# Magnetic Properties of Some New Polymeric Chelating Complexes. I.

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Received 22 October 1997; accepted 6 April 1998

ABSTRACT: A new series of metallopolymer complexes derived from the homopolymer poly(2-acrylamide) benzoic acid (PBA) through some transition metals, Cu(II), Ni(II), and Co(II), were prepared. The compounds were synthesized and characterized through different techniques. Their molecular structures were assumed based on the different spectral data [ultraviolet (UV) and infrared (IR)]. The magnetic behavior of these metallopolymer complexes was measured as a function of magnetic field strength [1.65–0.85 tesla (T)] at room temperature (RT) (300 K) and as a function of temperature (4.2–300 K) at a magnetic field strength of 1.7 T. Based on the magnetic data, the mechanisms of magnetic interaction are explained and related to the stereochemistry of these metallopolymer complexes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 409–414, 1999

**Key words:** magnetic susceptibility; metallopolymer complexes; magnetic properties; chelating

# **INTRODUCTION**

Polymers containing paramagnetic species constitute be a new type of potentially magnetic materials because magnetic ordering of unpaired electrons through exchange or dipolar interactions should be possible.<sup>1,2</sup> Polymers with paramagnetic centers may be classified under several aspects.<sup>1,2</sup> A classification that is rather arbitrary but useful, considering the structural features of coordination with respect to the polymeric backbone, is as follows.

- 1. The paramagnetic centers are bridged over discrete organic groups, forming linear (onedimensional) spin chains.
- 2. The paramagnetic centers are attached directly into the main polymeric backbone.

3. The paramagnetic centers are situated in the side chain of a main polymer.

A considerable number of mechanisms for ferromagnetic interactions have been established,<sup>3,4</sup> such as a real ferromagnetic interactions, which cannot be realized in one direction only. Thus, the existence of a nonzero Curie temperature<sup>5</sup> depends on an interchain interaction associated with the three-dimensional structure of the material. Nevertheless, an ordering effect should be possible due to dipole–dipole interaction or through bond interactions, even in amorphous polymers. However, excluding interchain interactions, a linear polymer chain is essentially one-dimensional.

The spin can originate from an organic radical or from a paramagnetic transition metal atom.<sup>6–8</sup> Only a few reports dealing with amorphous polymers with metal ions have been published.<sup>9,10</sup> In most cases, the metal ion is a part of the main chain.<sup>10</sup> Recently, Iskander et al.<sup>11</sup> showed the pos-

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Journal of Applied Polymer Science, Vol. 71, 409-414 (1999)

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**Scheme 1.** (A) PBA–Cu (II) acetate complex; (B) PBA–CU (II) chloride complex; (C) PBA–Ni (II) acetate complex; (D) PBA–Ni (II) chloride complex; and (E) PBA–Co (II) acetate complex

sibility of incorporating a metal ion via chemical functionalization of the side group of a polymer.

The aim of this work is to study the magnetic characteristics of some new transition metallopolymer complexes as a function of temperature (300-4.2 K) and magnetic field strength.

## MATERIALS AND METHODS

#### **Preparation and Characterization**

The polymer metal complexes of poly(2-acrylamide) benzoic acid (PBA) were prepared and characterized by elemental and different physical techniques.<sup>12</sup> The suggested structures for these metallopolymer complexes are represented by Scheme 1(A)–(E).

#### **Experimental Measurements**

The magnetic susceptibility measurements were carried out for 5 sample complexes [Scheme 1(A)–(E)] as a function of magnetic field strength (1.336,

1.152, 0.809, and 0.408 T) at room temperature (300 K) according to Faraday's method, <sup>13</sup> but the magnetic behavior for the complex of Scheme 1(A) only was also measured as a function of temperature (4.2–300 K) at field strength of 1.7 T.

Diamagnetic corrections (Pascal's constants),  $\alpha_{\rm diam}$ , were calculated using Pascal's constants.<sup>14</sup> The experimental magnetic susceptibility  $\chi_{\rm exp}$  was calculated as follows:

$$\chi_{\rm EXP} = \frac{\Delta m * g}{m_s * H \cdot \frac{dH}{dz}} \tag{1}$$

where  $\Delta m$  (the difference in wt) =  $\Delta m_s - \Delta m_h$ ;  $\Delta m_s$  is the difference in weight for the sample;  $\Delta m_h$  is the difference in weight for the holder; and g is the gravity constant since  $\Delta m_s$  can give by relation,

$$\Delta m_s = m_2 - \frac{m + m_3}{2}$$

Compound	Н	$\Delta m$	$\chi_{ m M} imes 10^{-6}$	$\chi^{Corr}_{Exp} imes 10^{-6}$	$\mu_{ m eff}$
Cu(II) acetate complex (A)	1.3658	-0.6364	1058.1085	1363.1085	1.7877
	1.1520	-0.4434	1050.9825	1355.9825	1.7830
	0.8090	-0.2114	551.2799	856.2799	1.4159
	0.4085	-0.0649	504.5296	809.5296	1.3777
Cu(II) chloride complex (B)	1.3658	-0.7196	955.5679	1369.2979	1.7917
	1.1520	-0.5018	949.2368	1362.9667	1.7876
	0.8090	-0.2365	231.2482	644.9782	1.2297
	0.4085	-0.0708	221.4387	635.1687	1.2203
Ni(II) acetate complex (C)	1.3658	-0.4914	3701.5824	4124.6124	3.1097
	1.1520	-0.3534	3491.5362	3914.5662	3.0295
	0.8090	-0.1448	3232.2960	3655.3260	2.9274
	0.4085	-0.0486	3005.8479	3428.8779	2.8353
Ni(II) chloride complex (D)	1.3658	-0.4831	2505.8098	2845.3298	2.5828
	1.1520	-0.3952	1872.7816	2212.3016	2.2774
	0.8090	-0.1846	1289.5059	1629.0259	1.9543
	0.4085	-0.0586	1171.7316	1511.2516	1.8823
Co(II) acetate complex (E)	1.3658	0.5769	9556.5015	9882.4415	4.8135
	1.1520	0.4106	9513.8291	9839.7691	4.8031
	0.8090	0.2123	9041.7539	9367.6939	4.6864
	0.4085	0.0369	8317.5570	8643.4970	4.5016

Table I Magnetic Properties at Room Temperature of Cu(II), Ni(II), and Co(II) Complexes Derived from PBA

where  $m_s$  is the mass of the sample without field at room temperature,  $m_1$  is the mass of the sample without field,  $m_2$  is the mass of the sample under field, and  $m_3$  is the mass of the sample after removing the field.

The correction of molar susceptibility was calculated as follows:

$$\chi_{\exp}^{\text{corr}} = (\chi_{\text{means}} * M_{\text{wt}}) - \alpha_{\text{diam}}$$
 (2)

where  $M_{\rm wt}$  is the molecular weight of sample, and  $\alpha_{\rm diam}$  is the diamagnetic correction.

The effective magnetic moment  $(\mu_{\text{eff}})$  was calculated from the following equation:

$$\mu_{\rm eff} = 2.828 \sqrt{\chi_{\rm exp}^{\rm corr} * T(\rm K)}$$
(3)

# **RESULTS AND DISCUSSION**

The effect of the magnetic field strength (1.366–0.408 T) on the magnetic susceptibilities of samples at room temperature are given in Table I.

It is observed that the magnetic moment values of Cu(II) polymer complexes (acetate and

chloride) are directly proportional to the magnetic field strength. This could be attributed to the possibility of the presence of ferromagnetic or antiferromagnetic interaction within the polymer matrix. Therefore, the paramagnetism for the Cu(II) polymer complexes is more complicated than expected. Their magnetic moment values are found to be higher than the spin only value  $(1.73 \ \mu\text{B})$  within the range of high magnetic field strength (1.366-1.15 T). This behavior may rise from paramagnetic impurities trapped within the polymeric matrix.

Under low magnetic field strengths (0.81–0.41 T), the magnetic moments of Cu(II) polymer complexes were smaller than the spin only value. This behavior indicates the existence of some sort of magnetic exchange interaction. This interaction mechanism could be attained via the bridging of acetate or chloride ions between 2 Cu(II) centers in the solid phase, as indicated from their infrared (IR) spectral data.<sup>12</sup> More structural information may be obtained by measuring the bulk magnetic susceptibility at absolute temperature.<sup>15</sup>

A number of investigations<sup>16–19</sup> have been devoted to study of Ni(II) polymer complexes and reported their magnetic susceptibilities at magnetic field strength in the range of  $2.8-4.1 \mu B$ . Magnetic susceptibility values may give an indication on the stereochemistry of the complex. In other words, Ni(II), in an octahedral structure, has a magnetic moment in the range of 2.8–3.3  $\mu$ B, while Ni(II) tetrahedral complexes have magnetic moments in range of 3.5–4.2  $\mu$ B.<sup>20–23</sup> The magnetic moment values of polymer Ni acetate complex (3.11–2.84  $\mu$ B) Table I at room temperature under field strengths 1.36–0.41 T were higher than the spin only value (2.83 BM) but still lower than the values obtained from spin-orbit coupling  $\mu_{S-L}^{theor}$  formula (4.47  $\mu$ B).

These values may be attributed to the slight mixing of the multiple excited states in which the spin-orbit coupling is appreciable.<sup>24</sup> This contribution is known as the second-order Zeeman effect, which is temperature-independent. The magnetic moments of Ni(II) acetate complex showed very slightly paramagnetism within the range of octahedral configuration.

The magnetic moment values of polymer Ni(II) chloride complex was in order of  $2.58-1.88 \ \mu\text{B}$ , as shown in Table I, which are lower than the spinonly value (2.83  $\mu\text{B}$ ) attributable to some sort of molecular association. The octahedral configuration for this Ni(II) polymer complex was adopted with certain distortion,<sup>24</sup> leading to decrease the magnetic moment values from that of the regular octahedral.

Pignalet et al.<sup>25</sup> reported several polymer Co(II) complexes with low and high magnetic moments. They pointed out that there is a direct relationship between the stereochemistry of Co(II) complexes and their magnetic moments. The Co(II) complexes were classified<sup>25</sup> into 2 main classes, based on their effective magnetic moment values, as follows: (1) low spin complexes with effective magnetic moment  $\mu_{\rm eff}$  in the range of 1.7–2.9  $\mu$ B; and (2) high spin complexes with  $\mu_{\rm eff}$ in the range of 3.96–5.60  $\mu$ B. The magnetic data of the first class is characterized by low spin octahedral or square planner complexes. The second class described the high spin octahedral or tetrahedral complexes.

The magnetic moment values of polymer Co(II) acetate complex were in the range of 4.81-4.50 BM at room temperature under field strengths of 1.366-0.408 T (Table I). These values are lower than the required for high-spin octahedral structure. It is of interest to mention that these values of magnetic moment could be due to some sort of molecular association.<sup>18-21</sup>

To study the variation of magnetic susceptibility as a function of temperature (4.2-300 K), the polymer complex [Scheme 1(A)], which showed a reduction in its magnetic susceptibility at room temperature, is chosen.

The change of magnetic susceptibility  $\chi$  and magnetic moment  $\mu$  as a function of temperature are shown in Figure 1, while variation of magnetic susceptibility  $\chi$  versus 1/T (K<sup>-1</sup>) for Cu(II) acetate complex is shown in Figure 2. The later variation showed a straight line, which did not pass through the origin but exhibited a negative Curie–Weise constant ( $\theta$ ), -53.7 K. However, the magnetic behavior of these complexes deviated from the simple Curie's law<sup>26</sup>:

$$\chi_M ext{ (molar magnetic susceptibility)} = rac{C}{T}$$
 (4)

but obeyed the Curie-Weise law, as follows:

$$\chi_M = \frac{C}{T - \theta}$$

where  $\theta$  is Curie–Weise temperature (K), and *C* is Curie constant and is given by the following:

$$C = \frac{Ng^2 \mu_B^2 S(S+1)}{3K}$$
(5)

where *N* is Avogadro's number, *g* is the gyromagnetic ratio ( $\mu$ /H),  $\mu_B$  is the effective magnetic moment, *S* is the total spin quantum number, and *K* is Boltzman's constant.

This behavior was attributed to presence of magnetic interaction in nonmagnetically diluted system for these Cu(II) polymer complexes. These polymer complexes, which have a negative Curie–Weise constant  $(-\theta)$  indicate an existence of antiferromagnetic interaction in the solid phase. This interaction mechanism could not be attributed to the direct Cu—Cu interaction because the nature of organic polymer compounds,<sup>9</sup> in which the bonded metal ions separated by a distance more than 3A°. This is supported by the absence of d-d transitions in its electronic spectrum due to the Cu—Cu bond.

It is assumed that the interaction takes place via a super exchange mechanism through bridging groups, such as acetate and chloride anions between Cu(II) centers. The magnetic susceptibil-



**Figure 1** Variation of magnetic susceptibility  $\chi$  and magnetic moment  $\mu$  as a function of temperature *T* for the Cu(II) acetate complex.

ity<sup>9</sup> values with increasing temperature for the polymer Cu(II) acetate complex were fitted in the Bleany–Bowers equation:

$$\chi = (1 - \chi_P - \chi_N) \frac{2N_L g^2 \mu_B^2}{KT} \cdot \frac{\exp(2J_1/KT)}{1 + 3 \exp(2J_1/KT)} + \chi_N \frac{2N_L g^2 \mu_B^2}{KT} \cdot \frac{\exp(2J_2/KT)}{1 + 3 \exp(2J_2/KT)} + \chi_P \frac{2N_L g^2 \mu_B^2}{3K(T - \theta)} \cdot S(S + 1) + 2N_\alpha \quad (6)$$

The susceptibility was expressed per Cu dimmer,  $\chi_P$  and  $\chi_N$  are the molar fraction of paramagnetic impurities, and  $J_1$  and  $J_2$  are coupling constants. The best fitted values were as follows:  $g = 2.27, J_1 = 22.95 \text{ cm}^{-1}, J_2 = -110.5$  $\text{cm}^{-1}, \chi_P = 3.5\%$ , and  $\chi_N = 3.5\%$ , and  $N_{\alpha}$  is the temperature-independent paramagnetism (TIP) =  $60 \times 10^{-6}$  (CGS).

The magnetic data of Cu acetate and chloride complexes shows subnormal magnetic moment values (that is, some of their  $\mu_{\text{eff}}$  values are lower,

and others are higher than the spin only value). The magnetic moment values, which are lower than the spin only values, are due to antiferromagnetic interaction, while that of moments higher than the spin only value may be attributed to ferromagnetic interactions of the small amounts of paramagnetic impurities in the polymeric matrix.

The magnetic moment data of Cu(II) complexes did not give any indication on the stereochemistry of these complexes<sup>13–16,26,27</sup> because of the unknown arrangement of the Cu(II) chelating units.<sup>5</sup> However, the actual model of Cu—Cu interaction is still uncertain.<sup>28</sup>

# CONCLUSION

The magnetic susceptibility of polymeric Cu(II) and Ni(II) complexes showed antiferromagnetic behavior at different temperatures (4.2–300 K) due to metal–metal interaction. In other words, the magnetic susceptibility of polymeric Cu(II) and Ni(II) acetate and chloride complexes showed subnormal magnetic moments, implying the exis-



**Figure 2** Variation of magnetic susceptibility  $\chi$  versus 1/T (K<sup>-1</sup>) for the Cu(II) acetate complex.

tence a condensed system where metal interaction takes place.

The authors thank Dr. Ali El-Desoky, Professor of Inorganic Chemistry, for his interest and valuable discussion.

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