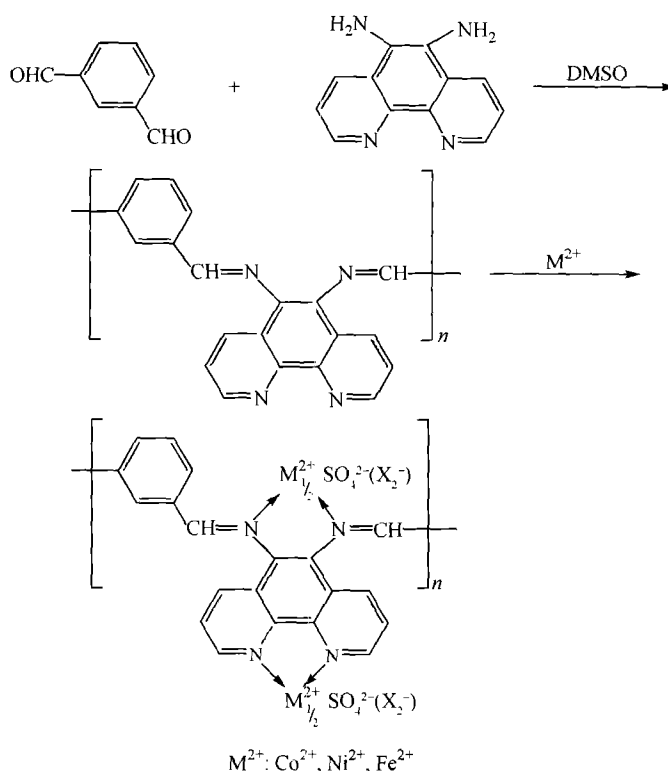
### Measurements

A Bruker Vector 22 Fourier Transform Infrared (FTIR) spectrometer was used for recording IR spectra in KBr pellets.  $^1H$ -NMR spectra were recorded on a Bruker Advance AMX-500 NMR instrument in DMSO- $d_6$  with tetramethylsilane (TMS) as internal standard. Intrinsic viscosity  $[\eta]$  was measured in DMSO at 30°C. Elemental analyses for C, H, and N were performed using a Flash EA112 elemental analyzer (ThermoFinnigan). The contents of metal (Fe, Co and Ni) were measured by complexometry. The magnetic properties of complexes (complexes powder in measuring tube) were measured with PPMS-9T magnetometer (Quantum Design).

## RESULTS AND DISCUSSION

Polymers and complexes were prepared as shown in Scheme 1.

To prepare the poly(Schiff base) with high molecular weight, we applied the polycondensation procedure and paid careful attention to dry the solvents used. It must be noted that low temperature was essential to obtain polymers successfully, and the complex reaction between polymer and metal ion should be carried out under purified nitrogen and about 80°C.



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

### Characterization of Polymers and Complexes

The structure of poly(schiff base) *DAPcIPA* was determined by IR (Fig. 1.) and  $^1\text{H-NMR}$  spectroscopy. In IR spectra, the stretching vibration band of  $\text{C}=\text{N}$  appeared at about  $1696\text{ cm}^{-1}$ , while  $1647, 1576, 1559, 1506\text{ cm}^{-1}$  are the stretching vibration band of aromatic rings. The band at  $803\text{ cm}^{-1}$  is the skeletal vibrations of aromatic heterocyclic rings containing nitrogen. As for  $^1\text{H-NMR}$  spectra,  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ):  $\delta = 7.8, 8.05, 8.6, 8.7, 8.9, 9.1$  are 1,10-phenanthroline and benzene protons resonances,  $\delta = 9.2$  is  $\text{CH}=\text{N}$  protons resonances,  $\delta = 10.2$  is polymer chain end  $-\text{CHO}$  protons resonances; In comparison with  $^1\text{H-NMR}$  spectra of monomer DAP, the  $-\text{NH}_2$  protons peak at  $\delta = 5.2$  disappear.

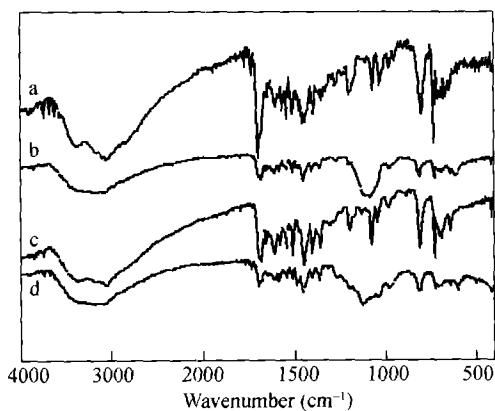


**Fig. 1** FT-IR spectra of polymer and complexes  
a) *DAPcIPA*; b) *DAPcIPA-Ni*<sup>2+</sup>; c) *DAPcIPA-Co*<sup>2+</sup>; d) *DAPcIPA-Fe*<sup>2+</sup>

In comparison with DAPcIPA, significant changes are observed in the IR spectra of DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> (Fig. 1.), e.g. the IR absorption bands of DAPcIPA at 1696 (C=N), 1647, 1576, 1559 cm<sup>-1</sup> are blue-shifted to 1698, 1651, 1606, 1583 cm<sup>-1</sup> of DAPcIPA-Ni<sup>2+</sup>, 1699, 1652, 1606, 1575 cm<sup>-1</sup> of DAPcIPA-Co<sup>2+</sup> and 1700, 1652, 1607, 1580 cm<sup>-1</sup> of DAPcIPA-Fe<sup>2+</sup>, respectively. This indicates that the coordination has taken place through the nitrogen atoms of phenanthroline rings or polymer skeleton, because the skeletal vibrations of phenanthroline rings will need higher energy after coordinating with Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>. Similar changes can be observed within the region of 1200–400 cm<sup>-1</sup> in IR spectra of these complexes.

On the basis of elemental analyses, three complexes have formulas of [C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>(NiSO<sub>4</sub>)<sub>0.36</sub>]<sub>n</sub>, [C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>(CoCl<sub>2</sub>)<sub>0.39</sub>]<sub>n</sub> and [C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>(FeSO<sub>4</sub>)<sub>0.33</sub>]<sub>n</sub> for DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup>, 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 coordination structure of the complexes is composed of one metal ion and two phenanthroline units from different polymer chains, in which nitrogen atoms act as coordinating sites. It seems reasonable in view of the stiffness of polymer chain and the strong chelating tendency of bidentate nitrogen ligands to metal ions.

### Magnetic Properties of Complexes

Figure 2 presents a typical ferromagnetic relationship between mass magnetization ( $\sigma$ ) and applied field ( $H$ ) for the complexes DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> at 5 K; their magnetizations ( $\sigma$ ) increase sharply below  $2.39 \times 10^6$  A/m. This indicates a spontaneous magnetization. The rising trend slows down above  $2.39 \times 10^6$  A/m and then nearly approaches saturation at about  $3.98 \times 10^6$  A/m. The relative saturation magnetization are 9.8 Am<sup>2</sup>/kg for DAPcIPA-Ni<sup>2+</sup>, 11.5 Am<sup>2</sup>/kg for DAPcIPA-Co<sup>2+</sup> and 5.7 Am<sup>2</sup>/kg for DAPcIPA-Fe<sup>2+</sup>, respectively.

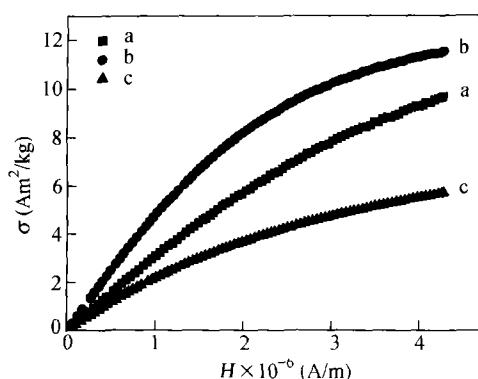


**Fig. 2** Mass magnetization ( $\sigma$ ) verse applied field ( $H$ ) curve at  $T = 5$  K for polymeric complexes  
a) DAPcIPA-Ni<sup>2+</sup>; b) DAPcIPA-Co<sup>2+</sup>; c) DAPcIPA-Fe<sup>2+</sup>

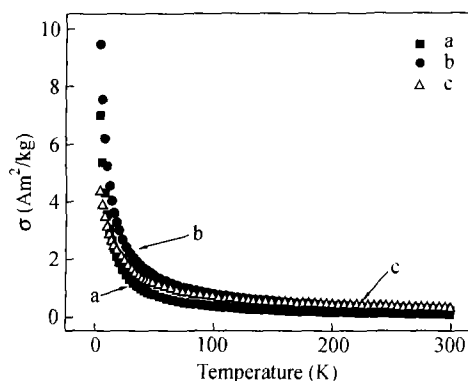


**Fig. 3** Mass magnetization ( $\sigma$ ) versus temperature ( $T$ ) curve at  $H = 2.39 \times 10^6$  A/m for polymeric complexes  
a) DAPcIPA-Ni<sup>2+</sup>; b) DAPcIPA-Co<sup>2+</sup>; c) DAPcIPA-Fe<sup>2+</sup>

Figure 3 shows the temperature dependence of magnetization of complexes DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> at an applied magnetic field of  $2.39 \times 10^6$  A/m from temperature 3 to 300 K. The magnetization decreases with increasing temperatures. Figures 4, 5 and 6 reveal that the temperature dependence of the reciprocal magnetic susceptibility for DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> under an applied field of  $2.39 \times 10^6$  A/m, respectively. Figure 4 indicates that the magnetic susceptibility ( $\chi$ ) of DAPcIPA-Ni<sup>2+</sup> obeys the Curie-Weiss relationship,  $\chi = C/(T-\theta)$ , from 240 to 300 K. The positive Curie-Weiss temperature ( $\theta = 49$  K) implies the existence of ferromagnetic coupling in the complex<sup>[16]</sup>. It can be deduced that DAPcIPA-Ni<sup>2+</sup> exhibits ferromagnetic character. Figure 5 also indicates that the magnetic susceptibility ( $\chi$ ) of DAPcIPA-Co<sup>2+</sup> obeys the Curie-Weiss relationship, in the temperature range from 260 to 300 K. With a positive Curie-Weiss temperature ( $\theta = 13$  K), implying the existence of ferromagnetic coupling in the complex. It can be deduced that DAPcIPA-Co<sup>2+</sup> exhibits ferromagnetic character too. Figure 6 indicates that the magnetic susceptibility ( $\chi$ ) of DAPcIPA-Fe<sup>2+</sup> also follows the Curie-Weiss relationship from 180 to 300 K, but its negative Curie-Weiss temperature ( $\theta = -118$  K) implies the existence of mainly antiferromagnetic interaction in this material.

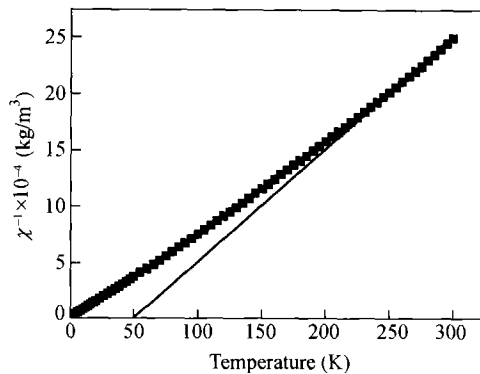


**Fig. 4** Temperature dependence of the reciprocal magnetic susceptibility ( $\chi^{-1}$ ) curve for DAPcIPA- $\text{Ni}^{2+}$  under an applied field of  $2.39 \times 10^6$  A/m. The straight line represents a fit to the Curie-Weiss law within 240–300 K.

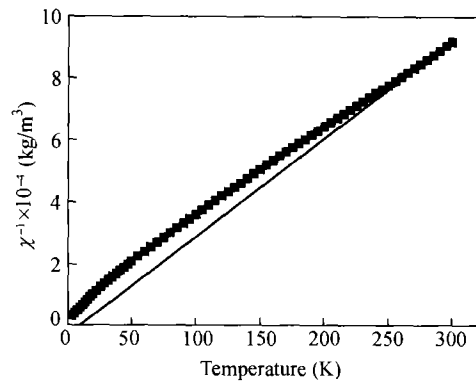


**Fig. 5** Temperature dependence of the reciprocal magnetic susceptibility ( $\chi^{-1}$ ) curve for DAPcIPA- $\text{Co}^{2+}$  under an applied field of  $2.39 \times 10^6$  A/m. The straight line represents a fit to the Curie-Weiss law within 260–300 K.

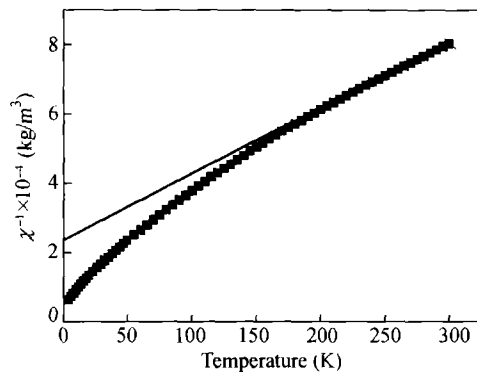


**Fig. 6** Temperature dependence of the reciprocal magnetic susceptibility ( $\chi^{-1}$ ) curve for DAPcIPA- $\text{Fe}^{2+}$  under an applied field of  $2.39 \times 10^6$  A/m. The straight line represents a fit to the Curie-Weiss law within 180–300 K.

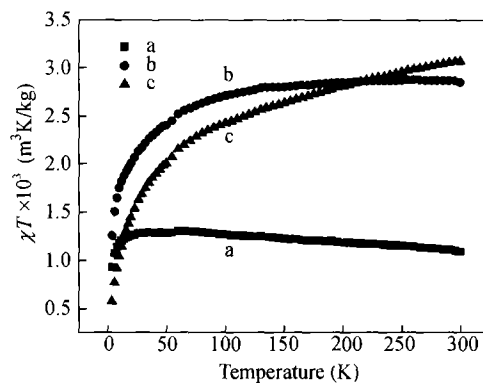


**Fig. 7** Temperature dependence of magnetic susceptibility data ( $\chi T$ ) curve for polymeric complexes a) DAPcIPA- $\text{Ni}^{2+}$ ; b) DAPcIPA- $\text{Co}^{2+}$ ; c) DAPcIPA- $\text{Fe}^{2+}$

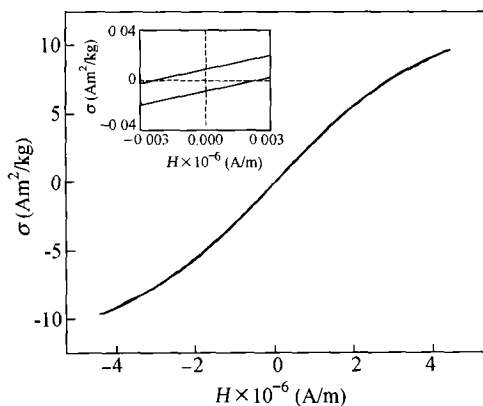


**Fig. 8** Magnetic hysteresis loop of DAPcIPA- $\text{Ni}^{2+}$  at 5 K (insert) Expanded view of the region from  $-3.18 \times 10^3$  A/m to  $3.18 \times 10^3$  A/m ( $\sigma$ : mass magnetization,  $H$ : applied field).

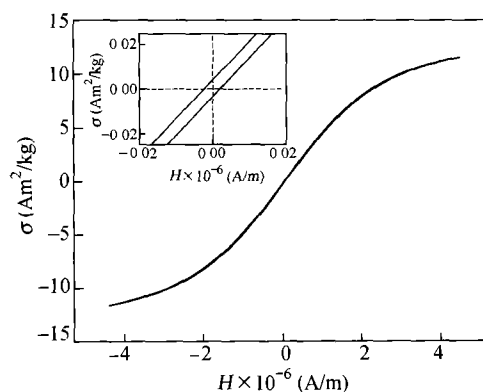


**Fig. 9** Magnetic hysteresis loop of DAPcIPA- $\text{Co}^{2+}$  at 5 K (insert) Expanded view of the region from  $-2.39 \times 10^4$  A/m to  $2.39 \times 10^4$  A/m ( $\sigma$ : mass magnetization,  $H$ : applied field).

**Table 1** Magnetic properties of DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> complexes

| Complex                  | Relative saturation magnetization (Am <sup>2</sup> /kg) | Remanence magnetization (Am <sup>2</sup> /kg) | Coercive field (A/m)     | Curie-Weiss temperature (K)   |
|--------------------------|---------------------------------------------------------|-----------------------------------------------|--------------------------|-------------------------------|
| DAPcIPA-Ni <sup>2+</sup> | 9.8 (5 K)                                               | 0.01 (5 K)                                    | $2.39 \times 10^3$ (5 K) | 49 ( $2.39 \times 10^6$ A/m)  |
| DAPcIPA-Co <sup>2+</sup> | 11.5 (5 K)                                              | 0.02 (5 K)                                    | $2.79 \times 10^3$ (5 K) | 11 ( $2.39 \times 10^6$ A/m)  |
| DAPcIPA-Fe <sup>2+</sup> | 5.7 (5 K)                                               | 0.04 (5 K)                                    | $1.35 \times 10^4$ (5 K) | -98 ( $2.39 \times 10^6$ A/m) |

The temperature dependence of  $\chi T$  for DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> are shown in Fig. 7. The  $\chi T$  for DAPcIPA-Ni<sup>2+</sup> changes little with a decreasing  $T$  above 50 K. Below 50 K, an abrupt increase in the slope of  $\chi T$  and also a decrease of  $\chi T$  with decreasing temperature is observed. It suggests that the system approaches a magnetic phase transition near 50 K. The change of  $\chi T$  for DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> are the same as DAPcIPA-Ni<sup>2+</sup> does.

Field dependence hysteresis loop of DAPcIPA-Ni<sup>2+</sup> and DAPcIPA-Co<sup>2+</sup> are generated at 5 K (Figs. 8 and 9). Table 1 summarizes the magnetic properties of DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup> complexes. The results indicate that these complexes possess the characteristic of a soft ferromagnet at low temperatures because the observed remanence magnetization and coercive field have low values. From the typical S shape and small area of hysteresis loop it can be deduced that DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> are all soft ferromagnets.

## CONCLUSIONS

The poly(schiff base)s DAPcIPA and their complexes, DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> and DAPcIPA-Fe<sup>2+</sup>, were synthesized and characterized. The magnetic properties of the complexes were studied. From the field and temperature dependence of magnetization and hysteresis loop it can be concluded that DAPcIPA-Ni<sup>2+</sup>, DAPcIPA-Co<sup>2+</sup> are soft ferromagnets, whereas DAPcIPA-Fe<sup>2+</sup> is an antiferromagnet.

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