

邻菲罗啉聚西佛碱金属配合物的合成及磁性能研究^{*}

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摘 要 以 5,6-二胺-1,10-菲罗啉与 2,6-吡啶二甲酸缩聚合成得到一种新的含邻菲罗啉结构的聚西佛碱,并制备了其相应的与过渡金属离子 Ni^{2+} 和 Fe^{2+} 以及稀土离子 Nd^{3+} 的配合物,通过红外光谱,核磁共振和元素分析等手段对聚合物及其金属配合物的结构进行了表征,并分析和讨论了它们的磁学性能. 结果表明,这一类金属配合物在低温区,磁化率倒数与温度的关系不服从居里-外斯定律,存在着铁磁耦合,其中聚合物的镍和钕的配合物是软铁磁体,而聚合物的亚铁配合物是反铁磁体.

关键词 合成, 邻菲罗啉聚西佛碱, 金属配合物, 磁性能

SYNTHESIS AND MAGNETIC PROPERTIES OF POLY(SCHIFF BASE) COMPLEXES CONTAINING 1,10-PHENANTHROLINE AND PYRIDINE UNIT

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Abstract A novel poly(Schiff base) containing 1,10-phenanthroline (DAPcPYA) was synthesized by the polycondensation of 2,6-pyridinedicarboxaldehyde (PYA) with 5,6-diamine-1,10-phenanthroline (DAP). Three polymeric complexes were first prepared by the reaction of polymer (DAPcPYA) with NiSO_4 , FeSO_4 , and NdCl_3 , respectively. The structures of the polymer and the complexes were characterized by IR, ^1H -NMR, and elemental analysis. The magnetic behaviors of these complexes were measured as a function of magnetic field strength ($0 \sim 4.0 \times 10^6$ A/m) at 5 K and as a function of temperature ($5 \sim 300$ K) at a magnetic field strength of 2.4×10^6 A/m. The results show that DAPcPYA- Ni^{2+} and DAPcPYA- Nd^{3+} were soft ferromagnets, whereas DAPcPYA- Fe^{2+} exhibited the features of an antiferromagnet.

Keywords Synthesis, Poly(Schiff base) containing phenanthroline, Polymeric complexes, Magnetic properties

1 INTRODUCTION

Organic and polymeric magnetic materials have been studied extensively, and great progress has been achieved in this field^[1-4]. Compared with traditional magnets, organic polymeric ferromagnets have many advantages, such as low density, various structures and easy processing, etc. For example,

the light soft ferromagnetic materials are applied in novel absorbents of microwave, micromotion of electron products, magnetic-optic materials, space kinetic systems and universe sail systems^[5-7].

Sun and coworkers have synthesized a variety of polymers containing bithiazole rings and the corresponding complexes with transition metal ions or rare earth metal ions, and in which most could show

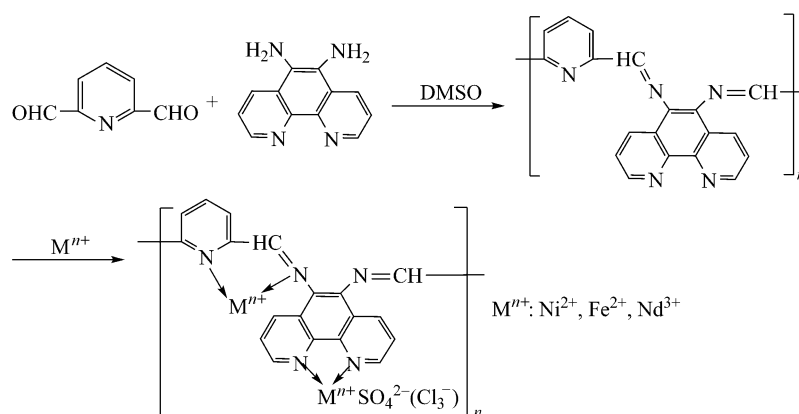
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interesting magnetic behaviors^[8~11]. 1, 10-Phenanthroline and its derivatives are vital ligands in organometallic chemistry because they can also provide bidentate N-donor sites for chelating with metal ions to form bridge ligands^[12,13], except that 5,6-diamino-1,10-phenanthroline can be condensed with a variety of carbonyl-containing compounds to form additional derivatives. In recent years, our group carried out a series of studies on the preparation of poly(Schiff base)s containing 1,10-phenanthroline rings and their metal complexes^[14~18], in which some of these complexes

showed soft ferromagnetic behavior.

Here, based on previous work concerning preparation and properties of polymeric complexes, we attempt to synthesize novel organic materials, which have better properties and multiple functions. In this article, we discuss the synthesis and characterization of a novel poly(Schiff base) incorporating phenanthroline units and pyridine units, and its transition metal and rare earth metal complexes (Scheme 1). The magnetic properties of these complexes were investigated for the first time.



Scheme 1 Synthetic routes of poly(Schiff base) DAPcPYA and suggested structures for the corresponding metal complexes

2 EXPERIMENTAL

2.1 Materials

Dimethyl sulfoxide (DMSO) was dried using a molecular sieve for several days and distilled prior to use. 5,6-Diamino-1,10-phenanthroline (DAP) was prepared according to the literature^[19], followed by several recrystallizations with ethanol. 2, 6-Pyridinedicarboxaldehyde (PYA) was bought from China National Medicines Corporation Ltd.

2.2 Synthesis of Poly(Schiff base) (DAPcPYA)

1.05 g (5 mmol) of DAP, 0.67 g (5 mmol) of PYA and DMSO (50 mL) as solvent were added into a round bottom flask. The mixture was magnetically stirred at room temperature under a purified N₂ atmosphere for 4 h. The solution was poured into a mixture of ethanol and water (1:1), and then the 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 1.21 g (78.6%). ¹H-NMR (CF₃COOD, δ): 7.5, 7.7, 7.9, 8.5 and 8.8 (H of 1,10-phenanthroline and pyridine), 7.4 (CH=N protons resonances); FTIR: 1643 (C=N), 1560, 1506, 1431, 1394, 1313, 1072, 993, 810, 738, 650 cm⁻¹; intrinsic viscosity [η] = 0.17 dL/g (DMSO, 30°C); the elemental analysis, Calcd. for [C₁₉H₁₁N₅]_n: C 73.77%, H 3.58%, N 22.64%. Found: C 74.21%, H 3.97%, N 21.82%.

2.3 Preparation of the Polymeric Complexes

NiSO₄ (or FeSO₄ or NdCl₃) and the polymer DAPcPYA (molar ratio = 2:1) were added slowly to a stirred DMSO solution under a purified nitrogen atmosphere. The mixed solution was stirred at 80°C for 12 h, and then, the precipitate was formed. After it was filtered and washed successively with water and methanol, the remaining precipitate was soaked in deionized water for 24 h to remove excess

physisorption of NiSO_4 (FeSO_4 or NdCl_3), and then isolated by filtration. After the filtrate was dried in vacuum at 60°C for 24 h, the polymeric complexes was obtained.

DAPcPYA- Ni^{2+} (the yield is 81.3%), IR (cm^{-1}): 1645, 1569, 1512, 1440, 1400, 1269, 1117, 813, 735, 617; the Ni content is 6.57%.

DAPcPYA- Fe^{2+} (the yield is 83.5%), IR (cm^{-1}): 1647, 1561, 1512, 1438, 1397, 1363, 1265, 1122, 1033, 978, 818, 739, 601; the Fe content is 7.32%.

DAPcPYA- Nd^{3+} (the yield is 76.1%), IR (cm^{-1}): 1645, 1562, 1508, 1433, 1395, 1288, 1190, 1072, 993, 810, 738, 650; the Nd content is 2.12%.

2.4 Measurements

A Bruker Vector 22 FTIR spectrometer (Ettlingen, Germany) was used to record IR spectra with KBr pellets. $^1\text{H-NMR}$ spectra were recorded on a Bruker Advance AMX-500NMR instrument in CF_3COOD with tetramethylsilane (TMS) 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, Ni and Nd) were obtained by complexometry. The magnetic properties of complexes were measured with a PPMS-9T magnetometer (Quantum Design, San Diego, CA).

3 RESULTS AND DISCUSSION

3.1 Characterization of the Polymer and Its Complexes

The polycondensation reaction of DAP with PYA can be examined by comparing their IR spectra. For example, the IR spectrum of DAPcPYA, compared with that of the monomer DAP is shown in Fig. 1. We can see the decrease of the broad absorption in the range of $3400 \sim 3200 \text{ cm}^{-1}$ of N—H stretching vibrations and a new bond ($\text{C}=\text{N}$) appeared at 1643 cm^{-1} , which indicate that DAPcPYA was obtained *via* polycondensation of DAP with PYA. As for the $^1\text{H-NMR}$ spectra, the resonance at $\delta = 7.4$ was that of $\text{CH}=\text{N}$ protons. The peaks at $\delta = 7.5$,

7.7, 7.9, 8.5 and 8.8 referred to 1, 10-phenanthroline and pyridine proton resonances. Compared with the $^1\text{H-NMR}$ spectra of monomer DAP, the peak of $-\text{NH}_2$ protons of DAPcPYA at $\delta = 5.2$ disappeared.

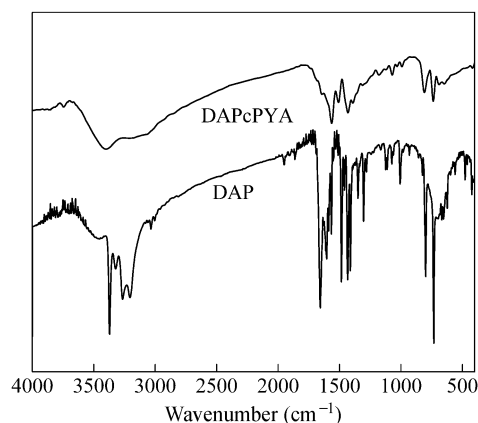


Fig. 1 IR spectra of DAP and DAPcPYA

According to the results of the element analysis, it is reasonable to infer that the formula for DAPcPYA is $[\text{C}_{19}\text{H}_{11}\text{N}_5]_n$ because experimental data were well in accordance with the theoretical values (For DAPcPYA, calcd: C 73.77%; H 3.58%, N 22.64%; Found: C 74.21%, H 3.97%, N 21.82%).

Because of two nitrogen atoms in the phenanthroline rings, the polymers presented in study can chelate various metal ions by form steady five-membered rings. The rare earth metal complexes and transition metal complexes were synthesized as described in Scheme 1 and examined by IR spectroscopy through comparing with the corresponding polymers. In comparison with DAPcPYA, significant changes were observed in the IR spectra of DAPcPYA- Ni^{2+} , DAPcPYA- Fe^{2+} and DAPcPYA- Nd^{3+} (Fig. 2); for example, the IR absorption bands of DAPcPYA at 1643 ($\text{C}=\text{N}$), 1560, 1506, 1431 and 1394 cm^{-1} blue-shifted to 1645, 1569, 1512, 1440 and 1400 cm^{-1} for DAPcPYA- Ni^{2+} ; 1647, 1561, 1512, 1438 and 1397 cm^{-1} for DAPcPYA- Fe^{2+} ; and 1645, 1562, 1508, 1433 and 1395 cm^{-1} for DAPcPYA- Nd^{3+} , 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 phenanthroline rings needed higher energy after coordination with Ni^{2+} , Fe^{2+} and Nd^{3+} . Similar changes were observed within the region $1200 \sim 400 \text{ cm}^{-1}$ in IR spectra of these complexes.

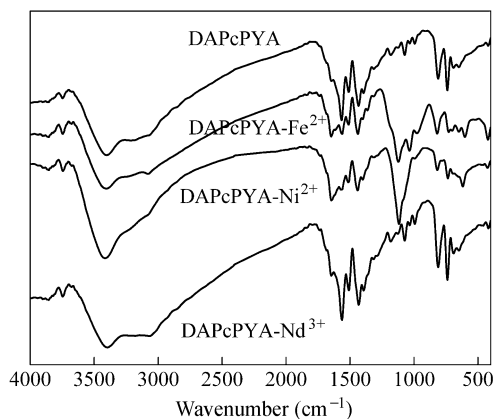


Fig. 2 IR spectra of DAPcPYA, DAPcPYA- Fe^{2+} , DAPcPYA- Ni^{2+} and DAPcPYA- Nd^{3+}

3.2 Magnetic Properties of the Complexes

Figure 3 shows the temperature dependence of the magnetization for the complexes DAPcPYA- Ni^{2+} , DAPcPYA- Fe^{2+} and DAPcPYA- Nd^{3+} at an applied magnetic field of $2.4 \times 10^6 \text{ A/m}$ from 5 K to 300 K. When the temperature was below 25 K, the magnetization decreased quickly with increasing temperature, and then decreased slowly till 300 K.

Figure 4 indicates that the reciprocal of the magnetic susceptibility (χ^{-1}) of DAPcPYA- Ni^{2+}

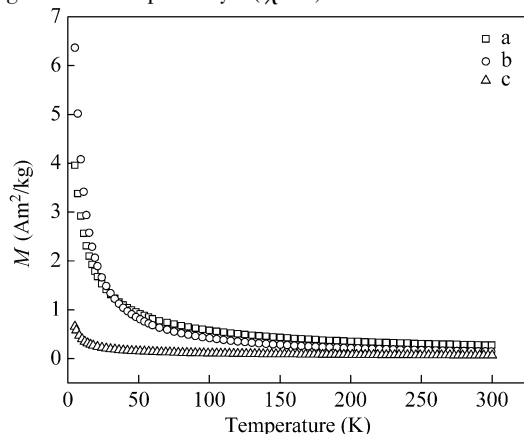


Fig. 3 Magnetization as function of temperature at an applied magnetic field of $2.4 \times 10^6 \text{ A/m}$ for DAPcPYA- Fe^{2+} (a), DAPcPYA- Ni^{2+} (b) and DAPcPYA- Nd^{3+} (c)

followed the Curie-Weiss relationship, $\chi = C/(T - \theta)$ (C is the Curie constant and T is the temperature), in the range $230 \sim 300 \text{ K}$ (θ is the Curie-Weiss temperature). The positive θ value (117 K) implies the existence of ferromagnetic coupling in the complex^[20]. It was deduced that DAPcPYA- Ni^{2+} exhibited ferromagnetism.

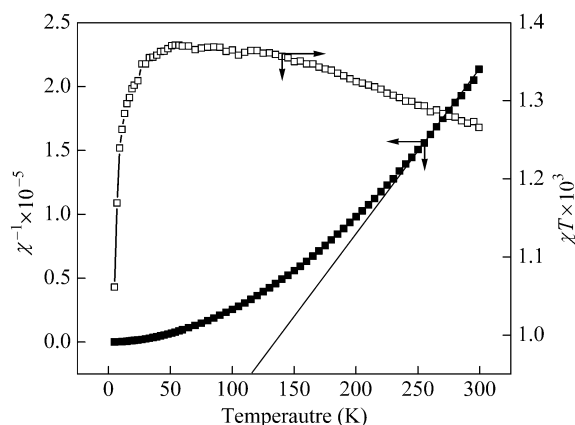


Fig. 4 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for DAPcPYA- Ni^{2+} at an applied magnetic field of $2.4 \times 10^6 \text{ A/m}$

The straight line is a fit to the Curie-Weiss law between 230 K and 300 K.

Figure 5 indicates that the magnetic susceptibility (χ^{-1}) of DAPcPYA- Nd^{3+} followed the Curie-Weiss relationship, $\chi = C/(T - \theta)$, in the range $220 \sim 300 \text{ K}$. The positive value (102 K) implies the existence of ferromagnetic coupling in the

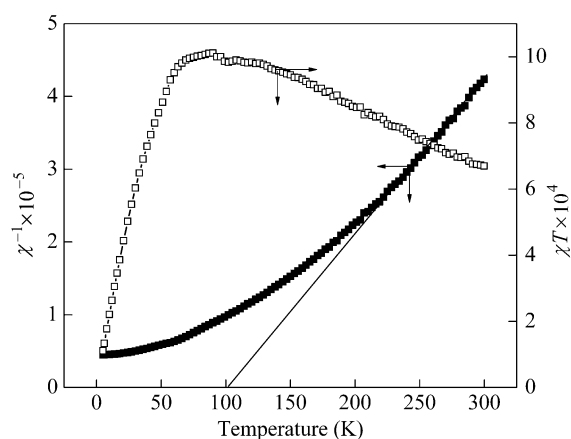


Fig. 5 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for DAPcPYA- Nd^{3+} at an applied magnetic field of $2.4 \times 10^6 \text{ A/m}$

The straight line is a fit to the Curie-Weiss law between 220 K and 300 K.

complex. We deduced that DAPcPYA-Nd³⁺ exhibited the characteristic phenomena of a ferromagnet.

Figure 6 indicates that the magnetic susceptibility (χ^{-1}) of DAPcPYA-Fe²⁺ followed the Curie-Weiss relationship, $\chi = C/(T - \theta)$, in the range 170 ~ 300 K. The negative value (- 179 K)

implied the existence of mainly antiferromagnetic interaction in this material.

Field dependence hysteresis loops of DAPcPYA-Ni²⁺ and DAPcPYA-Nd³⁺ were generated at 5 K (Figs. 7 and 8). Table 1 summarizes the magnetic properties of DAPcPYA-Ni²⁺, DAPcPYA-Nd³⁺ and DAPcPYA-Fe²⁺ complexes. The results

Table 1 Magnetic properties of DAPcPYA-Ni²⁺, DAPcPYA-Nd³⁺ and DAPcPYA-Fe²⁺

	Relative saturation magnetization (M_s)	θ (K)	Coercive field $\times 10^{-3}$ (A/m)	Remnant magnetization (Am^2/kg)
DAPcPYA-Ni ²⁺	9.1	117	0.96	0.0032
DAPcPYA-Nd ³⁺	0.92	102	2.56	0.0025
DAPcPYA-Fe ²⁺	5.1	- 179	21.68	0.055

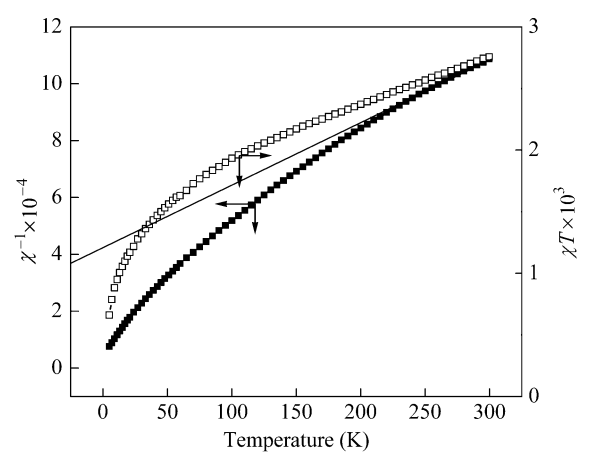


Fig. 6 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for DAPcPYA-Fe²⁺ at an applied magnetic filed of 2.4×10^6 A/m
The straight line is a fit to the Curie-Weiss law between 170 K and 300 K.

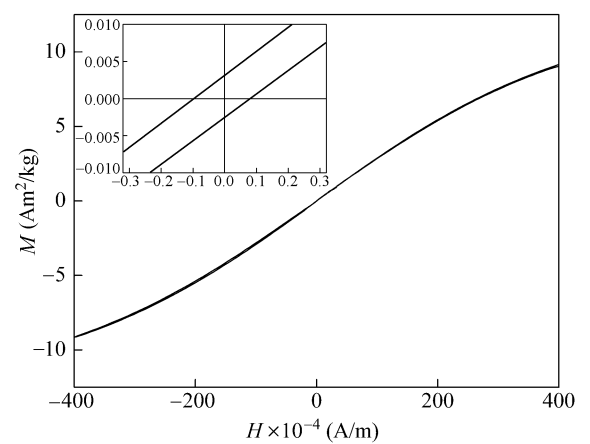


Fig. 7 Hysteresis loop (M versus H) at 5 K for DAPcPYA-Ni²⁺ complex
Inset: expanded view of the region from -3.2×10^3 A/m to 3.2×10^3 A/m

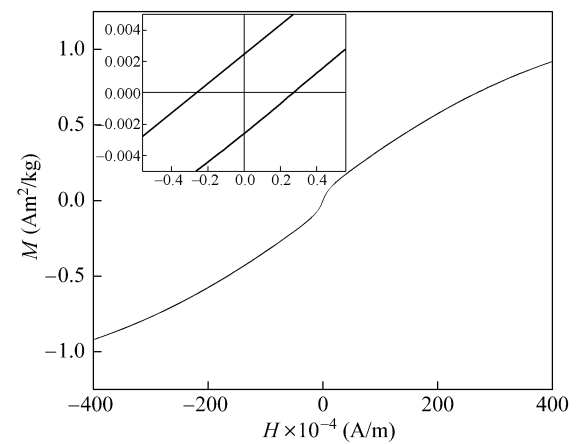


Fig. 8 Hysteresis loop (M versus H) at 5 K for DAPcPYA-Nd³⁺ complex
Inset: expanded view of the region from -5.6×10^3 A/m to 5.6×10^3 A/m

indicate that DAPcPYA-Ni²⁺ and DAPcPYA-Nd³⁺ 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 DAPcPYA-Ni²⁺ and DAPcPYA-Nd³⁺ were both soft ferromagnets.

4 CONCLUSIONS

The poly(Schiff base) DAPcPYA and the corresponding DAPcPYA-Ni²⁺, DAPcPYA-Nd³⁺ and DAPcPYA-Fe²⁺ complexes were first synthesized and characterized. Also, the magnetic properties of the complexes were studied.

DAPcPYA-Ni²⁺ has the highest relative

saturation magnetization among these complexes. On the basis of the field and temperature dependence of the magnetization and hysteresis loops, we concluded that DAPcPYA-Ni²⁺ and DAPcPYA-Nd³⁺ were soft ferromagnets, whereas DAPcPYA-Fe²⁺ was an antiferromagnet.

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